Life cycle thinking and general modelling contribution to chemical process sustainable design and operation

Life cycle thinking and general modelling contribution to chemical process sustainable design and operation

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A mis padres.

The world will not evolve past its current state of crisis
by using the same thinking that created the situation.

Albert Einstein (1879-1955)

Summary

Industry is often seen as a source of environmental degradation and resource depletion, however it is a vital part of societal development and wealth creation. Moreover, industrial systems cause and determine flows of materials and energy through the society. Sustainable development is associated to all the former issues, by encompassing them altogether under the same umbrella.

Sustainable services are those, which restrain resource consumption and waste generation to an acceptable level, considering Earth's existing capital, rates of replenishment and carrying capacity, make a positive contribution to the satisfaction of human needs, and provide enduring economic value to the business enterprise. The selection of appropriate processes for providing a given sustainable service is the main topic of this thesis.

This thesis presents a consistent framework for decision support towards sustainable design. It encompasses a set of methods and tools applicable to decision aid in process design, retrofit and operation considering sustainability criteria in terms of economic and environmental issues. In this sense special consideration is given to process simulation, general modelling programs and other multivariate statistical methods, as well as their supporting associated tools. The framework is materialised as a procedure for its application in four steps, which mimics other current applied methods; and a set of tools which are integrated. One of the framework aims is the consideration of the uncertainty associated to parameters and values. The tools, which in all cases are mathematical models, allow for an accurate representation of the reality they simulate. In the case of alternatives generation problem, the resultant multiobjective optimisation problem is solved by an strategy that permits narrowing-in the best solution compromise. A multitude of industrial case studies teaches the way to use the framework in different scenarios.

The framework is applied to different case studies which require decision aid. The case of continuous process design is first addressed along with three different studies. The first one is related to the selection of waste water treatment options for a phosphoric acid plant considering uncertainty in operating variables, another analysis considers the decisions related to raw material management in an integrated gasification combined cycle power plant, while the last one addresses the design of a reactive distillation system considering optimisation of operating variables. All case studies are modelled rigorously using state of the art commercial simulation tools in conjunction with other tools developed for the assessment of sustainability concerns, mainly economic and environmental issues.

The operational problem of selecting appropriate schedules, for the production of differ-

ent products, is addressed next. In this case, special attention is given to the selection of appropriate metrics, considering economic, efficiency and environmental concerns that reflect the sequence dependence features of this problem. The model proposed is built using mathematical programming and the production of acrylic fibres is the application considered.

Finally, the framework is applied to the design and retrofit of the whole chemical supply chain. Mid- to long-term planning decisions are modelled in this case, which studies a maleic anhydride production supply chain in Western Europe. Due to the problem nature, economic-environmental instruments such as emission trading and price subsidies are studied showing the viability of the presented approach for policy analysis.

The case studies and the proposed framework show that different trade offs appear at different decision making levels. Moreover, the framework provides with a robust approach for traceability and verifiability of different modelling hypothesis which strengthens the decision making process.

Resumen

La industria es vista comúnmente como una fuente de degradación ambiental y de consumo de recursos; a pesar de ello constituye una parte vital del desarrollo social y de la creación de riqueza. Del mismo modo, los sistemas industriales causan y determinan los flujos de materias y energía a través de la sociedad. El desarrollo sostenible está asociado a todos los aspectos anteriores pues engloba a todos ellos.

Los servicios sostenibles son aquellos que restringen el consumo de recursos y generación de residuos a un nivel aceptable, considerando las existencias y las velocidades de recuperación de los recursos así como la capacidad de soporte de La Tierra. Asimismo, contribuyen de forma positiva a la satisfacción de las necesidades humanas y otorgan valor económico a la empresa. La selección de procesos apropiados para la provisión de un servicio dado es el tópico principal de esta tesis.

Esta tesis presenta un marco consistente para el soporte a la decisión hacia alternativas sostenibles. El marco abarca un grupo de métodos y herramientas aplicables en cuestiones de diseño, actualización, y operación, considerando criterios de sostenibilidad en términos económicos y medioambientales. Se ha enfatizado la simulación de procesos, el modelado matemático y otros métodos de estadística multivariable, métodos que se han incluido como principales herramientas. El marco se materializa en un procedimiento de uso integrado por cuatro pasos que imitan los de otros métodos actualmente utilizados y en un set integrado de herramientas. Uno de los objetivos del marco es la consideración de la incertidumbre en parámetros y valores. Las herramientas usadas son, en todos los casos, modelos matemáticos que permiten una representación precisa de la realidad que simulan. El problema multiobjetivo resultante es resuelto mediante una estrategia que permite restringir la mejor solución de compromiso. Una multiplicidad de casos de estudio industriales muestra la forma de aplicación del marco en diferentes escenarios.

El marco se ha aplicado a casos de estudios que requieren de soporte a la decisión. El caso de diseño de procesos continuos se ha incluido tratando tres casos. El primero está relacionado con la selección de opciones de tratamiento de aguas residuales en una planta de producción de ácido fosfórico, considerando incertidumbre en variables operativas. El segundo considera las decisiones relativas al uso de diferentes materias primas en una usina eléctrica con tecnología de gasificación. El último caso se refiere a la optimización de las variables operativas en el diseño de un sistema de destilación reactiva. Todos los casos son modelados rigurosamente usando nuevas herramientas de simulación y modelado en conjunto con otras desarrolladas para el análisis de los aspectos económicos y medioambientales de la

sostenibilidad.

Posteriormente, se ha estudiado el problema operacional de la planificación de producción. En este caso se ha enfatizado en la selección de métricas apropiadas considerando aspectos económicos, medioambientales y de eficiencia que reflejen las características secuenciales del problema. El modelo propuesto se ha construido mediante herramientas de programación matemática y la producción de fibras acrílicas es la aplicación considerada.

Finalmente el marco se ha aplicado al diseño y planificación de una cadena de producción. En este caso se modelan decisiones de planificación a mediano y largo plazo y éstas se aplican a la producción de anhídrido maleico en Europa del Oeste. Dadas las características del problema, se han estudiado diferentes instrumentos económicos asociados al medio ambiente, como la venta de permisos de emisión y los subsidios a la producción. Esto permite mostrar las capacidades que tiene el marco propuesto para el estudio de políticas gubernamentales.

Los casos de estudio señalan las diferentes compensaciones que aparecen en varios niveles de decisión. Asimismo el marco ofrece un sólido enfoque para la trazabilidad y capacidad de verificación de las diferentes hipótesis de modelado, lo cual refuerza el proceso de toma de decisiones.

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Chapter 1

Introduction

1.1 Perspective

Global population growth and rising material expectations of people in industrialised countries coupled with expanding market economies in Asia and Latin America are causing a global increase in demand and consequently in production and consumption. The environment receives wastes and pollutants from all the echelons in any supply chain (SC), but it not only acts as a sink of emissions but it is also the source of raw materials. The overloading of the supply and sink function of the environment influences its activity support function and as a consequence the global ecological equilibrium is threatened (Christ, 1999, Ch 1.). Mankind as a whole is facing the realisation that planet Earth has constraints, i.e. the capacity of the planet to provide resources and absorb emissions is finite (Clift, 2006). Moreover, problems of environment and development are closely linked; degradation of ecosystem services harms people (UNEP, 2007). In this setting, industry is often seen as a source of environmental degradation and resource depletion, however it is also widely recognised that it is a vital part of development and wealth creation. Industry is one important part of the human society given that industrial systems cause and determine flows of materials and energy through the economy system. It is unlikely that humankind will give up the products that have improved the quality of life, thus is imperative for industry as a social factor and engineers as actors to learn how to evaluate the environmental impacts of a product and determine ways to minimise possible adverse effects (Azapagic & Perdan, 2000; Marteel *et al.*, 2003).

These threats have been discussed since the UN "Brundtland Report" (UNWCED, 1987). In this report the concept of sustainable development (SD) played a key role: "*Humanity has the ability to make development sustainable - to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs.*". An important principle that underlies this definition is *intergenerational equity*, where future generations have as much right to the Earth's resources as the current one. Another definition is given by Bakshi and Fiksel (2003), *"A sustainable product or process is one that constrains resource consumption and waste generation to an acceptable level, makes a positive contribution to the satisfaction of human needs, and provides enduring economic value to the business enterprise"*. This definition, closer to the industry, points out that SD encompasses three as-

pects: the *environment* considered via resource availability and waste generation; *technology and economy* that defines the ability to use those resources to meet human needs, and the *societal organisation* which determines the needs to be met. Moreover, it is more convenient for engineering-decision making given that it focus on products / process and it separates the objectives of each SD aspect, the social aspects are represented by the satisfaction of human needs while economic value is related to the economic aspect. However, the definition fails at defining *acceptable levels*, in this sense it is common to assert that resource utilisation should not deplete existing capital; meaning that resources should not be used at a rate faster than the rate of replenishment, and that waste generation should not exceed the carrying capacity of the surrounding ecosystem as proposed by Robèrt (1997). Social and economic SD is essential for further improving the quality of life of the world's population, while environmental sustainability ensures that this is achieved without causing deterioration in either this or future generations (Clift, 1998; SETAC, 1993).

Considering the former points and Bakshi and Fiksel (2003)'s wording, the following SD definition is proposed: "*A sustainable service*[1] *is one that constrains resource consumption and waste generation to an acceptable level, considering Earth's existing capital, rates of replenishment and carrying capacity, makes a positive contribution to the satisfaction of human needs, and provides enduring economic value to the business enterprise*".

However one- and two-dimensional metrics, focused on single SD aspects, while useful, cannot alone certify progress towards sustainability, it is widely agreed that significant progress in one or two of the three aspects, will aggravate the third, only when all three aspects are improved together progress towards sustainability can be made (Sikdar, 2003a,b).

If economic and societal aspects are considered then problem regards to socioeconomic considerations, such as job creation, equity and other impacts of the relationship between the economy and societal well-being. When societal and environmental aspects are discussed together then the focus is regarded as socio-environmental, including effects of natural resource degradation and environmental interventions on the livelihood, health, and safety of people today and of generations to come, generally regarded as liveability issues. Finally when economic and environmental concerns are discussed together eco-efficiency appears. Simply put, eco-efficiency means creating more goods and services with less use of resources while generating less waste and pollution (Tanzil & Beloff, 2006; WBCSD, 2000).

Regarding SD economic value, Fiksel (2003) identifies three pathways towards value creation while implementing SD initiatives into the business decision framework, (i) direct and tangible (SD initiatives can contribute directly to financial value by enabling growth, reducing costs, conserving capital, and decreasing risks); (ii) direct and intangible; or (iii) indirect and intangible.

The United States Environmental Protection Agency (USEPA) conducted an analysis (AIChE-CWRT, 2000), finding that an environmental design review[2] could generate great savings by considering (i) variable cost waste disposal savings (11%), (ii) improved product recovery (15%) and (iii) process improvements identified during the design review, including increased availability, increased capacity and improved product quality (74%) (Sylvester, 2001). Other industries found:

- Amoco Petroleum: "environmental costs made up at least 22% of the non-feedstock operating costs of Amoco's Yorktown oil refinery. The largest components were costs of waste treatment, maintenance of environment-related equipment and meeting environment-

[1] Throughout this thesis the chain idea of process manufacturing products, which in the end provide a service is used.

[2] Understood as an structured review of any chemical process with emphasis on waste generation and management.

related product specifications."
- DuPont: "for one DuPont pesticide, environmental costs represented 19% of the total manufacturing cost. The largest components were general overhead (including taxes and training and legal fees) and depreciation and operation of pollution control equipment."
- Novartis: "Environmental costs of one Novartis additive were a minimum of 19% and possibly a higher proportion of manufacturing costs (excluding raw material). The most obvious costs were operation and depreciation of waste water treatment and solvent recovery equipment, which alone totalled 15% of non-raw material manufacturing costs.

The points risen by Fiksel (2003) and the former figures could already justify the necessity of tackling with environmental problems from an economic point of view. However as pointed out by Adams (2006), "*The greening of business has grown to be a central issue in corporate social responsibility (CSR) for many global companies, although for many it is still a boutique concern within wider relationship management, rather than something that drives structural change in the nature or scale of core business*".

One reason for the widespread acceptance of the idea of SD is precisely this looseness, making it able to cover very divergent ideas. The SD concept is holistic, attractive, elastic but mostly it is imprecise. The idea of SD may bring people together but it does not necessarily help them to agree and measure such goals, but more importantly it does not agree on how to achieve such goals. In this sense the SD problem can be approached by different stakeholders, each of them having different points of view and ways of assessing SD. In this sense, the concepts of strong and weak sustainability have gone beyond the realm of economics to indicate the presence or absence of trade-offs between different SD issues (Gasparatos *et al.*, 2008), see section 2.2.2.

Summarising SD assessments should try to: (i) integrate economic, environmental, social and institutional issues as well as to consider their interdependencies; (ii) consider the consequences of present actions well into the future; (iii) acknowledge the existence of uncertainties regarding the result of present actions and act with a precautionary basis; and (iv) include equity considerations (intra- and intergenerational).

However, a sustainable planet and sustainability at different levels (such as communities, businesses and technologies) require of different actions to be performed at different levels and by different actors. Sikdar (2003a) defined such levels / systems so that necessary actions for progress become measurable and achievable; the author proposes the following levels[3]:

- *Type I system*: This system is the planet Earth, for which all solution frameworks would have to ultimately arrive by political negotiations.
- *Type II system*: This system is the community, for instance, a country city, commune or a watershed.
- *Type III system*: This system is integrated by enterprises, particularly multinational corporations that are motivated by both good business practise and government regulations.
- *Type IV system*: This system is cost-effective "*sustainable technology*". Included in this group diverse systems such as processing systems and chemical unit operations are found.

From the chemical engineering point of view systems of type III and specially type IV are deeply studied. In the case of type III emphasis is done in the whole SC of a given business while in type IV the emphasis is put on an echelon of a given SC.

[3]These levels are also referred as: micro, meso and macro, depending on the context.

Regarding type I and II systems, actors are governments and international bodies, these actors generally can act using policy instruments. UNEP (2007) classifies those instruments[4] into: (i) command and control regulations (e.g. standards, bans, permits and quotas, zoning, liability), (ii) direct provision by governments (e.g. eco-industrial zones, national parks, protected areas and ecosystem rehabilitation), (iii) engagement of public and private sectors (e.g. eco-labelling, voluntary agreements and public-private partnerships), (iv) use of markets (e.g. removal of perverse subsidies, environmental taxes and charges, deposit-refund systems, targeted subsidies and self-monitoring), and (v) creation of markets (e.g. tradeable permits and rights, environmental investment funds, payment for ecosystem services).

Consequently, the problem of decision making with regards to SD has to take into account:

- Different system boundaries, ranging from the whole planet to a small piece of equipment into a chemical plant,
- Different actors (decision makers) across those boundaries: such as management, NGOs, community, government and others, each one of them having a given set of objectives and a different vision of SD,
- Different set of actions that these actors can perform, and
- Different ways of measuring possible actions outcomes and its inherent uncertainty, i.e. a set of metrics proposed by these actors (each one of them selected following their own vision of SD).

Finally, decision making considering SD has an inherent multiobjectivity (economic, environmental and social), depends on the decision maker position and on the available set of actions that he/she can perform; and finally depends on the system upon decisions are being considered.

In this introductory section the complexity of the SD problem in general terms has been exposed. The next following sections discuss possible approaches for tackling it. In the following section 1.2 concepts and tools applied to the chemical industry are explored, while in section 1.3 the implications of SD in chemical engineering are outlined, framing the methodology and the object of study of this thesis.

1.2 Sustainability and the chemical industry

In the developed world, the business response to the then emerging environmental issues and later to the idea of SD has gone through three phases (Azapagic & Perdan, 2000).

- *Reactive phase* (early 1970s to mid-1980s), the main driver for improved environmental performance was regulation, and end-of-pipe solutions were almost the only options considered by industry at the time.
- *Proactive phase* (mid-1980s to early 1990s), it was realised that better environmental performance could improve the bottom line. This belief slowly changed the business response to environmental problems.
- *Integration phase* (mid-1990s till now), industry is integrating environmental performance into business strategy and development. This has been seen by an increment of external environmental reports required by diverse CSR strategies and the adoption of environmental management systems (EMS).

[4]Economic instruments provide market corrections, promote production efficiency or cost minimization, and facilitate flexible responses to changing circumstances. Moreover they may provide signals concerning resource scarcity and environmental damage which, in turn, can trigger more-efficient resource use and waste minimization. Instruments such as green taxes can raise revenues that may be used to improve environmental quality or reduce income taxes for the poor (UNEP, 2007)[Ch 10].

One of the important drivers for this attitude change was a realisation that, in addition to the more obvious costs, bad environmental practises brought other less tangible costs than those associated with the social perception and image of the business. Moreover, the increased public awareness of environmental problems and lobbying of various pressure groups have made some businesses more exposed and vulnerable, in some cases reflecting badly on their economic performance (Azapagic & Perdan, 2000; Fiksel, 2003).

For the case of systems III and IV several frameworks for measuring SD have been proposed, possible examples are: the Global Reporting Initiative (GRI), the United Nations Commission on Sustainable Development (UNCSD) framework, the Wuppertal Sustainability Indicators, the ICCA'sResponsible Care programme and the different sustainability metrics proposed by the Institution of Chemical Engineers (IChemE) and the American Institute of Chemical Engineers (AIChE). In Labuschagne *et al.* (2005) a review of SD frameworks is done concluding that common to all of them is the industries commitment to an EMS for an inclusion of SD considerations into their business approach. Most of these frameworks propose to measure SD in three dimensions economic, environmental and social while the UNCSD and the Wuppertal institute frameworks consider a fourth dimension related to institutional sustainability[5]. Most international chemical corporations have embedded SD into their corporate strategy and in all those cases, SD is addressed via CSR programmes[6].

CSR is seen as the business contribution to SD goals; essentially it is about how business takes account of its economic, social and environmental impacts in the way it operates maximising the benefits and minimising the downsides. Specifically, CSR takes the form of voluntary actions, over and above compliance with minimum legal requirements, to address both its own competitive interests and the interests of wider society[7]. CSR is mostly related to the institutional aspect of SD.

Besides the appearance and implementation of the former government and international SD frameworks via CSR programmes, several other concepts related to industry and environment are used. Some of these are: Life-cycle thinking (LCt), Life-Cycle Management (LCM), Industrial ecology (IE), Cleaner technology (CT), Cleaner Production (CP), Pollution Prevention (PP or P2), and Green chemistry/engineering.

1.2.1 Sustainability concepts

Life-Cycle thinking (LCt) and Life-Cycle Management (LCM) LCt reflects the acceptance that key societal actors cannot strictly limit their responsibilities to those phases of the life-cycle of a product, process or activity in which they are directly involved. It expands the scope of their responsibility to include environmental, economic and social implications along the entire life-cycle of the product, process or activity. Thus, it implies that all processors, manufacturers, distributors, retailers, users and waste managers involved in the life-cycle of a product share responsibility. The individual share of responsibility will be greater in the parts of the life-cycle under their direct control and lesser in distant stages of the life-cycle (SETAC, 1993).While LCM is the managerial set of practises and organisational arrangements that apply LCt (i.e. a procedural tool), the analytical tool that implements LCt is Life-Cycle

[5]This dimension is related to the manifestation of sustainability on a strategic level within a business (or industry); which can be seen as a prerequisite for sustainable operations, projects or even corporate sustainability. It implies that a prerequisite for all sustainability is a strategy that accepts the company's responsibility and its vital role in every society it operates in and also in the global environment.

[6]E.g. BASF, Bayer, Akzo Novel, British Petroleum, Dutch State Mines, Shell.

[7]According to the European Commission on Enterprise and Industry (ECDGEI, 2008), CSR is *"a concept whereby companies integrate social and environmental concerns in their business operations and in their interaction with their stakeholders on a voluntary basis"*.

assessment (LCA). Developments of LCA have been guided by the Society for Environmental Toxicology and Chemistry (SETAC), which developed its code of practise (SETAC, 1993) and encouraged the standardisation of the LCA steps undertaken by ISO (ISO, 1997, 1998, 2000a,b) and its updates (ISO, 2006a,b). Moreover the United Nations Environmental Programme (UNEP) has encouraged the use of LCt by providing tutorials for LCA and the launch of the Life-Cycle Initiative.In the European context the European Environment Agency (EEA), also promotes its use and has published a report to help on its implementation (Jensen *et al.*, 1998).

Industrial ecology (IE) as a term was conceived to suggest that industrial activity can be thought of and approached in the same way as a biological ecosystem and that in its ideal form it would strive towards integration of activities and cyclization of resources, as natural ecosystems do (Graedel, 1996)[8]. IE concentrates on the flows (mass and energy) between and within the industrial systems and ecosystems aiming to contribute to the efforts of controlling and reducing the impacts that the use of those flows generates on ecosystems. Besides flows, IE also focuses on the more structural and organisational characteristics and properties of industrial ecosystems (Korhonen, 2004). According to Lifset and Graedel (2002), IE is based on the combination of (i) a life-cycle perspective, (ii) use of materials and energy flow analysis and (iii) use of systems modeling.

Design for the environment (DfE) is a general term for a number of methods for incorporating environmental factors into the design process, which have been promoted by the USEPA. According to Lifset and Graedel (2002), DfE is a conspicuous element of IE, which incorporates environmental considerations into product ex ante, in this sense industrial ecologists seek to avoid environmental impacts and/or minimise the cost of doing so. The use of DfE is confined to the design of products being the World Business Council for Sustainable Development (WBCSD) a proponent of this approach, based on eco-efficiency.

Cleaner technology (CT) and Cleaner Production (CP) are two similar concepts aiming at "*the continuous application of an integrated, preventive environmental strategy applied to processes, products and services in pursuit of economic, social, health, safety and environmental benefits*" (Jackson, 2002; Yang & Shi, 2000). CP and CT lie in three basic principles (Jackson, 2002):

- *precaution*: mainly rising from the "precautionary principle", the main idea behind this principle is to take action to mitigate potential causes of environmental pollution in advance of conclusive scientific evidence about actual effects, see section 2.4.
- *prevention*: it requires actions to be taken upstream, before environmental impacts occur, is thus a directional strategy, it looks as far as possible upstream in a network of causes and effects; it attempts to identify those elements within the causal network which lead to a particular problem; and it then takes action at the source to avoid the problem.
- *integration*: it looks on all media sinks and not only to emissions on one echelon, but along the whole product life-cycle.

The operationalisation of CP and CT rely on two different aspects (i) efficiency improvements by reduction of material flows through process with out service loss and (ii) substitution; using non-hazardous or less hazardous materials in processes and products.

[8]Another way of referring to IE is industrial symbiosis, where the expression "symbiosis" builds on the notion of biological symbiotic relationships in nature, in which at least two otherwise unrelated species exchange materials, energy, or information in a mutually beneficial manner, the specific type of symbiosis known as mutualism (Chertow, 2000).

Pollution Prevention (PP or P2) Avoiding the formation of pollutants rather than capturing them is what leads to the definition of PP (Clift, 1998). It is clear that PP emphasises the reduction of risks, primarily, but not exclusively, from toxic substances at the facility or firm level. In this sense only when the use of such substances is eliminated or dramatically reduced the risks to humans and ecosystems can be lowered (Lifset & Graedel, 2002). According to Spriggs (1994) PP is all about process design, given that if the design is right then pollution will go away, but Rossiter (1994) states that PP is associated to a philosophy that aims at developing process to make products without creating pollution[9]. The PP concept is proposed together with a hierarchy; in order of decreasing priority, it strives for: (i) eliminate at source, (ii) reduce at source, (iii) recycle within process, (iv) re-use outside process[10], (v) treat to reduce environmental impact and (vi) dispose off in a responsible manner (Khor *et al.*, 2007)[11].

Green chemistry and engineering According to Marteel *et al.* (2003), green chemistry and engineering is the design of chemical manufacturing systems to minimise their adverse effects on the environment. In this approach the evaluation of the environmental impacts inherits a systems approach. The strategy of green chemistry is the operation of processes such that hazardous substances will not be used nor generated. In this sense the concepts of the PP are embedded within green chemistry. With regards to the levels at which P2 can be applied macroscale and mesoscale can be thought as green engineering while the microscale will fit as green chemistry one. A set of 12 "*green engineering principles*" were proposed by Anastas and Zimmerman (2003); McDonough *et al.* (2003), to be applied during the design stage of process.

Discussion No global umbrella has been conceived for bringing the former concepts all together. Each one of the proponents of these concepts remains isolated, a clear example of this is the appearance of different specialised journals related to each concept[12]. All former concepts include the life-cycle approach towards the definition of system boundaries or the analysis or solutions, and can be applied at different types of systems (micro, meso and macro). In the case of PP and CP, both concepts can be seen as good engineering practises , and consequently can be conceptually incorporated under a broader concept such as CT. According to Clift (1998) CT is a way of thinking, because it goes beyond PP and CP, given that it recognises that the product (that provides a given service) itself can be the actual problem. End-of-pipe and PP approaches can avoid emissions from the factory, but this approach misses the point where the product itself and not its production can be the problem. Jackson (2002), discusses that there is tendency for the CP approaches to focus its efforts on process technology improvements rather than on problems associated with consumption patterns or product take back and recycling initiatives.

With regards to green chemistry/engineering, it also shares the same level of IE or CT, given that it aims at designing products/services instead of focussing on the process. Moreover these principles, mimic some of the hierarchies already proposed in PP and strive for LCt. IE is interpreted with varying degrees of breadth or specificity, while under some inter-

[9] Berger (1994) states that successes in waste reduction have had a marked positive effect on the environment, and the most cost-effective reductions have been due to preventing the creation of the waste stream in the first place.

[10] With regards to recycling there is a difference between closed-loop recycling, which is a common practise in chemical process, where a stream is splitted and recycled back to a given unit operation, and open-loop recycling/reuse which involves recovery of material from one product life-cycle chain and fed it into a different often unrelated product life-cycle chain (Brennan, 2007).

[11] These guidelines are sometimes referred as the 4Rs - reduction, reuse, recycling and recovery.

[12] IE, "*Journal of Industrial Ecology*", CP, "*Journal of Cleaner Production*", and LCt, *International Journal of Life-Cycle Assessment*".

pretations it is simply a way of focusing attention on the use/reuse of generated wastes, it also focusses on the structure to make the industrial symbiosis possible. Currently, IE is not enforced by regulatory initiatives, it operates on the basis of industrial cooperation, driven mainly by the economic advantages of reusing waste resources.

Instead of adhering blindly to a fixed conceptual frame, in this thesis the following key points will be used as building blocks:

- a life-cycle perspective with regards to product production stages,
- the study of services instead of products, and the generation of processes for such "service delivery", and
- the selection of the appropriate system boundaries in terms of scale and level.

1.2.2 Sustainability tools

SD tools can be broadly classified into procedural or analytical tools. Procedural tools aim at organising integration of SD concerns into various activities, while analytical tools are quantitative tools which provide metrics to measure sustainability related issues. A great deal of procedural and analytical tools have been developed for the economic and environmental aspect. Regarding the last, some procedural tools are Environmental Impact Assessment (EIA), Environmental auditing (EAu), Environmental Managing Systems (EMS) and Environmental Performance Evaluation (EPE) (Baumann & Tillman, 2004)[Ch. 2].

The use of these procedural tools represent in many cases the CSR approach that many industries have with regards to the environmental aspect of SD[13]. In this sense the AIChE's and IChemE's SD frameworks have different qualitative metrics associated to environmental compliance (see section 2.2.1). Moreover, the usage of these procedures enables data gathering that is required by the quantitative tools, for example if EMS (ISO, 2004) is used then LCA (ISO, 1997) is used as analytical tool.

In a nutshell an LCA measures the cradle-grave environmental impacts that the provision of a given service entails. Section 3.4 contains a state of the art regarding LCA.An important feature of an LCA is that it is built around the service a product is providing, i.e. its functional unit (FU). A LCA follows a well established methodology (given by the ISO140X series) which encompasses four steps: (i) goal setting, (ii) inventory, (iii) impact assessment and (iv) interpretation of results. The inventory step requires gathering the environmental interventions associated to the provision of the FU, these are in most cases energy and material flows. The environmental impact assessment step uses the inventory results to generate a picture of the potential environmental impacts, which are interpreted in the last step in terms of the objectives set at step (i).

Other analytical tool such as, Material flow analysis (MFA)[14] is based on accounts in physical units (tons) quantifying the inputs and outputs of processes (Bringezu & Moriguchi, 2002). MFA is complementary to LCA, in both cases the flow of materials is studied, however in MFA its environmental impacts are not addressed. A typical metric derived from MFA is the material intensity per service (MIPS), which is applied in some cases to measure the dematerialisation effort of a system (Dewulf & van Langenhove, 2006a).

Environmental Risk Assessment (ERA) involves the estimation and evaluation of risk to the environment caused by a particular activity or exposure. Risk assessments (RA) are carried out

[13]While EIA is mandatory by law, according to each country legislation, EAu is the assessment of the compliance of an operating business with environmental protection requirements. EAu is usually used to test the effectiveness of EMS. EPE has been used by organisations in different sectors to improve environmental performance and provide a basis for performance benchmarking, its use is based on ISO (1999).

[14]There are differences between substance flow analysis (SFA) and MFA given that a substance is understood as atoms or molecules, while or a material/good which is a mixture (Brunner & Rechberger, 2004).

to examine the effects of an agent on humans (Health Risk Assessment-HRA) and ecosystems (Ecological Risk Assessment). In general risk is the combination of two factors: the probability that an adverse event will occur and the consequences of such event. In the chemical context risk depends on the following factors (EEA, 1998, USEPA-web).

- the inherent toxicity of the chemical (Hazard Identification),
- how much of a chemical is present in an environmental medium (Dose-Response Assessment), and
- how much contact a person or ecological receptor has with the contaminated environmental medium (Exposure Assessment).

ERA emphasises on reduction in the probability and/or consequences of occurrences (Burgess & Brennan, 2001), which is clearly different than the approach and objective in LCA. However, ERA is used in many of the impact assessment methodologies used in LCA.

Most approaches that tend to monetarise the environmental impact fall into the category of environmental cost accounting (ECA), these approaches are further discussed in section 2.2.3. In the case of Cost Benefit Analysis (CBA), projects are evaluated in economic terms by assigning monetary value (internalise) for any loss of environmental quality (externality), that is not normally accounted for in normal accounting structures.

Clearly the results of an MFA are required during the inventory phase of a LCA. It is important to note that making decisions around the flows of material is widely accepted, in this sense reduction of consumption of raw materials seems reasonable, however if impacts are considered the picture is different. In some cases the reduction of some emission flows might increase the flows of other species and render higher overall impact. The same line of thinking can be applied to the case of ECA. A LCA, which studies potential environmental impacts provides with a better set of metrics. In the case of ERA, LCA differs of it, in that the intrinsic risks of processes themselves are not addressed. This is a serious drawback with regards to LCA, where only potential impacts are addressed, however this is accepted due to the fact that LCA looks at broad picture than ERA; which focuses on a single site.

Thus, LCA is the appropriate analytical tool for implementing an IE, CT or green chemistry/engineering approach; given that "*virtually all modern approaches to environmental issues begin with the assumption that the appropriate scale of the analysis is the life-cycle of the material, product or service at issue*" (Seager & Theis, 2002). In this sense Kralish (2009), points out that LCA is being required by legislation, such is the case of the US Pollution Prevention Act[15], the EU Directive on Integrated Pollution Prevention (IPPC[16]) and the Integrated Product Policy (IPP[17]).

LCA helps in providing a framework which uses the appropriate (widely agreed) boundaries and provides with a set of metrics to analyse the product studied. The selection of metrics with regards to SD will be extensively discussed in section 2.2. However the problem of coping with different stakeholders remains. This problem where multiple stakeholder are present and where each of which understands the problem in a different manner is the core of the field of "decision analysis".

1.2.3 Decision analysis frameworks in SD

Decision analysis is a merger of decision theory and systems analysis. Decision theory provides a foundation for a logical and rational approach to decision making. Systems analysis

[15] http://www.epa.gov/p2/pubs/p2policy/act1990.htm
[16] http://europa.eu/legislation_summaries/environment/waste_management/l28045_en.htm
[17] http://ec.europa.eu/environment/ipp/

provides methodologies for systems representation and modelling to capture the interactions and dynamics of complex problems (Seppala *et al.*, 2002).

SD requires to measure a given system (product/process/alternative) with different types of metrics. Each one of the metrics can also have different meaning or value depending on who (i.e. each stakeholder) is assessing the value to it. In this sense, Cohon (2003) distinguishes two decision-making contexts namely, (i) multi-objective problems and (ii) multiple-decision maker (conflict resolution) problems. The former setting is related to situations in which there is a single decision maker, or a group (sharing similar objectives and preferences), who must make a decision about a problem with conflicting objectives. The latter is directed at those cases in which there are many stakeholders and each of which has its own conflicting objectives. In this case a particular decision maker must resolve internal conflicts among objectives and be aware of conflicts with others, this requires the predictions of preferences of others.

The methods to cope with these type of problems are generally known as multiple-criteria decision analysis (MCDA). These methods structure and model multidimensional decision problems in terms of a number of individual criteria where each criterion represents a particular dimension of the problem to be taken into account. A review of these methods has been performed under section 3.3.

In the multi-objective decision case, the analytical goal could be seen as finding the best compromise solution, which is the result of the resolution of the decision maker internal conflicts. For the selection of the appropriate multi-criteria decision framework, the most important question that requires to be answered is: are the criteria able to compensate each other?. This question separates broadly the methods to be used, but regardless of the selected methodology to tackle the multi-objective issue, the generation of different solutions is required.

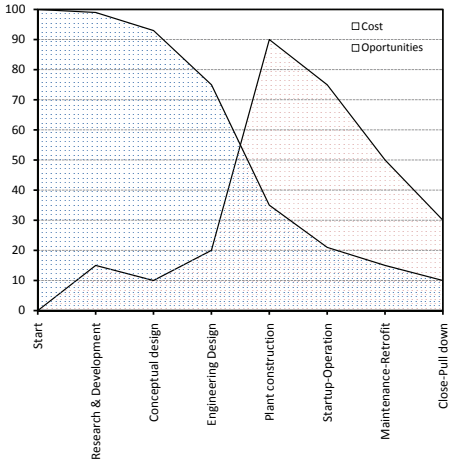
In the multiple-decision maker case, the agreement/disagreement between decision makers has to be modelled in order to cast the decision making problem into a multiobjective decision. Consequently another layer of modelling is required, which considers not only different objectives but different decision makers.

In this sense the approach of this thesis will be to treat problems as multiobjective, where a set of decision makers sharing similar objectives and preferences have to decide upon a given set of alternatives measured on different aspects.

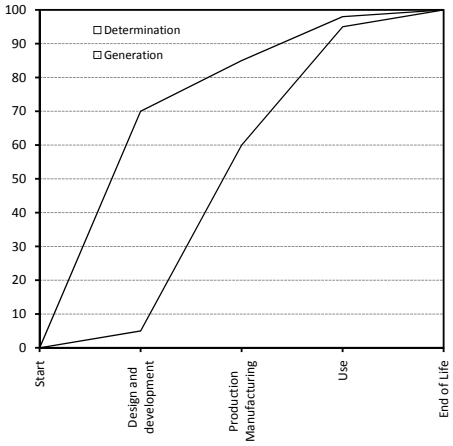
1.3 Sustainability and chemical process life cycle

According to (Cameron, 2005), different standards, such as ISO15288 (ISO, 2008) and ISO14001 (ISO, 2004) discuss the life cycle related to systems engineering. These standards introduce the following stages: concept, development, production, utilisation, support and retirement, which in the case of chemical process involve the following (Puigjaner & Heyen, 2006)[Sec. 4.2]:

- *Strategic planning*: initial ideas regarding resource utilisation or new product/service are generated, this phase is driven by new business opportunities.
- *Research and development (R&D)*: ideas are tested in lab, market research is done for promising products. From a process perspective research covers areas such as product qualities, reaction kinetics, product yields and physicochemical prediction models.
- *Conceptual design*: promising ideas are further developed and input-output process are generated. Initial process feasibility is assessed by means of general mass and energy balances. Simple models in steady state are used, some structural optimisation can be considered. Study of alternate reaction/production routes is performed.



(a) Modification cost and opportunities for sustainability considerations along process life-cycle phases adapted from Yang and Shi (2000).



(b) Determination and generation of environmental impacts along life-cycle stages, adapted from Rebitzer *et al.* (2004).

Figure 1.1: Cost and environmental considerations along chemical process life cycle.

- *Detailed design*: here the final engineering flowsheet is obtained (piping, controls and instrumentation). Models used are more complex and unit specific, steady state assumptions are dropped and dynamic behaviour is modelled for start-up, shutdown, emergency response and regulatory control.
- *Plant Installation/Construction and Commissioning.*
- *Operations*: it involves process day-to-day operations, problems associated to debottlenecking for retrofit, start-up or maintenance.
- *Decommissioning or Close/pull down*: this is an important consideration in the life-cycle given that most product and process have an "expiry" date and inevitably come to a natural end.
- *Remediation or rehabilitation*: this stage might involve significant financial resources and specialised chemical modelling and experimentation to consider ways of achieving remediation of land and environment.

Khor *et al.* (2007) makes a difference between phases and stages, where phases are the ones related to the process being developed while stages are the one that relate to the process being operative[18], this differentiation is not really important and consequently phase and stage will be used interchangeably.

According to Yang and Shi (2000) the opportunities for considering environmental concerns in particular, and SD in general, differ sharply along each of the phases of the process life-cycle. The earlier the phase is, the greater the freedom of changes is, i.e. the more the opportunities of inclusion of SD considerations are, and the lower the cost for modification is, see Fig 1.1(a). If no attention is paid until the construction stage, many practical opportunities still exist that could be disregarded, making the cost for retrofit increase. With regards to the number of technology options available for reducing environmental impact, it is larger in earlier phases of the process life-cycle, while costs associated with resolving environmental

[18]There are other life-cycle views, given that the interpretation of the term life-cycle differs. This is discussed by Emblemsvag (2003, Ch. 1), a product marketing perspective will detail (i) introduction, (ii) growth, (iii) maturity and (iv) decline; while a customer perspective will detail (i) purchase, (ii) operation, (iii) support, (iv) maintenance and (v) disposal.

issues typically increase exponentially as the process matures and the scale of equipment becomes larger (Khor *et al.*, 2007) (see Fig. 1.1(b)). According to Heinzle *et al.* (1998), it is found that 70% of the final costs were already determined during the development phase, and that the development phase itself, contributed only 5% to the total costs.

It is clear that the key phases in the whole process life-cycle to include SD considerations are those associated to design and R&D. Moreover it can be seen that during the conceptual design, modification costs are even lower than during R&D and detailed engineering design. The conceptual design phase lies between laboratory research and engineering design, and serves as the connecting link between them.

1.4 Remarks

Main conclusion from this chapter is the selection of diverse aspects from LCt and other concepts as framework required to tackle with SD. In this sense the unique feature of LCt in its perspective is used, this comprehensive scope along product/service life-cycle stages is useful for avoiding problem-shifting issues. This conceptual framework fits over the concepts of PP and CT, and shares the same level with IE. Furthermore, LCt allows for the usage of EMS and LCA as the procedural and analytical tools for the analysis of different process/product systems. However, the use of LCt does not only focus on the environmental dimension but also on social and economic aspects as well. Another important feature is the past, consideration of products using a functional unit. However, the SD idea, which, according to the UN definition of "fulfilling the needs", makes a shift from product to service: products are only a vehicle to deliver the service one uses to fulfil the needs of the population.

The inherent multidimensional nature of the SD problem requires the use of different metrics to measure each of the problem dimensions: environment, economic, social and institutional. Regarding SD institutional concerns are commonly considered in CSR programmes, and its measurement in this thesis will be disregarded.

The requirement of multidimensionality, due to the inability of summarising all possible metrics into a single one that entails all objectives simultaneously, is a key aspect of the SD problem. Apart from multidimensionality the SD is more complex due to the inclusion of different points of view rising from the different stake holders which assess different value to the metrics. Furthermore, in any future prediction related to complex systems, such as the design or operation of a chemical plant, there is always uncertainty.

In this section, a brief but comprehensive introduction to the variety of challenges that SD entails with regards chemical industry and specially to chemical process design has been presented.

The following thesis chapters try to address SD problems related to the chemical process design. Chapter 2 provides a state of the art regarding different areas of sustainability. First of all different applicable metrics are discussed in section 2.2, next methodologies that apply the former metrics and concepts are enumerated and critically revised in section 2.3. Due to the nature of the decision making process, special attention to put to the treatment of uncertainty in the case of chemical process design and operation, which is briefly revised under section 2.4. To end chapter 2 a discussion of presented literature results is done (section 2.5). Typical methods and tools used in the reviewed papers and in the thesis are described in chapter 3, which puts special emphasis on .

This thesis Part II, in its chapter 4 contains the proposed framework and guidelines towards inclusion of SD in process design and operation. The framework application to different case studies is performed in Part III which entails three different chapters. Continuous process design is considered in chapter 5, which discusses the selection of waste water treat-

ment options for phosphoric acid plant in section 5.1; the effects of raw materials changes in coal-coke co-gasification environmental profile, section 5.2; and the sustainability considerations of isopropyl myristate production via reactive distillation, in section 5.3. Batch process operation SD considerations are studied in chapter 6 focusing on the process's operational phase of its life-cycle. The design and retrofit of chemical process plants is studied in chapter 7. Part IV, contains conclusion and future research needs that this thesis has identified.

Chapter 2

State of the art and literature review

In the introductory chapter 1 the concept of SD is discussed in terms of the possible concepts and tools that can be used in industry. Moreover the different phases and stages of a process life-cycle (LC) were presented and the process design phase was selected for further study. This chapter presents a literature survey of current methodologies proposed for the design and operation of chemical processes and their associated supply chains (SC) taking into consideration sustainability aspects.

2.1 Incorporating sustainability into chemical process design and operation

The design of chemical processes consists of a series of steps where different refinements on a given process flowsheet are done aiming at generating a final design for the production of a given product. Two main approaches are available: one based on mathematical programming and the other centred on a hierarchical decomposition of decisions. In the latter the flowsheet is solved in layers, first the reaction steps, then separations, then heat integration and subsequently other layers as proposed by Douglas (1985). The former approach is based on the appropriate representation of all possible flow sheets for the production of a given product from different raw materials using different processing units by means of a process "superstructure". This superstructure is commonly coded using a mathematical program which is subsequently optimised. The principal proponents of this approach are Biegler *et al.* (1997).

A deep review of the inclusion of environmental concerns in process design was done by Cano-Ruiz and McRae (1998). These authors recognise four trends towards consideration of environmental impacts:

- inclusion of waste treatment infrastructure inside system boundaries; making the waste handling problem to be incorporated into process synthesis step.
- materials integration as an extension of the successful application of energy integration techniques, with efforts towards potential matches of wastes as raw materials across process and plants within a SC.

- use of Life-Cycle thinking (LCt). Under this concept fit all attempts that include the possible environmental impacts that rose during the whole life-cycle stages of a product, focusing mainly in raw material and energy.
- emphasis shift in the problem formulation, from effluent concentration towards environmental impacts.

The most important conclusion of the previous review is that the adoption of strategies that consider the environment as design objective instead of an operation constraint can lead to the discovery of novel processing alternatives that achieve both improved economic and environmental performance. Other recent reviews in the field by Grossmann (2004) and Li and Kraslawski (2004) emphasise on the current research needs regarding the incorporation of environmental issues, using an extended system boundary and different metrics.

Several methodologies have been developed within the chemical engineering community including SD considerations for the design of chemical processes. Any design methodology which addresses process design proposes different ways of (Li & Kraslawski, 2004):

- *problem representation*; it should allow for all possible design alternatives to be included;
- *solution strategy*; it should aim at finding the best alternative without enumerating all the possible alternatives;
- *solution evaluation*; it should ensure that all alternatives are evaluated and compared effectively.

Regarding the design problem a classification can be done based on the:

- (i) *Detail level*, from conceptual (very broad flowsheet description) to detailed design (specification of process control loops).
- (ii) *System boundary*, from mesoscopic (a set of processing units within a flowsheet) towards macroscopic (possible inter-plant connections or the whole product SC).
- (iii) *Subjects of design*, which can encompass from unit operation (unit operations specifications and flows will be the variables) downwards to molecular (design of solvents or materials) design[1].

The former three points can be combined in several ways. Typical conceptual and detailed design are done at unit operation considering connectivity between unit-ops, which is commonly regarded as the mesoscopic scale. Design of materials which is considered microscopic scale only uses a detail level that considers input-output molecules or preferred properties for different molecules structures. In the case of macroscopic design input-output relationships are used to model each of the echelons that encompass a chemical SC (Gani, 2005).

Several books treat the design of chemical processes, each one of them emphasises chemical process design in a different way, but just a handful of them define clear guidelines regarding inclusion of SD considerations. Sikdar and El-Halwagi (2001), focusses on tools applicable for process design and identifies three main areas (i) conceptual process design [Chs. 1-11], where they discuss application of mathematical programming and hierarchical approaches to design single plants, (ii) macroscopic design [Chs. 12-14], where they discuss approaches that take into account inter-plant connections, and finally (iii) molecular design [Chs. 15-17], where they discuss different strategies towards solvent and chemical synthesis steps selection. In the case of Allen & Shonnard (2002a, Chs. 8-11), their design approach consists in evaluating the process performance at different detail levels, namely: (i) situations where only the chemical structure is known (input-output relationships), (ii) conceptual/preliminary process designs, which also include wastes and emissions estimation, and (iii) the evaluation of

[1] This area is also known as Computer Aided Molecular Design (CAMD).

flow sheet alternatives. In the case of point (i) they measure the environmental aspects of the process by using metrics that can be calculated on the chemical structure of the compound such as the persistence, bioaccumulation and toxicity. In the case of point (ii) the most important aspect according to the authors is the estimation of environmental releases (emissions and wastes), while for point (iii) detailed information is required. Ayres & Ayres (2002, Chs. 8-13), present a different approach where emphasis, in the sense that the facility is seen as one of the members of an ecosystem and the focus is on the model of plants as a whole. The authors propose a methodology which is based on MFA-SFA and process simulation. A similar approach is adopted in Kutz (2007). Other books emphasise the selection of appropriate metrics (Lapkin & Constable, 2009), and a LC point of view (Sonnemann *et al.*, 2004). In general all these methodologies require of multiple objectives and the application of a "systems perspective". All reviewed authors coincide in the need of the implementation of LCt in process design, emphasising the extension of the system boundaries to include the LC of different echelons and the use of LCA as part of a toolbox combined with others and not as a single stand alone method.

Uncertainty of different types and magnitudes exists in all decision making frameworks, may it be pure engineering decisions, policy making or environmental assessments. It has been already pointed out that, there is a need for approaches that account for uncertainty that rises from the "*precautionary principle*"[2] being taken into account. It is increasingly a requirement in model-based decision support that uncertainty has to be communicated (Walker *et al.*, 2003).

A better understanding of how uncertainty impacts on decision making support frameworks helps in identifying and prioritising effective and efficient research and development activities. It has been also emphasised that the ultimate goal of decision making in the face of uncertainty should be to reduce the undesired impacts from surprises rather than trying to eliminate them (Dewar, 2002).

Due to the fact that SD multidimensionality requires the use of different metrics a review of them is done, in next section 2.2. Besides the former methodologies presented in books, the chemical engineering literature has proposed a great deal of other approaches to tackle the process considerations related to the SD problem; a review of the current state of the art regarding methodologies for SD process design is done in section 2.3. The consideration of uncertainty given that decisions are being assessed on future events is considered under section 2.4.

2.2 Sustainability indicators applicable to chemical industries

Any metrics selection is a complex issue, due to problems encompassed by the different users of these indicators, and the different scope of each metric (Olsthoorn *et al.*, 2001). Each stakeholder will interpret SD in a given way defending the interests of the group that he/she represents. Table 2.1, shows the potential alignments of different stake holders regarding SD concerns.

Stakeholders point of view is a matter not of disagreement about facts but due to differences in values rising from the interest and concerns that each group has. While this problem of values seems appealing to be tackled, the objective of a framework towards SD should be aimed at providing the least biased information regarding the different processing options. Consequently many different metrics should be provided and consensus on which ones should be used has to be achieved by the decision makers. The consensus achieving part will

[2] See section 1.2. This principle deals with situations where uncertainty prevails regarding decisions about activities potentially generating harm.

not be further studied[3], and this thesis will emphasise on the different metrics and methodologies available.

Many indicators proposed are not quantitative, and might only be "*yes*" or "*no*", or some formal expression of compliance to a standard. Although in every-day life situations decision making relies on highly subjective and qualitative indicators, in formal decision-making situations it is difficult to make assessments without using quantitative measures, regardless of their true meaning and reliability (Azapagic & Perdan, 2000). Consequently the review will emphasise on quantitative metrics while disregarding the possible use of qualitative metrics. In the case of mathematical optimisation metrics are also known as objective functions (OF).

There is consensus on the requirements for effective metrics, they should satisfy the following criteria (Sharratt, 1999; Tanzil & Beloff, 2006):

- simple and understandable to a variety of audiences;
- reproducible and consistent in comparing different time periods, business units, or decision alternatives;
- robust, unbiased and non-perverse;
- relevant and complementary to existing regulatory programs;
- cost-effective in terms of data collection, making use of data already collected or available for other purposes, while minimising the effort of gathering new data-sets;
- stackable along the SC or the product/process LC stages;
- scalable for multiple boundaries of analysis; and
- protective of proprietary information.

However, Sharratt (1999) states that this list should be understood as an unachievable ideal, and some compromise is inevitable. Metrics should be able to reproduce changes at all levels in the system, it would be a fallacy to have a set of metrics that does not take into consideration the closely knit network of cause-effect relationships that comprise chemical processes (Constable *et al.*, 2009). This systems-wide approach requires the collection of more than one single metric, which implies a multivariate view of the system. The selection of one set of metrics in favour of the others will rely on the agreement between the decision makers and in the underlying principles of each of the metrics calculation methodologies.

Table 2.1: Potential interests in sustainability issues of process design related stakeholders, adapted from Azapagic *et al.*,(2006; 2005a) and Fiksel (2003)

Stakeholders	Sustainability interests and concerns		
	Economic	Environmental	Social
Employees	++++	+++	++++
Trade Unions	++++	+	++++
Contractors	++++	++	++
Suppliers	++++	+	+
Customers	++++	+++	+++
Shareholders	++++	+++	+++
Creditors	++++	+++	+++
Insurers	++++	++++	++++
Local communities	++++	++++	++++
Local authorities	++++	++++	++++
Government	++++	++++	++++
NGOs	+	++++	++++

\+ no interest/concern
++ little interest/concern
+++ some interest/concern
++++ strong interest/concern

[3]Some methodologies for studying possible trade offs are summarised in section 3.1.3.

Table 2.2: Comparison between sustainability frameworks proposed for chemical engineering projects.

SD area	Azapagic and Perdan (2000)	IChemE	AIChE
Environmental	Environmental impact Environmental efficiency	Environmental efficiency	Resource use Emissions measurement Compliance management
Economic	Financial metrics Human Capital	Financial metrics Investments	Value chain management
Social	Ethics Welfare	Workplace Community benefit	Safety performance Social responsibility
Institutional	Voluntary actions		Sustainability innovation Product stewardship

2.2.1 Current metrics in sustainability frameworks

Typical frameworks for assessing the SD of enterprises (type III systems), separate metrics in three main areas: environmental, economic and social, and present guidelines regarding the measurement of institutional SD. As discussed in section 1.2, institutional SD metrics are more related to the enterprise CSR strategies and are not easily linked to process operation.

Azapagic and Perdan (2000) proposes a general framework of SD indicators for industry, using both quantitative and qualitative indicators. The amount of indicators included in their framework is large (more than 30) using the following classification:

- *Environmental indicators*: *Environmental impacts*, *Environmental efficiency*, and *Voluntary actions*.
- *Economic indicators*: *Financial indicators*, and *Human-capital*.
- *Social indicators*: *Ethics indicators*, and *Welfare indicators*.

They propose a modular application of them due to the large number of available metrics. Assessments can be done with some of them based on data availability and the analysis objective.

A similar set of metrics is the one proposed by the IChemE (Tallis, 2002). They provided a classification of metrics as follows:

- *Environmental indicators*: *Resource use*, and *Emissions*.
- *Economic indicators*: *Profit, value and tax*, and *Investments*.
- *Social indicators*: *Workplace*, and *Society*.

In the case of the Sustainability Index developed by the Institute for Sustainability (IfS) of the AIChE, it is proposed to measure companies with respect to seven items: strategic commitment, SD innovation, environmental performance, safety performance, product stewardship, social responsibility, and value chain management (Cobb *et al.*, 2009).

While former approaches can help the comparison of different enterprises and show how each enterprise deals with different SD related issues, the IChemE and AIChE's metrics are mostly qualitative and specially suited for assessing the sustainability of enterprises (as a whole), but are not suitable for single process designs alternatives, see Table 2.2. Moreover, most of the former metrics are qualitative and are not helpful for process design, where for example the implementation of an EMS or the compliance with REACH are not part of the decision boundary when dealing with decisions at the process design level. Process design entails a type IV system boundary; a flowsheet, a set of plants interconnected, a given unit operation are the typical boundaries drawn. Within these boundaries and from the available information there is no way of assessing many of the qualitative metrics. Despite the fact that adhering to a given CSR program is seen as good sustainable practises, its quantification remains not feasible.

A different approach towards metric formulation is done by Constable *et al.* (2009); they propose a different classification for metrics closely related to the process, considering metrics in the following areas:

- *Materials*: physical form and properties; mass; inherent hazard (toxicity, stability and reactivity); cost; renewability and recyclability.
- *Equipment*: unit operation type; number of unit operations; size; scalability and controllability.
- *Operability*: throughput/cycle time; robustness; energy consumption; ease of cleaning and maintenance.
- *Environmental, Health and Safety (EHS) risk*: occupational exposure; environmental impact; process safety.
- *Quality*: purity/impurity profile.

In most cases, the former metrics are the summation of mass flows, analysis on the number of unit operations and other similar considerations, all of them are quantitative and closely related to the process flowsheet. On the contrary AIChE's and IChemE's metrics are closer to the enterprise as a whole and not to a single part of it and consequently its application to type IV systems is difficult. In the case of continuous plants there are opportunities to look at the collection of the unit operations/processes and develop metrics that will enable to work towards significant mass and energy integration amongst processes. However in the case of the batch industries, this is not generally the case given the employment of a multi-purpose campaign approach, with a wide variety of nature of processes over time. It is argued that metrics in the batch context are different than in the continuous one case (Constable *et al.*, 2009), but despite its way of operation (i.e. continuous or batch), emissions and raw material consumption are measurable and both type of plants can be assessed in those terms.

It is noteworthy that all of the quantitative metrics proposed before are of two possible types: (i) mass/energy/money flows normalised using some reference value that it is set according to the objective of the study; or (ii) a set of weighted sum of values of the former, that are normalised accordingly.

2.2.2 Metrics selection, normalisation and weighting

Very few contributions have been regarding metrics selection for measuring SD. In most cases, the authors present a broad set of metrics and the reader is supposed to select the ones that appropriately fit the analysis objectives. In this sense Wehrmeyer *et al.* (2001) discuss, in the environmental context, that metrics depend on the purpose of the application (reporting, interpreting or comparing behaviour), and that the existence of several indicators, shifts the decision-makers problem from "*how can sustainability performance of a company/process be measured?*" towards "*which of these indicators do make most sense in given circumstances?*". Thus, the question the decision-maker has to answer is "*how many (and which) indicators are the minimum necessary to give an approximate yet reasonably robust description of the comparative sustainability performance of alternatives?*".

Reductionist approaches tend to quantify and aggregate different dimensions of SD with a single unit of measurement. It has been argued that reductionism is the dominant paradigm regarding SD assessments. Recently, Gasparatos *et al.* (2008) reviewed different reductionist approaches for measuring SD, the authors classify these approaches into three: (i) monetary tools, (ii) biophysical models and (iii) composite indices. They conclude that none of these reductionist approaches seems capable of assessing SD in a holistic manner. Reductionist approaches shortcomings are due to the multitude of environmental/economic and social issues combined with intergenerational and intragenerational concerns.

Olsthoorn *et al.* (2001) and Wehrmeyer *et al.* (2001) reported that many environmental variables have substantial correlations between them (multicollinearity). In this sense there is a strong correlation between CO_2, SO_2 and NOx emissions in fossil-fuel fired power stations and a strong correlation between BOD and COD in water emissions of paper companies. As a result, they propose that redundant variables can be excluded for the benefit of one variable that represents a set of highly correlated variables. The selection procedure presented by the authors relies on the use of principal component analysis (PCA), see section 3.3. Variables that show a high degree of correlation (i.e. are present in any of principal components (PC) with a high coefficient value), can be substituted by the PC itself.

It has often been advocated that quantitative indicators should be normalised to a unique measure of performance across different sectors in order to be comparable and used in weighting decision alternatives and comparing operational units (Azapagic & Perdan, 2000; Tanzil & Beloff, 2006). In this sense all MCDA techniques (see section 1.2.3) require that alternative's attributes are normalised before weighting. Some of the examples include normalisation to the physical flows in the system (e.g., per tonne of product output), to a measure of economic performance (e.g. turnover of sales, shipment value, value added, operating profit, number of employees or total investments), or to a defined functional unit (FU) of the system under study (as is the case of LCA, see section 3.4.1). With regards to the use of value added, its use at the macroeconomic level in systems of type II, does not pose problems, but at corporate or process levels, it is difficult depending on the assumptions adopted and the socio-economic and industrial context under consideration (Olsthoorn *et al.*, 2001). In the context of LCIA (see section 3.4.3) normalisation is conducted to obtain a comprehensive view of impact category indicator results. Normalisation values in LCIA are calculated on the basis of chosen reference systems, e.g. all society's activities in a given area and over a specified period of time, or the interventions of the world as a whole in a certain year (Heijungs *et al.*, 2007; Huijbregts *et al.*, 2003)

It has been argued by Azapagic and Perdan (2000) that it is not possible to fix a single measure of normalisation that would apply uniquely in all cases and for all industrial sectors. To support such argument the authors consider the case of the extractive industry and two sub-sectors within it: production of coal and diamonds.The former example sheds light into a key aspect of indicator normalisation; it shows that depending on the service that the product provides, which can be taken into account in terms of production volume or value generation, the indicator will be biased.

Therefore, it is only logical to express any indicator of SD per unit of service that the system delivers. This implies that alternative comparisons of the level of SD can only be made between systems that deliver the same set of services. The set of services that a given system provide is closely related to the FU that it is defined for such system. It is clear that depending on assessment goal the appropriate normalisation has to be decided upon. For product-oriented analysis, i.e. compare different products delivering an equivalent service or function, the indicators can be expressed per unit mass of product. While in process-oriented assessments, i.e. comparison of different processes providing similar services, total (annual) output, or the process flow may be a more appropriate units of measure. In company-oriented analysis both measures can be used depending on the context (Azapagic & Perdan, 2000). The selection of FU and system boundaries are closely related and are further discussed under section 3.4.1.

Weighting, can be defined as the quantitative element in which the relative importance of different metrics is assessed. Such assessment requires of political, ideological and or ethical values to be addressed and valued (Finnveden, 2000). Different metrics weighting and aggregation is generally performed in order to reduce the number of aspects that have to be

considered altogether. It is a common feature of many of the ready to use LCIA end-point methods, and it is widely used in MCDA techniques to generate a single score for a set of indicators (see section 3.1.3). With regards to weighting in LCIA, Finnveden *et al.* (2009) classify weighting methods in (i) monetisation, (ii) panel based or (iii) distance-to-target methods. In the first case and similarly to the case of SD metrics, the values are expressed in money values (see section 2.2.3), while in the panel based ones a group of people is asked about their values. In the third case, weighting factors are calculated in terms of some type of target value, but in this last case different targets are not weighted against each other. Any weighting set, for any kind of metrics, embeds the subjectivity of the decision maker and no general agreement can be found. No unique set of weighting can be constructed that fits for all SD problems, given that weights are essentially value judgements and consequently no "objective" value can be given to them.

Indicators aggregation provides a mean for compensation, higher performance of indicator X has the ability to compensate for lower performance of indicator Y. This compensation ability is highly questioned in SD, with two strong divergent points of view: *strong sustainability*, where trade-offs are not allowed or are restricted, and *weak sustainability*, where they are permissible. In the case of weak sustainability different forms of capital can be substituted aiming at non-declining utility while the concept of critical natural capital is also used to describe elements of the biosphere that cannot be traded off (e.g. critical ecosystems or species), due to physical or technological constraints. Many of the criticism present in weak sustainability approaches is shared by any Cost Benefit Analysis (CBA) as discussed in section 2.2.3. The effect of compensation could be diminished if geometric aggregationis used instead of additive aggregation (Gasparatos *et al.*, 2008).

2.2.2.1 Remarks

It seems that the normalisation factor is defined mainly from the scope of the problem being taken into account. In its definition the concept of the service that the process/product is providing is the most important aspect. Regarding weighting it depends on the set of metrics used and the value assigned by the decision maker (or the methodology employed). It has to be emphasised that the compensability obtained using weights and aggregation to generate a composite index implies the existence of trade-offs and renders a weak-sustainability approach, this is not necessarily a disadvantage but is ts a feature of the methodology that the decision maker has to be aware of (Gasparatos *et al.*, 2008).

Following current state of the art classifications, SD metrics in this thesis will be classified into three aspects: economic (see section 2.2.3, where economic reductionist approaches are also discussed), social (see section 2.2.4, process safety related metrics are further discussed there) and environmental (see section 2.2.5, LCIA methods are also reviewed there). Another important set of metrics that have a weighting embedded are the ones that rise from ecological demands, such are the cases of the sustainable process index (SPI) (Krotscheck & Narodoslawsky, 1996; Narodoslawsky & Krotscheck, 1995) and the Ecological footprint (EF) (Huijbregts *et al.*, 2007), and the ones derived from thermodynamic functions as the case of Cumulative Energy Demand (CED) (Huijbregts *et al.*, 2006) and other metrics based on Exergy (CExD) or Emergy (CEmD) (Bakshi, 2002). These indicators based on thermodynamic or ecological concerns are also known as biophysical and they will be reviewed in section 2.2.6.

2.2.3 Economic indicators in process design and operation

Economic aspects have travelled side by side to chemical engineering since its very beginning, and different indicators are used to check the economic-viability of different processing

options.

In both retrofit and starting up (green-field) projects standard industrial practise calls for estimation of potential investment, working capital, sales revenue, and operating expenses, to assess long term impact of the project. The financial evaluation of a project, known also as Cost Benefit Analysis (CBA)comprises basically three major steps:

(i) *Estimation of capital costs*: these represent discrete expenditures comprising a fixed capital (also known as investment costs) and working capital. Fixed capital can be estimated using factored methods while working capital is associated to inventories, cash and accounts receivables. Capital costs are expressed in monetary units [(U$D, EUR)].

(ii) *Estimation of cash flows*: these represent the surplus of incomes over expenditures for all periods, calculation of these cash flows requires estimation of expected revenues and operating costs. Cash flows are expressed as monetary time flows [(U$D, EUR)/(year, month, week)].

(iii) *Evaluation of economic indicators*: this last step comprises the use of cash flows for the calculation of the selected metric. Besides cash flows, other parameters such as interest rate, depreciation and savage costs are also required.

Regarding the calculation of cash flows, (Eq. 2.5) gets complex when dealing with environmental and social aspects, the complexities are related to the possibility of generating realistic accounting for internal and external costs associated with pollution, waste minimisation, waste treatment and waste management and its social implications (Brennan, 2007), some of which are further discussed in section 2.2.3.1. In general the calculation of an economic metric can be summarised in the following Fig. 2.1.

Surprisingly, a recent survey by Pintaric and Kravanja (2006) of economic OFs used in optimisation problems related to chemical process design, revealed that the most common OFs are different types of costs (see Eq. 2.1). Optimisation of profit or economic potential (see Eq. 2.3) is found less common, while the usage of net present worth or value (NPW, NPV, see Eq. 2.4) or monetary value added are found rarely. This issue could be traced to some discouraging arguments that are found in process design books (Luyben, 2006)[4]. However, other process design books emphasise on the use of metrics where the time value of money is taken in to account (Biegler *et al.*, 1997) [Ch. 5], in some cases the application of NPV and discounted cash flow for profitability evaluation and the economic comparison of alternatives, are the most acceptable, as recommended by Peters & Timmerhaus (1991, Ch. 10).

The following are the operational definitions of commonly used economic indicators (Pintaric & Kravanja, 2006).

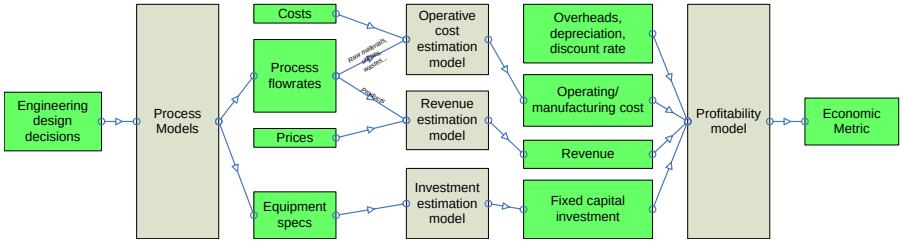


Figure 2.1: Overall variables and models relationship in the calculation of an economic metric.

[4] "*The prediction of future sales, prices of raw materials and products, and construction schedule is usually a guessing game made by marketing and business managers whose track record for predicting the future is almost as poor as that of the weather forecaster.*"

- Total Annual Cost (TAC, C_t), it comprises annual operating costs (C_t^{op}) and the annual depreciation D_t for fixed capital goods for period t. D_t is customarily estimated usually by the straight line method, I_f and t_d, represent the fixed capital cost and the depreciation period respectively.

$$C_t = C_t^{op} + D_t = C_t^{op} + \frac{I^f}{t_d} \qquad \forall t \tag{2.1}$$

$$I^f = IFC_0(S/S_0)^{\alpha} \tag{2.2}$$

  Fixed capital costs (I^f) are usually calculated using factored methods, which are correlations based on equipment geometry. There are correlations using Eq. 2.2 for each equipment type, see Biegler *et al.* (1997, Ch. 4)[5]. IFC_0 is an investment base cost which is usually selected on the basis of material used and working pressure; and S, is a given equipment characteristic (e.g. S is the area in the case of heat exchangers while is the diameter and height in vessels); the value of α aims at reflecting economies of scale[6]. Working capital is mainly associated to stream flows, being the stream a product, raw material or utility use. Prices of each stream are required, for the calculation of the associated monetary flow for each stream, see Eq. 2.5.
- Profit before taxes (PB_t), is calculated considering revenues (R_t), minus total cost for the same period t.

$$P_{Bt} = R_t - C_t \qquad \forall t \tag{2.3}$$

- Net Present Value (NPV, see Eq. 2.4), is the arithmetic sum of all cash flows present worth. It combines the discrete and continuous cash flows for each of the Np periods (F_t^C) into the net cash flow of the project.

$$NPV = -I_f + \sum_{t=1}^{Np} \frac{F_t^C}{(1+r_d)^t} \tag{2.4}$$

  usually I_f is the project investment on fixed capital goods, which is usually performed in the first projected period, however if its done in different periods its discounted value is used instead.
- Corporate Value (CV), is calculated from the cash flows and is used as a financial indicator that is able to properly assess the trade-off between net operating income (i.e., profit) and capital efficiency (i.e., fixed assets and net working capital), and liabilities (e.g. debt borrowed).

Eq. 2.5 provides a simple way of assessing cash flows based on input and output mass flows per t period (M_t^{in}, M_t^{out}) and their associated period prices ($P_t^{M^{out}}, P_t^{M^{in}}$). At the conceptual stage of process design where only material flows are known expression 2.5, can be applied, however in the case of whole chemical supply chains different expressions are used, see section 7.3.3.

$$F_t^C = M_t^{out} P_t^{M^{out}} - M_t^{in} P_t^{M^{in}} \qquad \forall t \tag{2.5}$$

While the application of NPV as defined in Eq. 2.4 is the backbone of the CBA of any project, the use of annual equivalent metrics (such as annual equivalent profit AEP, see Eq. 2.6), is

[5] Correlations are available for vessels, heat exchangers, columns/trays, compressors, pumps and others, with different accuracy; which can range from 40% to 3% error in the estimate.

[6] In many cases the heuristic sets $\alpha = 0.6$, but its value depends on the actual cost being estimated.

sometimes preferred over NPV analysis, this is due to current practise of corporations, which commonly issue annual reports and develop yearly budgets.

$$AEP = \sum_{t=0}^{Np} \frac{F_t^C}{(1+r_d)^t} A_f = \sum_{t=0}^{N_p} \frac{F_t^C}{(1+r_d)^t} \frac{r_d(1+r_d)^{Np}}{(1+r_d)^{Np}-1} \tag{2.6}$$

$$TAPPS = \frac{AEP}{FU} \tag{2.7}$$

The second term of Eq. 2.6 is known as the annualization factor (A_f) (Gollapalli *et al.*, 2000). Other possibility is the use of total annualised profit per service unit (TAPPS) as calculated per FU, see Eq. 2.7. FU, is the number of functional units provided during project's life. TAPPS can be understood as the potential maximum profit per unit of product, this metric is more convenient to compare with other environmental metrics which are typically calculated per unit of service. Generally AEP and TAPPS are preferred when (i) consistency of report formats is desired, (ii) there is a need to determine unit costs or profits, specially when projects must be broken into unit cost (or profits) for easy comparison with alternatives, (iii) or when project lives are unequal.

Regarding the use of NPV or CV, both metrics analyse discounted cash flows, the difference between them is related to which items are considered for its calculation. NPV and CV will provide with the same results if (i) there are no delays in payments for services received or product delivered, (ii) throughput time is small and the product in process value can be disregarded, and (iii) enterprise assets are financed only by shareholders capital and not by debt (Laínez *et al.*, 2007). To sum up, CV will provide with more information for cases where the cost structure is heavily influenced by the net working capital and debt.

The selection of the discount rate (r_d) for any time discounted metric is also subject of controversy, given that it represents the trade-off between the enjoyment of present and future benefits and affects directly intergenerational aspects of SD. Higher r_d's devaluate future impacts and consequently they count little on long time horizon projects, which could be perceived as contrary to the interest of future generations[7]. In some cases it has been suggested to adopt very low discount rates (even zero), in cases where mortality or extinction of species is possible (Gasparatos *et al.*, 2008).

It is generally recognised that in environmental accounting words like "*full*", "*total*" and "*life-cycle*" are used to indicate that not all costs are captured in traditional accounting and capital budgeting practises (Sinclair-Rosselot & Allen, 2002a). According to Bartelmus (2002), environmental economists attempt to put a monetary value on the loss or impairment of environmental services as a first step towards "internalising" these "externalities" into the budgets of households and enterprises. Similarly to environmental accounting, social externalities can be also considered. The principle followed in these practises is that if costs are properly accounted for, business management practises that foster economic performance will also foster superior environmental/social performance.

2.2.3.1 Methodologies that Internalise Costs

These methodologies aim at including costs which are not usually considered in the bill of materials, extending the attention not only to costs derived from chemical purchases and plant operation. Precise definitions of different terms in this area are elusive given their current evolution. However some of them need to be clarified: *internal* and *external costs*, the

[7]This could lead to a non-equitable distribution of costs and benefit through time by forcing future generations to bear a disproportionate cost.

Table 2.3: Pollution control capital expenditures, for selected industrial sectors in the US (Sinclair-Rosselot & Allen, 2002a)

Industry sector	As a % of sales	As a % of value added	As a % of total
Petroleum	2.25	15.42	25.7
Primary metals	1.68	4.79	11.6
Chemical manufacturing	1.88	3.54	13.4

former are costs borne by a facility while the later, also known as societal costs, are the costs to society by the facility's activities. *Overhead* or *indirect costs* as opposed to costs of direct materials, consists of any cost that the accounting system pools facility-wide and does not allocate among facility's activities. Examples of these accounting practises are Full Cost Assessment (FCA) (USEPA, 1997)and the Total Cost Assessment (TCA) (AIChE-CWRT, 2000). These methodologies are also known as Environmental Cost Accounting (ECA) practises.

TCA can be briefly defined as "*the identification, compilation, analysis, and use of environmental and human health cost information associated with a business decision*". The TCA method uses five tiers for costs as follows:

- Type 1 costs *are direct costs for the manufacturing site*, such as direct costs of capital investment, labour, raw materials, and waste disposal. May include both recurring and non-recurring costs. Includes both capital and operating and maintenance costs. This type of costs are the ones that traditional accounting practises take care.
- Type 2 costs *are potentially hidden corporate and manufacturing site overhead cost*s, such as indirect costs not allocated to the product or process. They may include both recurring and non-recurring costs, both capital and operating and maintenance costs and outsourced services.
- Type 3 costs *are future and contingent liability costs*, such as potential future contingent costs include fines and penalties caused by non-compliance, future liabilities for clean-up, personal injury and property damage lawsuits, natural resource damages, and industrial accident costs.
- Type 4 costs *are internal intangible costs paid by the company*, these are difficult to measure cost entities such as, consumer acceptance, customer loyalty, worker morale, worker wellness, union relations, corporate image, and community relations.
- Type 5 costs *are external costs that the company does not pay directly*, including those borne by society and from deterioration of the environment by pollution within compliance regulations.

From Type 1 towards type 5, the difficulty of estimation/measurement of costs increases greatly (Emblemsvag, 2003). USEPA (1997) emphasises on the difference between liabilities and intangible costs, while the first is cost resulting from legal actions (e.g. personal injury, property damage or natural resources damage liabilities), the other are not possible for easy estimation due to fact that environmental or social degradation can not be easily remedied or measured.

Among the easiest environmental costs to track are the ones associated with treating emissions and disposing of wastes (Tier 1). These costs have already been proven to be a high percentage of the expenditures and of the value added for several industrial sectors, see Table 2.3.

One form of Type 1 cost are eco-taxes; these are different economic instruments that are available for the government to encourage greater environmental responsibility. Brennan (2007) and UNEP (2007) classifies them as (i) emission charges related to quantity and quality of pollutant and damage done; (ii) user charges for treatment of discharges, related to cost of collection, disposal and treatment; (iii) tradable/marketable permits, and (iv) deposit refund systems involving refundable deposits paid on potentially polluting products. Point

(iii) enables pollution control to be concentrated amongst those who can do it economically without increasing total emissions. The idea behind these schemes is to make firms pay for their emissions so that a financial incentive to decrease emissions is provided. A cap is set on emissions, businesses are allowed to buy or sell from each other the right to emit a certain pollutant. Firms exceeding their emissions cap have to buy extra credits to cover the excess, providing an incentive for them to operate under the capped level, while those that do not use up all their allowances can sell them, providing the least-polluting firms with an extra revenue and an incentive to further reduce emissions (Young, 2008). Such a setup is already in effect in some countries and for certain industries under the European Union-Emissions Trading Scheme (EU-ETS)[8]. Similar schemes are available for SO_2 (acid rain program) and NO_x air emission markets for some zones in the USA by a US-EPA programme. According to Matthews *et al.* (2008) the scope of these government schemes varies, estimating only direct emissions (Tier 1) and emissions from purchased energy (Tier 2), with less focus on the SC context which leads to large underestimates of the overall emissions. Other estimations include the total SC up to the production gate, also known as cradle-to-gate approach (Tier 3) while Tier 4 emission estimations considers the whole product LC, by considering emissions occurring during distribution and product end of life stages. These extended scopes are expected to better aid effective environmental strategies since both firms and consumers have an important influence over the emission footprints through their "purchase" decisions.

Indirect costs (Type 2) are more difficult to estimate, given that these costs are borne by facilities regardless of whether they choose to quantify them or to assign them to project or product lines, and consequently "hide" them as overheads or indirect costs. This is one of the main reasons that environmental considerations are lost, given that they are not appropriately allocated and cost or benefits of green engineering projects get masked. These costs can be grouped into (i) waste treatment costs ($Cost_t^{WT}$, see Eq. 2.8), (ii) regulatory compliance ($Cost_t^{com}$, see Eq. 2.9) and (iii) hidden capacity costs. Many facilities have centralised waste treatment plants[9], given that these facilities provide a service for the whole chemical complex the cost of waste treatment is usually divided for the whole plant, however its costs should be considered depending on the needs of each product line. Sinclair-Rosselot and Allen (2002a) and Chakraborty and Linninger (2002) provide order of magnitude estimates for treatment of water, air and soil effluents ($Price_s^{WT}$), depending on the selected sink s. For the case of point (ii) these tasks are performed by managerial employees which divide their working efforts in different tasks, and the assessment will depend heavily on the company structure. One possibility for its estimation is given in Eq. 2.9, which relies on the estimation of the reporting frequency required for document d ($Freq_d$) and the cost for its emission ($Cost_{dt}^{com}$) . With regards to (iii), these costs are usually hidden due to the inability of the costs structure to accurately discriminate the source of costs.

$$Cost_t^{WT} = \sum_s Price_s^{WT} Flow_{st}^{WT} \qquad \forall t \tag{2.8}$$

$$Cost_t^{com} = \sum_d Freq_d Cost_{dt}^{com} \qquad \forall t \tag{2.9}$$

Potential future costs (Type 3) include several different categories all related to liabilities, due to the different sources of these liabilities (compliance obligations, civil/criminal fees, remedial costs, compensation/punitive damages or natural source damage, $Cost_t^{liab}$),

[8]Which considers an estimated economic damage of about US$85 for each ton of CO_2 and caps on GHG emissions (Stern, 2006)

[9]These facilities could be a waste water plant (WWT) for aqueous effluents, a flare or an incineration plant for air effluents.

sources are very different, but in general the procedure for their estimation relies on risk estimation and the expected cost of such risk. Sinclair-Rosselot and Allen (2002a) propose to calculate them making an assessment, based on enterprise historical data, on (i) the probability/frequency of that a liable event l might occur ($Freq_l$) and (ii) the costs associated to that event ($Cost_{lt}^{liab}$). These type of costs can be estimated similarly to the case of compliance costs, see Eq. 2.10.

$$Cost_t^{liab} = \sum_l Freq_l Cost_{lt}^{liab} \qquad \forall t \tag{2.10}$$

With regards to internal and external intangible costs (Type 4 and 5), the TCA methodology, provides of possible data sources and examples, but no standardised method to fulfil such estimations. The major proportion of costs arising from environmental damage is borne by the natural environment and the wider community, since these costs fall outside the conventional accounting framework of the polluter, they are called external costs or externalities. These costs are associated to (i) air pollution, such as degradation of buildings and human health; (ii) water pollution, such as loss of marine life or recreational value and (iii) soil pollution, such as loss of biodiversity (Brennan, 2007). Different techniques can be used to provide with value to environmental services, Bartelmus (2002) classifies them as follows:

- *Market valuation*: it uses prices for natural assets which are observed in the market. It is usually applied to economic assets of natural resources (such as fisheries, forests and mines), though trading of pollution permits could also generate a market value for environmental assets of waste absorption capacities.
- *Maintenance valuation*: allows for costing of losses of environmental functions that are typically not traded in markets. Maintenance costs are defined as those that: would have been incurred if the environment had been used in such a way as not to have affected its future use. They refer to best available technologies or production processes with which to avoid, mitigate or reduce environmental impacts. Of course, these costs are hypothetical since environmental impacts did occur.
- *Damage valuations*: these are contingent valuation methods (CVM), in a CVM the stated preference of the public regarding a particular environmental service (not traded in a real market), is measured by its Willingness To Pay (WTP) for that service, or its Willingness To Accept (WTA) compensation for the loss of such service. WTP and WTA are inconsistent with market prices because of their inclusion of consumer surplus. Some environmental impact assessment techniques (e.g. Steen (1999a)) use this approach.

Regarding CVM is highly subjective and controversy will always rise regarding how surveys are performed and how to apply such results at small scale system boundaries such as a chemical plant. Regarding its current state, there are some EU funded projects that study externalities mainly associated to energy and electricity production (ExternE, CASES).

2.2.3.2 Remarks

Environmentally benign designs are bound to be more profitable, given that they incur in lower waste treatment and environmental compliance costs while converting a higher percentage or raw materials into saleable products (Khor *et al.*, 2007). It has been pointed out by Sinclair-Rosselot and Allen (2002a) that savings due to increased production capacities and increased use of raw materials can often be more substantial than avoided treatment costs. This is also true for the case of recycle options where the benefits from avoiding manufacturing impacts tend to dwarf energy/materials used for recycling the materials (Constable *et al.*, 2009). However all these issues should be backed by the use of sound economic metrics to actually measure environmental friendliness.

The single use of TAC or NPV which is the basis of CBA, is rooted in the concept of economic efficiency and not on distributional equity and justice that sustainable development advocates, consequently the use of these economic indicators solely is prone to controversy. Most environmentalists and even some ecological economists, reject the commodification or commoditization and pricing of the environment[10]. In their view, the value of the environment cannot be expressed in money. For them, physical indicators of sustainable development are preferable, which might cover a broader set of social values and amenities. However, these metrics do not have the integrative power of monetary aggregates generated in accounting systems, which are also able to show the people's subjective preferences, which physical indicators can not. These two divergent points of view can not be satisfied and consequently environmental concerns have to be quantified separately and preferably using non-economic metrics. Despite this fact, the economic burden of complying with environmental legislation (in terms of cost as discussed in section 2.2.3.1), is a different issue and has to be dealt by assigning an appropriate economic value.

The selection of the appropriate economic metric to measure the problem at hand is also related to the level at which the process LC phase is in place. At early phases where information is scarce typical simple metrics such as cost or profit can be used to screen different process alternatives. At more detailed phases the estimation of cash flow can be performed and NPV can be more insightful. In the case of the design of a single unit operation the use of TAC could be the most convenient, and is the approach used by many authors in the case of distillation units, heat exchanger design, and complete process flowsheets (Biegler *et al.*, 1997; Doherty & Malone, 2001; Luyben, 2006). It has to be emphasised that the system under study will imply different set of economic metrics, while the instalment of a new process equipment can be globally grasped by cost calculations the implementation of a whole supply chain will require broader metrics such as NPV.

Much of the opportunity to address CO_2 emissions rests on SCM, compelling companies to look for new approaches to manage carbon emissions effectively. And most certainly, this charge will force a change in the way organisations run their SCs (Butner *et al.*, 2008). One of the key aspects to have a successful policy is the definition of the free emissions allowance cap for each industry type.

Several economic metrics have been reviewed aiming at its application to the chemical process design, it was found that the use of TAPPS and AEP instead of NPV is envisaged due to its "service" instead of project emphasis. It was found that despite the good efforts at including complex economic metrics, when SD issues are incorporated it is more important to estimate LC associated costs using methodologies such as TCA rather than using complex metrics.

2.2.4 Social indicators in process design and operation

Traditionally, social aspects in the chemical industry are only seen as safety and health problems and consequently two ways of addressing them are available: (i) the use of shortcut or (ii) detailed methodologies. Shortcut methodologies encompass the Dow Fire and Explosion Index (F&EI[11]), the Control of major accident hazards related metrics (COMAH), the exposure to unhealthy chemicals using the chemical exposure index (CEI), or other metrics such as the oned developed by Koller *et al.* (2000) or the intrinsic safety metrics developed by Heikkilä

[10] In this sense, Burgess and Brennan (2001) claim "*that the ability to put reliable dollar value on environmental impacts is unlikely to be practicable in the framework of engineering decisions*".

[11] F&EI, is a system to quantify the expected property damage and business interruption in the event of an accident.

(1999). On the other hand, the use of other detailed hazard assessment methods include hazards and operability analysis (HAZOP), the fault tree analysis (FTA) and the failure model effect analysis (FMEA), which are proven tools of detailed engineering design are possibilities (Cameron & Raman, 2005). While the application of shortcut methodologies seems straightforward there is no agreement between which one to choose given that each author states the merits of their own method whether the limitations are pointed out by proponents of others (Adu *et al.*, 2008). In the case of detailed methods, their application has one main drawback, they require a very large amount of data and a detailed design of the process.

Despite the fact that safety and health issues impact a society as a whole, an enterprise also affects the society in other aspects. Some of these social aspects of SD could be measured at the enterprise level, in this sense Azapagic and Perdan (2000), proposes two generic types of indicators: ethics and welfare indicators. Within ethics indicators the authors use label indicators, qualitative in nature and reported as descriptive statements. While for the case of welfare indicators, they propose quantitative indicators; such as: income distribution, work satisfaction and satisfaction of social needs. A similar trend in found in the case of the social metrics proposed by AIChE and IChemE. In the latter case they propose to measure *Workplace* regarding employment situation (using five indicators); and health and safety at work, and *Society* which is measured with four metrics all of them expressed per unit of value added.

Within the LCA community a similar approach to the one used to assess environmental impact (Environmental LCA or ELCA) was taken, consequently a "Social LCA" (SLCA) was proposed[12]. The SLCA methodology draws from the ELCA methodology in all aspects. In the case of ELCA the areas of protection (AoPs) are the ones used in environmental considerations see section 2.2.5, whereas, in the case of Social LCA, different AoPs are proposed by different authors. These areas should be regarded as complementary to the existing areas of environmental protection. In the review of Jørgensen *et al.* (2008) a list of possible impact categories used for social impact assessment is done, where four AoPs (Human rights, Labour practises and decent work conditions, Society and Product responsibility) and possible mid-point indicators affecting them is done. Labuschagne and Brent (2006); Labuschagne *et al.* (2005), propose a framework of social indicators relevant for operational initiatives in the process industry. Their framework considers four AoPs relevant to social SD as follows: Internal Human, External Population, Stakeholder participation and Macro social performance. Some of the AIChE's indicators partially address some of the former AoPs. Labuschagne and Brent (2006) propose to use the methodological framework of LCA, extending it to encompass the social aspects and propose a social impact indicator SII, calculated as in Eq. 2.11.

$$SII^G = \sum_{c}^{SIP_C} \sum_{x}^{SI_X} Q_{xc} Cf_c^G N_c S_c \tag{2.11}$$

SII is calculated for a main social resource group G, through the summation of all social impact pathways SIP_C of all categorised social interventions SI_x of an evaluated LC system. Q_{xc}^G considers a quantifiable social intervention (x) of the LC system in a midpoint social impact category c, CF_c^G represents the characterisation factor (CF) for a social impact category within the pathway associated to the G social resource, N_c is a normalisation factor for the impact category based on the social objectives in the region of assessment and S_c is the significance (or relative importance) of the impact category in a social group based on a distance-to-target method.

[12] Dreyer *et al.* (2006) proposes the differentiation of the ELCA from the SLCA, while according to O'Brien *et al.* (1996) there is the possibility of combining both into a SELCA which brings together the different aspects of SD producing a comprehensive analysis.

There is still no agreement on the impacts to society that should be accounted for, the system boundaries or the connections between social stressors that create impact and the AoPs (Jørgensen *et al.*, 2008). With regards to system boundaries, Dreyer *et al.* (2006), argue that social impacts have no relation to the process themselves, but rather to the companies performing the process, consequently the SLCA inventory phase should focus on the companies involved in the product system. Dreyer *et al.* (2006) goes further in the boundary selection by narrowing it to those parts of the LC where the company has influence on, this justifies the extension of the boundaries to include the company and its closest suppliers and distributors. On the other hand Jørgensen *et al.* (2008) cite some methodologies such as Socio-Eco-Efficiency Analysis (SEEbalance, Schmidt *et al.* (2004)) where the main focus of the assessment is the same basis as for the assessment used in an LCA. Clearly two possible points of view are available regarding social system boundary definition, being in one case the whole company (and/or some suppliers), while in the other certain parts of it. In the first case site specific data is required, while in the second, the possibility of using generic process data is open.

The former points of view define broadly how to select system boundaries and allocation procedures, in the first case the whole company is assessed and no allocation is required, while in the other case, similarly to an ELCA, the boundaries are selected accordingly to the FU and the allocation should mimic such boundary.

Remarks

Current social impact assessment has several shortcomings: (i) social impact mechanisms are not as well developed compared to environmental impact mechanisms, (ii) system boundaries can not be drawn appropriately and (iii) due to the lack of appropriate social mechanisms and system boundaries; data can not be gathered in a systematised way.

Two different ways of social impact measurement were found, (i) the health-safety approach, which is based on shortcut or detailed engineering methodologies, and (ii) the LCA approach, which embeds the first. The state of development of social impact assessment is not the same as environmental impact assessment and social characterisation factors are not widely developed. In this sense most metrics for social impact are extensions of environmental impacts using the same LCI.

In the case of process design the use of health-safety indices can be done, and is the approach used by several authors (see section 2.3), but these indices only explain a small part of the possible impacts due to the presence of a chemical facility. In this sense, the system boundary associated to process design is different, and usually does not consider the whole chemical complex consequently many of the social impacts related to wages, labour practises, compliance with law, can not be assessed properly, or are not affected by a given process design. As previously discussed and emphasised by Dreyer *et al.* (2006) most social impacts are due to the enterprise as a whole, and not to a certain part of the process.

2.2.5 Environmental indicators in process design and operation

In the case of environmental metrics no information is easily available to chemical process designers for its computation. There are two main reasons for this:

- Relevant properties of chemicals (e.g. toxicity, environmental degradation constants) are not readily available in the tools commonly used by chemical engineers (e.g. process simulators, chemical process design handbooks).

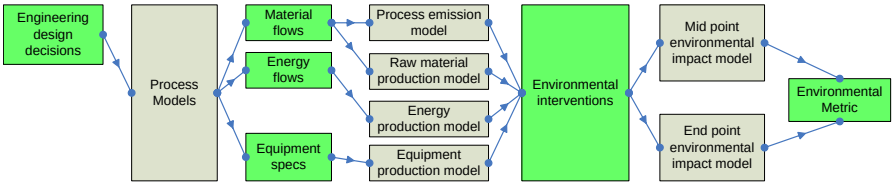


Figure 2.2: Overall variables and models relationship for the calculation of an environmental metric.

- Location-specific knowledge is needed to estimate environmental impacts, with the exception of environmental problems that are global in nature (e.g. ozone layer depletion and increase of greenhouse gas concentration).

Sharratt (1999) states that all environmental effects can in principle be linked to the concentration, dispersion and persistence of materials in the environment. Most chemicals in recent years have been categorised according to their potential for persistence[13], bioaccumulation[14] and toxicity[15]. Consequently the environment is compromised by industry mainly in two ways: emissions and the consumption of raw materials. This broadly separates typical environmental metrics in two (Bare *et al.*, 2003):

1. Pollution categories associated to system's output flows such as: ozone depletion, global warming, human toxicology, eco-toxicology, smog formation, acidification, eutrophication, odour, noise, radiation and waste heat.
2. Depletion categories associated to system's input flows: abiotic resource depletion, biotic resource depletion, land use, and water use.

The calculation of environmental metrics requires the estimation of environmental interventions (inputs and outputs) from the system. While inputs to the system can be easily gathered from the raw material and energy consumption, the estimation of emissions is not straightforward and several authors propose different ways to assess them, they are discussed under section 2.2.5.1. Once environmental interventions, are estimated, it is important to know how the chemical compound will distribute along the different environmental compartments, this requires the use of environmental models, which are briefly reviewed in section 2.2.5.2, and given than some impacts are not directly related to the chemical concentration on a given environmental compartment, but to the exposure of this chemical to the subjects of impact, another layer of modelling is required, namely the impact model. The calculation of an environmental metric can be summarised in the following Fig. 2.2, which shows the different models required to calculate an environmental metric. As pointed out in section 2.2, indicators have to comply to certain number of requirements. In the case of early phases of the process LC (i.e. R&D and design), reliable data is limited making necessary to compromise the use of certain indicators against others. This compromise gave birth to a series of simplified (streamlined) versions of metrics that can be used at the conceptual design stage. The paper of Curran and Todd (1999) provides a deep review of shortcut methodologies in the

[13]Persistence is related to what extent materials will accumulate; at one extreme of behaviour are materials that are not degradable and thus accumulate while at the other extreme are highly degradable materials that will quickly reach an essentially steady level in the environment as their rate of release is balanced by their destruction. In this sense, persistence is associated to the substance resistance to chemical (hydrolysis, photolysis, etc.) or biological (biodegradation, metabolism, etc.) degradation or breakdown.

[14]Bioaccumulation is related to the chemical tendency to become increasingly concentrated (in fat tissues) as one moves up along the food chain from microorganism to mammals.

[15]Toxicity is the most contentious/disagreeable area of concern where multiple tests are available depending on the endpoint (lethality, fecundity, endocrine disruption, etc.), each chemical has different effects and consequently different toxicity.

LCA context[16]. In the context of chemical process design Allen *et al.* (2002), Sharratt (1999), and Constable *et al.* (2009) propose the use of a set of simple indicators that do not require of emission estimation, emission fate analysis and impact modelling, these are simpler metrics that provide a proxy image of the impact, to assess the environmental performance of the a process. Many of them are based on the Canadian National Round Table on the Environment and the Economy (1999), and have been used by AIChE as well. These indicators are:

- *Energy consumed* from all sources within the process per unit of manufactured output[17].
- *Total mass of materials* used directly in the product, minus the mass of product, per unit of manufactured output. Within materials the amount of water consumption is also important.
- *Release concentration or release amount*; both concentration [kg/m^3] or amount [kg/h] of certain species have already an environmental meaning, examples of such are: CO_2, non methane volatile organic compounds (NMVOC), sulphur and nitrogen oxides (SO_2 and NO_xs), particulate material (mu<2.5), BOD/COD or emission of metals such as cadmium. The selected species could be present in the USEPA Toxic Release Inventory.
- *Atom efficiency*, in certain process this measure can be calculated as the proportion of atoms in raw materials appearing in final product. The atom utilisation or atom selectivity are defined as the ratio of the molecular weight of the desired product to the sum of the molecular weights of all materials produced in the process. These metrics are widely used in the case of the analysis of reaction sets, to assess in a very simple metric the greenness of a given reaction (Sheldon, 1997).
- *Environmental load factor* (ELF) is defined as in Eq. 2.12, it is similar to atom efficiency but related only to wastes and considering mass flows instead of number of atoms/moles.

$$ELF = \frac{(weight\ waste)}{(weight\ product)} \tag{2.12}$$

- *Best Practicable Environmental Option* index (*BPEO index*), these indexes are defined as in Eq. 2.13.

$$BPEO\ Index = \frac{(process\ contribution)}{(allowable\ concentration)} \tag{2.13}$$

- *Critical volumes* (CVs), measure the volume of environmental sink that is polluted to a reference concentration level (some environmental standard) by a given release of a given compound i, calculated as in Eq. 2.14[18].

$$CV_i = \frac{(total\ process\ emission_i)}{(maximum\ allowable\ concentration_i)} \tag{2.14}$$

All former metrics shed light in the way material and energy flows are affected by the process, but they do not help in devising the environmental impact of such material/energy flows, specially in the case of emissions, in this sense they can serve as proxy.

[16]In these report the authors state that streamlining is an inherent part of the goal-and-scope definition process of LCA, in which designers do not decide whether to streamline or not, rather than where and how to streamline. Streamlining in the LCA context is therefore, a disciplined process of designing an LCA study to gather sufficient information to make a sound decision or to meet the requirements of other applications.

[17]This item requires the conversion of electricity consumption to equivalent energy use, using a given production/consumption factor. Cumulative energy demands are discussed in section 2.2.6.

[18]For example lethal doses from toxicological studies (LC_{50}), can be used as the maximum allowable concentration.

2.2.5.1 Emission estimation guidelines

The chemical process emits directly and indirectly. Direct emissions are associated with the process and are known as foreground process, while and indirect are associated with other parts of the LC and are known as background emissions. Releases may be further classified as intended (such as stacks and flares) or accidental (such as leaks and spills). Stefanis and Pistikopoulos (1997) classify direct emissions in four groups as follows:

- accidental releases mainly due to the occurrence of scenarios such as leakage, equipment failure, human error, etc.
- fugitive emissions that involve small leaks or spills from pumps or flanges which are generally tolerated in industry.
- releases from normal process operations such as: start-up, shutdown, maintenance / cleaning procedures and from operation conditions changes.
- episode releases as a result of sudden weather changes or other occurrences.

Regarding fugitive emissions, Burgess and Brennan (2001) cite several sources stating that 70-90% of total air emissions for some plants in the United States are result of unintentional releases of volatile liquids (spills and handling) and that 40-60% of total VOC emissions are due to fugitive emissions. Typical sources of fugitive emissions are valves, flanges, pump and compressor seals, process drains and open-ended lines. In this sense Allen *et al.* (2002), state that common sources of releases that are overlooked in flowsheet are fugitive emissions (leaks) and venting of equipment (breathing and displacement losses), periodic equipment cleaning and transport container residuals.

Emissions arising from process models are usually based on the routine operation of a plant, it means they can assess for the amount of CO_2 being emitted through a chimney in normal process conditions, or the volatile remaining in an air stream after some pollution abatement system. In order to reduce the emission model complexity, the use of emission factors is a possibility, such as in Eq. 2.15.

$$E_{ij} = A_R EF_{ij} \tag{2.15}$$

where E_{ij} is the emission rate of pollutant i into environmental sink j, A_R is the actual activity rate usually measured as a mass flow and EF_{ij} is the emission factor of pollutant i into environmental sink j for a given activity. An emission factor EF_{ij} is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. Several lists of uncontrolled emission factors are available for different activities, being the usual environmental sink air, examples are available: UN (IPCC), Europe (EEA), Australia (Environment-Australia (2000) and Emission Estimation manuals), United Kingdom (UK National Atmospheric Emissions Inventory) and United States (AP 42, Compilation of Air Pollutant Emission Factors). Other emission calculation procedure is based on the process unit and not on the activity performed, in this case Eq. 2.16 is used (Allen *et al.*, 2002).

$$E_{ij} = m_i EF_j^{av} M \tag{2.16}$$

In Eq. 2.16, $m_i M$ is identical to A_R of Eq. 2.15, while EF_j^{av} is tabulated for different chemical process units (reactor vents, distillation column vents, absorber units, strippers, sumps / decanters dryers and cooling towers). In some cases the emission factor is a function of process parameters, such is the case of organic liquid storage tanks (USEPA, 2006) or in single-stage vent control devices (vent condensers, liquid-ring vacuum pumps, and vacuum steam jets, Hatfield (2008)). Other ways of generating fugitive loss estimations, consider the state and boiling point of the stream as in Jimenez-Gonzalez *et al.* (2000) , while other authors apply

a given factor to estimate fugitive emissions, such is the case of Smith *et al.* (2004), where 0.1% of each stream in a flowsheet is lost as a fugitive emission. Within the literature no clear agreement is found the consideration of non-routine emissions and it has to be considered in a case basis, depending on the process under study, and the compounds and the state at which are present in the plant.

Cleaning emission estimations According to Allen *et al.* (2002), the nature of the cleaning process should be considered taking into account several aspects: (i) nature of the vessels to be cleaned (capacities, materials of construction and shape), (ii) the cleaning schedule, (iii) the residual quantity of chemical left to be cleaned in the vessel, (iv) the cleaning agent (aqueous/organic, chemical solubility/miscibility), and (v) the requirements of waste treatment for the used cleaning agent. In the batch industries where individual unit operations are utilised for multiple products, many pieces of equipment may be subject to long clean-out periods using large solvent volumes and/or aqueous detergents, however cleaning operations are also common in the continuous process industries. It is current practise to try to use clean-in-place (CIP) procedures instead of break down and rebuild approaches where unit operation allows it (Constable *et al.*, 2009). While in some cases the unit operation requires its break down and rebuild (e.g. plate filtration), most vessel cleaning is performed using CIP. Regarding clean up scheduling (ii), it depends on the process/product given that cleaning between batches could be due to product requirements (e.g. colour changes in paint manufacturing), or process requirements (e.g. solidification of product in a filter requires it cleaning). In order to make an estimation of the cleaning emissions due to scheduling, information regarding product and process requirements is needed. Estimation of point (iii) requires knowing vessel characteristics and some rough estimate of the viscosity and surface tension of the liquid to be cleaned.With regards to (iv) in the case of aqueous cleaning agents, these are sent to waste water treatment plants, while in the case of organic solvents these are recycled back to process or incinerated. In general, the actual amount of clean up agent will depend on the amount of this agent that can be recycled/reused in other cleaning operations.

2.2.5.2 Environmental models and impact estimation

Once emission has been estimated, via process models, emission factors or measured; the question of the fate of the compound must be addressed.Chemical environmental fate is highly component dependant and is modelled by means of environmental fate models. Sinclair-Rosselot and Allen (2002b), describes the appearance of two types of environmental model approaches: (i) focusing on a single compartment and (ii) taking into account multimedia compartment models (MCMs). In the first case typical examples are: prediction of air concentrations downwind from a stationary source, or the estimation of concentration using ground water dispersion models, their main disadvantage is that they provide of concentration in only one compartment.

The complexity in MCMs rises from characteristics such as: number of environmental compartments considered, homogeneity and heterogeneity of each one of them and steady or unsteady conditions. In Mackay (2001) an environmental models taxonomy is provided in levels of increasing complexity:

- *Level I*: corresponds to multiple phase closed systems, where pollutants do not react, i.e. are conserved in their chemical form. Each phase is considered as a closed vessel that attains thermodynamical equilibrium, see Mackay (2001, Ch. 2).
- *Level II*: corresponds to steady state multiple phase open systems, where pollutants are

subject to advective flows[19], chemical reactions[20] and attain physicochemical equilibrium. Each phase is considered as a CSTR where outlet concentrations equal phase concentrations, see Mackay (2001, Ch. 6).
- *Level III*: corresponds to steady state multiple phase open systems, where pollutants are subject to advective flows, chemical reactions and diffusive flows between environmental compartments, so chemical equilibrium is used but not attained, see Mackay (2001, Ch. 7).
- *Level IV*: corresponds to level III models where some compartments are taken into non-steady state conditions.

In all MCMs where equilibrium is hypothesised the partitioning of a chemical between environmental phases is described using the concept of fugacity for the description of mass transfer and reaction phenomena.

The concept of environmental impact is closely related to the concept of risk, which in many cases is embedded in the way fate, dose and impact of a chemical compound are calculated. As discussed in section 1.2.2 and in the case of risk there are two analytical tools available for such analysis: Environmental risk assessment (ERA) and Impact pathway analysis (IPA). Both tools put emphasis on impacts to humans, in the case of ERA emphasis is put on ingested dose, while in the case of IPA the focus is on air concentration, see Sonnemann (2002, p.27).

Risk in the environmental sense is defined by Allen & Shonnard (2002b, Ch. 2) as "*the probability that a substance or situation will produce harm under specific conditions*". This risk will be the combination of two factors (Cameron & Raman, 2005)[Ch. 9]: (i) the probability that the adverse event will occur and (ii) the consequences/effects of such event. It is generally accepted that risk is a function of a given hazard and the exposure to such hazard; considering that *hazard* is the potential of a given substance/situation to produce harm or adverse effects in people or the environment, while *exposure* is the contact time or exposition to such hazard. In order to assess the risk, the following items have to be addressed properly:

- *Hazard assessment*, which addresses the question of which are the adverse effects that a given substance or situation produces (mortality, shortened life-span or impairment).
- *Dose response*, is the mathematical relationship between the dose of a given substance and the appearance of negative effects.
- *Exposure assessment*, this is linked to dose measurement and it studies how much and which subjects are "exposed" to the substance or situation.
- *Risk characterisation*, addresses how big is the adverse impact of the chemical/situation.

Most of the environmental metric methodologies reviewed under section 2.2.5.3 consider a given set of emissions into some compartments which are modelled using a given environmental model. These emissions are assessed in terms of hazard/dose/exposure/risk and a given characterisation factor (CF)[21] is obtained which relates the emission to its impact. In this sense all environmental impact metrics related to LCA follow Eq. 2.17.

Several environmental metrics have been developed within the LCA context for LCIA, where two important terms are crucial to be defined appropriately, these are: impact category and environmental mechanism (EM). An impact category represents environmental issues of concern to which some LCI results may be assigned. According to de Haes *et al.* (1999), all

[19]Advection flows are the ones related to "*the direct movement of a chemical by virtue of its presence in a medium that happens to be flowing*".

[20]The most important chemical reactions considered are biodegradation, hydrolysis, oxidation and photolysis.

[21]Several names are given to the CF such as "harm factor", or "potency factor", however CF is the standardised terminology adopted by the ISO.

physical process and variables starting from extractions, emissions or other types of interaction between the product/process system and the environment, which are connected with a given impact category, are called the EM[22] of that impact category. Within and connected to a given EM it can be distinguished:

- *environmental interventions*: such as extractions, emissions from and to the environment, or different types of land use[23].
- *areas of protection* (AoPs), these are variables of direct societal concern, also known as classes of *end-points* which have some well recognisable value for society. Each impact assessment methodology has a predefined set. Common AoPs are: human health, natural resources, natural environment and man-made environment (de Haes *et al.*, 1999).
- *category mid-points*: these variables which appear within the EM of an impact category fit between environmental interventions and the impact category end-points. Examples are: concentration of toxic substances, deposition of acidifying substances, global temperature or sea level.

With regards to EIA two schools of methods have evolved (Finnveden *et al.*, 2009; Humbert *et al.*, 2005):

- *Problem oriented or mid-point methods* like CML (Guinee *et al.*, 2001a; Heijungs *et al.*, 1992), EDIP (Hauschild & Potting, 2004; Wenzel *et al.*, 1997) and TRACI (Bare, 2002; Bare *et al.*, 2003), which restrict quantitative modelling to relatively early stages in the EM to limit uncertainties and classify and characterise emission results in mid-point categories. Themes are common mechanisms (e.g. climate change) or commonly accepted grouping (e.g. aquatic ecotoxicity).
- *Damage oriented or end-point methods* such as Eco-indicator 99 (Goedkoop & Spriensma, 2001) or EPS (Steen, 1999a), try to model the EM up to the damage to a given area of protection, sometimes with high uncertainties. These methods differ on the way end-point impacts are measured and in the way that weights are assessed for each impact. Moreover not all methods consider the same AoPs, nor how each mid-point indicator affects the end-point.

2.2.5.3 Environmental impact assessment calculation

Mid-point environmental impacts for any category are calculated using Eq. 2.17.

$$mid\ impact^{cat} = \sum_{j}^{all\ sinks} \sum_{i}^{all\ species} m_{ij} CF_{ij}^{cat} \tag{2.17}$$

$$end\ impact^{AoP} = \sum_{cat}^{all\ Cats} W_{cat}^{AoP}\, mid\ impact^{cat} \tag{2.18}$$

$$end\ impact^{AoP} = \sum_{j}^{all\ sinks} \sum_{i}^{all\ species} m_{ij} CF_{ij}^{AoP} \tag{2.19}$$

In Eq.2.17, m_{ij}, represents the environmental intervention amount related to the emission of specie i (it is usually a mass flow) into environmental compartment j, while CF_{ij}^{cat}, is the

[22] The term cause-effect chain is also used.

[23] Other synonyms are "elementary flows" or "environmental inputs and outputs". Environmental interventions are also called stressors.

mid-point CF, relating the environmental impact to impact category cat of species i intervention into sink j. In other methodologies end-point impacts are aggregated metrics from mid-point results (see Eq. 2.18), in which different weights are assigned to mid-point categories (W_{cat}^{AoP}), or are calculated from CFs (CF_{ij}^{AoP}), that relate the impact of the environmental intervention directly to the end-point AoP, see Eq. 2.19[24]. Eqs.2.17 to 2.19 are linear in terms of the environmental intervention, linearity means that characterisation is based on CFs that are independent of the magnitude of the environmental intervention. A deep revision of different methods for available for impact assessment at mid-points is performed under section D.1, while ready to use mid-point and end-point impact assessment methodologies are discussed under section 3.4.3.

Besides the LCIA methods, from the chemical engineering community some environmental metrics have been developed. Most of these metrics will be discussed in next section 2.3, but its worth mentioning the WAste Reduction (WAR) algorithm, first developed by Hilaly and Sikdar (1994) who introduced the concept of pollution balance based on the mass balance of pollutants. Cabezas *et al.* (1997, 1999); Young and Cabezas (1999) later improved the original WAR algorithm and developed a generalised WAR algorithm based on the potential environmental impact (PEI) balance of pollutants, which simply states that PEI can enter, leave, be generated within and accumulate within the system boundary. Two metrics are proposed to be calculated using PEI balances: fractions of total PEI output related to the total mass of products and total generated PEI over the total mass of products. In general, the lower the value of these indexes the higher the environmental efficiency of a process, i.e. the less potential impact the process is likely to have on the environment (Young & Cabezas, 1999). One important drawback of the WAR algorithm is due to the difficulty, ambiguity, and subjectivity involved in combining the different impacts generated by the process into a single value , however this is a common feature of end-point metrics. Second, the WAR assumes that pollutants emitted into a particular environment compartment (air, water or soil), exert the impact in that compartment solely (Cabezas *et al.*, 1997; Shonnard *et al.*, 2001). Also, the WAR algorithm does not directly provide any guidance on the actual origin of the waste in the process or the modifications that would minimise the waste.

Remarks

Currently the mid-point approach, is considered best available practise for impact assessment, according to SETAC guidelines (de Haes *et al.*, 1999). Analysis at mid-points minimises the amount of forecasting and modelling effect incorporated into the LCIA, thereby reducing the modelling complexity which might simplify communication. Other factor supporting the use of mid-point modelling is the incompleteness of model coverage for end-point estimation, i.e. not all mid-point indicators have a modelled effect on end-points (Bare *et al.*, 2003). Decision-making at mid-points has several advantages according to Lenzen (2006), first instead of providing a few aggregated numbers, the more multi-facetted mid-point information clearly reveals the multi-dimensionality of the problem at hand, and the possible trade-offs between the inherent aspects. Second, compared to mid-points, end-point assessments require additional steps of data collection, modeling and computation, and hence requires more time, labour and resources, with potentially little gain in decision certainty. Third, aggregation of impact categories and pathways may cause uncertainty to swamp certain endpoints; while reverting to mid-point levels opens the opportunity of carrying out an iterative

[24]Some methodologies present two sets of CFs, one for mid-point characterisation (CF_{ij}^{cat}) and other for end-point characterisation (CF_{ij}^{AoP}), see for example Humbert *et al.* (2005).

procedure, where too uncertain indicators are excluded[25]. Fourth, MCDA at mid-point levels is able to include characteristics that impact modeling and valuation has trouble quantifying, but mid-point indicators form a very difficult input for any weighting scheme. According to Finnveden (2000), people with a positive view of the model's ability for predicting environmental impacts may choose to define category indicators closer to end-points, on the other hand persons with a less positive view (emphasising the precautionary principle, see section 2.4), will suggest that effects should be defined earlier in the EM. Approaches used to derive end-point metrics are typically more complex but have a number of potential advantages, in addition to improved perceptions of defensibility and some opportunities to link emissions to observed effects, consequently end-point results can be readily aggregated. Most important disadvantages of end-point methodologies include reduced transparency, limitations in scope and significant uncertainty (Pennington *et al.*, 2000). The key feature of the problem-oriented approach is that the category indicators are defined at places along the EM congruent with environmental policy themes and therefore can be modelled with relative accuracy.

In all the mid-point and end-point metrics reviewed under section 3.4.3 and appendix D.1 and it is found that the environmental impacts caused by an emission depend on (i) the quantity of substance emitted, (ii) the properties of the substance, (iii) the characteristics of the emitting source, and (iv) the receiving environment (Finnveden *et al.*, 2009). In most impact characterisation models points (i) and (ii) are included as variables (i.e. emission amount and its corresponding CF), while points (iii) and (iv) are fixed and depend implicitly on the assumed model for properties of the receiving environment in terms of a global/regional or average/standard conditions. For truly global environmental impacts such as climate change and ozone depletion, the constraints adopted in points (iii) and (iv) are not problematic, given that the impact is independent of where emission occurs. However for the other impact categories the situation is different, the global set of standards disregards large and unknown variations in the actual exposure and the sensitivity of the receiving environment[26]. In this sense, the different approaches used to derive these metrics range in their site-specificity, complexity, comprehensiveness, sophistication and uncertainty. It is therefore often necessary to consider the use of more than one approach within the context of a given impact category to help support a decision (Pennington *et al.*, 2000).

The principal discrepancy between mid- and end-point modelling lies in the evaluation of whether the uncertainty is justified by the interpretation of the results. This answer varies depending on the categories of impact and the authors. While reliable end-point modelling seems within reach for some categories such as acidification, cancer effects and photochemical ozone formation, it is still under development for climate change[27], where the end-point modelling is encumbered with large uncertainties due to many unknowns of the global climate system and due to the long time horizon of some of the involved balances (Finnveden *et al.*, 2009).

[25] Comparison at mid-points may not however always account for all factors in the EM and can result in a reduced ability to later aggregate the results across impact categories.

[26] This has risen the need for site spatial differentiation in LCIA, which requires of more information regarding the emissions and the impact assessment itself. Finnveden *et al.* (2009) reviews the literature with regards the availability of region CFs for non global impact categories, which are available for different countries and for regions within the same country. There are also available different CFs depending on the stack height, which affects human health related impacts.

[27] A mid-point indicator is still used early along the EM, i.e. increase in radiative force.

2.2.6 Sustainability indicators based on thermodynamic functions and footprinting

In most of chemical industries many of the raw materials used, especially those derived from oil, gas, and some plants and animals, have been, and in some cases continue to be, depleted at rates either large compared to known reserves, or faster than their replenishment capacity (Grossmann, 2004). This abiotic (in the case of non-renewables) and biotic (for renewables) depletion increases the attention to the use of renewable resources[28]. However, the use of such renewable resources also raises some concerns regarding its possible depletion.

Former concerns are related to resource use, which is measured by considering the mass or energy consumed, which are thermodynamic functions. Thermodynamic techniques include the approaches for process heat integration (pinch analysis), others related to waste minimisation (El-Halwagi, 2003), and also exergy analysis (Dewulf & van Langenhove, 2006b; Dincer & Rosen, 2005; Kotas, 1995). These methodologies are based on applying the first and second laws of thermodynamics to the design of thermodynamically optimal process. In this sense the most simple thermodynamic functions to measure are related to mass and energy.

In the case of mass, the use of material intensity per unit service (MIPS) is widely used as an eco-efficiency metric, while in the case of energy the Cumulative Energy Demand (CED) is defined as the sum of the energy content of the fuels used directly or indirectly to make a product/service. In the case of MIPS, several material intensities are found already calculated by different raw materials and fuels (Ritthoff *et al.*, 2002). The CED calculation in Simapro/Ecoinvent takes into account five different types of energy sources: non-renewables nuclear and fossil; and renewables biomass, water and solar/wind/geothermal. Different CFs are available for each raw material consumption. Huijbregts *et al.* (2006) studied, using the Ecoinvent database, the application of CED as a proxy indicator, the authors found that for many product groups (excluding waste treatment sectors), the fossil CED correlates well with many impact categories, such as climate change, resource depletion, acidification, eutrophication, tropospheric ozone formation, ozone depletion, and human toxicity. They concluded that the use of fossil fuels is an important driver of several environmental impacts and thereby indicative of those environmental problems. However the authors also pointed out that the use of CED as a single metric is limited by the large uncertainty in the product-specific fossil CED based impact scores.

Similarly to CED two other metrics are defined: exergy and emergy. Exergy or availability analysis focuses on the amount of energy that is available for conversion into useful work from any product or process, while emergy is related to the amount of embodied solar energy in different materials. The Cumulative Exergy Demand (CExD), in all process starting from natural resources present in the ecosystem, has been suggested as a measure of the ecological cost of any process, given that it considers the "quality" of energy which can be associated to its capacity to cause change (Dewulf & van Langenhove, 2006b). Exergy is generally treated as a mix of different energy sources: kinetic and potential are related to the state of movement of the system while physical and chemical are related to physical (pressure, temperature, state changes) and chemical (composition change) processes that the system may undergo to produce work. Dewulf and van Langenhove (2005); Dewulf *et al.* (2000) propose the use of different ratios of exergy to quantify renewability ($Renew_\rho$, $Renew_\alpha$), the efficiency (Eff_η) and

[28] Features like CO_2 neutrality and biodegradability, are mainly responsible for the environmental attraction of renewable sources based technologies and products (Narodoslawsky, 2003). Products from renewable resources are considered to contribute less to global warming and consequently are CO_2 neutral, it is generally accepted that renewable materials have a shorter C-cycle and are preferable compared to non-renewables.

degree of recovery ($Recov_\tau$) as in Eqs. 2.20 to 2.23.

$$Renew_\rho = \frac{B^{re-used}}{B^{re-used} + B^{extr}} \tag{2.20}$$

$$Renew_\alpha = \frac{B^{prod}}{B^{extr}} \tag{2.21}$$

$$Eff_\eta = \frac{B^{prod}}{R^{re-used} + B^{extr}} \tag{2.22}$$

$$Recov_\tau = \frac{B^{recov}}{B^{prod}} \tag{2.23}$$

In Eqs. 2.20 to 2.23 B are exergy flows associated to the different resources. Different flows are recognised associated to re-used waste materials ($B^{re-used}$), virgin extraction of materials (B^{extr}), product (B^{prod}) and the fraction of recoverable exergy (B^{recov}), see also de Swaan-Arons *et al.* (2004, Chs. 13-14). Exergy and availability are calculated in most process simulation environments.

Energy and exergy metrics do not consider the fact that natural resources require different amounts of "ecological effort" for making more "concentrated sources" of energy such as coal and petroleum, than for "diluted sources" such as sunlight or wood (Bakshi, 2002). Shorter carbon cycles are related to smaller ecological efforts. Systems ecology, aims at analysing ecosystems as networks of energy flow, since solar energy is the main source of energy for the planet, the ecological input/effort put in any product or service may be measured by the equivalent solar energy embodied in it. The solar embodied energy or solar emergy can be used as a common currency analysis of industrial or ecological systems alike (Odum, 1980). Eq. 2.24 defines the relationship between exergy (B) and emergy (M), by means of an emergy transformity (τ^{em})[29].

$$M = \tau^{em} B \tag{2.24}$$

The units of τ are [sej/J] where sej states for solar embodied joules (emjoules). The value of a given transformity (τ^{em}) increases as the energy becomes more concentrated and consequently with higher quality. The values of emergy will depend on the transformity selected, i.e. depend on the path taken to reach a given state. By using Eq. 2.24 the Cumulative Emergy demand (CEmD) of a given process can be calculated in the same way as in the case of CED and CExD.

Ecological footprint analysis was introduced explicitly to reopen the debate on human carrying capacity. An ecological footprint (EF) is understood as "*the area of land and water ecosystems required on a continuous basis to produce the resources that the population consumes, and to assimilate (some of) the wastes that the population produces, wherever on Earth the relevant land/water may be located*" (Rees, 2006). Nation wide metrics can be calculated for the national footprint and the national biocapacity considering net consumption and total existing areas (Wackernagel *et al.*, 2005). Huijbregts *et al.* (2007) define the EF of a product as the sum of time-integrated direct land occupation (EF^{direct}) and indirect land occupation ($EF^{indirect}$), measured in [m^2·yr]. The authors relate indirect land occupation to nuclear energy use ($EF^{nuclear}$) and to CO_2 emissions from fossil energy use and cement production (EF^{CO_2}), see Eq. 2.25.

$$EF = EF^{direct} + EF^{indirect} = EF^{direct} + EF^{nuclear} + EF^{CO_2} \tag{2.25}$$

$$EF^{direct} = \sum_a A_a Eq F_a \tag{2.26}$$

[29] Emergy transformities values can be found in the works of de Swaan-Arons *et al.* (2004) and Odum (1980).

EF^{direct} is calculated using Eq. 2.26, where A_a is the occupation of area by land use type a [m²·yr] and EqF_a is the equivalence factor of land use type a[30]. The EF^{CO_2} footprint estimates the additional biologically productive area required to sequester atmospheric fossil CO_2 emissions and calcination CO_2 from cement burning through afforestation, see Eq. 2.27.

$$EF^{CO_2} = M_{CO_2} \frac{1 - F_{CO_2}}{S_{CO_2}} EqF_f \tag{2.27}$$

M_{CO_2} is the product-specific emission of CO_2 [$kgCO_2$], F_{CO_2} is the fraction of CO_2 absorbed by oceans, S_{CO_2} is the sequestration rate of CO_2 by biomass [$kgCO_2 \cdot m^{-2} \cdot yr^{-1}$] and EqF_f is the equivalence factor of forests. This results in an EF^{CO_2} of 2.7 [$m^2 \cdot yr \cdot kg^{-1}$] CO_2 emitted. In the case of $EF^{nuclear}$ a factor (I_{CO_2}) relating the CO_2 emission per MJ produced energy ($E^{nuclear}$), is used following a similar approach to EF^{CO_2} estimation, see Eq. 2.28.

$$EF^{nuclear} = E^{nuclear} I_{CO_2} \frac{1 - F_{CO_2}}{S_{CO_2}} EqF_f \tag{2.28}$$

Huijbregts *et al.* (2007) compared the EF results to the EI99 results using the ecoinvent LCI data and found that, although the two methods follow a different philosophy, the majority products have an EF/EI99 ratio around 30 m²·yr/ecopoint. This implies that both methods will typically produce the same gross ranking results. An advantage of the EF method is that relatively low uncertainty is attached to the interventions included, such as land occupation, fossil energy use and CO_2 emission factors, and equivalency factors of different land use types.

Narodoslawsky *et al.*, (1996; 1995; 2006), introduced the sustainability process index (SPI). This index also measures the EF or necessary area (A_{tot}), in [m²], required for a specific process to take place into the ecosphere as in Eq. 2.29.

$$A^{tot} = A^R + A^E + A^I + A^S + A^P \tag{2.29}$$

where A^R is the area necessary to produce raw materials, A^E the area requirement to provide process energy, A^I takes into account the area attached to physical installations, A^S is the area required for staff and A^P denotes the area to accommodate products and by-products in the ecosphere. A^{tot} is the total area of the overall process, then it should be normalised for the considered FU. If the FU is a given mass of given raw material i then a series of A_i^{tot} [$m^2 \cdot kg^{-1}$], can be used to formulate other products j as in Eq. 2.30, given the knowledge on the M_{ji} consumption's of i material to give product j.

$$A_j^{tot} = \sum_i M_{ji} A_i^{tot} \tag{2.30}$$

Further normalisation can be done if the figures are divided by the area per inhabitant in the region relevant to the process. This area (a^{inhab}) [m²/cap] is the area available for the yearly supply of goods and energy for each person[31]. The SPI is defined as in Eq. 2.31.

$$SPI = \frac{A^{tot}}{a^{in}} \tag{2.31}$$

A key advantage of the SPI is that it discerns raw materials according to their origin. Thus, the inherent advantage of renewable resources as being neutral for global material cycles, like the carbon cycle, can included in the technological evaluation (Narodoslawsky & Niederl, 2006).

[30] Different EqF_a for a set of land uses can be found in Wackernagel *et al.* (2005).

[31] It may roughly be estimated by dividing the total area of a region by the number of its inhabitants per year.

Remarks

Irrespective on the assumptions made to calculate these metrics, they rely on a given way proposed of assessing value/quality to different types of energy and raw materials and in all cases they assess the process inlets. MIPS, CED and CExD are straightforward to understand and rely on sound thermodynamic underlying principles in its calculation. However Dewulf and van Langenhove (2006b), points out that the use of CExD can not be the sole indicator used to analyse the sustainability of processing options, given that not only efficiency and renewability should be taken into account, but the nature of the resources as well, thus propose the use of CEmD or EF/SPI.

In the case of emergy if it is calculated only for raw materials and types of energy then it mimics a valuation of different type of energies/raw materials and the information is similar to the one provided by CExD. In fact, emergy analysis is equivalent to exergy analysis if the analysis boundary includes ecosystems as pointed out by Hau and Bakshi (2004). Most of the criticism that emergy rises is referred to its link to money, and the use of the Maximum Empower Principle[32] however for engineering applications, agreement with this principle is not essential for using this analysis. According to Hau and Bakshi (2004), the emergy theory of value, as other theories of value based on energy and exergy, focuses on the supply side and ignores human preference and demand[33]. Modern economics, which is focused on humans and their values and not the biophysical world, has doubted the ability of all such theories to capture the value of products to humans. The SPI distinguishes itself here clearly from consumption-based valuation concepts. It not only values conventional eco-efficiency in terms of reduced material input to a process, but sends a strong signal concerning the quality of the input to (as well as emissions from) a process.

A major drawback of this section metrics (MIPS, CED, CExD, CEmD, EF and SPI), is that toxicity aspects are not dealt with. Moreover in the case of thermodynamic metrics, these only deal with the "effort" to get such resources, but they do not consider the actual scarcity of such mineral/fuel. However the simplicity and straightforward methodology for its calculation can surpass the former drawbacks.

2.2.7 Metrics remarks

In this section SD metrics have been discussed, the three dimensions of sustainability have been surveyed in terms of the metrics being used. With regards to the use of a single metric, being these monetary, biophysical, thermodynamical or other, the literature agrees on that this assumption reduces the diversity of information present in possible information feedback's (Korhonen, 2005), consequently multiple metrics have to be used altogether.

In section 2.2.3 economic metrics were reviewed and it was found that despite the availability of different metrics, just a few of them are used namely the TAC and NPV. Due to its simplicity and scope these metrics are appropriate for any process design problem. Another finding is the use of cost assessment methodologies, for addressing the problem of proper cost identification and quantification. In this sense Full/Total Cost Accounting practises have been reviewed and guidelines have been outlined (see section 2.2.3.1). The inclusion of these concerns increases the information and modelling hypothesis required for the calculation of economic metrics.

[32] This principle claims that all self-organising systems tend to maximise their rate of emergy use (empower). This principle can determine which species or ecosystems or any system will survive (Odum, 1980).

[33] Odum (1980) argued that "*money cannot be used directly to measure environmental contributions to the public good, since money is paid only to people for their services, and not to the environment service generating resources or assimilating wastes. Price is often inversely related to the contribution of a resource, because it contributes most to the economy when it is easily available, requiring few services for delivery*".

In the case of social metrics, which were reviewed in section 2.2.4, it was found that their current degree of development makes the application to process design to be very difficult. This is due to two reasons mainly: (i) the actual impacts of a chemical complex are mostly due to the enterprise wide organisation than to actual parts of it separately, and (ii) methodologies which use LCt for social assessment do not have the same common agreed social impact mechanisms and the metric is not widely accepted. A list of possible candidates metrics candidates was done and specifically for the case of process design, proxy metrics related to process safety can be used. Regarding system boundary definition, one possible way to circumvent this problem is to use similar approaches than in environmental assessment: system boundary extension or allocation.

Regarding environmental metrics, studied in section 2.2.5, the needs for its calculation have been elucidated in terms of information and modelling effort: emission estimation, environmental distribution and impact. The different "ready to use" environmental impact methodologies have been compared and the main differences between mid- and end-point modelling have been discussed. In this sense, within the literature there is no agreement between which one of the methodologies should be used, however there is consensus in the use of mid-point approaches when uncertainty wants to be minimised and end-point metrics when ease of understanding of the results is preferred. In the case of metrics based on thermodynamics or ecological footprint they focus mainly on the input side of the process and not on the impacts due to emissions. This simplification makes them robust and easy to understand, but they have to be used together with emission impact related metrics.

2.3 Methodologies for inclusion of sustainability concerns into process design

The following paragraphs review some of the most promising frameworks that arise from the computer aided process engineering community to tackle with the chemical process design problem considering different design boundaries, detail and subject while adopting SD concerns. Diverse methodologies are currently available to cope with the chemical process design problem, and as briefly outlined in the introductory section 2.1, they can be broadly divided in two: (i) mathematical programming approaches and (ii) hierarchical decomposition of solutions.

The following paragraphs contain the most relevant methodologies that have been proposed to tackle with the problem of design/retrofit of chemical process. The focus has been put on methodologies that implemented different metrics, and on the implementation details of each methodology, the incorporation of uncertainty considerations has been addressed separately in section 2.4.

2.3.1 Methodologies based on mathematical programming and optimisation

In the approach proposed by Biegler *et al.* (1997) the process synthesis problem is formulated as a mathematical programing problem. The whole superstructure[34] of all possible combinations of equipment, raw material and products is programed as a mixed integer non linear problem (MINLP). Integer (binary) variables are related to the presence or not of a given equipment in the solution while real variables represent equipment parameters such as tem-

[34]The ensemble of all feasible flow sheets.

peratures, pressures or flow rates.

$$\begin{array}{lll} minimise & \mathbf{f}(\mathbf{x},\mathbf{y}) = & [f_1\ f_2 \ldots f_p] \\ subject\ to & \mathbf{h}(\mathbf{x},\mathbf{y}) = & 0 \\ & \mathbf{g}(\mathbf{x},\mathbf{y}) \leq & 0 \\ & \mathbf{x} \in \mathbf{X} \subseteq \mathbf{R^n} & \\ & \mathbf{y} \in \mathbf{Y} \subseteq \mathbf{Z^q} & \end{array} \tag{2.32}$$

In 2.32, **f** is a vector of economic and environmental objective functions (OF), or commonly known as key performance indicators (KPIs); $\mathbf{h}(\mathbf{x},\mathbf{y}) = 0$ and $\mathbf{g}(\mathbf{x},\mathbf{y}) \leq 0$ are equality and inequality constraints, and **x** and **y** are the vectors of continuous and integer variables, respectively[35]. Algorithms and software available for solving such problems are discussed in section 3.1.1.

A review of models and structures formulations and algorithms to solve them was performed by Grossmann *et al.* (2000). The authors conclude that there has been extensive development of mathematical programming models for subsystems such as reactor networks, distillation systems, heat and mass exchange networks, utility plants, and total process flowsheets. All these models have the feature that they can be used as a basis for developing automated design tools that can effectively help to support design engineers. Azapagic (1999) reviews the use of LCA in process selection, design and optimisation. The review concludes, that process selection should be done considering the environment as a whole, including indirect releases, consumption of raw materials and waste disposal. It also concludes that LC considerations, can ensure that the best environmental option is identified. Moreover the author proposes the use of multiobjective optimisation (MOO) as the most important tool to be used (section 3.1.2 briefly reviews current applied techniques).

The use of these models is not solely a feature of process design, similar approaches have been proposed to the operation problem, and the supply chain design considerations. A review on such modelling approaches is done in sections 6.1 and 7.1, and emphasis is put here on the design considerations. The following sections review the approaches that tackle the design problem using mathematical programing tools.

Methodology for Environmental Impact Minimisation (MEIM)

The MEIM was developed aiming at capturing diverse environmental concerns as objectives within a formal quantitative process design and optimisation framework. Pistikopoulos *et al.* (1994); Stefanis *et al.* (1995) propose the main steps of the MEIM; which include: (i) definition of a process system boundary, (ii) selection of an environmental impact assessment and (iii) incorporation of environmental impact criteria explicitly as process design objectives together with economics in a moO setting. In Stefanis *et al.* (1995), MEIM is applied to design considerations for the production of VCM from ethylene. The conventional process system boundary (which is considered to be the production of VCM only); is expanded to include all processes associated to raw material extraction and energy generation. The advantage of the expanded boundary is that input wastes (to the VCM process) can be also accounted for together with output emissions. As impact categories six indicators are proposed, air pollution by accounting Critical Air Mass (CTAM); water pollution using Critical Water Mass (CTWM) and solid wastes measuring Solid Mass Disposal (SMD). Global warming, photochemical oxidation and stratospheric ozone depletion potentials are the remaining three categories used.

[35] If the integer set Z is empty and the constraints and OFs are linear, then 2.32 becomes a Linear Programming (LP) problem; if the set of integer variables is nonempty and non-linear terms exist in the OFs or constraints, then 2.32 is a mixed-integer non-linear programming (MINLP) problem. Mixed integer linear programming (MILP) problems incorporate integrality and linear functions.

The authors proceed on calculating the former six impact indicators forming an Environmental Impact vector (EI_w) for each pollutant w, each element of EI_w is a category indicator. The Global Environmental Impact (GEI) of the process system is then a summation over w for all pollutants ($GEI = \sum_w EI_w$). The authors proceed on performing optimisation of the process in two ways considering the conventional system boundaries, and including suppliers of raw material and energy (global system boundaries, cradle-gate). They found that the optimal solution obtained from the minimisation of process operating cost rises the environmental impact metrics and that the optimal environmental metrics obtained from the solution of the four independent optimisation problems (min CTAM, min CTWM, min GWI, min POI) for the conventional system are lower than the corresponding values when the optimisation was carried out for the global system. Moreover the estimated operating costs in the optimisation of the environmental metrics within the global system are consistently lower compared to the corresponding operating costs in the optimisation runs performed within the conventional process. Therefore, targeting for minimum "global" waste results in less expensive plant operation. These points are in clear favour that optimising the "whole system" reduces the possibility of pollution shifting between echelons. In Stefanis *et al.* (1997), MEIM is extended to the design and scheduling of batch processes. Instead of optimising a single OF individually the authors propose a MOO formulation to generate the family of designs and the corresponding operating policies that refer to the Pareto curve of solutions trading-off cost versus pollution metrics. The solution of the MOO problem, using the ϵ-constraint method, shows that zero discharge may not necessarily be the best environmental policy, since frequently output wastes are minimised at the expense of increased input waste generation (due to raw material or energy consumption).

In Stefanis and Pistikopoulos (1997) and Vassiliadis *et al.* (2001), MEIM is further extended to quantify environmental degradation caused by unexpected or non-routine events such as equipment breakdown, measurement errors etc. Qualitatively, environmental riskrepresents the probability of environmental damage due to undesired events multiplied by the severity of the environmental degradation. Point (i) of the MEIM is further extended by examining: (a) wastes that are regularly emitted into the air, aquatic, or soil environment and (b) various non-routine releases. In the case of the fully operable state (routine process system status), the EI vector remains unchanged, however, when an event that causes the system to significantly deviate from its normal operating status occurs, they introduce the concept of a "non-routine release environmental impact" ($NREI$). On the basis of models to describe the design and operational characteristics of a given process (e.g. equipment reliability and maintenance policy), an optimisation problem is formulated and solved parametrically to detect the optimal operation of each degraded operating state and the optimal process maintenance schedule that is economically acceptable and at the same time features minimum environmental risk. The OFs used are related to environmental risk, maintenance cost and process revenue (Vassiliadis *et al.*, 2001).

In Hugo *et al.* (2004) and Buxton *et al.* (1999), the authors combine a material design technique with the optimisation of process topology. Their approach is based on the estimation of a given substance properties, using UNIFAC,and then using such desired compound in the flowsheet model. The optimisation of the flowsheet is performed using TAC and EIs are calculated using EI99. The combined molecular structure and flowsheet topology problem is formulated as a MINLP and solved using decomposition techniques in GAMS.

Finally in Hugo and Pistikopoulos (2005) the MEIM methodology is further extended to the field of strategic decisions related to design and planning of SCs. The problem that the authors tackle is the planning and design of a chemical SC network. The authors aim at designing a SC network of integrated production facilities satisfying a given set of market demands,

using technologies from a set based available raw materials over a given planning horizon. They consider maximising NPV while minimising EI (measured using EI99).

The MEIM has an inherent LC thinking, it allows for routine and non-routine emissions and has been used for the design, operation and strategic decisions. However effluents treatment, emissions estimations and the actual use phase of the product have been disregarded or grossly simplified and emphasis has been put on showing the mathematical capabilities. Moreover, its broad coverage of different problems is based on the use of several simplifying assumptions on models, which is a common feature of mathematical programming approaches.

Optimum LCA Performance (OLCAP)

Azapagic and Clift (1999) propose Optimum LCA performance (OLCAP) an approach for incorporating LCA into system optimisation comprising four main steps: (1) carrying out an LCA study; (2) formulation of the design problem as an optimisation problem in the context of LCA; (3) MOO considering environmental and economic criteria and (4) MCDM for selection of the best compromise solution. Regarding point (2), in Azapagic and Clift (1995) the authors propose the application of Linear Programming (LP) to LCA for analysing and managing the environmental performance of a complete product system. The authors first solve the LP considering economic performance function and then introduce environmental considerations by inclusion of other OFs. The case study proposed is the production of different polymers. Operations and activities from the extraction of raw materials up to production of thermoplastic products are all included (cradle-gate).

In Azapagic (1999) and Azapagic and Clift (1999), OLCAP's step (2) is extended to a MILP, by considering some decisions related to product manufacture, the case study presented is associated to the boron mining industry. Step (3) is performed using ϵ constraint. The authors use the mid-point approach of Heijungs *et al.* (1992) for the EIs while cost and profit are used as economic indicators; total production is also used as objective. For step (4) Azapagic and Clift (1999) emphasise that if all objectives are considered to be of the same importance, then possible compromise solution could be the one where all objectives differ from their optimum values by the same percentage. However, if the objectives are not considered to be equally important, then a given MCDA technique has to be used to identify the best compromise solution.

One of the main drawbacks of OLCAP is the looseness of the definition of the first step, where a LCA has to be performed, this issue has been addressed in other methodology proposed by the author, process design for the environment (PDfS), see next section 2.3.2.

Combinatorial process synthesis

Chakraborty and Linninger (2002) propose a combinatorial process synthesis, which combines informed search for systematic synthesis of structural alternatives with mathematical programming. The solution strategy is two-tiered, (1) first superstructure generation, followed by (2) superstructure optimisation. In the enumeration and estimation of Pareto efficient structures, cost and EI estimations are used. EI is calculated using the global EI vector based on MEIM. This step uses a LP algorithm based on previous author's works (Linninger & Chakraborty, 1999, 2001). As a result a Pareto frontier (PF) with different super structures is obtained. MOO using the ϵ-constraint method, is used to generate the PF for each superstructure, taking into account economic and environmental objectives. The economic function is operating cost and the environmental function takes into account a global pollution index using WAR, the decision variables in this case are operative variables which depend

on the superstructure being optimised. The case study presented is the design of plant-wide waste treatment facilities. This methodology has been further extended to cope with uncertainty in input variables for the design of waste treatment plants (Chakraborty & Linninger., 2003; Chakraborty *et al.*, 2004), (see section 2.4.4.2). Chakraborty *et al.* (2003), extended the methodology to long term operation and planning. Their proposed framework uses as a MILP that considers the estimation of waste production and the objective is to find the plant-wide waste treatment facility taking into account this estimation from a given business plan. The business plan also incorporates a forecast on environmental regulation and a CO_2 emission cap is enforced as a constraint in the model.

Other mathematical programming approaches

Hertwig *et al.* (2002) propose a methodology for the consideration of chemical complexes which incorporates economic, environmental and sustainability costs combined in a single OF to be optimised. The economic function includes TCA considerations while the EI is assessed using the WAR methodology and its included in the optimisation function as a given percentage of the raw material costs (Xu *et al.*, 2005). The case study consists of an agrochemical complex plant which also incorporates several CO_2 processing facilities. The model includes the material and energy balances, rate and equilibrium equations that describe the performance of the individual plants and how they are connected. The problem obtained is a MINLP which is programmed using GAMS and solved using DICOPT. Singh *et al.* (2007) studied the same problem using TRACI metrics. The authors found that improving the environmental performance for some impact potentials worsens others. Thus, attempts to optimise global warming end-up increasing fossil fuel consumption, human health and photochemical smog.

Recently, Guillen-Gozalbez *et al.* (2008), study the HDA production problem stated in Douglas (1988), using a mathematical programming model. The problem is a MINLP for which different objectives are used as optimisation functions. The EI is calculated using EI99, while the economic metric considers the overall cost. The ϵ-constraint MOO formulation is used to generate the PF of possible process flow sheets. The results show that significant environmental improvement can be achieved through structural modifications in the process flow sheet, as well as changes in the operating conditions.

2.3.2 Methodologies based on hierarchical decomposition and optimisation

The most widely used decision hierarchy in process design has been proposed by Douglas (1985, 1988), stating a decomposition of decisions as follows[36]:

Level 1: type of process batch or continuous.
Level 2: input-output structure of the flow sheet.
Level 3: possible recycles.
Level 4: separation network: general structure (i.e. phase splits), vapour recovery system; liquid recovery system; solid recovery system.
Level 5: heat integration[37].

[36]This hierarchy is based mainly on problem complexity, each layer corresponds to a different problem. The core decision (level 1) is process type, the input output and recycles are mainly defined by reaction path. Separation network synthesis is performed in four stages done after recycles flows is outlined, while heat integration comes last.

[37]Heat integration was tackled first using pinch analysis. Energy pinch was introduced by Linnhoff *et al.*, (1982) aiming at synthesising heat exchanger networks (HENs). Several other pinch methodologies rose after energy pinch, such as water pinch or hydrogen pinch. El-Halwagi *et al.* (2003; 1998; 1995), exploited the analogy between mass and

In each layer different flow sheet options are generated, and the best is selected to pass to the next layer. The number of sub-levels within separation level is proposed in other paper (Douglas, 1992), trying to address minimisation of wastes, a brief classification of waste minimisation problems is also proposed and based on waste origin[38]. Recently in an attempt to mimic these hierarchies, and serve as heuristics for "green engineering", the 12 principles of green engineering have been proposed by McDonough *et al.* (2003) and Anastas and Zimmerman (2003). These principles provide a structure to create and assess the elements of design relevant for maximising sustainability of a given process. Engineers can use these principles as guidelines to help ensure that designs for products, processes, or systems have the fundamental components, conditions, and circumstances necessary to be more sustainable (Anastas & Zimmerman, 2003).

The main tool used for alternative flowsheet comparison is process simulation[39]. Current steady-state process simulation is deterministic, the basic plant configuration is decided and the simulator is used to size unit operations and estimate process energy requirements, product yields and chemical separation profiles. Despite its excellent capabilities regarding material and energy bookkeeping, based on their thermodynamic and unit operation models, simulators have critical omissions that prevent its effective application with regards to economic, environmental or safety applications. In this sense, simulators lack of (i) waste separation and treatment technologies models which are not part of their libraries; (ii) environmental data and parameters are not tabulated; (iii) kinetic data regarding product and byproduct formation is scarce in simulators databases, and (iv) information regarding process safety is not available (Shonnard *et al.*, 2001).

Another drawback of the use of process simulation lies in the time required for the simulation to run. In many cases and due to the presence of material recycles and its sequential modular approach, this computation time rises significantly. One approach towards minimising this effect is to change the simulation into an equation oriented approach.Several methodologies that are based on the use of simulation are available. The following sections review the most relevant regarding process design considerations.

Environmental fate and Risk Assessment Tool (EFRAT)

EFRAT is introduced by Shonnard and Hiew (2000), it performs in-process gate-to-gate environmental assessments including the impact of energy consumption and is organised into three calculation modules: (a) air emission estimation, (b) environmental fate and transport, and (c) relative risk assessment. Output results from a process design simulator (Hysys) are used to calculate emissions and energy consumption. The algorithm is demonstrated for the comparative assessment of different design alternatives for VOCs recovery and recycle; for a gaseous waste streams. EFRAT includes energy consumption within the process for impact analysis, regardless of where energy is produced (on site or off site). Within EFRAT only waste streams are considered, emissions to air are estimated on a unit operation by unit operation basis. A general relative risk assessment dimensionless metric (I_i^*) is proposed based on Eq. 2.33, which is independent of environmental sink and is valid for environmental and health

heat transfer to develop the concept of mass exchange network (MEN) synthesis, based on the pinch method for HEN synthesis. As applied to pollution prevention, the goal of mass exchange networks is to transfer species that are potential pollutants in effluent streams to streams in which they may have positive value. A deep review of application of these methodologies is presented in Dunn and El-Halwagi (2003).

[38]The recommendations obtained by this procedure are fairly general (e.g. change the chemistry, change the solvent, look for different separation system), and serve as starting points for search of design alternatives (Cano-Ruiz & McRae, 1998).

[39]Details of different process simulation tools and its use joint with optimisation are further discussed in section 3.1.

risks.

$$I_i^* = \frac{[(EP)\cdot(IIP)]_i}{[(EP)\cdot(IIP)]_{benchmark}} \tag{2.33}$$

Where IIP is the inherent impact or toxicity parameter and EP_{ij} corresponds to the exposure potential of compound i calculated as in Eq. 2.34, where D_{ij} correspond to the i-th compound in the j-th sink[40] distribution factors, and τ_{ij} is the environmental persistence of chemical i in compartment j usually expressed in [day].

$$EP_{ij} = D_{ij}\tau_{ij} \tag{2.34}$$

The different EFRAT indices are referred to the following categories[41]:

- Abiotic indexes: global warming, ozone depletion, smog formation and acid rain.
- Health related indexes: human toxicity and human carcinogenicity, in both cases by ingestion and inhalation routes.
- Ecotoxicity index: fish toxicity.

These indices are the same proposed in the WAR algorithm methodology, however a single process composite index is developed by applying a normalisation factor using national emission data for each impact index. The normalised impacts are further combined using a valuation step that uses EI95 weighting factors for each EI category based on their "distance to target".

Chen *et al.* (2002b) provide design guidelines for VOC recovery and recycling based on results generated from a software tool SCENE[42], that generates process designs considering the NPV and environmental metrics (calculated using EFRAT). The AHP technique is used to weight economic and environmental criteria, while optimisation is carried out by exhaustive enumeration (brute force method). LCA cradle to gate data is gathered from EIO-LCA[43], together with data from SCENE the authors complete a cradle to gate inventory. The authors found differences when comparing different process options regarding different EI; they also report that in all cases both the environmental and economic assessments provided similar optimum design configurations; suggesting that performing only economics based optimisation is sufficient to minimise design EIs. In the case of VOC recovery, pre-manufacturing LC impacts for global warming and for acidification are less important compared to the manufacturing stage impacts. The authors also found that including pre-manufacturing LC stages can have a profound effect on the environmental assessment and optimisation.

Chen *et al.* (2003) propose other integrated software tool for environmental and economic optimisation. Key points of this tool are the implementation of a genetic algorithm (GA) for optimisation and the selection of optimisation process variables based on a scaled gradient analysis (SGA, proposed by Douglas (1988)), where each design variable is changed slightly, increasing and decreasing its value relative to the base case values; consequently a ranking of "better to modify" variables is formed and used by the GA.

In Chen and Shonnard (2004) a systematic and hierarchical approach for incorporating environmental considerations into all stages of chemical process design is proposed and applied to early and detailed stages. At early stages of process design, environmental assessment includes emission estimates from major process equipment, considers pollution control efficiency, and generates nine risk-based EI indices (using EFRAT). The economic assessment is

[40] Air, water and soil are considered as possible sinks.
[41] Explicit definitions of them are given in Sinclair-Rosselot and Allen (2002b).
[42] Simultaneous Comparisons of Environmental and Non-Environmental criteria.
[43] http://www.eiolca.net/

based on the cost of raw materials and reaction stoichiometry. In their case study these metrics allowed for the selection of the appropriate production route. The detailed stage includes more detailed emission estimations based on the use of process simulation for the alternatives selected in early stages. The case study is the production of maleic anhydride and the whole problem resides in route selection from n-butane or benzene as raw materials. The authors use a combination of economic and environmental indicators using AHP for formulating a single OF. GA is used for optimisation. The authors show that the early stage metrics are able to hint on the correct route.

In Kemppainen and Shonnard (2005) comparative LCAs based on commercial process simulation (Aspen Plus) for biomass to ethanol production are presented. Process modifications considering reactor recycles and heat integration were simulated and process stage LCIs were accordingly generated. A database of LCIs (Boustead database[44]) is used to gather pre manufacturing LC, while process simulation results complete the LCI. EI assessment is performed using EFRAT.

Several conclusions from the work associated to EFRAT can be drawn. First, economic and environmental objectives can be minimised at the same time. The inclusion of pre-manufacturing LC stages is key for some impact categories, and finally in order to design flow sheets based on optimisation the selection of variables is critical. Moreover the use of simple metrics such based on SGA seems feasible and helpful. Furthermore, process simulation can and has been actually proven to be a robust tool for gate-gate LCI information generation.

Process Design for Sustainability (PDfS)

Azapagic *et al.* (2006), propose the use Process Design for Sustainability (PDfS), a methodology for the integration of SD considerations into process design. It is based on LCt and it is implemented by adding more tasks to what the authors consider "traditional process design stages" (project initiation; preliminary design; detailed design; and final design).PDfS is based on the metrics defined in (Azapagic & Perdan, 2000), and also uses metrics from the CML and EI99 methodologies. Regarding social metrics the authors use the Dow's F&EI for measuring risk from fire and explosion. The authors apply their methodology for the design of a vinyl chloride monomer (VCM) production plant, no optimisation is done and the selection of different processing options is not explicitly made, instead pros and cons of different raw materials and flowsheets are elicited. The authors point out the need for the selection of a given MCDA technique for the elicitation of preferences and consequently for aiding decision making with multiple objectives. The selected processing option at early stages is simulated using ChemCAD and the results serve as start for the LCI and the calculation of other metrics. The application of LCA to their process identified different environmental "hot spots" related to indirect activities and mainly stem from the LC of chlorine, ethylene and generation of electricity and heat.

Environmental optimisation (ENVOP) and ENVOP Expert

ENVOP is a qualitative approach towards pollution prevention based on a waste minimisation procedure introduced by Halim and Srinivasan (2002a,b,c) used in continuous process plants and further extended to the case of batch industries (2006). The procedure follows the approach of Hazard and Operability (HAZOP) analysis in process safety. During an ENVOP study, each process line and unit operation is analysed to identify potential waste minimisa-

[44] http://www.boustead-consulting.co.uk/

tion alternatives that meet the desired environmental objectives[45]. The authors claim that one common shortcoming of the quantitative approaches is the complexities involved in modelling industrial-scale process with a large number of interconnections between the streams and the processing units, which renders an optimisation problem usually difficult to solve. The ENVOP framework proposed comprises the following steps

1. Base-case process flow sheet simulation using a process simulator.
2. EI calculation using WAR algorithm and process economic analysis.
3. Qualitative waste minimisation analysis using ENVOP Expert to generate alternatives[46].
4. Modification to the base process based on the alternatives proposed[47].
5. Comparison between the modified and the base-case process in terms of EI and economics.

The application of the ENVOP is tested in the production of HDA that is simulated using a commercial process simulator (AspenHysys).

Path flow decomposition

The methodology developed by Uerdingen *et al.* (2005, 2003) is based on a detailed economic analysis of the process under investigation by decomposing it into component path flows and assigning to each path a given cost. Their method consists of three steps, (i) path flow decomposition which decomposes a process flowsheet into a set of flow trajectories for each of the components in the process; (ii) path flow assessment which assigns a given value to each path according to different metrics and (iii) identification of retrofit options based on the former indicators.The decomposition technique used in step (i) is based on graph theory and aims at identifying recycles within the flowsheet. In step (ii) each component path flow is characterised using the following indicators:

- *Material-Value Added* (MVA) which is based on the raw material and product prices;
- *Energy and Waste Cost* (EWC) which is calculated using related to utility consumption and waste treatment costs;
- *Reaction Quality* (RQ)[48], positive values indicate a positive effect on overall plant productivity defined as the total mole flow rate of the reactants required per total mole flow rate of the desired products produced, whereas negative values identify undesirable located component path flows in the process and thus highlight potential for cost savings through mass-flow reduction or rerouting of a path flow;
- *Accumulation Factor* (AF)[49], this indicator rates the accumulative behaviour in recycle flows and, therefore, only applies to component cycle path flows; a large AF often indicates unfavourable buildup in a cycle and can be caused by non optimal separation or too low reaction conversion;

[45]These alternatives are derived by combining a set of qualitative guide-words (such as more, less, etc.) with process variables (pressure, temperature, flow rate, etc). The algorithm is based in Douglas (1988) hierarchical decomposition, extended to incorporate potential strategies to reduce waste generation right from the early stages of design.

[46]ENVOP Expert, uses a two step procedure: (i) waste detection and diagnosis followed by (ii) waste minimisation option generation.

[47]Step (4) uses a p-graph representation of the process, which allows for every waste stream to be traced upstream to track waste sources. All waste sources are further studied by using digraph models, representing cause and effect of different variables in each process unit, and detailed knowledge.

[48]Defined as $RQ = \frac{(extent of reaction)\cdot(reaction parameter)}{(sum of desired products)}$.

[49]Defined as $AF = \frac{(mass of component in recycle)}{(sum of component mass leaving recycle)}$.

- *Energy Accumulation Factor* (EAF)[50], calculates the accumulative behaviour of energy in an energy cycle path flow, Since it is of interest to recycle or recover energy, the EAF should be as large as possible in order to save energy.

Step (iii) ranks path flows in terms of Total-Value Added (TVA), which is defined in terms of MVA and EWC, and defines different retrofitting actions depending on the signs of RQ and AF. Other metrics that the authors use are the Tallis (2002)'s SD metrics related to material, energy and water consumption. Also the indices developed by Heikkilä (1999) and WAR are used in this methodology to measure the process intrinsic safety and EI respectively.

The generation of retrofit alternatives and assessment is performed in such a way that alternatives show differences regarding the a base case. A local sensitivity analysis is performed for different input variables (X_i) affecting the path flows and the indicators former indicators (Y) are checked for changes using Eq. 2.35.

$$\Delta Y = 100 \left[\frac{f(X_r) - f(X_r + \Delta X_r)}{X_r} \right]^2 \tag{2.35}$$

The case studies presented in Jensen *et al.* (2003), showed that rather than a trade-off between competing factors, the generated retrofit alternatives either improve some indicator or are neutral to them. This means that the process optimisation becomes easier and multiple objectives can be satisfied without resorting to trade-offs between them. In the case of Uerdingen *et al.* (2005) and Carvalho *et al.* (2008) an SQP optimisation based step is performed to set design variables values[51]. The methodology has been applied to the HDA of toluene, where it showed different retrofit options.

ETH group methodology

Heinzle *et al.* (1998) and Koller *et al.* (1998) present a methodology based the use of Mass-loss indices (MLI), combined with environmental and economic weights. The MLIs are considered for flow sheet different sections separately, following a hierarchy similar to the one proposed by Douglas. MLIs are defined in the same way as an environmental load factor (see Eq. 2.12) and are a ratio of mass flows. The reference flow (which is used in denominator), changes depending on the flow sheet section (e.g., in the reactor section is used the outlet mass flow of the product). They take into account mass/energy balances regarding the formation of coupled products or by-products, loss of un-reacted reactants, impurities contained in substrates, solvent consumption, catalyst consumption, auxiliary materials (e.g. neutralisation agents), and equipment utilisation (based on equipment's life span and its use) and energy use. These balances over smaller sections of the flow sheet are used as estimates of the overall emissions around the whole plant. The authors propose calculating environmental indices based on the product of an environmental factor and a MLI defined as before. In order to estimate the environmental factors, the authors introduce an ABC method, where they classify environmental problems in classes[52]. These classes take into account three different aspects of environmental concerns with regards to input streams: (i) complexity of synthesis of raw materials, (ii) critical materials used for the production of raw materials and (iii) availability of raw material resources; while in the case of effluent streams they take into account air and water pollution, and special problems such as downstream processing or special landfill system. The authors

[50] Defined as $EAF = \frac{(energy recycled)}{(energy leaving the recycle)}$.

[51] The selection of optimisation variables and weights coefficients used in the single objective optimisation takes into account the sensitivity of variables with regards to each optimisation function term as in Eq. 2.35.

[52] Class A characterises serious problems, C are non critical ones, while B lies in between. Class C problems are assigned an environmental factor of 1, while for class A a value of 4 is used.

assume that high complexity in the processing steps of a product is a significant indication of the degree of pollution associated to it.

Koller *et al.* (2000) introduces different categories for environmental and health effects and also considers safety issues, this way the authors provide a short-cut methodology for the assessment of safety, human health and environment (SHE) considerations. The number of classes for the ABC methodology is increased and depends on each category taken into account. In the case of safety these categories are: mobility (relative amount of substance releasable into air), fire/explosion (probable potential energy with O_2 reaction), acute toxicity and reactivity (substance decomposition probability and rise in adiabatic temperature). For the assessment of health aspects, irritation and chronic toxicity are taken into account; while in the case of the environmental aspects, water and air effects are considered separately, as well as degradation and accumulation; finally solid waste is also considered. In the case of Koller *et al.* (2000, 1998), the examples used are from the batch industries.

Hoffmann *et al.* (2001) propose a methodology applicable for the early stages of design, taking into account economic and environmental objectives. They aim at identifying different technologies and guiding principles rather than a detailed assessment of process. The authors divide the design problem into three phases: (i) early, (ii) detailed and (iii) final. The authors use a database of unit operation inventories as the source for the alternatives generation step. For the evaluation of each alternative the metrics used are: total annualised profit per service unit (TAPPS, see Eq. 2.7, instead of NPV), and the material intensity per service (MIPS[53], see section 2.2.6). They argue that complex environmental metrics can be very helpful for a detailed evaluation of complete inventory data, however the information they provide is questionable for early decision making. This suggests the use of proxy measures (i.e. MIPS, TAPPS), for the environmental evaluation in early design phases.

Recently, Sugiyama *et al.* (2008) have proposed a methodology for chemical process design at the early stages, with four stages, where at each stage selection of process routes are modelled and evaluated and promising options survive to the next design stage. They consider decision of two type: process chemistry and process conceptual design. The selection of indicators is based on the relevant available information, at each stage. For the case of process chemistry raw materials cost, CEDs and MLIs are computed, while at conceptual design stages, NPV and methods for calculation of potential EI as well as safety proxy indicators. In order to select which process/reaction survives next stage the authors aggregate the metrics into a single score by using different weights. These weights are defined at each stage depending on the metrics used. A weights sensitivity analysis is performed, the authors changed the values of a set of three weights which add up to 1, and show in a ternary diagram which alternative is selected depending on the weights values. They present a case study of methyl methacrylate production. Despite the fact that the methodology provides quantitative results the authors emphasise that results of it should be used when differences are very significant.

Other approaches based on hierarchical decomposition

In Alexander *et al.*, (2000), a process simulation (Hysys) based approach is presented. The process simulation is used together with a spreadsheet (MS Excel) to calculate economic (rate of return) and environmental objectives (acidification and direct GWP). The authors consider the optimisation of single objectives first and then apply certain weights (calculated using AHP), to normalised OFs to calculate trade off options. The case study represents a medium-pressure nitric acid plant using the Uhde technology.

[53]They propose a MIPS calculation divided in five categories: abiotic resources, biotic resources, water, air and movements in agriculture and forestry.

Fu *et al.* (2001) propose a three level optimisation framework for the design of chemical processes taking into account EIs, with metrics based on WAR, and profit as design objectives. Their framework is based on AspenPlus for the calculation of the process flowsheet data, a non linear optimiser and on top of those a MO optimiser. The authors only explore solutions at bounds for each of the OFs, which correspond to all the Pareto surface bounds. The case studied is the HDA of toluene to benzene. The WAR algorithm use is exemplified by a case study based on acrylic acid production. The ChemStations simulation software is used for estimating mass flows and energy consumption's.

Regarding the use of metrics based on thermodynamic functions or footprint concepts (see section 2.2.6), the SPI has been used together with process optimisation (AspenPlus) by Narodoslawsky and Krotscheck (2000). Bakshi (2002), presents a methodology based on thermodynamics to join the process systems approach, systems ecology and LCt. The author proposes the use of exergy and emergy analysis for SD assessments, combined with LCA. He argues that both approaches are complementary given that LCA focuses on the impact of emissions while emergy analysis focuses on the ecological and economical interventions. The author proposes to use the transformities reported in literature, which mainly rise from the works of Odum (1980), to calculate the associated emergy of a process and based on it make the corresponding assessments. The calculation of emergy requires previous analysis in terms of mass and energy balances over a given system boundary.

In Biwer and Heinzle (2004) a method for environmental assessment, based on the environmental relevance of a substance referred to 14 EI categories. The methodology classifies all compounds using an ABC methodology depending on the compound behaviour regarding each impact category. The methodology is applied to a case study or early stage design in the batch industry (Biwer *et al.*, 2005). Kralish (2009), proposes other methodology which is based on the data available in R&D stage, the author proposes three metrics (i) energy demand, (ii) risks concerning human health and environment using the environmental and human factor and (iii) costs. The energy factor incorporates the CED resulting from all processing steps, using it as a proxy metric for LCIA categories such as ADP, GWP, POCP, ODP, AP and EP. The results for each of the processing alternatives being assessed (related to the synthesis of different ionic liquids processes), are ranked using the MCDA method PROMETHEE.

2.3.3 Methodologies remarks

The methodologies proposed in sections 2.3.1 and 2.3.2 are few examples of how the process design complexity increases when dealing with SD considerations. Table 2.4, aims at summarising those findings. Two approaches are available for problem representation when dealing with topological changes in the flowsheet: (i) use of superstructure, or (ii) the use of a hierarchy of decisions. In the first case, the surveyed literature related to superstructure, solves the problem using a mathematical programming formulation (MILP-MINLP). However in the second case the hierarchy of decisions allows for generating different topologies (i.e. fixed flowsheets), which are tested using process simulation.

Most of the methodologies tackle the conceptual design problem at the mesoscopic scale. In all the methodologies that consider the input-output problem the approach considers the use of different models of increasing complexity, starting with mass balances and at higher detail levels (including conceptual level) using process simulation. In this sense the application of shortcut/simple model results to drive further modelling seems to be the current trend as shown in Chen and Shonnard (2004).

In the case of the macroscopic boundary the problem is simplified and the reviewed approaches use a mathematical programming approach.

None of the current process synthesis approaches has proven better than the other in all senses. The selection of one of the former methodologies is highly problem dependant, mainly due to different boundary setting and detail. In the case of mathematical programming techniques the ability to solve large process superstructures depends highly on the type of simplifications that are within each of the unit operations modelled, however its application provides with the ability to cope with all possible processing structures at the same time. In the opposite side of superstructures lies the hierarchical decomposition, where the model's complexity rises when each layer is previously solved, in this sense once the composition change is solved (reaction), then reactor effluent separation problem is tackled and so on; this approach allows for the use of more complex models but process topology changes are more difficult to treat.

Regarding the integration of SD concerns, two main strategies were found in all methodologies reviewed: the use of MCDM techniques (see section 3.3) for aiding in the selection of a single optimal solution, and the provision of a set of non-dominated solutions, a Pareto Front. The approach that seems less restrictive is the generation of a non-dominated solutions set. This set can be used if consensus is achieved between decision-makers, after all alternatives are elucidated and compared.

The adoption of different process design steps is done in most of the methodologies proposed. All authors coincide on a sequential approach towards the selection of processing routes using different indicators. Being the processing route selected the process design is performed. In all the methodologies the approach adopted is iterative requiring the return to previous steps if new information is available or required.

With regards to the inclusion of LCt in the methodologies proposed it is important to note that OLCAP, PDfS and MEI, readily incorporate the concepts while some other such as EFRAT does not, while WAR and Path flow decomposition focus attention only on the processing stage. Focussing in one echelon more than in others allows for a better estimation of the actual EI of that LC stage, this implies a bigger modelling effort, but allows for the possibility of problem shifting, thus EI is risen somewhere else along the production SC.

Many of the methodologies propose emission estimation methods, such is the case of EFRAT, MEI, OLCAP and PDfS, while others also propose the use of proxy estimations (Path Flow Decomposition and ETH). All reviewed methodologies strive for a better estimation of emissions, by using many different estimation methods and take into account the emission and waste treatment as a part of the design process. These facts are fundamental for the identification of hot-spots which could render new process alternatives.

Regarding the environmental fate of compounds some methodologies propose their own environmental models, as in the case of (i) MCMs: EFRAT or (ii) single compartment as the case of WAR and ETH. Other methodologies rely on ready to use CFs that embed the environmental model in them, such is the case of MEIM, OLCAP, PEPA and others, where the EI modelling approach is not emphasised. The application of environmental models to accurately asses the EI of an emission is a matter of the goal and scope of the study. While at the micro and mesoscopic scales the use of mid point or proxy indicators is done, at the macroscopic level, ready to use methodologies are used, where the trade offs of a single environmental metric and a economic metric are studied.

Former approaches are appropriate for the level of detail that they aim at studying, however very few of them have studied the uncertainty that its inherent in the models used, and how SD indicators are affected by it. Next section discusses how uncertainty is addressed when SD is considered in process design and operation.

Table 2.4: Comparison of reviewed process design methodologies.

Design problem	Representation	Evaluation and Strategy	Detail Level			System Boundaries		
			Input-Output	Conceptual	Detailed	Microscopic	Mesoscopic	Macroscopic
MEIM	MILP-MINLP	mo-EpsConstraint	X	X		X	X	X
OLCAP	LP-MILP	MCDM + mo-EpsConstraint	X	X			X	
PDfS	Process Simulation	Heuristics	X	X			X	
Combinatorial process synthesis	MILP-MINLP	mo-EpsConstraint		X			X	X
EFRAT	Hierarchical decomposition/Process Simulation	MCDM, SGA and heuristics for optimisation	X	X			X	
ENVOP	Graph theory	Heuristics based on HAZOP		X	X		X	
Path Flow Decomposition	Graph theory	Heuristics based on material loops		X			X	
ETH group	Hierarchical decomposition/Process Simulation	Heuristics based on MLIs	X	X			X	
Hertwig *et al.*	MILP-MINLP	single objective optimisation	X					X

2.4 Including uncertainty in sustainable process design and operation

The following sections aim at summarising key issues related to different uncertainty definitions and classifications (section 2.4.1). The identification of uncertainty sources and its representation is briefly reviewed under section 2.4.2.

Two main approaches are found with regards to uncertainty in models. One of them, aims at analysing how uncertainty in model inputs affects model outputs, and the other goes further at including a decision as model output. The analysis of input-output relationships is a prior step in using the model for decision making, such methodologies are reviewed under section 2.4.3, while others that aim at decision making under uncertainty and are reviewed under section 2.4.4.

2.4.1 Uncertainty definitions and classifications

Uncertainty is very difficult to define, and many authors propose different definitions and possible classifications of sources and means to quantify it. The ISO standard for expression of uncertainty in measurement (GUM) (ISO, 1995), is vague in its definition "*the word uncertainty means doubt, and thus in the broadest sense uncertainty of measurement means doubt about the validity of the result of a measurement*". The former considers only uncertainty related to a measurement, but uncertainty is also related to the prediction of future events. Clearly both measurement and future predictions are related if a model is considered; in this sense measurements are fed to a model which predicts future conditions.

Walker *et al.* (2003), in an attempt to clarify the situation with regards to uncertainty in modelling, discuss to assign three uncertainty dimensions being: *location*; where uncertainty manifests in the model, *level*, how large is it ranging from deterministic knowledge to total ignorance and *nature* whether is due to knowledge imperfection or to phenomena inherent variability. Within *location* the authors discuss that model uncertainty can be found in: boundaries selection (model context), model structure, model inputs (i.e external forces that drive the system), model parameters and model outcomes. In the case of uncertainty *level*, it increases from complete determinism, statistical uncertainty, scenario uncertainty, recognised ignorance, indeterminacy and total ignorance. Regarding the *nature* of uncertainty, epistemic uncertainty which is due to knowledge imperfection, can be reduced by more research and empirical efforts, while variability uncertainty is inherent variability associated to human and natural systems specially concerning social, economic and technological developments, that can not be reduced and should only be assessed.

de Rocquigny *et al.* (2008), emphasise on the following terms related to uncertainty:

- *irreducible-aleatory* vs. *reducible-epistemic*; irreducible refers to events which remain unpredictable whatever the amount of data available while reducible/epistemic refers to uncertainty types which can be directly reduced by an increase of available data.
- *ambiguity* vs. *imprecision*; as used by Kraslawski (1989) are related to the establishment of the *truth value* of a proposition, and to the *sufficient determination of its value* in a given scale.
- *variability* vs. *uncertainty*; variability is used when unpredictable behaviour is modelled while uncertainty in the other case. Huijbregts (1998a) uses uncertainty when referring to the use of inaccurate measurements, lack of data or model assumptions; while variability in the case that doubt rises from inherent variations in the real world.
- *parameter* vs. *model uncertainty*: the first refers to the uncertainty associated to model inputs and to the level of information available on such inputs, while the second con-

cerns the model's adequacy to represent reality in terms of its structure (equations, discretization, numerical resolution, etc.).

No matter how it is classified all uncertainties should be dealt with in an appropriate way (Granger *et al.*, 1990; Heijungs & Huijbregts, 2004). All sources of uncertainty have a certain degree of subjectivity given that subjectivity manifests in the model building phase when decisions are made concerning which elements will be taken into account within the analysis. Thus, subjectivity affects the manner in which modelers build the model (Walker *et al.*, 2003).

According to Granger *et al.* (1990, Ch 4. p50), empirical parameters (or chance variables) are the only ones that are susceptible of description by a probabilistic measure a probability distribution function (pdf, based on frequentist or Bayesian analysis[54].). Bode *et al.* (2007) link the frequentist approach to objective probabilities, where the realisation probability of an outcome A ($p_f(A)$) is defined as the limit of actual realisations of A ($n_f A$) divided by the total number of experiments (n_f) as in Eq. 2.36.

$$p_f(A) = \lim_{n \to \infty} \frac{n_f A}{n_f} \tag{2.36}$$

The use of Bayesian analysis allows subjective probabilities as in the case of Eq. 2.37, where the probability of an outcome A depends ($p_B(A|Info)$) on the observer experiences and knowledge ($Info$).

$$p_B(A|Info) = \frac{p_B(Info|A)p(A)}{\int_{-\infty}^{+\infty} p_B(Info|A)p(A)dA} \tag{2.37}$$

where $p(A)$ is the probability that the outcome A is realised, while $p_B(Info|A)$ expresses the probability that the information would be realised if the true state of nature would be A. Empirical variables have to be measurable either now or at some time the past or future to be susceptible for description via pdf. These variables are the only type of quantity that are uncertain and can be said to have a *true* value as opposed to *appropriate or good* values that are subject of bias due to value decision. This definition of true and good values rises only from the way these pdfs were generated, Bode *et al.* (2007) argue that using measurement data does not mean that the probabilities are objective, data may differ between scientists, trust on data will be different and may be rejected, consequently distributions derived from experimentation are subjective and will depend on the scientist knowledge (trust/experience) and consequently will always be Bayesian.

If uncertainty rises from the subjectivity that is embedded in the models and in the reality that these models are trying to explore, then no further clarification is required. However an uncertainty classification might shed some light with regards to which parameter or model parts are uncertain and why. In this thesis the following classification is proposed, using the uncertainty location proposed by Walker *et al.* (2003). For any given model $y = f(X)$ uncertainty will be located in:

- *Model uncertainty*: raises from the selection of a model which is motivated by belief of model's capability to represent the reality it simulates. This uncertainty is associated to the appropriateness of a given f in representing the values obtained of y, and to the inclusion of the appropriate set of X to represent the reality.
- *Parameters uncertainty*: despite the model's shape (f), each model parameter is subject to uncertainty due to its nature, its a parameter of a model which tries to model reality.

[54] In practise most assertions regarding uncertainty in data are based on subjective informed estimates, when classical statistical analysis are applied, the assumptions underlying Bayesian statistics are implicitly made (Bjorklund, 2002)

Model parameters and process variables come from different sources, however both can be treated in the same way. In this case the uncertainty is associated to the use of uncertain parameters or variables X within the model.
- *Variability*: all other uncertainty that its not coped with in models and parameters, and that it is due to subjective valuation.

Note that no difference is made between model parameters and model inputs, and both are treated in the same way, however and this is discussed later (see next section), different uncertainty settings can be associated to them.

2.4.2 Uncertainty representation and identification of sources

Zimmermann (2000) discusses sources or causes of uncertainty, and identifies the following: (i) lack of information, (ii) abundance of information and consequently increased complexity, (iii) conflicting evidence, (iv) ambiguity, (v) measurement and (vi) belief. While Granger *et al.* (1990, Ch. 4 pg. 56), identify as sources of uncertainty (i) statistical variation (random error), (ii) subjective judgement, (iii) linguistic imprecision, (iv) inherent randomness, (v) disagreement and (vi) approximation. According to Heijungs and Huijbregts (2004), uncertainty rises from the problem of using information that is unavailable, wrong, unreliable, or that shows a certain degree of variability.

Uncertainty representation is commonly referred as the uncertainty setting of the problem. There are different uncertainty settings (de Rocquigny *et al.*, 2008):

- (i) *deterministic*: uncertain variables are taken at penalised values, the treatment implies the calculation of model outputs at these penalised values. This approach can be combined with the use of interval arithmetic.
- (ii) *standard probabilistic setting*: uncertain variables are considered as random variables with a pdf for each (or a joint distribution function if they are non-independent). Other model inputs are considered to be deterministic, making this setting a mixed deterministic-probabilistic setting. No explicit separation is performed between natures of uncertainty, all sources of uncertainty are randomised together. In this case the parameters which describe the pdfs are considered to be fixed.
- (iii) *standard probabilistic setting with level-2 deterministic treatment*: in this case the parameters used for the pdfs describing the uncertain model inputs are considered to be also uncertain but a given discrete number of choices is available for them. The values of the pdfs describing the 1st level uncertain variables are taken at penalised values.
- (iv) *double probabilistic setting*: similarly to the former, however the pdf's parameters are also random variables.

It can be seen that level-2 representations (iii) and (iv) will require more information than single level, and are used when a single level representation does not provide with accurate representation of the uncertain variables behaviour.

With regards to a measure for uncertainty, the possible metrics can be mainly of two types: variance ($Var(y)$, see Eq. 3.21), expectation ($E(y)$, see Eq. 3.20) or other central dispersion quantities (standard deviation or coefficient of variation) of a given output variable[55].

In most cases the uncertainty in input variables is modelled using the standard probabilistic setting (ii) and X is modelled as a random vector. If inputs are independent from each other then a one dimensional analysis can be used. Expert judgement is mostly used when information regarding the uncertain model inputs is scarce, parametric modelscan then be

[55]Other metrics can be probability of exceeding a given threshold value ($P(y = f(X,d) > y_s)$), quantiles ($z^{95\%} < z_s$) or probabilities of relative exceedance ($P(f(X,d_1) > f(X,d_2))$).

used to translate these judgements as accurately as possible into a pdf (de Rocquigny *et al.*, 2008). Some model pdf parameters can be assigned a certain value for its quality, in this sense some authors have proposed the use of a Pedigree Matrix for its consideration (Huijbregts *et al.*, 2001)[56]. May and Brennan (2003) review these methodologies and found that some of them assign different Beta pdfs based on the % of attainable data quality, while other simply uses normal distributions with a standard deviation based on the quality of data.

In the case of the parametric approach, the most common method for pdf's parameter fitting is the usage of maximum likelihood and the method of moments.It is clear that the amount of information or degree of belief regarding a given parameter value or model hints which kind of uncertainty representation has to be used. This step is of paramount importance given that it shapes results.

2.4.3 Analysis of input-output relationships

Most uncertainty treatment frameworks reviewed by Bjorklund (2002), converge on similar aspects to the ones proposed by de Rocquigny *et al.* (2008) or Campolongo *et al.* (2000b), that propose the following steps: (i) scoping the uncertainty analysis, (ii) selecting the method for modelling uncertainties, (iii) assessing the uncertainties in input data, (iv) propagating the uncertainty through models and (v) reporting the uncertainty in output data.

Methodologies performing the former steps are broadly known as sensitivity analysis (SA). Saltelli *et al.* (2000) provide a clear definition, a SA is: "*the study of how the variation in the output of a model can be apportioned, qualitatively or quantitatively, to different sources of variation and of how the given model depends upon information fed into it*".

Sensitivity analysis (SA) can be classified into three groups of methods: screening, local SA and global SA (Saltelli *et al.*, 2000). Screening methods aim at devising which are the input parameters that roughly affect the most to the output parameters, in this sense the most widely used method is the Morris plot, see Campolongo *et al.* (2000a) for the underlying assumptions and examples. In the case of local SA metrics, they rely on a Taylor series decomposition of the output values in terms of the input values, and consequently they are also called analytical approaches, their underlying assumptions are presented in section 3.2.1.

Despite the important information that a SA provides with regards to models, its use in chemical engineering is not wide spread. Some authors have studied the problem of uncertainty in parameters; mostly in the case where these parameters are found in thermodynamic models used in process simulation. This problem is associated to the parameter estimation problem. In that context, a naive approach would use the minimum global residual error as the solution of any estimation problem. However, this minimum is not guaranteed to represent the true physical phenomena. Consequently, the problem of uncertainty in parameters is two-folded, one the one hand it is a consequence of the uncertainty associated to the physical world measurement and on the other it is associated to the selection of the model parameters fitted. In this regard Zhang *et al.* (2006), point out that the selection of the true solution from multiple candidates based on physical principles is a challenge that requires further investigation given that no proven approach is available.

In the case of commercial process simulation tools, none of the sequential oriented based platforms provides with a structured way of calculating SA metrics. The user is left with the ability to run the simulation for any given set of input parameters but no structured approach is provided as a tool. In the case of AspenHysys, a SA can be performed using the *DataBook* provided, where independent and dependant variables can be recorded, while in AspenPlus

[56]The data pedigree is expressed by means of a matrix; where each of the characteristics of data are assessed and given a score. In the LCA context the use of the data quality pedigree matrix of Weidema and Wesnas (1996) is usually done.

under *model analysis tools* a rudimentary SA can be done provided the user sets all required scenario runs. No information regarding derivatives of the output values can be extracted from process simulation excepting its possible numerical calculation[57].

Most of the literature surveyed relies on the assumption that no information regarding the model structure is available, and consequently for these models (black-box like) sampling approaches are better suited. In a nut-shell, sampling approaches rely on a certain number of model runs (scenarios), to generate the model's output pdf. The most simple uses random sampling and is called Monte Carlo Sampling (MCS). A MCS varies model's input data according to given pdfs, runs the model and stores model output results. Differences in these methods appear regarding the sampling methodology and the metrics calculated (see sections 3.2.2 and 3.2.3). Other set of tools that can be applied to analyse input-output relationships is multivariate analysis, main tools are described in section 3.3, while its application to chemical process is reviewed here.

Sensitivity analysis in process simulation Whiting (1996), Xin and Whiting (2000) and Vasquez and Whiting (2006), in the context of thermodynamic models in process simulation, propose to analyse model and parameters uncertainty. Model uncertainty is evaluated by using thermodynamic models of different expected accuracy, but the authors do not provide with a ranking of best suited models, and the analysis ends up in checking parameters uncertainty. Metrics used to analyse thermodynamic model parameters in simulation results are the standardised regression coefficient (SRC) and partial correlation coefficient (PCC), see section 3.2.3 for their definition.

Whiting *et al.* (1993) studied a fractionator problem using the Soave-Redlich-Kwong (SRK) equation of state (EOS), and found that critical temperature and pressure, and acentric factor for some components were the most significant variables (in terms of PCC and SRC). Chakraborty and Linninger. (2003) found in distillation columns that a small reduction in the relative volatility already impedes the operability of the separation tasks even with adjustable controls. The authors conclude that uncertainty in the physical properties, along with the feed composition, drastically could reduce the flexibility of a design to almost zero. Clarke *et al.* (2001) studied the design of heat exchangers and how it is affected by uncertainty in thermodynamical parameters. They found that critical properties as well as transport properties (heat exchanger material and fluid conductivities), affect importantly the design results.

Vasquez and Whiting (1998) and Whiting *et al.* (1999) studied the uncertainty effect on LLE and VLE estimation using activity coefficient models (NRTL and UNIQUAC). They propose a methodology to generate correlated samples (required due to parameters fitting) called Equal Probability Sampling (EPS) (Vasquez & Whiting, 2000). When comparing EPS with Latin Hypercube Sampling (LHS), they have shown that EPS produces less unfeasible simulations and narrows the uncertainty distribution significantly, however the implementation of the EPS is far from being straightforward, as the LHS or the Cholesky factorisation.

Whiting (1996) and Vasquez and Whiting (2004) studied the effects of uncertainty in thermophysical properties on the evaluation of environmental performance metrics, in their case study, environmental performance is based on the estimation of the VOCs and other emissions of a plant using environmental risk indexes. They found that VOCs estimations are very sensitive to uncertainty in thermophysical properties such as infinite-dilution activity coefficients and vapour pressures; and also concluded that detailed model of the given chemical process might not be required for the estimation of the total emissions, given that simpler

[57] Sensitivity information is provided in the case of optimisation in AspenPlus, moreover AspenPlus when running in equation oriented mode allows for the calculation of local sensitivity metrics, which calculate the derivative values at the converged values obtained.

process model can perform the same task just as well, due to the variations caused by uncertainty in the thermophysical properties.

Other approaches (multi variate analysis) In the context of LCA, Sonnemann (2002); Sonnemann *et al.* (2000) based their work on MCS for the estimation of environmental risk. MCS is used to generate uncertain LCIs for the different emissions which were then used to estimate impacts, the authors use Crystal Ball an MSExcel addin for modelling uncertainty. Basson (2004), also uses MCS for generation of scenarios outcomes, based on the selection of input parameter pdfs; the author proposes the application of PCA and a Distinguishability Index (DI), see section 2.4.4.1. Chen *et al.* (2005) present a framework for the study of LCA results based on MCS and the use of rank correlation coefficients. Risk analysis software @Risk, other MSExcel addin is used to perform a 2000 samples using the LHS method to obtain the distributions and the correlation coefficients of the uncertain parameters.

The application of multi variate analysis techniques to LCA and process design has also been done (see section 3.3, for references regarding the implementation of these methodologies). Le-Teno (1999) proposes the use of PCA to analyse the results of LCI. His methodology "adds" uncertainty according to a normal pdf centred on the mean value of LCI results. PCA is computed using mean values and the results from sampling produce clouds of points. The hulls of such clouds indicate how variable alternatives positions are. Basson (2004) has used PCA in her work, she points out that PCA should be performed on the correlation matrix instead of the covariance, which renders scores that are unit independent. She points out that PCA biplots[58] do not necessarily provide reliable information for decision making, biplots provide a general impression of the structure of the performance information. She also argues that in the case that clouds of points in the biplot overlap, then it is to be expected that alternatives will be indistinguishable, while if the clouds do not overlap then alternatives will be distinguishable.

Despite the great deal of available analysis tools developed to help interpret uncertain results, there are no standardised methods available, and all authors propose their own set which is mainly driven by the goal of their study. Most authors agree on analysis that aim at incorporating uncertainty in input data in order to address the confidence of their results. It was found that in all non-local approaches a model is used for the generation of output variables scenario results. While in the context of LCA the use of MSExcel addins (Crystal Ball or @Risk) might be feasible due to the possibility of MSExcel of coping with the simplicity of LCA models, in the case of process simulation models, that are more complex, a more robust approach is required. This approach requires the use of a commercial simulator in tandem to other platform which serving as input scenarios generator and output results receiver.

Remarks Despite the availability of software tools allowing for SA analysis very few publications using process simulation as their main tool have used it under a systematic approach towards the identification of the relationships between input and output variables. Consequently most simulation results do not have an error which provides an incomplete picture of the reality.

In the case of EOS comparison the authors conclude that most design differences relate to the different pure component information registered in each simulation package database and that EOS results were comparable, while in the comparison of activity coefficient based estimation, pure component information is the same and models provide with good fit. Consequently, differences might be due to systematic error in the experimental data used to regress

[58]The axes in a biplot represent the pcs, vectors usually represent variables loading's while points are the PCA scores.

the model parameters and the fact that highly non-ideal systems can push methods to their limits (Xin & Whiting, 2000).

Different thermodynamic and transport properties have been found to influence heavily on the model results, this requires the inclusion of them in the analysis of uncertainty.

2.4.4 Decision making under uncertainty

As discussed in previous sections, any decision making process is accompanied by variability related to several factors: decision-maker's value systems, elicitation and modeling of preferences (i.e. MCDA technique) and uncertainty related mainly to the information used to support such decision-making, i.e. model results. As a consequence it is necessary to carry out robustness, sensitivity and uncertainty analysis before making a decision (Seppala *et al.*, 2002). As Sahinidis (2004), points out the approaches to optimisation under uncertainty have followed a variety of modeling philosophies, including expectation minimisation, minimisation of deviations from goals, minimisation of maximum costs, and optimisation over soft constraints. Several of them have introduced risk formulations or flexibility formulations.

Most approaches revised present a two-stage stochastic approach towards the optimisation of process designs. The problem that contains uncertain values is transformed into a deterministic one where the expected value of the OF is optimised (see section 3.1.2.1). In all cases some first stage decisions (regarding flowsheet connectivity, i.e. integer variables and flowsheet operation) are defined by a given algorithm and the estimation of the expected value of such design is assessed using sampling methods.

In chemical process models, equality constraints (conservation balances, reactions, or phase relations) model steady-state process operation, while inequalities enforce design specifications or physical operating limits. In the uncertain case, variations in variables or parameters deteriorate the design performance and change its proximity to design constraints. In severe cases, the design optimised at nominal conditions may violate specifications in some scenarios, rendering the flowsheet inoperable.

Flexibility is defined as the range of uncertain parameters that can be dealt with by a specific design or operational plan (Sahinidis, 2004). The flexibility index of a particular process flowsheet measures the maximum tolerable deviations from the nominal values of uncertain design variables or parameters without violating any design constraint. The concept of the flexibility index and its computation via mathematical programming techniques has been studied intensively, (see Biegler *et al.* (1997, Ch. 21)). This index quantifies the vulnerability of a design against any constraint violation caused by continuous parameter variations. It considers the nominal amount and expected deviations, ignoring the probability of their occurrence or the expected cost of the design in the presence of uncertainty. As reviewed by Chakraborty and Linninger. (2003) other metrics such as the flexibility measure for decisions in production planning and the resilience index for processing plants have been similarly defined. The term robust is also used in this context; robust decision making involves choosing designs with good average performance and minimum variance.Other metrics involve the calculation of risk, which in general can be defined as the probability of achieving a given value for a metric. In the ERA context it is related to hazards and likelihood of exposure (see section 2.2.5.2). In this sense Janjira *et al.* (2007) have used ERA combined with financial risk, for the assessment of different processing alternatives.

2.4.4.1 Alternative selection problem under uncertainty

The incorporation of uncertainty into alternatives selection, brings another issue with regards the dominance of options in front of others. Fig. 2.3 shows the case where no clear dominance

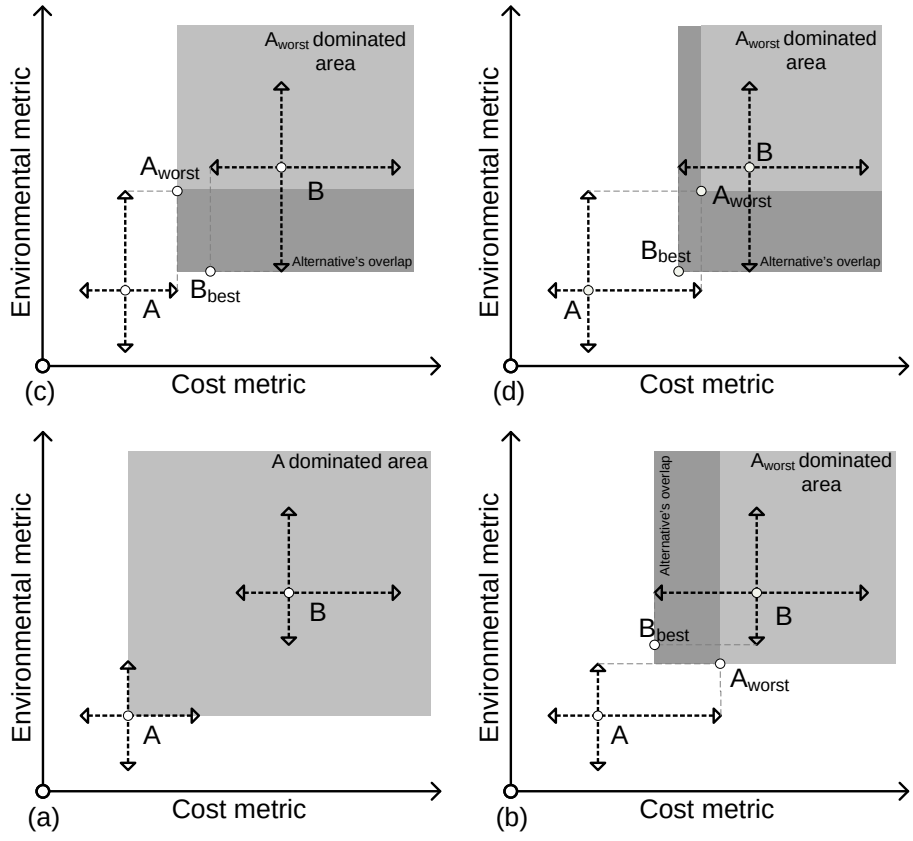


Figure 2.3: Representation of solutions with error bars associated, (a) Dominance of Option A over B based on mean values and no metrics overlapping, (b,c) Case A_{worst} is worse than case B_{best} for one of the metrics, (d) Case A_{worst} is worse than case B_{best} for both metrics. In cases (b,c,d) option A does not dominate over B, adapted from Jankowitsch *et al.* (2001).

of one option over the other can be assessed due to the overlapping of the error bars. With regards to Fig. 2.3, it has to be pointed out that in many cases A_{worst} and B_{best}, will represent model evaluations in which the simulation besides being evaluated at different decision variables has also very different underlying parameters. Instead of examining deviations from a mean value, the discrete points resulting from the MC runs (using the same underlying parameters, i.e. the same random numbers[59]), should be compared and the dominance should be studied in that sense

A *discernibility analysis* is proposed in Heijungs & Suh (2002, Ch. 8) aiming at comparing MCS results. They state that comparisons based on confidence intervals are not valid, arguing that it is more reasonable to compare products pair-wise in each MC scenario. The ratio or the difference (see Eq. 2.38) between MC results for each option is computed and the resulting distribution is analysed. The ratio is known also as the comparison index (Huijbregts, 1998b).

The discernibility analysis, effectively comes down to counting the number of times that alternative A has a higher score than B ($n_{(A>B)}$) and the number of times that alternative B has

[59]According to Law & Kelton (1999, Ch. 11), alternative configurations should be compared under similar experimental conditions, then any observed differences in performance are due to the differences in the system configuration rather than to fluctuations in the experimental conditions. This might be accomplished by using common random numbers (CRN) a common variance reduction technique.

a higher score than A ($n_{(B>A)}$). If there are N runs available then $n_{(A>B)}$ should be at less equal than $0.95N$, to say that A has a significantly higher score than B, while if $n_{(B>A)} \geqslant 0.95N$, then B has a significantly higher score than A. However, if neither $n_{(A>B)}$ or $n_{(B>A)}$ are greater than $0.95N$, the null hypothesis of indiscernibility can not be rejected[60]. This could be extended to analyse more products via always pair wise comparisons (Heijungs & Kleijn, 2001). Other method involves the generation of a normalised difference pdf characterised as the ratio given in Eq. 2.38.

$$KPI_{diffNorm} = \frac{KPI_A - KPI_B}{KPI_A} \tag{2.38}$$

in this case, if the KPI_{Norm} is positive and equal to 0.XX then alternative A is said to be better than alternative B by the magnitude of the ratio (XX%). Conversely, if the ratio is negative, B is better than A by the magnitude of the ratio.

In general, the problem of elucidating if an option A is superior to B in terms of any metric under uncertainty is equivalent to determine the probability of option A being better than option B (see Eq. 2.36). These concepts of distinguishing alternatives under uncertainty are embedded in the stochastic-dominance principle. This principle, as described by Bode *et al.* (2007), is based on the assumption that all alternatives are correlated. Consequently a change in the input values' realisations would cause all alternative's outputs values to make the same shift. The difference or quotient of the alternatives output values would stay the same regardless of each alternative's output value uncertainty, and consequently one alternative would always be the better choice.

In the context of distinguishing alternatives measured using different metrics, Basson (2004, Ch. 5), has developed a distinguishability index (DI), which is based on interval overlapping. Each process alternative is evaluated for different possible indicators, and upper and lower bounds are calculated. The DI is defined as the ratio between the number of indicators for which alternatives do not overlap (n_{non}) over the total number of indicators (n_{total}) (see Eq. 2.39).

$$DI = \frac{n_{non}}{n_{total}} \tag{2.39}$$

This DI then serves as a MCDA selection tool, if DI=1, then the evaluation can be done using any MCDA tool, while for DI<1 then more information regarding the decision maker preferences is required, such as thresholds to decide if alternatives are different, or more in depth analysis to reduce the uncertainty. This index is profited in other works Basson and Petrie (2007a,b) where an integrated approach for the consideration of uncertainty in decision making is presented, the method is based on LCA, PCA and MCDA. Their approach is based on three different strategies (i) placing appropriate bounds on particular aspects, (ii) ensuring that the quality of information is such that the generated alternatives are "adequately distinguishable" between them and (iii) propagating technical uncertainties and performing SAs for uncertainty valuation. Two uncertainty sources are considered in this work: *valuation uncertainties* due to the potential consequences of the activities under consideration and *technical uncertainties* that pertain to variables which are used for the evaluation of these consequences. Propagation of technical uncertainties is performed by MCS, while valuation uncertainties are treated performing SAs.The effect of several of the model parameter uncertainties are investigated in a parametric manner to obtain an overall impression of their relative significance. For elicitation of stake holder preferences the ELECTRE TRI method is used.

[60] In the case that the metric is a real number the probability of a tie is vanishing small, it is considered that $n_{(A>B)} + n_{(B>A)} = N$, assuming that $n_{(A=B)}$=0.

2.4.4.2 Approaches

Diwekar (1994) and Chaudhuri and Diwekar (1997) have pioneered flow sheet synthesis using commercial simulation under uncertainty, using sampling approaches. Their approach uses the simulation tool as a black box which provides with the output variable values for each of the scenarios, where expected value of economic metrics are used. Fu *et al.* (2000) analyse the chemical processes design problem using economic (annualised profit) and environmental metrics (calculated using WAR), they consider uncertainty associated to the calculation of the PEI. The authors found that several indicators behave similarly, which allows for simplifying the problem by reducing the amount of OFs to be considered. Due the inclusion of uncertainty only in the EI, the same flowsheets are obtained in the stochastic and deterministic optimisation, however differences on the OF value are found.

Chen and Frey (2004), proposed two different algorithms for coping with parameters uncertainty represented using pdfs in a double and simple probabilistic setting (see section 2.4.2). in process design. One of the algorithms proposed is the Coupled Stochastic Optimisation and Programming (CSOP), the result of it is a given pdf for the different solutions. The other algorithm is the Two-Dimensional Stochastic Programming (TDSP), in which no difference between the uncertainty setting is done and the problem is optimised for each variable's realisation. In this sense both the CSOP and TDSP are used as sensitivity analysis, the authors use the Pearson correlation coefficient , to rank input variables with high influence on the OF. The problem being solved is the design of NOx controls for an IGCC plant, which is simulated using AspenPlus (Frey & Zhu, 2006). Given the high number of simulation runs required to represent uncertainty, a response surface model RSM of the underlying simulation model is used instead.

Hoffmann *et al.* (2004), extend their previous work, (Hoffmann *et al.*, 2001) to the cope with uncertainty. Their approach calculates the probability of a given process alternative of being economically and environmentally better than other. The authors present a 3 level model hierarchy (i) technical equilibrium based models in the process simulator (which are substituted by RSM), (ii) input-output models which tackle the connection between the RSM models and (iii) evaluation models which calculate the OFs. The RSM is based on polynomial chaos expansion, and fitting of these models required 50-100 simulation runs. These black box models are used to run the MCS (using 1000-10000 samples) which generates the OF expected values that are optimised using a GA. Several variables and parameters are considered uncertain, such as concentrations, reactor yields, distillation efficiencies, equilibrium parameters and others. The OFs used are TAPPS (see Eq. 2.7) as economic indicator and the EI99 for the EI. The case study is the selection of different processing routes for HCN production, AspenPlus is used as simulation environment. As design variables equipment sizes and some operating specifications are used. The analysis of PF is realised using the mean values of the OFs referred to a base case.

In Dantus and High (1999), the approach presented in Dantus and High (1996) for process retrofit is extended to process design taking into account uncertainty and analysing economic (AEP, Eq. 2.6) and EI (based on WAR, but considering human and environmental effects due to VOCs) OFs. The algorithm uses AspenPlus for the calculation of mass and energy balances. The MOO problem is solved using a weighted sum approach, where the normalised distance to the single objective optimal solution is weighted. Two parameters are used to weight the decision maker preferences a typical weight factor (γ_i) and a exponent (K_i), that represents the concern regarding the maximal deviation (see Eq. 2.40).

$$L_j = \sum_{i=1}^{nObjs} [\gamma_i (obj_i^* - obj_i(x))]^{K_i} \tag{2.40}$$

No Pareto fronts are shown, but the results to a given selection of preferences (γ_i and K_i). The case study is the manufacture of methyl chloride using methane and chlorine as raw materials. As optimisation variables temperatures, flows and reactor type were used, while prices, release factors, and reaction kinetic values were selected as uncertain parameters.

Kheawhom and Hirao (2002, 2004); Kheawhom and Kittisupakorn (2005) propose a methodology for process design including environmental, economic and process robustness metrics. In the case of EI the SPI is used while TAC is the economic aspects. The methodology is based on two-stage optimisation technique, which incorporates a filtering based on process robustness metrics. The OFs (environmental and economic), are separated in two parts, one part is due to the selection of a given set of design variables (1st stage), while the second is based on the values of uncertain values and only a given expected value is calculated. The inner layer is the one that deals with the uncertain variables and calculates (using HSS) the expected value of the OFs, this optimisation is performed using the Matlab's SQP algorithm. The outer layer which fixes the values of the 1st stage variables uses a multiobjective genetic algorithm (MOGA). Aspen Hysys is used for the process model, using Matlab's solvers and Visual Basic for the OF calculation.

Diwekar (2003, 2005) propose an algorithmic framework containing five levels for the design of processes considering uncertainty. The innermost level holds the process model (simulated using AspenPlus), above it, in the second level a sampling module works (using Hammersley Sequence Sampling HSS); which provides OF expected values and constraints values to a continuous optimiser, that provides continuous variable decisions. Above the continuous optimiser a discrete optimiser works, which receives continuous feasible solutions and provides with discrete solutions to the third level. In the top fifth level a MO programming layer is in place that receives optimal solutions (integer and continuous feasible) and defines the optimisation problem accordingly to generate a trade-off surface. The framework is tested in two case studies, the synthesis of a hybrid fuel cell plant, and a solvent and process design coupled problem.

2.4.5 Inclusion of uncertainty remarks

Different approaches to represent uncertainty have been discussed briefly in section 2.4.2, showing that in most cases uncertainty is represented via pdfs. It has been found that the inclusion of uncertainty is done following two different goals: (i) devise how model outputs are modified by uncertain inputs, and (ii) take a decision based on model results which is fed with uncertain inputs.

For the first goal the use of sensitivity analysis is done, examples of this approach were considered in section 2.4.3, in all cases they involved a sampling method, which could require covariates generation. Regression based metrics are used to analyse model input output relationships.

In the context of decision making using optimisation two different strategies are found: stochastic optimisation (SO) and stochastic programming (SP). The main difference between them is the objective function that is considered. In the first case the OF expected value is optimised for a given set of scenarios while in the SP context, each optimisation is performed on each scenario. The SP approach can then be interpreted as a sensitivity analysis that incorporates optimisation as part of the model. Further details are discussed in section 3.1.2.1.

Hoffmann *et al.* (2004) points out that the use of process simulation in the context of MOO under uncertainty causes considerable computational requirements due to (i) multiobjectivity which requires the simulation to be run as multiple single objective optimisation problems for a given set of constraints or weights while (ii) uncertainty requires the single objective

problem to be solved for a given number of scenarios depending on the SO (estimation of expected values of the OFs values) or SP/SA (estimation of each scenario optimal value) context applied. The application of these approaches require multiple layers of models as described in the works of Diwekar (2005).

Regarding the SO approach both the use of weighted sum or ϵ-constraint methods are found to be used to generate Pareto curves. The application of heuristic based optimisation methods and meta-modelling is also found. In all cases the methodologies dealt with process design at the mesoscale and considered uncertainty in parameters and variability.

Independently of the SO or SP/SA context reliable estimates of the model inputs are required, one feature that is scarcely discussed in the literature is the estimation of the appropriate number of samples required to model accurately the model input parameter and consequently its influence in the model output considering or not optimisation. Different methods applied to answer such question are reviewed in section 3.2.2, with special focus on sampling methods.

Specially suited for sampling methods, where the model is computationally expensive to be run for all scenarios, is the use of a surrogate model or meta-model which can be implemented using different response surface methods (RSM). This meta-model replaces the pre-existing model with other that produces comparable results with respect to output variables and quantities of interest, but which is quicker to compute. Section 3.1.4 discusses the rudimentary aspects of metamodels implementation.

2.5 Identification of research needs

The amount of different strategies/tools/frameworks available, shows the clear desire of the scientific community, governments and society as a whole, for the inclusion of SD into process and product design, but it also shows that there is no consensus in how to achieve it. Most frameworks include a LC perspective and different set of objectives to measure SD, which in general are different from author to author. The discussion between monetisation of environmental and social issues is not closed and different perspectives are used. Normalisation of metrics has a certain similitude with monetisation, however there seems to be consensus between authors in pointing out the use of the process/product FU as normalising constant. But no clear and general guidelines are for its definition.

Regarding the FU definition, it is widely agreed that the irrational production of waste is undesirable, but it is a more difficult challenge to identify what level of production and its associated waste is acceptable. None of the reviewed methodologies addressed the definition of production level, in most cases a given demand was defined to be met or a given production rate was fixed. In this sense, the definition of the FU could improve this issue, given that its normalisation effect will render more efficient solutions. However the actual reduction of production with its consequent reduction of emissions and waste seems out of the scope of most of the methodologies proposed.

All reviewed frameworks coincide in pointing the design phase during the synthesis of processing alternatives as the most promising for the inclusion of sustainability. However, a process design unified framework is still lacking, there is no agreement in how many steps this framework should have nor in the metrics to be used in each stage. As a common trend found in all frameworks is the use of very simple models (and metrics) in earlier stages, followed by more complex models if required. It has also been found that there is a clear trend in making the design process iterative, where first estimations are done using simple models which are further improved with more complex models at later stages. One trend is the use of process simulation for checking the viability of simple model solutions, i.e. from mathematical

programming.

Regarding metrics for SD measurement (see section 2.2), at the design phase different trends have been found. While in the case of economic and environmental aspects of SD several metrics are available, in the case of social metrics the picture is different. Economic and environmental metrics have evolved and are easily linked to process variables such as flows and emissions, while social metrics can not. In the case of social issues, the designer has to rely on safety related metrics or on qualitative assessments, which only provide a proxy/glimpse of the social impacts of a design. In this sense, social impacts; related to work force generation or enterprise-community relationships, are mostly due to the enterprise structure and not directly associated to the process design itself as discussed in section 2.2.4. Consequently its measurement at earlier process design stages, seems pointless. Moreover the focus and use of safety metrics shows a clear anthropocentric point of view that bias decision making.

In the case of SD economic aspects, the discussion of properly assessing environmental damage cost is open, not only regarding externalities of goods production, but also due to the modelling of production cost properly. Given that the application of current tools (e.g. TCA), has not been widespread, it seems an important place to focus further research, (see section 2.2.3). In this sense the estimation of waste treatment costs has to be explicitly added to the cost assessment scheme, and any possible regulation on emissions should be handled by the models used. Regarding the possible metrics to be used, no agreement is found while some authors propose using TAC and NPV, others prefer normalised metrics such as TAPPS, however its use has not been widespread nor its convenience proved.

Regarding SD environmental issues, most frameworks agree in considering these metrics as the ones that measure intergenerational equity. In this sense the use of resource depletion and global climate change metrics provide with an appropriate yardstick to measure the possible losses of future generations. However, the broad amount of modelling perspectives in terms of environment and impact models shows a lack of consensus and guidelines which makes metrics selection and application a difficult task. In this sense most frameworks use mid and end point modelling depending on the goal objective and on the amount of uncertainty that they are willing to accept. Mid points are considered to be less uncertain than end point due to the inclusion in the latter of subjective weights to add mid point categories together. The use of solely EI metrics is not recommended given that would clearly bias towards an ecocentric point of view.

Despite the emphasis put on appropriate emission estimation, its application to different process and different systems has been addressed in very few occasions and the literature showed scarce examples (section 2.2.5). In this sense emissions and cost estimations should be improved and modelled with higher detail levels. In many cases the use of emission factors (as described in section 2.2.5.1), can be avoided if adequate models are built and used. Environmental models (discussed in section 2.2.5.2), can be properly integrated to current process models results and hence improve the detail level of emission estimation. One important aspect that seems to be disregarded in the literature is the match of impact assessment CFs and the emission estimations, which has to be checked in order to generate data appropriately. More importantly not all impact assessment methods provide with the same CFs and in some cases the methods' underlying modelling assumptions are different.

In terms of how the design problem is tackled two main approaches were found: (i) one based on mathematical programming, which is best suited for optimisation and the use of simple models, and (ii) a hierarchical approach which is mainly used for testing complex models and used in optimisation less frequently. In all cases, authors seek to generate a set of non-dominated solutions (or Pareto Front, see section 2.3), clearly showing that there exists trade offs between metrics. While many methodologies stop at this point some others

proceed to the selection of the "best" process alternative which in all cases is done by the application of a predefined MCDA technique to join together all objectives taken into account. Regarding the MCDA techniques chosen, no clear trend is found, and every author proposes to use a different one.

Uncertainty is inherent to modelling as discussed in section 2.4.1, and many authors propose different ways to deal with it. Current methodologies associated to process design lack of a systematic way of addressing different sources of uncertainty and there is no consensus in the literature regarding possible classification of uncertainty sources. One of the classifications proposed, relates uncertainty to three aspects (i) model adequacy, (ii) model parameters and (iii) all other sources (specially bias and subjective decisions). This classification was adopted in this thesis, and a discussion of different uncertainty settings was done. Moreover it was found that the current frameworks proposed seldom address the relationship between model input-output variables and select optimisation/decision variables on heuristics, despite the fact that different methodologies are available for its selection.

The main objective of this thesis is obtaining a framework for decision support towards chemical process sustainable design. This objective embraces the following issues.

- Building a consistent framework considering appropriate methodologies to be used together with appropriate integration of information flows.
- Selection, construction and possible integration of appropriate tools, for framework implementation. In this sense tools selected have to be able to provide with a given degree of precision and be subject of uncertainty analysis.
- Application of the framework to different benchmark case studies, for testing purposes and results analysis.

Chapter 3

Methods and tools

In this thesis different methods and tools have been applied. This chapter aims at describing and detailing the concepts underlying them and describing in details some aspects of its implementation in this thesis.

Section 3.1, presents a wide variety of aspects related to process modelling, considering optimisation using multiple objectives and under uncertainty. Section 3.1.3 reviews the typical methods applied to multi criteria decision making (MCDA), which are of high importance with regards to the sustainability problem where each alternative is meassured with different metrics and where each decision maker assigns different importance to each metrics. Section 3.1.4, briefly comments on possible approaches to metamodeling and its possible connection to process simulation.

In section 3.2, different tools for the consideration of uncertainty in modelling are introduced, attention to two types of approaches are done, one based on analytical approaches requiring of model derivatives, while other is based on the model results solely. To end this chapter a deep revision of the LCA methodology is done in section 3.4.

3.1 Process simulation and optimisation

Process simulation is understood as the use of computer software resources to develop mathematical models for the construction of an accurate, representative model of a chemical process aiming at understanding its behaviour during regular plant operations and to explore other possible working conditions (Diwekar, 2005; Diwekar & Small, 2002). The complexity of process simulation rises from the mathematical functions that are used in the model. Simulation environments can be classified considering the way that equations are solved, and which type of equations are solved.

In the case that variables are not changing along time or position a non-linear set of equations such as Eq. 2.32 appears in chemical problems, where both the number of functions in the **f** vector function plus design specifications equal the number of variables **x**. If Eq. 2.32 is considered as a system of two equations and three variables: $f_1(x_1, x_2, x_3) = 0$ and $f_2(x_1, x_2, x_3) = 0$, having defined one single x_i the system is square. Two main approaches regarding process simulation are available: the *equation oriented* (EO) and the *sequential mod-*

ular (SM). In the EO approach any x_i can be set freely and the system is solved altogether using the algorithms described next in section 3.1.1. In the SM approach the availability of partial information is used, lets say that x_1 is selected as fixed degree of freedom (DOF), the SM approach solves the system using explicit expressions: $x_2 = F_1(x_1)$ and $x_3 = F_2(x_1)$, and uses custom made algorithms for the case of presence of cycles between variables and functions.

In the case of steady state continuous plant modelling, Eq. 2.32, is perfectly suited. However in batch process simulation or the dynamic simulation of continuous plants the problem being solved can not be described using Eq. 2.32, but due to the inherent characteristics of transient process the assumption of steady state has to be dropped. The system 2.32 is transformed in a system of ordinary differential equations (ODE) where the time derivatives of variables ($\mathbf{x}$) are defined. The solution of ODEs is done using Euler algorithms or its higher order Runge-Kutta generalisations (Lee & Schiesser, 2004).

Commercial simulators for SS using the SM approach are AspenPlus - AspenHysys[1], CHEMCAD[2] or PRO II[3], ProMax[4], and Prosim[5]. Due to the former way of handling equations, these simulators have developed different ways of handling with material and energy recycles and specifications of values for calculating model outputs. AspenPlus requires the use of design specification blocks for fixing the DOFs to variables which are model outputs[6], while AspenHysys has a different way of handling model's DOF that allows the simulator to solve if a certain number of DOF are fixed for each model. The EO approach is used in gProms[7], VMGSim[8], AspenCustomModeler and AspenPlus in EO mode. For non SS simulation the commercial options are: AspenHysys, AspenDynamics - AspenCustomModeler and gProms. In the case of batch process SuperPro designer[9] or AspenBatchPlus can be used, however in this case, commercial software has not reached the same maturity as in the case of continuous process modelling.

Thermodynamic insights based on thermodynamical principles, are used to analyse whole processes and consequently point in the direction towards creating good designs[10]. These methods offer a degree of assurance that the "best" design has been found. The alternatives obtained are "best" designs from a thermodynamical point of view, in this sense reducing energy consumption in a plant is translated into reduced flue gas emissions, but minimising energy consumption may not always result in minimising environmental impact of utility systems given that the minimisation should consider not only on-site combustion (furnaces, boilers), but also off-site emissions (power generation plants), adoption of this broader view has been already emphasised (Cano-Ruiz & McRae, 1998). Thermodynamic insight approaches provide systematic means to evaluate the optimal way to cut down waste generation by the process, however, they do not account for the waste associated with inputs to the process (i.e. waste associated with raw materials, energy generation, capital plant, etc.). Furthermore, they lack of a systematic quantification of the environmental impact of the different kinds of process wastes in a consistent way. Examples of commercial software for HEN

[1] http://www.aspentech.com/

[2] http://www.chemstations.net/

[3] http://www.simsci-esscor.com/us/eng/products/productlist/proII/default.htm

[4] http://www.bre.com/promax/interface/flowsheet-drawing.aspx

[5] http://www.prosim.net/en/index.html

[6] Different ways for changing input variables are available: direct substitution, secant, Broyden and Newton methods.

[7] http://www.psenterprise.com/gproms/index.html

[8] http://www.virtualmaterials.com/index.html

[9] http://www.intelligen.com/superprofeatures.shtml

[10] The process performance is first targeted and then a structure is proposed (if possible) to achieve such targeted performance. In other words, the best achievable system performance is determined thermodynamically before the structure (design) of the system is known.

synthesis are Aspen HX-Net and Super Pro[11] while in the case of MEN synthesis AspenWater.

The techniques for solving non linear equations overlap in their motivation, analysis, and implementation with optimisation techniques (Nocedal & Wright, 2006). In unconstrained optimisation, the objective function is the natural choice of merit function that gauges progress towards the solution, but in non linear equations various merit functions can be used, all of which have some drawbacks[12]. The sequence of estimates converging to the optima can be generated using only first derivatives of the objective function (for example, steepest descent, conjugate gradient), or second order derivatives (Newton method, quasi-newton methods or SQP).

The discussion of optimality conditions and optimality conditions regarding constrained optimisation can be found in different optimisation books such as: Steuer (1986), Statnikov and Matusov (1995), Nocedal and Wright (2006) and Griva *et al.* (2009). In all these books the constrained optimisation basics regarding Karusch-Kuhn and Tucker (KKT) conditions is discussed.

With regards to optimisation, process simulation environments provide the user with optimisation capabilities for NLP. The problem is non-linear in constraints and objective function. Constraints are required to enforce mass and energy balances, for which thermodynamic properties estimations are also required. Unit operation performance also introduces constraints as well as the calculation of objective function metrics.

In AspenPlus, PRO/II, and AspenHysys, the optimisation problem is solved first calculating the process models before evaluating the constraints and objective function value. Due to its SM approach the optimisation problem is solved in an outer loop, while the model equations are converged in an inner loop[13]. AspenPlus, in the SM approach, has coded two algorithms, the complex algorithm which is a feasible path "black-box" pattern search, and a sequential quadratic programming (SQP) method[14]. In the case of AspenHysys the optimiser algorithms available are several, differing mainly in the ability in handling inequality and equality constraints, most of them are based on different quasi-Newton or SQP implementations (AspenTech, 2005a). None of the commercial simulation environments provide with the capabilities to solve multiobjective optimisation (MOO) problems, see section 3.1.2.

Caballero *et al.* (2007), points out that the process simulators capabilities involving integer variables or discontinuous domains for the equations are very limited. Moreover the optimisation capability for process topology changes is rather small and the usage of complex objective functions[15] can only be done in a posteriori after the simulation has converged. In this sense the combined usage of commercial simulation coupled with stand alone optimisation algorithms has been proposed by several authors. The combined use of AspenHysys together with MS Excel optimiser has been done by Alexander *et al.* (2000), while its connection to GA is exemplified by Chen *et al.* (2003). While the former authors dealt with NLP, Caballero *et al.* (2005, 2007), proposed different algorithms for MINLP, where they combined AspenHysys with Matlab[16] using different decomposition strategies for tackling with integer

[11] http://www.kbcenergyservices.com/

[12] The merit function is a scalar-valued function of **x** that indicates whether a new iterate is better or worse than the current iterate, in the sense of making progress towards a root of **f**. The most widely used merit function is the sum of squares.

[13] At least a single process model evaluation is required every time the objective and constraint functions are evaluated for optimisation (Caballero *et al.*, 2007).

[14] It provides with three different implementations one of them is based on the work of Biegler and Cuthrell (1985); Lang and Biegler (1987) while other implements the Broyden-Fletcher-Goldfarb-Shanno (BFGS) approximation to the Hessian of the Lagrangian (AspenTech, 2005c).

[15] Such as complex cost models or detailed size models, involving discontinuities.

[16] Matlab has already a set of optimiser codes for solving NLP problems but it can also access other stand alone solvers easily.

variables (see section 2.3.1 and Diwekar *et al.* (1992)). In the case of AspenPlus, Chaudhuri and Diwekar (1997) and Fu *et al.* (2001) proposed the use of simulated annealing included as a calculation block within the simulator, which requires to use the input language of ASPEN and FORTRAN to implement the simulated annealing algorithm.

The following section 3.1.1 discuss algorithms implemented in commercial simulators, while section 3.1.2 and 3.1.3 discuss of how to treat multiobjective (MO) information, in terms of generating Pareto solutions and deciding on them. To end this section the use of metamodelling techniques in process simulation has also been emphasised in section 3.1.4.

3.1.1 Algorithms used in process simulation

Several algorithms and software packages are available for solving optimisation problems. In the simplest case of linear problems (LP), two main strategies are available: simplex or interior point methods. In these problems the optimal solution lies in a "vertex" of the feasible region. In a nutshell, simplex methods solve the LP by exploring the vertices of the problem's feasible region while interior points generate a sequence of solutions that explore the interior of the feasible region. Commercial LP algorithms usually have a hybrid implementation of those algorithms. MILP solvers use different strategies for solving the integrality constraints, one is the use of Branch & Bound (B&B), cutting planes or its combination in Branch and Cut strategies.

Some of the algorithms for solving MINLP optimisation include the branch and bound (B&B) method, the Generalized Benders Decomposition (GBD) and the Outer Approximation (OA) method (Diwekar *et al.*, 1992).One serious drawback of MINLP solving algorithms is that they require the functions to satisfy convexity conditions to guarantee convergence to the global optimum, however this is also a requirement for solving NLPs. The B&B algorithm consists of solving a series of NLP subproblems where constraints are added depending on the solution obtained and the variables desired integrality. NLP subproblems are formed by splitting (branching) the search space including a bound constraint (that serves as integer constraint). Commonly B&B can be visualised using a tree structure, these problems are solved and bounds are calculated[17]. The GBD and OA algorithms consist of solving at each major iteration an NLP subproblem (with all integer variables fixed) and an MILP master problem (Diwekar *et al.*, 1992). The NLP subproblems have the role of optimising the continuous variables and provide an upper bound to the optimal MINLP solution, while the MILP master problem has the role of predicting a lower bound to the MINLP as well as new integer variable values for each major iteration. The predicted lower bounds increase monotonically as the cycle of major iterations proceeds, and the search is terminated when the predicted lower bound coincides or exceeds the current upper bound. The main difference between GBD and the OA method lies in the definition of the MILP master problem[18]. The OA and GBD algorithms are in general more efficient than the B&B method, however in the B&B only NLP problems are solved while in the OA and GDB a series of NLP and MILP is required (Diwekar *et al.*, 1992).

Different commercial software is available for mathematical optimisation, some examples are GAMS[19], AMPL[20] or AIMMS[21], former software provides a GUI that allows implementation of mathematical models, and allows for the connection to different optimisation libraries

[17]The key idea behind the B&B algorithm is: if the lower bound for some tree node A is greater than the upper bound for some other node B, then A may be safely discarded from the search (i.e. that branch is pruned).

[18]The master problem in GBD is a dual representation of the continuous space, while the master problem in OA is given by a primal approximation (Diwekar *et al.*, 1992).

[19]http://www.gams.com/

[20]http://www.ampl.com/

[21]http://www.aimms.com/aimms/product/overview.html

such as CPLEX[22], Xpress[23] or Baron[24].

In the case of commercial optimisation, Matlab's optimisation algorithm (fmincon) implements a quasi-newton method where the required Hessian matrix of the objective function is substituted by an approximation calculated using the BFGS formula. GAMS provide with the following NLP solvers: CONOPT, MINOS and SNOPT, while it also provides connectivity to several MILP solvers such as CPLEX. More importantly GAMS provides with different strategies to solve MINLP (e.g. BARON or DICOPT), these strategies generally require NLP solvers and MILP solvers working in combination to solve the problem as previously described.

There are other optimisation techniques, called meta-heuristics or heuristics, that do not require nor use the information of derivatives of the objective function, they propose different ways of exploring different solutions towards the optimal point. They can be broadly classified in two groups: deterministic or stochastic. Deterministic techniques are based on different ways of exploring a region or a tree, examples are: greedy search, depth first, breadth first, best first or pattern search[25]. Stochastic techniques have a breadth of approaches ranging from the simplest "random search" where random input values are tested for optimality towards more informed search. These informed techniques incorporate a set of rules to generate the sequence of points to be explored (Coello-Coello *et al.*, 2007).

- *Evolutionary computation* techniques which encompass *genetic algorithms* (GAs), evolution strategies, and evolutionary programming (EP), collectively known as Evolutionary Algorithms. These techniques are loosely based on natural evolution and the Darwinian concept of survival of the fittest[26]. These algorithms are easily coded for single or MOO, where a Pareto filtering technique is used to select the "best" solutions, see Pham (2006, Ch. 42). One of the most commonly used algorithms is the Non-dominated Sorting Genetic Algorithm (NSGA-II)[27].
- *Simulated annealing*, is an algorithm based on an annealing analogy, where a liquid is heated and then gradually cooled until it freezes[28]. Simulated Annealing picks a random move for each iteration. If the move improves the current optimum it is always executed, else it is made with a probability $p < 1$. This probability exponentially decreases either by time or with the amount by which the current optimum is worsened; the analogy for SA is that if the "move" probability decreases slowly enough the global optimum is found.
- *Tabu search*, is a meta-strategy developed to avoid getting "stuck" on local optima. It keeps a record of both visited solutions and the "paths" which reached them in different "memories". This information restricts the choice of solutions to evaluate next. Tabu search is often integrated with other optimisation methods.
- *Ant colony*, is based on the analogy of ants pheromones to mark shortest paths from colony to resources. The optimisation problem has to be casted into finding paths through graphs, in which shorter paths are associated to better solutions.
- *Particle swarm*, is based on the use of swarm intelligence, that is rooted in evolution in social science, where decisions made at individual level are determined by the views of the group. Each particle, that is allowed to move, is modelled considering its position

[22] http://www.ilog.com/products/optimization/archive.cfm

[23] http://www.dashoptimization.com/

[24] http://www.aimms.com/aimms/product/overview.html

[25] Such as the complex or the Nelder & Mead simplex. These methods use simplex (a convex hull of n+1 points) to select directions of further improvement.

[26] Common to them are terms such as individual, reproduction, random variation (mutation), competition, and selection of contending individuals within some population.

[27] http://www.iitk.ac.in/kangal/codes.shtml

[28] If a liquid's temperature is lowered slowly enough it attains a lowest-energy configuration. This method is also known as stochastic annealing (Kim & Diwekar, 2002).

and velocity, and it has two capabilities (i) memory of former positions and (ii) global best particles position and value. The next position of a particle is evaluated using a velocity which considers others particles position and their values.

The former optimisation methodologies are specially suited for SM simulation, given that they only require of the objective function values and consequently can treat the simulation flowsheet as a "black-box" model. Given the difficulty of coding new optimisation algorithms inside the commercial simulation tools, the application of the former optimisation methods requires of connecting the simulation to other mathematical environment (e.g. Matlab) or programming environment (e.g. VisualBasic or MS Excel) where the metaheuristic is coded, see section 4.2.2 and Alg. C.1.

The selection of the appropriate optimisation algorithm to be used depends mainly on the type of model that is going to be optimised. In commercial process simulation, variable derivatives are not available and their estimation by numerical methods is necessary for the application of derivative based optimisation. The algorithms based on numerical derivatives might run into convergence issues due to round off errors. Moreover the lack of knowledge regarding the convexity of the objective function and the solution space rises the issue of local optimality. On the other hand the use of meta-heuristics is straightforward given that the process simulation is used as a black box model. However the usage of meta-heuristics requires of an enormous amount simulation runs[29] and do not provide with any hint regarding the quality of the optimal solution.

Regarding the MOO problem there are several methods divided into two basic types: preference-based methods and generating methods. Preference-based methods attempt to quantify the decision-maker's (DM) preference, and with this information, the solution that best satisfies the DM's preference is then identified, they are also known as multiple criteria decision analysis (MCDA). Regarding generating methods, the most commonly used is multiobjective optimisation (MOO).

3.1.2 Multi Objective Optimisation (MOO)

Alternative strategies can be applied to solve a MOO problem (Gandibleux *et al.*, 2004), a deep review of currently used methods has been done in Ehrgott and Gandibleux (2003). One typical approach consists of optimisation of alternating objectives, that is, solving the problem for one objective, and next an additional objective function (OF) subject to constraints for the objectives already optimised. The optimisation process usually leads to different solutions depending on the order in which the OF are selected and optimised. Mathematical tools can not isolate a unique optimum solution when there are multiple competing objectives, at most they aid in the identification of the solution alternatives that are dominated by others.

Since there is not a unique optimal solution for MO problems, but rather a set of feasible solutions, the preferred approach consists of providing a set of Pareto optimal solutions. A Pareto solution[30]. is one for which any improvement in one objective can only take place if at least another objective worsens (Messac *et al.*, 2003), the solutions that are not dominated by others is know as the Pareto Front (PF).

The techniques for generating a set of Pareto optimal solutions should have some desirable properties (Messac *et al.*, 2003). Namely, they should be able to find all available Pareto points, generate them evenly along the possible solutions in the feasible region, and they

[29] In GAs, the population size is usually set considering 15 points per optimisation variable.

[30] Given a set of k, z_k criteria, the vector $\mathbf{z}$ considering the values of such criteria is the criterion vector. Vector $\mathbf{z}^1$ will *dominate* $\mathbf{z}^2$ if and only if $\mathbf{z}^1 \geqslant \mathbf{z}^2$, i.e. $z_i^1 \geqslant z_i^2$. Strongly dominates happens when equality is dropped $\mathbf{z}^1 > \mathbf{z}^2$. A point $\mathbf{x}$ is efficient if its criterion vector is not dominated by others, see Steuer (1986, Ch. 7).

should not generate and explore dominated solutions. However, the available techniques present deficiencies in some of the former aspects. In all cases a MO problem is cast into a single objective one.

The weighting method is easy to implement; it uses weights w_p of a weighted sum (WS) of the objectives f_p which are varied parametrically, and the weighted sum is used as objective function (see Eq. 3.1).

$$\begin{array}{lll} \min & WS_i = \sum_p f_p^N w_{ip} & \\ ST. & \mathbf{h}(\mathbf{x},\mathbf{y}) = & 0 \\ & \mathbf{g}(\mathbf{x},\mathbf{y}) \leq & 0 \\ & \mathbf{x} \in \mathbf{X} \subseteq \mathbf{R^n} & \\ & \mathbf{y} \in \mathbf{Y} \subseteq \mathbf{Z^q} & \end{array} \tag{3.1}$$

WS_i represents the objective function for the set of w_{ip} weights, different sets are defined to explore different objective function trade offs. Normalisation of the objective functions is performed by using Eq. 3.2, where f_p^{MAX} and f_p^{MIN}, represent the maximum and minimum single objective optimisation results.

$$f_p^N = \frac{f_p - f_p^{MIN}}{f_p^{MAX} - f_p^{MIN}} \tag{3.2}$$

In the case of the constraint technique, one single objective k is optimised while all others remain constrained at some value ϵ_i, which is varied along the possible values ($[f_i^{MIN}, f_i^{MAX}]$) (Cohon, 2003).

$$\begin{array}{lll} \min & f_k & \\ ST. & \mathbf{h}(\mathbf{x},\mathbf{y}) = & 0 \\ & \mathbf{g}(\mathbf{x},\mathbf{y}) \leq & 0 \\ & f_i \leq \epsilon_i & \forall i \neq k \\ & \mathbf{x} \in \mathbf{X} \subseteq \mathbf{R^n} & \\ & \mathbf{y} \in \mathbf{Y} \subseteq \mathbf{Z^q} & \end{array} \tag{3.3}$$

The weighted sum must be carefully applied since it does not generate all available Pareto points; the compromise solution cannot represent an evenly set of solutions of the feasible region (Steuer, 1986). Fu *et al.* (2001) points out that each optimal solution in the Pareto set that is derived from a combination of weights by the weighting method can also be generated from a corresponding combination of constraints using the ϵ-constraint method. The constraint method offers the advantages of better control over exploration of the non-dominated set and of locating points anywhere along this surface, while the weighted sum is easier to implement but it might generate dominated solutions.

3.1.2.1 Optimisation under uncertainty

The deterministic problem stated in 2.32, if some parameters are uncertain is formulated as in Eq. 3.4.

$$\begin{aligned} \min \quad & \mathbf{f}(\mathbf{x},\mathbf{y},\omega) = \quad [f_1\ f_2 \dots f_p] \\ subject\ to \quad & \mathbf{h}(\mathbf{x},\mathbf{y},\omega) = \quad 0 \\ & \mathbf{g}(\mathbf{x},\mathbf{y},\omega) \leq \quad 0 \\ & \mathbf{x} \in \mathbf{X} \subseteq \mathbf{R^n} \\ & \mathbf{y} \in \mathbf{Y} \subseteq \mathbf{Z^q} \end{aligned} \tag{3.4}$$

where **f** is a vector of key performance indicators KPIs; **h**(**x**,**y**, ,ω) = 0 and **g**(**x**,**y**,ω) $\leq$ 0 are equality and inequality constraints, and **x** and **y** are the vectors of continuous and integer variables, respectively. ω is a vector of uncertain parameters which affects KPIs, equality and inequality constraints.

The decisions that are made on the variables value are two depending on when they are done. Some variables' values are defined before the particular values of the uncertain values are known, these are called first-stage decisions and the period is know as the first stage. While there is a number of decisions that can be taken after uncertainty is revealed they are called second-stage decisions and this stage is the second stage as described by Birge & Louveaux (1997, Ch. 2).

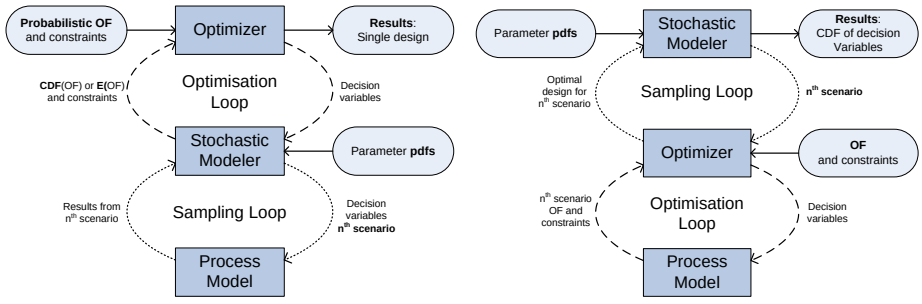
The first-stage variables are those that have to be decided before the actual realisation of the uncertain parameters. Once the random events are calculated, further design or operational policy improvements can be made by selecting, at a certain cost, the values of the second-stage, or recourse variables. Traditionally, the second-stage variables are interpreted as corrective measures or recourse against any infeasibilities arising due to a particular realisation of uncertainty (Sahinidis, 2004).

Stochastic optimisation (SO) involves selection of one optimal design based upon consideration of selected statistics, such as expected value, variance, or others, for the objective function, constraints, or both. The numerical implementation of SO involves two iterative loops: (1) an inner sampling loop (see section 3.2.2), in which uncertainty is simulated conditional on point estimates selected for each design variable, and (2) an outer optimisation loop in which the values of the design variables are manipulated (see Figure 3.1(a)). SO is used to make a decision now regarding a system for which uncertainty cannot be further reduced (Chen & Frey, 2004).

Stochastic programming (SP) involves estimation of optimal decision variable values for each sample, thereby resulting in a pdf for each decision variable. SP features: (1) an inner optimisation loop, in which the system is optimised conditional on a given realisation of uncertainty, and (2) an outer Monte Carlo sampling loop in which realizations of uncertainty are simulated (see Figure 3.1(b)). SP is used to assess the probable range of optimal solutions if uncertainty is first realised before choosing an optimal design (Chen & Frey, 2004). SO is a "here-and-now" formulation, while SP is a "wait-and-see" formulation.

SP mimics SA approach where the model incorporates optimisation and where input and output variables have associated pdfs. On the other hand SO has pdfs only for the model input variables given that the decision variables do not; Figure 3.1 clarifies the differences.

In both cases, this problem could be solved using MINLP techniques, however in the case of problems with process simulation MINLP methods get trapped into some neighbourhood within the search region leading to a local solution and failing to find a global optimum (Chaudhuri & Diwekar, 1997; Dantus & High, 1999). This issue has prompted the usage of random search methods to circumvent this issue, the use of simulated annealing has been



(a) Stochastic Optimisation (SO) (b) Stochastic Programming (SP)

Figure 3.1: Simplified algorithms for the implementation of SO and SP, adapted from Chen and Frey (2004); Diwekar *et al.* (1997).

proposed by Chaudhuri and Diwekar (1997); Dantus and High (1999), while the genetic algorithm was used by Hoffmann *et al.* (2004), as was previously discussed in section 2.4.4.2.

3.1.3 Multiple criteria decision analysis (MCDA)

All MCDA techniques require that alternatives are generated as a first step, which can be done using moO or using heuristics. Once all alternatives are generated the selection of the "best compromise" alternative requires input about the values and preferences of the decision makers (DMs)[31]. Design teams working on a problem with multiple objectives are faced with the need to apply multi-attribute decision analysis (MADA) techniques. A brief outline of them is done here, and the reader is referred to the reviews of Seppala *et al.* (2002) and Azapagic and Perdan (2005b) for further information.

Elementary methods do not require explicit evaluation of quantitative trade offs or any inter criteria weighting, and some cases nor a relative ranking. They can be of the following types (i) *maxi-min* selects the alternative based on importance of the attribute with respect to which alternative performs worst[32]; (ii) *maxi-max* selects based on the attribute with respect to which alternative performs best[33]; (iii) *conjunctive* and *disjunctive* methods are screening methods that select different alternatives if attributes are exceeding threshold values for all alternatives (conjunctive) or for some (disjunctive). In general they allow for selection of "satisfactory alternatives" instead of "best alternatives", and are mainly used as "gates/filters" for shortening the list of alternatives; and (iv) *lexicographic* methods require a ranking of attributes; they select the best alternative by choosing the one that has the best value for the first ranked attribute.

Value- and Utility-based Methods require that a real number is associated to each alternative based on the DM's value judgements. *Multi Attribute Utility Theory* (MAUT) methods require that the stakeholders articulate preferences according to strict preference or indifference relations, which provide a clear axiomatic foundation for rational decision making. **Multi Attribute Value Theory** (MAVT), is considered a special case of MAUT that does not consider uncertainty in the consequences of an alternative[34]. Both approaches can use an additive or multiplicative formulation, in order to asses the value (or utility) of a given alternative (see

[31] This kind of analysis is also known as goal programming.
[32] Its equivalent to assess the strength of an alternative by its weakest link.
[33] Its equivalent to assess the strength of an alternative by its strongest link.
[34] There is certainty of the outcomes of each alternative, while in MAUT, it has to be explicitly incorporated.

Eqs. 3.5 and 3.6).

$$V(a_j) = \sum_{i=1}^{nCriteria} w_i v_i(x_i(a_j)) \tag{3.5}$$

$$V(a_j) = \prod_{i=1}^{nCriteria} v_i(x_i(a_j))^{w_i} \tag{3.6}$$

where $V(a_j)$ represents the value associated to alternative a_j, w_i are criteria weights and $v_i(\cdot)$ are single attribute functions. If utility functions ($u_i(\cdot)$) are used instead, the calculation of the utility of the option ($U(a_j)$) can be assessed by using Eq. 3.7.

$$U(a_j) = \sum_{n=1}^{allConsequences} p_n u_n(a_j) \tag{3.7}$$

where p_n is the probability that the consequence j will occur, and the $u_n(a_j)$ is the utility of alternative a_j if its selection leads to consequence j. In general the higher the value of $V(a_j)$, the better the option. Examples of $v_i(\cdot)$ are found in Eqs. 3.8 and 3.9.

$$v_i(x_i(a_j)) = \frac{x_i(a_j)}{x_i^*} \tag{3.8}$$

$$v_i(x_i(a_j)) = \frac{x_i(a_j) - x_i^o}{x_i^* - x_i^o} \tag{3.9}$$

Eq. 3.8, scales alternative scores according to the distances from the origin to the best option x_i^*, while Eq. 3.9 scales scores relative to the distances between lowest x_i^o and highest scores x_i^*.

The *AHP*, (Analytical Hierarchy Process) proposed by Saaty (1980), calculates criteria scores (w_i) through pairwise comparison using a pre-specified 1 to 9 point scale that quantifies verbal expressions of strength of importance between attributes or preference between alternatives. More importantly is the fact that alternative's attributes are grouped in hierarchies. A ratio of 1 means that both criteria are equally important, 3 that a criteria is moderately more important while a ratio of 9 means that one criterion is most important. Having evaluated all comparisons, weights are calculated via a so-called principal eigenvalue method and consistency of preferences can also be assessed using an index provided by the method.

Outranking methods require that the DMs express their preferences when comparing one alternative to other. If such binary relations hold, then by performing pairwise comparisons between each pair of alternatives under consideration for each criteria the decision of which alternative is best can be achieved. Like AHP, they use pairwise comparison between every pair of alternatives (rather than criteria) being considered, but the aim is to eliminate alternatives that are dominated. The ranking of alternatives is obtained by out-ranking of an alternative over the others. Several methods of this type are available, such as ELimination Et Choix Traduisant la REalité (ELimination and Choice Expressing REality) (ELECTRE), Preference Ranking Organisation METHod for Enrichment Evaluations (PROMETHEE) and others. All these methods use a certain calculation reflecting the idea that beyond a certain level, bad performance on one criteria cannot be compensated for by good performance on another criterion. However, this non-compensatory approach to decision making lacks of strong theoretical foundations which is not the case of MAVT (Seppala *et al.*, 2002). In other methods such as Technique for Order by Similarity to Ideal Solution (TOPSIS) (Hwang & Yoon, 1981), the best solution is selected according to the alternative that has the shortest distance (euclidean) from the "utopian" best possible alternative, formed by the best possible scores for

each attribute (see section 6.3.1, Eq. 6.30). The same metric but measured fixing the worst (nadir) possible alternative also provides with other alternatives ordering (see section 6.3.1, Eq. 6.31).

In all former cases decision criteria can be of different type: (i) cardinal or measurable criterion (with or without indifference/preference thresholds), (ii) ordinal or qualitative criterion, (iii) probabilistic criterion and (iv) fuzzy criterion. MOO and value based MCDA techniques require cardinal metrics, while elementary or outranking methods can deal with mixed ordinal or cardinal information. Regarding compensation it can be treated in different ways: (i) *Single, all-important indicator*: where one criterion whose importance is deemed to be overriding[35]; (ii) *criteria of ranked importance combined with performance uncertainty*: quantified uncertainty can aid DMs in setting threshold values of difference and confidence that are required to distinguish between alternatives (eliminating possible ties). After ties are eliminated non compensatory methods requiring rank order can be used; and (iii) *Performance thresholds*, in this case the assessment of such thresholds can help in identifying situations where compensation does not hold.

The use of the former methods requires of elicitation the DM preferences, in this sense this thesis does not consider this path and generates the Pareto front as the problem solution, or proposes solutions considering all objective functions as equally important.

3.1.4 Metamodeling

Any meta-model or surrogate model methodology consists in building a mathematical function, which is cheaper from the computational point of view, and which approximates the behaviour of the pre-existing model over the domain of variation of its inputs (Fang *et al.*, 2006).

The primary goal of metamodeling is to predict the true model $y = f(x)$ at an untried point x by using $g(x)$, the metamodel built on a computer experiment sample $(x_i, y_i), i = 1...n$. Intuitively, it is desired to have the residual or approximate error, defined as $f(x) - g(x)$, as small as possible over the whole experimental region T. In order to do that the mean square error (MSE) defined as in Eq. 3.10 is minimised.

$$MSE(g) = \int_T [f(x) - g(x)]^2 dx \tag{3.10}$$

Most metamodels can be written as in Eq. 3.11, where the set of $B_0(x)...B_L(x)$ is a set of basis functions which depend on the type of metamodel selected.

$$g(x) = \sum_{j=0}^{L} B_j(x)\beta_j \tag{3.11}$$

Fang *et al.* (2006) state that since outputs of computer experiments are deterministic, the construction of a metamodel is in fact an interpolation problem. To interpolate the observed outputs $y_1...y_n$, over the observed inputs $x_1...x_n$ using the basis $B_0(x)...B_L(x)$ a L value is taken large enough such that equation 3.12 has a solution.

$$Y = BB\beta_G \tag{3.12}$$

where $Y = (y_1, ..., y_n)^T$, $\beta_G = (\beta_1, ..., \beta_n)$, and $BB_{ij} = B_j(x_i)$ for i=1:n and j=1:L.

[35] This is related to the question of strong-sustainability (non compensation) and weak-sustainability (compensation is allowed).

Diverse basis functions are available for usage, most commonly used are polynomials and splines. Other methods are Kriging and artificial neural networks (ANN), Fang *et al.* (2006), makes the following recommendations:

- Polynomial models are primarily intended for regression with random error; Polynomial modelling is the best established metamodeling technique, and is probably the easiest to implement. They are recommended for exploration in deterministic applications with a few fairly well-behaved factors.
- Kriging may be the best choice in the situation in which the underlying function to be modelled is deterministic and highly non-linear in a moderate number of factors (less than 50).
- Multi-layer perceptron networks may be the best choice (despite their tendency to be computationally expensive to create) in the presence of many factors to be modelled in a deterministic application.

Other methodologies rise from the design of experiments and response surface techniques. In these cases the models to be fitted are the same as for ANOVA see Eq. 3.29. Examples of using RSM in the context of optimisation are the works of Chen and Frey (2004) and a brief consistent review is done in Almeida-Bezerra *et al.* (2008).

An ANN is formed by simple processing elements called neurons, which are activated as soon as their inputs exceed certain thresholds. Neurons are arranged in several layers, which are inter-connected in such a way that input signals are propagated through the complete network to the output. Thus, they provide a way of correlating complex relationships between input and output responses in a model. The choice of the transfer function of each neuron (e.g. a sigmoidal function) contributes to the overall non-linear behaviour of the network. In general four characteristics define an ANN (Kasabov, 1998)[Ch. 4]: type of neurons/nodes, architecture of the connections between neurons (presence of loops, separates feedforward and feedback architectures) and learning algorithm.

In this thesis metamodels have been used in the context of process simulation. Two different process simulation software's: AspenPlus and AspenHysys required the use of results from the other. AspenPlus provides with good built in modelling capabilities for some aspects, but AspenHysys has the possibility of building custom models easily. In order to use AspenPlus results in AspenHysys a metamodel is constructed, in this case a multi layer perceptron network is used. Data fitting to the ANN was done using the Matlab's toolbox for ANNs (a description is provided in section 5.2.2.1).

3.2 Uncertainty management

Various methods have been proposed to make uncertainty operational[36] due to parameter uncertainty, such as the use of analytical uncertainty propagation methods; calculations based on intervals; applied fuzzy logic computations[37]; Bayesian statistics[38], and stochastic modelling which describes parameters as uncertainty distributions (Huijbregts, 1998a).

Performing uncertainty analysis is commonly done on real (physical) experimental results. Forrester *et al.* (2008) make a important distinction between physical versus computational experiments. Physical experiments are almost always subject to experimental error due to human error, that is error introduced simply by the experimenter making a mistake;

[36]Operationalization is understood as the process of turning abstract concepts into observable and measurable quantities.

[37]Which can be seen as an extension of the interval concept.

[38]Which makes it possible to treat subjective uncertainty estimates with the usual statistical calculation rules.

systematic error, due to a flaw in the philosophy of the experiment that adds a consistent bias to the result and random error, which is due to measurement inaccuracies inherent to the instruments being used. Repeatability differentiates the former two sources of experimental error, if there is a systematic component in the experimental error, this will have the same value each time the experiment is repeated, while in the case of the random error, it will be different every time and, given enough experiments, it will take both positive and negative values[39].

In the case of computational experiments experimental error, results from human error[40], and systematic error rises mainly from the inherently finite resolution of the numerical modelling process[41]. The main difference is that computational experiments are not affected by random error, they are deterministic. Therefore, the statistical theory and methods that have been constructed to address random errors cannot be directly applied to analyse data from computer experiments. Conceptually the application of these methods requires a fictional "physicalization" of computer experiments, in this sense it is required to view the outputs (results) of computer experiments, known to be deterministic values, as realisations of a stochastic process (Forrester *et al.*, 2008).

This section discusses approaches towards the analysis of input-output model relationships considering optimisation, while section 3.1.2.1, considered the inclusion of uncertainty within and optimisation procedure. In this sense two main approaches are available: analytical and sampling based methods.

3.2.1 Analytical methods

First order or Gaussian approximation is widely used while higher order approximations (method of moments) have been also used. In this case the model upon calculations are performed is an NLP, and complexity increases given that constraints have to be taken into account. In this sense the Karusch-Kuhn and Tucker (KKT) conditions allow to obtain the multiplier values once an optimal solution is found and the sensitivity values can be obtained from the differentiation of that set of equations. The problem of finding sensitivity information due to model parameters analytically in optimisation problems is thoroughly discussed in Conejo *et al.* (2006, Part III) and Fiacco (1983, Ch. 3).

One metric used in the chemical engineering community is the one proposed by Fisher *et al.* (1985). This methodology is based on the assumption that commonly used objective functions (OF) used in engineering have the following shape, see Eq. 3.13.

$$OF_k = \sum_{i=1}^{nTerms_k} OF_{ik}^{term} \tag{3.13}$$

where each OF_{ik}^{term} is a given function of the different engineering decision variables x_j. The SA in this context aims at devising (i) how each OF_{ik}^{term} of Eq. 3.13 affects the overall OF_k value and, (ii) how each optimisation variable (x_j) impacts each term and consequently the overall OF_k value. The first point allows for focusing attention on which OF_{ik}^{term} contributes the most to the overall OF_k, while the second shows which input variables affect the most, to the most important OF_{ik}^{term}. Two parameters can be used to calculate how far from the optimal conditions a given design is, and how each input variable affects a given the k-th OF (OF_k). Fisher

[39] This error can often be assumed to be distributed as a normal distribution ($N(0,\sigma^2)$) in most experiments.

[40] Bugs in the analysis code, incorrectly entered boundary conditions in the solution of a partial differential equation, etc.

[41] This type of error can lead to underestimates or overestimates, but it will do so in exactly the same way if the experiment is repeated (Forrester *et al.*, 2008).

et al. (1985) based their metrics on the assumption that process design optimisation problems can be characterised by a trade-off between monotonically increasing or decreasing functions (see Eq. 3.13).

- Rank-order parameter (ROP_{jk}): this parameter indicates whether large positive incremental changes are being trading off by large negative changes.

$$ROP_{jk} = \sum_{i=1}^{nTerms_k} \left| \frac{\partial OF_{ik}^{term}}{\partial x_j} \right| \Delta x_j^{MAX_k} \tag{3.14}$$

- Proximity parameter (PP_j): this parameter is equal to zero at optimum because the gradient is zero, but as the design is away from the optima this parameter tends to 1.

$$PP_{jk} = \frac{\left| \sum_{i=1}^{nTerms_k} \frac{\partial OF_{ik}^{term}}{\partial x_j} \Delta x_j^{MAX_k} \right|}{\sum_{i=1}^{nTerms_k} \left| \frac{\partial OF_{ik}^{term}}{\partial x_j} \right| \Delta x_j^{MAX_k}} \tag{3.15}$$

According to Granger *et al.* (1990, Ch 8. p192), the analytical approach has two important advantages, (i) once all algebraic analysis is performed the numerical calculations are simple, and (ii) it provides a very clear approach for decomposing the variance of each output into the sum of contributions. One example of the use of rank parameters is shown by Doherty & Malone (2001, Ch 6. p276), for testing the accuracy and sensitivity of their proposed OF. They propose to use an analytical approach by expanding the cost function in a Taylor series around a base cost design (C_0). Without proper knowledge of input parameter error distribution they use Root Mean Squared error (RMSE)[42]. Based on the absolute value of the $\delta \frac{C_i}{C_0}$, they establish a ranking of importance for variables, this way the authors focus attention on the i-th parameters that show highest values for such metric. Similarly Chen *et al.* (2002a) provide an analysis of uncertainty characterisation of model uncertainty for human inhalation toxicity (derived using EFRAT). In order to quantify parameter uncertainty the authors use the analytical method for error propagation. Other authors (Noykova & Gyllenberg, 2000) use derivatives evaluated at different operating points.

Despite its stated simplicity, local approaches suffer from complexity in algebra that increases rapidly with the complexity of the model. The method produces moments of distributions making hard to obtain reliable estimates for the tails of the output distribution. This local approach will not be accurate if the uncertainties are large, if the model is not smooth or if important covariance terms are omitted.

3.2.2 Sampling methods

A Monte Carlo Simulation (MCS) uses a simple procedure, it varies input data according to a given probability distribution function (PDF), runs the model and stores its results. This procedure is repeated until the appropriate uncertainty ranges are obtained for the output variables. Any sampling method has five steps: selection of PDFs for input variables, input variables sampling, model evaluation, output variables uncertainty analysis and finally input-output variables sensitivity analysis.

Uniform of log-uniform distributions may be assumed and physical plausibility arguments might be used to establish the ranges. According to Saltelli *et al.* (2000, Ch. 2), sensitivity

[42]This is equivalent to assume that the errors in the parameters are normal; the RMSE is the square root of the average of the squared deviations from the mean output function value, see Eq. 3.10.

analysis results generally depend more on the selected ranges than on the assigned distributions. However distributional assumptions can have an impact on the estimated distribution for output variables. Law & Kelton (1999, Ch 9.), state that the output random variables which are the results from a simulation will be neither independent nor identically distributed. However if each of the simulations is performed using different random numbers, then there is independence across runs and in this sense simulation results can be studied as realisations of an stochastic process.

Sampling can be random (such as MCS), or stratified and variables correlation can be handled by a correlation matrix or by the model. One of the stratified sampling techniques involve Latin Hypercube Sampling (LHS), in this method the range of each input factor is divided in a given set of intervals and one observation from each interval is drawn, generating non-overlapping realisations. This method has the advantage of ensuring that the input factor has all portions of its distribution represented by input values, further details can be found in Campolongo *et al.* (2000b) and Granger *et al.* (1990).

3.2.2.1 Number of scenarios required

Sampling methodologies suffer from a severe problem, which rises from the lack of knowledge of the amount of scenarios required to generate statistically reliable output model distributions.

One possible way is the use of bootstrapping, which in general is used for approximating a continuous PDF by discrete samples. The idea in bootstrapping is to choose the sample size n^* large enough so that repeated experiments with the same number of samples n^* will exhibit results with the same statistical properties. Consequently these samples are used to calculate the properties desired. Martinez & Martinez (2002, Ch. 6) state that there is no consistency in the literature to what bootstrapping methods mean. For some authors bootstrapping is used when a single population sample is generated and bootstrap samples are taken from that sample by replacement[43], while other use it when re-sampling is done by gathering new simulations. In both cases finding the correct sample size n^* requires performing a certain number of different trial runs and the computation of the studied statistic for each run.

While Granger *et al.* (1990) states that in general 10000 runs will yield reliable results, other authors propose an algorithm to determine it iteratively. (Chakraborty & Linninger., 2003) use the standard error of the mean (SEM) value of 0.3% as the stopping criterion and Law & Kelton (1999, Ch. 9), use two ways of defining errors, an absolute error (β, see Eq. 3.16) and a relative error (γ, see Eq. 3.17).

$$|\bar{X} - \mu| = \beta \tag{3.16}$$

$$|\bar{X} - \mu|/|\mu| = \gamma \tag{3.17}$$

In order to estimate n^* required to reach a certain precision on the mean value ($\bar{X}$) of the simulation output, there is need to define the error. The number of required scenarios can

[43] This means that in bootstrapped samples individual values from the original population, could appear several times and some other might not appear at all.

then be estimated as in Eqs. 3.18 and 3.19 for the absolute and relative errors respectively.

$$n_a^*(\beta) = \min\left\{ i \geq n : t_{(i-1,1-\alpha/2)}\sqrt{\frac{S^2(n)}{i}} \leq \beta \right\} \tag{3.18}$$

$$n_r^*(\gamma) = \min\left\{ i \geq n : \frac{t_{(i-1,1-\alpha/2)}\sqrt{\frac{S^2(n)}{i}}}{|\bar{X}(n)|} \leq \gamma \right\} \tag{3.19}$$

However, the former estimations use $\bar{X}$ and $S^2(n)$ which may not be precise estimates of their corresponding population parameters (μ and σ). In this sense $n_r^*(\gamma)$ or $n_a^*(\beta)$ might be too small or too big, consequently a sequential procedure should be adopted in which a given number of scenarios is added to the estimation of $\bar{X}$ and $S^2(n)$.

Algorithm 3.1: Determination of n^* using Law & Kelton (1999) bootstrapping technique.

Data: Initial values n^0, desired tolerance (γ).
Result: Number of desired scenarios n^*
begin
  $k \longleftarrow 1$;
  $n^k \longleftarrow n^0$;
  $\delta(n^k,\alpha)/|\bar{X}(n^k)| \longleftarrow \infty$;
  while $\delta(n^k,\alpha)/|\bar{X}(n^k)| > \gamma$ **do**
    calculate $\bar{X}(n^k)$;
    calculate $\delta(n^k,\alpha)$ using $\delta(n^k,\alpha) = t_{(i-1,1-\alpha/2)}\sqrt{\frac{S^2(n^k)}{n^k}}$;
    $k \longleftarrow k+1$;
    sample 1 extra point for X;
  $n^* \longleftarrow n^k$;

Algorithm 3.1 can be easily implemented for the case of the MCS method where a new scenario, or a new batch of scenarios using Eqs. 3.18 and 3.19, can be easily generated without any requirement of dependence of the previous samples scenarios. Special care has to be taken if other sampling strategy is adopted due to prior generated scenarios as in the case of LHS (Kurowicka & Cooke, 2006).

Not only the mean value can be assessed using the algorithm but any other metrics can be calculated based on model results, such as standard statistics (mean, standard deviations, and confidence intervals) or regression analysis metrics.

Uncertainty analysis simply involves calculation of output variables typical statistical metrics (e.g., mean and variance). On the other hand, in order to assess the relationships between nIn input variables (x_i), and $nOut$ output variables (y_l), several authors have proposed the use of two different type of metrics (i) regression based metrics and (ii) variance decomposition metrics (Saltelli *et al.*, 2000; 2008; 2004, Heijungs & Huijbregts, 2004, Cacuci *et al.*, 2005, Kurowicka & Cooke, 2006).

3.2.3 Uncertainty metrics

Classical statistics Considering that $nScen$, scenarios are available, and that there are available nIn input variables (x_h) and $nOut$ output variables (y_l) mean or expected value (see Eq. 3.20), standard deviation or variance (see Eq. 3.21) can be calculated.

$$E(y_l) = \bar{y}_l = \sum_{i}^{nScen} \frac{y_{il}}{nScen} \tag{3.20}$$

$$V(y_l) = \sigma_{y_l}^2 = \frac{1}{nScen} \sum_{i}^{nScen} \left(y_n - \bar{y}\right)^2 \tag{3.21}$$

The standard deviation (SD_{y_l}) is calculated from the variance as in Eq. 3.22, while the coefficient of variation is defined as in Eq. 3.23.

$$SD_{y_l} = \sigma_{y_l} = \sqrt{Var(y_l)} \tag{3.22}$$

$$CV_{y_l} = \frac{\sigma_{y_l}}{\bar{y}_l} \tag{3.23}$$

The confidence interval for the mean ($\bar{y}_l$) can be calculated considering the value of σ_{y_l} as in Eq. 3.24.

$$CI(\bar{y}_l) = \left[\bar{y}_l - t_{(nScen-1,0.975)}\sigma_{y_l}; \bar{y}_l + t_{(nScen-1,0.975)}\sigma_{y_l}\right] \tag{3.24}$$

where $t_{(nScen-1,0.975)}$, is the Student-t distribution value for nScen-1 DOF, which makes the probability be 0.975. The former is based on assuming normal distribution for the errors and a 95% coverage of the CI, as described in (Law & Kelton, 1999).

It is always important to compare the estimated results from sampling runs and the results without uncertainty, if mean and the value with out uncertainty coincide its a clear result of symmetrical distributions being used for the input parameters (Heijungs & Kleijn, 2001). With regards to the coefficient of variation, values below 10% suggest reasonable certain results.

Linear regression based metrics These metrics are based on a linear correlation defined as in Eq. 3.25.

$$\hat{y}_l = b_{l0} + \sum_{h=1}^{nIn} b_{lh} x_h + \epsilon_i \qquad \forall l = 1, nOut \tag{3.25}$$

An important value related to the regression is the model coefficient of determination $R_{y_l}^2$, for output variable y_l, which is defined traditionally as in Eq. 3.26.

$$R_{y_l}^2 = \frac{\sum_{f=1}^{nScen} (\hat{y}_{lf} - \bar{y}_l)^2}{\sum_{f=1}^{nScen} (y_{lf} - \bar{y}_l)^2} \qquad \forall l = 1, nOut \tag{3.26}$$

the closer $R_{y_l}^2$ is to unity the better the regression model results $\hat{y}_{lf}$ fit the actual model realisations y_{lf}. This issue is important, given that the validity of regression based metrics depends on the degree to which the regression model fits the data.

- *Standardised regression coefficients* (SRC), require the standardisation of input variables and output results which is performed by subtracting the mean value ($\bar{x_h}$, $\bar{y_l}$) and normalising its value by dividing it by the variable's standard deviation (σ_{x_h}, σ_{y_l})[44]. The SRCs represent the following relation between input variables which are the nIn uncertain variables x_h and the $nOut$ output variables y_l, see Eq. 3.27.

$$\frac{y_l - \bar{y_l}}{\sigma_{y_l}} = \sum_{h=1}^{nIn} SRC_{lh} \frac{x_h - \bar{x_h}}{\sigma_{x_h}} \qquad \forall l = 1, nOut \tag{3.27}$$

  A value of SRC_{lh} close to zero indicates that the output variable l is not correlated to input variable h, moreover the sign of SRC also indicates the relationship between them, a positive SRC_{lh} indicates that increments of the input variable h, are followed by an increase of the output variable l, and the opposite behaviour if the SRC_{lh} is negative.
- *Partial Correlation Coefficients* (PCC), are calculated by performing several regressions which include or not the input variable under consideration. In this case a PCC shows how much each input variable affects the behaviour of the output variables, by performing two separate regressions, the first one considering all input variables and the second without the subject input variable as depicted in Eq. 3.28.

$$PCC_{hl}^2 = \frac{\sum_{f=1}^{nScen} (y_{lf} - \widehat{y_{lf}^{\sim x_h}})^2 - \sum_{f=1}^{nScen} (y_{lf} - \widehat{y_{lf}^{full}})^2}{\sum_{f=1}^{nScen} (y_{lf} - \widehat{y_{lf}^{\sim x_h}})^2} \qquad \forall l = 1, nOut; h = 1, nIn \tag{3.28}$$

In Eq. 3.28, $\widehat{y_{lf}^{\sim x_h}}$, represents the estimation of the y_l variable value using a regression that does not include input variable x_h, while $\widehat{y_{lf}^{full}}$ represents the y_l variable value estimated using a regression that considers all input variables.

An iterative methodology can be used for calculating the variance explained by each of the variables, one proposed algorithm is the one of Helton and Davis (2000) which is depicted in Algorithm 3.2.

Different algorithms have been implemented in this thesis for the calculation of the former set of metrics. All of them rely on the use of the statistical toolbox of Matlab. Linear regressions are calculated using the `regress` command which calculates multilinear regressions[45], it provides with confidence intervals for the coefficients calculated and basic statistics such as $R_{y_l}^2$.

Rank transformation To all regression based metrics the rank transformation can be applied and the same metrics (SRC and PCC) can be calculated. Ranks can cope with non linear (but monotonic) relationships between input-output distributions allowing the use of linear regression. Rank transformed statistics are more "robust" allowing a useful solution in the presence of long-tailed input-output distributions. But conclusions drawn from this analysis are not easy to translate back to the original model (Campolongo *et al.*, 2000b).

[44] Standardising the data set makes the measurements of different lengths comparable, i.e., the importance of the different measurements does not depend on the scale (Häardle & Hlavka, 2007)[Ch. 8].

[45] The algorithm is based on the fact that if $y = Xb$ then $b = (X^T X)^{-1} X^T y$, but X is expressed using a QR orthogonal-triangular decomposition. The decomposition makes X=Q·R, where R keeps the same size as X (m x n) while Q is m x m; this way no matrix inversion is required.

Algorithm 3.2: Variance explained by each variable using Helton and Davis (2000) method.

Data: y, x
Result: x^{rank}, holds the ranking of variables in terms of output variable's variance explained by linear regression.
begin
  $x^{totest} \longleftarrow x$;
  $x^{tested} \longleftarrow empty$;
  $\bar{y} \longleftarrow y$;
  for *all* i *columns in* x^{totest} **do**
    perform single variables regressions $\bar{y} = b_{0i} + b_i x_i^{totest}$ for all i columns in x_i^{totest};
    select column i^* that has max R_i^2 (Eq. 3.26) and CI for b_i does not contain zero;
    $x^{tested} \longleftarrow [x^{tested} | x_{i^*}^{totest}]$;
    remove $x_{i^*}^{totest}$ from x^{totest};
    perform multiple variable regression $\hat{y} = c_{0i} + c_i x_i^{tested}$;
    $\bar{y} \longleftarrow \bar{y} - \hat{y}$;
  $x^{rank} \longleftarrow x^{tested}$;

Variance decomposition metrics To cope with some of the drawbacks of linear based regression metrics other sensitivity metrics can be used. One of the most widely variance decomposition's types is the one performed in analysis of variance (ANOVA). The experiment result (y) is described as in Eq. 3.29.

$$y = \mu + \sum_t \tau_t + \epsilon \tag{3.29}$$

where μ is the overall experiments mean, τ_t is the deviation associated to treatment t and ϵ is the associated error. ANOVAs are collection of statistical models, and their associated procedures, in which the observed variance is partitioned into components due to different explanatory variables. One-Way ANOVA takes a set of grouped data and determine whether the mean of a variable differs significantly between groups (de Sá, 2007)[Ch. 5]. Often there are multiple variables, and there is interest in determining whether the entire set of means is different from one group to the next (MathWorks, 2005). The comparison is performed between variances calculated over the whole data, and over treatment data as discussed by Box *et al.* (2005, Ch. 2). Different experimental designs are available a brief review is presented in Almeida-Bezerra *et al.* (2008) aiming at the optimisation of a given variable.

Other metrics are based on different possible decomposition's of the model output's variance ($V(y_l)$). They resemble an ANOVA, however the model used to calculate the decomposition is different, due to the use of conditional statements as in Eq. 3.30.

$$V(y_l) = E_{x_i}(V_{x_{\sim i}}(y_l|X_i)) + V_{x_i}(E_{X_{\sim i}}(y_l|x_i)) \qquad \forall l = 1, nOut \tag{3.30}$$

These metrics are based on the partial or conditional variance of the model output; it is expected that the variance of y_l will be reduced if an input variable which is influential is fixed to a given value (Homma & Saltelli, 1996). Based on the former idea, the use of first order, and total sensitivity metrics can is extensively discussed (Chan *et al.*, 2000; Homma & Saltelli, 1996; Saltelli *et al.*, 2008).

3.3 Multivariate analysis techniques

Multivariate analysis represents a class of analytical techniques that aim to detect structural patterns in a data set. When row observations from a model are arranged as matrix, usually the number of observations is bigger than the number of columns (variables observed). Many different techniques are developed for such objective, such as Principal components analysis (PCA), Linear Discriminant Analysis (LDA), canonical correlation analysis (CCA) and Multidimensional Scaling (MDS). The former techniques decrease the dimensionality of the problem to a set of 2 to 3 dimensions. These dimensions, in the PCA and LDA cases, are a linear combination of the variables which are selected using different criteria. In the case of PCA, the variables contained in the selected dimensions (principal components) are the ones that explain most of the variance. In the case of LDA the criterion used is the Fischer criterion (see Eq. 3.40), while in the case of MDS, the criteria is to find a set of output values which has the same distance structure as the original sampling set (Duda *et al.*, 2000).

3.3.1 Principal components analysis

The basic idea of the PCA method is to describe the variation of a set of multivariate data in terms of uncorrelated (linearly independent) variables each of which is a particular linear combination of the original variables. The new variables are derived in decreasing order of importance so that, for example, the first principal component (pc) accounts for as much as possible of the variation in the original data. The objective of this analysis is usually to see whether the first few pc account for most of the variation in the data. If so, it is argued that they can be used to summarise the data with little loss of information, thus providing a reduction in the dimensionality of the data, which may be useful in simplifying later analysis (Jackson, 1991). Further details can be found in de Sá (2007, Ch. 7).

The method of principal components is based on a key result from matrix algebra, a (p x p) symmetric, non-singular matrix, such as the covariance matrix **S** (defined as in Eqs. 3.31 and 3.32.), may be reduced to a diagonal matrix **L** by pre-multiplying and post-multiplying it by a particular orthonormal matrix **U**.

$$s_{ii}^2 = \frac{\sum_{j=1}^{nScens} \left(x_{ij} - \overline{x}_j\right)^2}{nScens - 1} \tag{3.31}$$

$$s_{ij}^2 = \frac{nScens \sum_{k=1}^{nScens} \left(x_{ik} - x_{jk}\right)^2 - \sum_{k=1}^{nScens} (x_{ik}) \sum_{k=1}^{nScens} \left(x_{jk}\right)}{nScens(nScens - 1)} \tag{3.32}$$

$$\mathbf{U}^{-1}\mathbf{S}\mathbf{U} = \mathbf{L} \tag{3.33}$$

The diagonal elements of **L**, $[l_1, l_2, ..., l_p]$, are the characteristic roots, latent roots or eigenvalues of **S**. The columns of **U**, $([u_1|u_2|...|u_p])$, are the characteristic vectors or eigenvectors of **S**. Geometrically, PCA is a principal axis rotation of the original coordinate axes. The principal axis transformation will transform p correlated input variables $(x_1, x_2, ..., x_p)$ into p new uncorrelated variables $(z_1, z_2, ..., z_p)$. The coordinate axes of these new variables are described by the characteristic vectors u_i which make up the matrix **U** of direction cosines. The transformed variables are called the principal components of x or pc's, and will have a zero mean and a l_i variance[46]. To distinguish between the transformed variables and the transformed

[46]The i-th characteristic root of **S**.

observations, the transformed variables are called pc and the individual transformed observations are called z-scores (Jackson, 1991). The variability explained and associated to the i-th pc is proportional to l_i, the first being the biggest and sub sequentially decreasing. The number of components that a system can be reduced to is associated then to the amount of variability that the new uncorrelated model is supposed to assume.

3.3.2 Linear discriminant analysis

Linear Discriminant Analysis (LDA) searches for vectors that best discriminate among classes, rather than those that best describe the data as in the case of PCA. In this sense discriminant analysis is used in situations where the clusters are known a priori. The aim of discriminant analysis is to classify an observation, or several observations (Häardle & Hlavka, 2007)[Ch. 12]. Formally, given a number of independent features relative to which the data is described, LDA creates a linear combination of these which yields the largest mean differences between the desired classes (Martinez & Kak, 2001). Duda *et al.* (2000, Ch. 4), describe the algorithm for the calculation of these vectors. LDAs are calculated based on n p-dimensional samples $x_1 ... x_p$ where c subsets D_c, are described. The following means can be calculated, the total mean as in Eq. 3.35 and the class mean as in Eq. 3.34.

$$\mathbf{m_i} = \frac{1}{n_i} \sum_{x \in D_i} \mathbf{x} \tag{3.34}$$

$$\mathbf{m} = \frac{1}{n} \sum \mathbf{x} = \frac{1}{n} \sum_{k=1}^{c} n_k \mathbf{m_k} \tag{3.35}$$

To obtain good separation of the projected data it is desired that the difference between the means to be large relative to some measure of the standard deviations for each class matrix. The method uses scatter matrices, instead of the covariance matrix in PCA, defined as in Eqs. 3.36 to 3.39.

$$\mathbf{S}_k = \sum_{\mathbf{x} \in D_k} (\mathbf{x} - \mathbf{m}_k)(\mathbf{x} - \mathbf{m}_k)^T \tag{3.36}$$

$$\mathbf{S}_W = \sum_{k=1}^{c} \mathbf{S}_k \tag{3.37}$$

$$\mathbf{S}_T = \sum_{\mathbf{x}} (\mathbf{x} - \mathbf{m})(\mathbf{x} - \mathbf{m})^T \tag{3.38}$$

$$\mathbf{S}_B = \sum_{k=1}^{c} n_k (\mathbf{m}_k - \mathbf{m})(\mathbf{m}_k - \mathbf{m})^T \tag{3.39}$$

In the former equations eq:scatteri to eq:scatterbetween, $\mathbf{S}_W$ represents the *within-class scatter* matrix, while $\mathbf{S}_B$ is the *between-class scatter* matrix and $\mathbf{S}_T$ the *total scatter* matrix, which are related as follows: $\mathbf{S}_T = \mathbf{S}_W + \mathbf{S}_B$. According to Duda *et al.* (2000, Ch. 4), what is desirable is a transformation matrix $\mathbf{W}$ that in some sense maximises the ratio of the between-class scatter to the within-class scatter. Moreover the authors state that "*a simple scalar measure of scatter is the determinant of the scatter matrix, thereby measuring the square of the hyper ellipsoidal scattering volume*", which can be expressed as in Eq. 3.40[47].

$$J(\mathbf{W}) = \frac{|\mathbf{W}^T \mathbf{S}_B \mathbf{W}|}{|\mathbf{W}^T \mathbf{S}_W \mathbf{W}|} \tag{3.40}$$

[47] This criterion is also known as Fisher's linear discriminant, i.e. the linear function yielding the maximum ratio of between-class scatter to within-class scatter.

Finding **W** is difficult, however it can be found the columns w_i of an optimal **W** are the generalised eigenvectors that correspond to the largest eigenvalues in Eq. 3.41.

$$\mathbf{S}_B w_i = \lambda_i \mathbf{S}_W w_i \tag{3.41}$$

In this thesis Matlab's statistical toolbox has been used for the calculation of PCA. The method princomp performs principal components analysis on the data matrix X, and returns the principal component coefficients. For the calculation of LDA, the Matlab toolbox developed by Cai (2009)[48], has been used.

3.4 Life-Cycle Assessment (LCA)

Life-Cycle Assessment (LCA) is an environmental management tool that enables quantification of environmental burdens and their potential impacts over the whole LC of a product, process or activity. Although it has been used in some industrial sectors for about 20 years, LCA has received wider attention and methodological development since the beginning of the 1990s when its relevance as an environmental management aid in both corporate and public decision making became more evident[49]. Two main trends appeared, one from the Society of Environmental Toxicology and Chemistry (SETAC) and other from the International Standards Organisation (ISO). The methodological framework for conducting LCA, as defined by both SETAC (SETAC, 1993) and ISO (ISO, 1997), comprises four main phases.

- (i) Goal Definition and Scoping, (ISO, 1997).
- (ii) Inventory Analysis, (ISO, 1998).
- (iii) Impact Assessment, (ISO, 2000a).
- (iv) Interpretation and Improvement Assessment, (ISO, 2000b).

Two attractive features of LC thinking techniques are: (i) the inclusion of input and output wastes associated with a process, and (ii) the emphasis on environmental impact rather than emissions as a means of comparing different alternatives. In this sense an LCA takes into look all possible flows that a product/process incurs as in the case of Figure 3.2. The focus on a product/service system in LCA has many important implications for the nature of impacts that can be modelled; Finnveden *et al.* (2009) emphasises that (i) the product system is

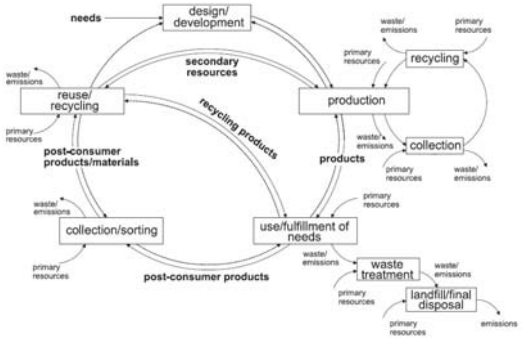


Figure 3.2: Mass and energy flows taken into account in a LCA. From Rebitzer *et al.* (2004).

[48] http://www.cs.uiuc.edu/~dengcai2/Data/code/LDA.m

[49] According to Azapagic (1999), LCA originates from "net energy analysis" studies, which were first published in the 1970s and considered only energy consumption over a LC of a product or a process. Some later studies included wastes and emissions, but none of them went further than just quantifying materials and energy use.

extended along time[50] and space, and the emission inventory is often aggregated in a form which restricts knowledge about the geographical location of the individual emissions, and (ii) the LCA's FU refers to the assessment of an often rather small unit. The emissions to air, water, or soil in the inventory are determined as the FU's proportional share of the full emission from each process. The LCIA thus has to operate on mass loads representing a share (often nearly infinitesimal) of the full emission output from the processes. Point (i) forces emission's impacts to represent the sum of impacts from releases years ago, releases today, and releases in the future. These emissions generate harm at different ecosystems in different parts of the world. Consequently LCA can not be a substitute for ERA, given that LCIA results reflect the potential contributions to actual impacts or risks pending on the relevance and validity of the reference conditions assumed in the underlying models (Finnveden *et al.*, 2009).

3.4.1 Goal and scope definition

The goal and scope definition of an LCA provides a description of the product system in terms of the system boundaries and a FU (Rebitzer *et al.*, 2004). In this stage the reasons for carrying the study, the intended application and the intended audience are defined. The methodology is fully described in ISO (1998). In this step the LCA most critical points are decided.

- *Functional unit* (FU), is a measure of the function or service that the system delivers, its selection generally disregards production and consumption volumes, and assumes linearity.
- *Data* used in some cases technology averaged values will be enough, but for cases when the study modifies a consumption distribution then marginal data should be used.
- *Impact assessment* procedure to be used, commonly a set of environmental impacts is chosen from one of the ready to use LCIAs, see section D.1.
- *System boundaries* are drawn from "cradle to grave" including all burdens and impacts in the LC of a process, its definition is specially important when dealing with interrelated products.

In setting the system boundaries, it is useful to distinguish between *foreground* and *background* subsystems (Azapagic, 1999; Mellor *et al.*, 2002).

- The *foreground* system is defined as the set of processes directly affected by the study delivering a FU specified; environmental emissions from foreground system are termed *direct burdens*.
- The *background* system is the one that supplies energy, materials and other services (e.g. transportation, inventory), to the foreground system, usually via a homogeneous market so that individual plants and operations cannot be identified. The primary resource inputs and emissions from the background system comprising the upstream and downstream SC echelons are termed *indirect burdens*.

Differentiation between foreground and background systems is also important for deciding on the type and quality of data to be used[51]. According to Tillman *et al.* (1994) system boundaries must be specified in many dimensions:

[50] The LCI results are typically unaccompanied by information about the temporal course of the emission or the resulting concentrations in the receiving environment.

[51] According to Azapagic (1999), the foreground system should be described by specific process data, while the background is normally represented using data from a mix of different technologies or processes, or by generic industry data, obtainable from commercial or public LCI databases.

- *Technological system and nature*. These boundaries are expected to be clear, but for cases which include forestry, agriculture, emissions to external waste water systems and landfills; these boundaries need to be explicitly defined.
- *Geographical areas*, various parts of a product may be produced all around the world; infrastructure, such as electricity production, waste management and transport systems, differs in different regions and the sensitivity of the environment to pollutants varies from one area to another.
- *Time horizon*, similar considerations to the former point have to be taken for products which are used over long time horizons.
- *Production of capital goods*, is specially important in the case of an LCA that analyses whether it is environmentally beneficial to invest on new process equipment in order to reduce emissions from a process[52].
- *Boundaries between product's LCs*, it is important to distinguish between significant and insignificant products/processes; three different methodologies are available for performing these decisions (Tillman *et al.*, 1994):

  – (i) process tree system (PTS): it only includes processes and transportation directly involved in the production, use and disposal of the product studied, the ancillary materials and the equipment. All flows are followed upstream, to the acquisition of raw materials or other resources.
  – (ii) technological whole system (TWS): it includes all processes and transports affected by the choice between the alternatives compared, assuming that the demand for the functions fulfilled by the systems is constant; ignoring economic and social forces.
  – (iii) socio-economic whole system (SEWS): in addition to TWS, it considers economic forces and social factors which further expands the system's boundary.

Rebitzer *et al.* (2004) uses the term *attributional* LCA to denote a description of a product system and the term *consequential* LCA denotes a description of the expected consequences of a product system change. In attributional LCAs, the processes included within boundaries are those that are deemed to contribute significantly to the studied product and its function[53]. In consequential LCAs, the processes included are those that are expected to be affected on short and/or long term by the decisions to be supported by the study. Thus, the linearity that appears from the connection between processing units disappears and the production changes impacts upstream and downstream processes, considering its demand and capacities. According to Rebitzer *et al.* (2004), different hypothesis regarding the SEWS must be addressed such as marginal production costs and elasticity of supply or demand[54]. One possible way

[52]To answer such a question it is necessary to compare the production and operation of the new equipment with continued use of the existing equipment. Tillman *et al.* (1994) recommend that capital goods should be included only when the investment is significantly different in compared alternatives, which is consistent with the principle of excluding identical activities.

[53]This implies that material and energy flows are followed systematically upstream from the process associated with the reference flow to the extraction of natural resources and downstream to the final disposal of waste, by using the PTS or TWS methods.

[54]Neither production nor demand are always fully elastic, which means that the demand for one unit of product in the investigated LC affects not only the production of this product but also its consumption in other systems. In most cases individual suppliers or markets may be unconstrained, which means that they are unaffected by an increase in product demand, this is usually due to small changes, compared to the total market, that only affects the marginal upstream production processes. However big production changes might produce effects which include some rebound. Korhonen (2005) describes one possible situation related to energy policy, which refers to increases in fuel efficiency, where "*Increases in fuel efficiency lead to reduced production costs; reduced costs affect the prices of end-products that go down making the purchasing power of consumers increase, which will make the overall energy use increase*".

of dealing with these issues is the application of partial equilibrium models to analyse them (Bouman *et al.*, 2000).

Selection of data sources is also heavily modified by the selection between attributional or consequential LCA. Attributional LCA excludes the use of marginal data, they use average data reflecting the actual physical flows. On the other hand, in consequential LCAs marginal data is used when relevant for the purpose of assessing the consequences. A general approach can be to include all easily accessible data, check its importance and refine if necessary by performing LCI and LCIA in an iterative fashion until the required precision has been achieved. In the case of process industries, attributional LCAs are done, where downstream processes are generally excluded, given that use and disposal phase of chemicals are the same regardless of its production method[55].

The boundary between the product system and other products system also rises issues with regards to allocation. A narrowly defined system requires less data collection and analysis, but it may ignore critical features of a system (Sinclair-Rosselot & Allen, 2002c). There are three types of allocation problems (Finnveden *et al.*, 2009):

- (i) multi-output or multi functional[56], one process which generates multiple products such as a refinery,
- (ii) multi-input, one process which receives several waste products, such as a waste incinerator, and
- (iii) open-loop recycling[57], in which one waste product is recycled to another product, such as the case of newspaper waste used for energy production.

In the case of multi-output process two ways of handling with allocation are available, (i) allocate/partition the burdens between the products using different principles (physical, chemical, economic or arbitrary)[58], or (ii) avoid allocation by system expansion to include the other LC parts[59], or by dividing the process into sub processes. In the case of attributional LCAs partitioning is often considered to be the correct method, and system expansion can be used for investigating individual LCs but also combinations (Finnveden *et al.*, 2009).

The allocation problem remains a subject of current discussion and consequently referred as a source for bias and uncertainty. Burgess and Brennan (2001) states that regarding allocation procedures "a single solution to the problem will never be agreed on", therefore the only way of dealing with it is the application of sensitivity analysis.

3.4.2 Life Cycle Inventory Analysis (LCI)

LCI is the most important step in a LCA, given that the whole environmental relevant interventions of the system under study are gathered; its methodology has been defined by ISO (1998). Three main stages can be differentiated when developing an LCI:

- (i) Flow model construction: a small system flow sheet is constructed, which helps visualising data requirements and flow.
- (ii) Data collection: it is by far the most time consuming step of the LCI and LCA.

[55] An example of such case is an LCA for nitric acid production reviewed by Burgess and Brennan (2001).

[56] A single process that performs several other functions besides producing a given product, or that produces different products, is considered to be multi-functional.

[57] Differences between open loop and closed loop where discussed in section 1.2.1.

[58] Tillman *et al.* (1994) argue that allocation should reflect the process/product objective, which is to create value, based on all the functions the process helps to fulfil. Consequently it makes sense to allocate based on the economic value, if that is not feasible then the weight fraction or other physical property.

[59] The problem resides in building a single function system from multi-product systems. This approach depends on the existence of technically and economically feasible alternative processes for the production of the co-product.

- (iii) Data normalisation: calculation of all flows related to the selected FU.

In the case of attributional LCAs, calculation of the LCI responds to mass balances, where the FU is the calculation basis for it. Linear algebra is sufficient for solving it, given that the models considered are linear and in steady state (Heijungs & Suh, 2002)[60]. Several schemes are available for LCIs calculation, a review of them is found in the following paragraphs.

3.4.2.1 LCI calculation procedures

In total, six methods are distinguished and classified by Suh and Huppes (2003), (i) LCI computation using process flow diagram (PFD); (ii) matrix expression of product system, extensively discussed by Heijungs and Suh (2002)[61]; (iii) input-output (IO) based LCI; and three different forms of hybrid analysis namely (iv.a) the tiered hybrid analysis, (iv.b) the IO-based hybrid analysis, and (iv.c) the integrated hybrid analysis.

Process flow diagrams PFDs show how different processes for manufacturing a product are interconnected through commodity flows. In PFDs, boxes represent processes while arrows the commodity flows. Each process is represented as a ratio between a number of inputs and outputs. The LCI of the product system is calculated using plain algebra, the amount of commodities fulfilling a certain FU is obtained, by multiplying the amount of environmental interventions generated to produce them (Suh & Huppes, 2003). The computation of an LCI is more complex if some of the following situations are not met:

a. each production process produces only one material or energy flow,
b. each waste treatment process receives only one type of waste,
c. the product system under study delivers inputs to, or receives outputs from another product system, and
d. material or energy flows between processes do not have loop(s).

The first three conditions refers to the issue of multi-functionality and consequently have to be handled with an appropriate allocation procedure. The last condition requires that all processes in the product system under study do not utilise their own output indirectly, and is commonly addressed by setting appropriate system boundaries or calculating net consumption.

Castells *et al.* (1994a,b) introduce an algorithm for assessing the LCI of process system, based on the use of the eco-vector concept. The eco-vector includes for every input stream, information about process environmental interventions from a cradle to grave perspective. Each element of the eco-vector consists of the amount of environmental load per unit of mass or energy, subsequently two types of eco-vectors are introduced associated to mass or energy streams. Eco-vectors are calculated once mass balance of all process/product flows have been solved, moreover their source are such mass-energy balances.

Matrix representation of product system Each process involved in the production of a given product can be represented as an n-dimensional vector, that contains information regarding

[60] Regardless of the calculation procedure, it has to be emphasised that while some LCI values are seen as objective values given that are calculated using sound material and energy balances, other quantities depend on choices and assumptions and can be seen as subjective. In general all of them have a certain uncertainty associated to them.

[61] LCIs calculated using process flow diagrams or matrix expression of product system are referred to as LCIs based on process analysis (Suh & Huppes, 2003).

economic flows and environmental interventions. Economic flows are used between process, and a mass balance performed on them holds.

$$\mathbf{P} = \begin{bmatrix} p_{11} & p_{1I} \\ p_{I1} & p_{II} \\ p_{j1} & p_{jI} \\ p_{J1} & p_{JI} \end{bmatrix} = \begin{bmatrix} \mathbf{A} \\ \mathbf{B} \end{bmatrix} \tag{3.42}$$

Each column vector $\mathbf{p}_i$ represents a given unit process, in this case I production processes are modelled. The first I rows of **P** correspond to matrix **A**, that represents the technology matrix, while the remaining j rows (with $j = I+1..J$) represent the intervention matrix **B**, that represents the environmental interventions for every I process[62].

The production of the I products before mentioned can be represented by a column vector **f**, each (f_i) element of **f**, will be set according to the FU.

$$\mathbf{As} = \mathbf{f} \tag{3.43}$$

Eq. 3.43 supposes that **f** is produced by **A**, where **s**, is a scaling vector that indicates how much each process is used in order to produce the products concerned in **f**. If matrix **A** is invertible then **s** is easily calculated as in Eq. 3.44[63].

$$\mathbf{s} = \mathbf{A}^{-1}\mathbf{f} \tag{3.44}$$

Upscaling or downscaling a given i process by a scale factor s_i, not only affects economic flows f_i, but also environmental interventions g_j, consequently the environmental interventions (**g**) associated to the production of **f** can be calculated as in Eq. 3.45.

$$\mathbf{g} = \mathbf{Bs} \tag{3.45}$$

Based on Eqs. 3.44 and 3.45; **g**, can be calculated straightforward as in Eq. 3.47 provided the intensity matrix ˜ is calculated as in Eq. 3.46.

$$\mathbf{g} = \mathbf{BA}^{-1}\mathbf{f} \qquad ^{\sim} = \mathbf{BA}^{-1} \tag{3.46}$$

$$\mathbf{g} = ^{\sim}\mathbf{f} \tag{3.47}$$

Matrix ˜ can be interpreted as formed by environmental intensity coefficients per unit of economic flow, hence a column of the intensity matrix (λ_i) is associated to the system wide interventions for supplying one unit of the good or service that is referred by that column.

Heijungs and Suh (2002), describe problems associated to the inversibility of matrix **A**, rising from cut-off criteria associated to economic flows, multifunctional unit process, choices between alternative process and closed loop recycle. Although helpful, the use of eco-vectors or PDFs is less broad than the matrix representation. This approach is more useful for the case of tackling with consequential LCAs, however linearity between production process will drop and other functions relating input output relations should be used.

[62] Heijungs & Suh (2002, Ch. 2), propose a convention regarding the sign of each p_{ij} element, flows to a process are considered negative, while flows leaving the process are positive. The basis for this convention, which is the opposite to the general convention for chemical processes, is to consider the environment, as system. To be consequent to chemical engineering point of view; flows leaving the environment system, such as raw material are then negative, while flows entering the environment (i.e. leaving the process system) are positive.

[63] From a geometric point of view the inventory problem can be interpreted as finding the linear combination of the unit process vectors, such that the resulting vector falls on the hyperplane that is defined by the final demand vector, and locating the exact coordinates of this resulting vector, see Heijungs & Suh (2002, p. 26).

Input-Output Analysis (IOA) based LCI As pointed out by Heijungs & Suh (2002, Chs. 5 and 7), the technology matrix **A** holds more information than just process data, it also contains information regarding the structure of inter-industry dependence of processes. In general all processes in an economy are directly or indirectly connected with each other and LCIs based on matrix or PFD are always truncated to a certain degree. Since all transaction activities within a country are, in principle, recorded in the national IO table, it is often argued that the system boundary of an IO-based LCI is more complete than that of process analysis (Suh & Huppes, 2003).

This broad and complete view of the whole inter-industry relations is an important source of LCI data, but it should be used with care given that several limitations rise. The IOA method itself can provide LCIs only for pre-consumer stages of the product LC, while the rest of the product LC stages are outside the system boundary. The amount of imported commodities by the product system under study should be negligible; otherwise errors due to truncation or miss specification of imports may well be more significant than those due to cut-off in process-based. Nonetheless, the biggest practical obstacle in applying IOA for LCI calculation is the lack of applicable a sector environmental emission data in most countries (Suh & Huppes, 2003).

Hybrid approaches IO-based inventory is relatively fast, and upstream system boundary is more complete within the national level, while process-based LCI provides more accurate and detailed process information with more recent data. Hybrid approaches link process-based and IO-based analysis by combining the strengths of both (Suh & Huppes, 2003). So far hybrid analysis has been adopted to LCI compilation in different ways:

- tiered hybrid analysis: uses process-based analysis for the use and disposal phase as well as for important upstream processes, remaining input requirements are imported from an IO-based LCI. They are performed by adding IO-based LCIs to the process-based LCI results (Suh & Huppes, 2003).
- IO-based hybrid analysis: is carried out by disaggregating industry sectors in the IO national data table.
- integrated hybrid analysis: uses former approaches, assuming that information from IO accounts is less reliable than process-specific data due to temporal differences between IO data and current process operation, aggregation and import assumptions. Therefore, the IO table is interconnected with the matrix representation of the physical product system only at upstream and downstream cut-offs where better data is not available.

PFD and matrix approaches to the calculation of LCIs are inherently more time consuming than one based on IOA or hybrid approach (Rebitzer *et al.*, 2004). IOA-LCA is not mathematically different from process LCA both are linear, with constant coefficient models, which can be readily cast in matrix form (Heijungs & Suh, 2002). Instead their differences lie in data sources (unit process data vs. economic national accounts), commodity flow units (physical units vs. economic value), level of process/commodity detail, and covered life-cycle stages (complete life-cycle vs. pre-use/consumption stages) (Rebitzer *et al.*, 2004).

LCI computation methods using PFD and matrix representation are considered to be compatible with ISO standards, and are typically used. With regards to the use of other methods, if clear model assumptions are noted then LCI based on IOA could be used for calculation of upstream process environmental interventions and could be accepted by ISO standards. Regarding uncertainty associated to LCIs rising from different calculation approaches, Suh and Huppes (2003) clearly states that PFD and matrix representation are inherently less uncertain than IOA, provided that process specific (and not sectoral) emission data is gathered for

them, but if questions regarding uncertainty is due to completeness's, IOA provides of better estimates.

3.4.2.2 LCI data sources

A review of currently available LCA software and LCI databases was performed by Curran (2006). In the review is emphasised that many of the LCI databases are freely available given that they have evolved from publicly funded projects. LCI databases provide inventory data for a variety of processes, such as raw material generation, electricity production, transport processes and waste treatment services. Most databases (commercial and public), are based on data from numerous business organisations worldwide, which have created their own inventory databases. Such is the case of the LCIs for industries related to aluminium, cooper, iron and steel, plastics, and paper and board (Finnveden *et al.*, 2009). A few examples of public LCIs are the case of the Swedish SPINE@CPM[64], the German PROBAS database[65], the Japanese JEMAI database[66] and the US NREL database[67]. There are also commercial providers of LCI data such as EcoInvent database[68] and DEAM Database[69]. Most of the public and commercial available databases comply with the ISO standard for LCI database information exchange (ISO, 2001), and there are available tools for the format change between different databases (Finnveden *et al.*, 2009). Another source for LCI data, is the result of IOA, several economies have been studied this way and there are LCI results available for the US, Denmark, Japan and the Netherlands.

LCI data in databases appears in two different forms as *aggregated data*, and as *unit-process sets*. Most of the industry related data sets are in aggregated form, which specify the elementary flows (resource expenditures, emissions, and wastes) aggregated for all processes involved, for example, per mass unit of product manufactured[70]. In the case of the unit-process data sets the inventory is given for each processing step up to the gate. These data sets refer to average data for specific technologies, which provides the ability for creating tailored inventories according to the selected technology. Unit process data also allows for reviewing methodological choices, make changes in the inventory data set and the ability to choose easily different allocation principles (Finnveden *et al.*, 2009)[71].

A straightforward extension of the calculation of LCIs based on PFDs is the use of process simulators. Using a mass balance is clearly superior to a total disregard of it, given that it can be used to test for errors present, while in other cases might provide a way of "disguising" them (Ayres, 1995; Huijbregts *et al.*, 2001). The use of process simulation is based on the application of 1st principle conservation laws (mass and energy), which are enforced in all unit operation models. Its use for the calculation of environmental interventions has been proposed and exemplified by several authors in the case of continuous (Alexander *et al.*, 2000;

[64] http://www.globalspine.com/
[65] http://www.probas.umweltbundesamt.de/php/index.php
[66] http://www.jemai.or.jp/english/index.cfm
[67] http://www.nrel.gov/lci/
[68] http://www.ecoinvent.ch/
[69] http://www.ecobalance.com/ukdeam.php
[70] This kind of data is widely used by industry given that it preserves confidentiality and is commonly used as background data for modelling production of aluminium, steel, electricity, etc, given that the exact source of material or energy is not know exactly. Regarding confidentiality, Ayres (1995) argued that this issue is a severe drawback of current LCI data, given that the user depends largely on the validity of process and emissions data obtained in this way.
[71] In the case of the EcoInvent database, it provides data sets in both ways, aggregated data sets are identified as process data sets, while, unit process data sets as units. Aggregated data sets show only elementary flows as inputs and outputs, while unit data sets are constituted by the material flows linking different unit operations. Furthermore, the EcoInvent database allows for the inclusion or not in the LCI of the infrastructure impact.

Azapagic *et al.*, 2006; Cabezas *et al.*, 1999; Chen & Shonnard, 2004; Herrera *et al.*, 2002; Shonnard & Hiew, 2000) and batch (Benko *et al.*, 2006) plants. The authors showed, that the use of process simulation provides a robust approach that helps overcome the lack of reliable data[72].

Concerning uncertainty in LCI, some aspects have to be pointed out (i) data aggregation, Sinclair-Rosselot and Allen (2002c) discuss this issue with regards to electricity production and refineries emissions in the US context, showing that different results are obtained depending on the geographical aggregation adopted and (ii) data origin, Sugiyama *et al.* (2005) discuss the possible mismatch in temporal distribution or geography between the available data and the LCA scope. In some databases as in the case of the Ecoinvent which provides with probability distributions for inventory data, the former points can be studied by using sensitivity analysis.

3.4.3 Life Cycle Impact Assessment (LCIA)

The LCIA stage tries to summarise in a minor number of results the findings of the LCI, this stage is fully described in ISO (2000a). Values of environmental interventions are changed to impact category indicator results by using characterisation factors (CF). The number of factors taken into account for interpretation can be reduced from thousands or even hundreds to about 10 to 20. From a DM's perspective, impact category indicator results are more manageable forms than the actual environmental interventions. Impact assessment of emission inventories and environmental interventions requires the following decisions to be made (ISO, 2000a):

i. *Selection of categories and classification*, each LCI result should be classified according to which environmental impact category it affects.
ii. *Selection of characterisation methods and characterisation*: The selection is previously done for each IA methodology, and the model result is a set of CFs, which are used to calculate the potential impacts.
iii. *Normalisation*: results from the previous step are related to reference values; expressing the relative magnitude of the impacts scores on a scale common to all impact categories[73]. The aim of normalisation is two-folded (i) to place LCIA indicator results into a broader context and (ii) to adjust the results to have common dimensions.
iv. *Grouping and/or weighting*: aggregate category indicator results according to their relative importance. This point is one of the most controversial issues, due to the fact that it requires the incorporation of social, political and ethical values. Grouping requires to create a broad ranking or hierarchy or impact categories, from which the relative importance of each impact category can be drawn (Pennington *et al.*, 2004). This issue is further discussed under section 2.2.2.

Points (i) and (ii) have been previously developed by several authors which provide with ready to use methodologies, and are mandatory of an LCIA (ISO, 2000a), while points (iii) and (iv) are optional and depend on how results should be interpreted. In general steps (i) and (ii) are addressed by impact assessment methodologies where different LCI results have been already classified and characterised.

Appendix D contains a review of the difference found in the calculation of some of the used metrics in LCIA. The list of metrics reviewed is long but no conclusive, many other impacts can be modelled. Such is the case of odour related impacts or solid waste impacts. Met-

[72] There are ready to use methodologies for the generation of gate-gate LCI information such as Jimenez-Gonzalez *et al.* (2000), which are used in combination with process simulation.

[73] Typical normalisation values are associated to the background impact from society's total activities (Finnveden *et al.*, 2009).

rics for such categories can be found in other references (Baumann & Tillman, 2004; Finnveden *et al.*, 2009; Guinee *et al.*, 2001a)

The following section reviews the current methodologies which use many of the metrics described in the appendix D, however some differences between methods are outlined.

Centre for Environmental Studies (CML) The CML v2 baseline 2000 (Guinee *et al.*, 2001a) is an update from the CML 1992 method (Heijungs *et al.*, 1992) developed by the Centre of Environmental Science (CML)of the University of Leiden in The Netherlands. Both versions use a mid-point approach, and the most recent method considers normalisation factors for four situations: world population (1990) and (1995), Western Europe (1995), and The Netherlands (1997), provided in Huijbregts *et al.* (2003). No weighting procedure is included in the methodology see Table 3.1. The method considers ten impact categories as a baseline (default) and proposes several other (50 in total), for studying other impacts (Ecoinvent, 2008).

Resource Depletion is considered only for abiotic resources as abiotic depletion (AD) (Guinee *et al.*, 2001a), and is calculated as in Eq. 3.48 and 3.49.

$$AD = \sum_{i}^{all\ species} m_i ADP_i \tag{3.48}$$

$$ADP_i = \frac{DR_i}{R_i^2} \frac{R_{ref}^2}{DR_{ref}} \tag{3.49}$$

ADP_i is the Abiotic Depletion Potential of resource i[74] (dimensionless), m_i is the quantity of resource i extracted [kg], R_i is the ultimate reserve of resource i [kg], DR_i extraction rate of resource i [kg·yr^{-1}], R_{ref} ultimate reserve of the reference resource [kg], and DR_{ref} is the extraction rate of reference substance [kg·yr^{-1}]. The indicator result is expressed in [kg of reference resource], in this case antimony (Sb).

In the case of eutrophication all emissions of N and P to air, water and soil and of organic matter to water are aggregated into a single measure, allowing for both terrestrial and aquatic eutrophication to be assessed. The methodology uses the same concept and factors as in Eq. D.3. For acidification it uses Eq. D.2 but includes emissions of NOx, SO_2 and NH_3 to air only; no consideration of emissions to water or soil are considered within this impact category. In the case of climate change impacts, the GWP as in Eq. D.7 is used; a time horizon of 100 years is selected as the baseline and climate change impact is calculated using Eq. 3.50.

$$GCC = \sum_{i}^{all\ species} m_i GWP_i \tag{3.50}$$

Similarly to GCC, SOD is calculated using Eq. D.5 and D.6, the CF selected is the one related to steady state concentrations. POF is calculated by using Eqs. 3.51 and D.4; the characterisation is based on the most recent POCPs (Guinee *et al.*, 2001a).

$$POF = \sum_{i} m_i POCP_i \tag{3.51}$$

To assess toxicity impacts, this methodology adopts a multimedia fate and exposure model called Uniform System for the Evaluation of Substances (USES-LCA). The USES model con-

[74] While most ADP_is are available only for elements (mostly metals) and non renewable resources (e.g. oil, coal), it is also available for some minerals (e.g bauxite).

sists of Mackay Type III multimedia fate model (Huijbregts, 2001; Huijbregts *et al.*, 2000b)[75]. For Human Toxicity (HT) the model calculates a single CF for each emission compartment, by aggregating the four factors calculated at global and continental scales on a population basis, the larger the population the greater the weight of the associated factor.

$$HT = \sum_{i}^{species} \sum_{j}^{sinks} m_{ij} HTP_{ij} \tag{3.52}$$

HTP_{ij} the human toxicity potential of substance i emitted to environmental compartment/sink j, calculated as in Eq. 3.53.

$$HTP_{ij} = \frac{\sum_{r}\sum_{s} PDI_{ijrs} E_{ir} N_s}{\sum_{r}\sum_{s} PDI_{ref,jrs} E_{ref,r} N_s} \tag{3.53}$$

where PDI_{ijrs} is the predicted daily intake via exposure route r at geographical scale s for substance i emitted to environmental compartment j measured in [day^{-1}]; E_{ir} is the effect factor representing the human toxic impact[76] of substance i via exposure route r (inhalation or ingestion) [day]; N_s is the population density at scale s. The reference component selected is 1,4 dichclorobenzene ($C_6H_4Cl_2$)[77]. Similarly to the calculation of HT, this method calculates Fresh water Aquatic EcoToxicity (FWET), Marine Aquatic EcoToxicity (MAET) and Terrestrial EcoToxicity (TET). In Eq. 3.54 PEC_{ij}^{FW} is the predicted concentration of specie i in freshwater (FW) due to its emission into compartment j while E_i^{FW} is the effect factor representing the toxic impact of substance i on FW ecosystems.

$$FWETP_{ij} = \frac{PEC_{ij}^{FW} E_i^{FW}}{PEC_{ref,FW}^{FW} E_{ref}^{FW}} \tag{3.54}$$

Similarly as in Eq. 3.54, CFs (potentials) are defined for MAET, ($MAETP_{ij}$) and TET, ($TETP_{ij}$). The calculation of the impact is done using similar equations to the case of HT (see Eq. 3.52), but using the corresponding CFs. Despite of its broad acceptance and use, this toxicity approach based on the USES model lacks of some shortcomings. Data required for models such as vapour pressure, water-octanol distribution coefficient (K_{ow}), photodegradation, water solubility or bioconcentration factors (BCFs) are not widely known for many of the modelled species.

EcoIndicator 95 and 99 versions The Eco-Indicator-99 (EI99) method (Goedkoop & Spriensma, 2001) is an update of EI95 (Goedkoop, 1995); this version is based entirely on the endpoints and links inventory results into three damage categories (see Table 3.1):

- *Human Health*, impact is measured using Disability Adjusted Life Years (DALY). Damage to human health has its roots in infectious diseases, cardiovascular and respiratory

[75]The distribution model consists of local fate models nested into a multimedia fate model where three spatial scales are used (regional, continental and global) and three climate zones (arctic, moderate and tropic). Regional and continental scales are defined within the moderate climate zone and each of them consists of six compartments: air, fresh water, seawater, natural soil, agricultural soil and industrial soil. Global scale comprises three compartments air, seawater and soil, this scale is assumed to be closed with no transport across its boundaries. The model distinguishes seven protection targets: aquatic ecosystems, terrestrial ecosystems, sediment ecosystems, fish eating predators, worm eating predators, microorganisms and humans (Huijbregts *et al.*, 2000b). The exposure model calculates exposure levels for fish eating predators, worm eating predators and humans.

[76]The acceptable daily intake is used.

[77]Also known as 1,4-DB, para-dichlorobenzene, p-DCB or PDB.

diseases, as well as forced displacement due to climate change. It also considers cancer as a result of ionising radiation and ozone layer thinning, while respiratory diseases and cancer are due to toxic chemicals in air, drinking water and food. A four steps (Fate, Exposure, Effect and Damage, as described in section 2.2.5.2) analysis is performed in order to arrive to the impact to human health. The damage analysis links health effects to the number of Years Lived Disabled (YLD) and Years of Life Lost (YOLL).

- *Ecosystem Quality* uses the species diversity as an indicator, which is measured as a percentage of species that are threatened or that disappear from a given area during a certain time[78]. It is assessed using two different approaches (i) toxic substances emissions concerning ecotoxicity and acidification/nutrification, and (ii) land-use and land transformation.
- *Resources depletion*, is measured in MJ of surplus energy and is modelled in two steps: (i) resource analysis, which links a resource extraction to a decrease of resource concentration and (ii) damage analysis, that links lower concentration to increased efforts to extract that resource in the future.

The normalisation procedure considers the total inventory of mass and energy used in Western Europe by person·year. The weighting procedure was carried out by means of a written panel procedure among the Swiss LCA interest group. Three perspectives can be applied: individualist (higher weight to human health and considering only proven effects), egalitarian (higher weight to ecosystem quality, while considering effects with minimum scientific proof), and hierarchist (equal weight distribution) (Bovea & Gallardo, 2006). The authors recommend using the hierarchist perspective as default, and the remaining two for sensitivity analysis[79].

Environmental Design of Industrial Products (EDIP) method was developed by Wenzel *et al.* (1997). and distinguishes between ecotoxicity, human toxicity and between acute and chronic toxicity. Normalisation is based on person equivalent for 1990, while weighting is based on the distance-to-target approach (see Table 3.1), considering as a targets the Danish political target emissions for 1990 (Baumann & Tillman, 2004; Bovea & Gallardo, 2006).

Environmental Priority System (EPS) method was initially developed in 1993 and later revised by Steen (1999a,b). This method evaluates environmental impact according to the willingness to pay (WTP) to restore changes or to protect the following five AoPs: human health, ecosystem production capacity, abiotic stock resources, biodiversity and cultural and recreational values[80] (see Table 3.1). In the case of effects to biological production, the units used are decreased production of 1 kg of crop seed or wood or fish, while in human health the metrics range from excess death owing to pollution and severe nuisance due to pollution. In the case of biodiversity the method focuses on genetic resource value, consequently the characterisation model is based on the extinction rate of "red listed" species, the indicator used is normalised extinction of species (NEX), which is dimensionless given its normalisation with respect to the species extinct during 1990 (Baumann & Tillman, 2004). The EPS method counts both pollution and resource depletion as environmental impacts, in fact resource depletion

[78] The unit used is: [% vascular plant species·km^2·year].

[79] The individualist view coincides with a short term perspective, the egalitarian perspective uses a long term perspective, being this last perspective the most complete in number of CFs but also the one that introduces most uncertainty.

[80] In general no CFs are given for the case of cultural and recreational values. The methodology states that there are so far no general values that have been identified for the estimation of cultural and recreational values loss. The WTP has to be found for each specific case.

weights heavier, in order to emphasise that future generations should have the same access to resources as the current one. In the case of Human Health indicators, the ones used are life expectancy, expressed in YOLL [person·year], morbidity, suffering and nuisance (Steen, 1999a), in most cases CFs are available for air emissions. The default impact categories of ecosystems are decreased yields of crop, fish & meat and wood, mainly due to air emissions, and freshwater for irrigation and drinking due to its usage. Abiotic stock resource indicators are depletion of elemental or mineral reserves and depletion of fossil reserves, measured in Environmental Load Units (ELU)s. The threat to bio-diversity lies mainly in the alteration of habitats for species that has no possibility to adapt to the moving climate zones; biodiversity loss is measured using NEX. All impact categories results are expressed in monetary terms, consequently there is no need for a normalisation step.

TRACI stands for Tool for the Reduction and Assessment of Chemical and other environmental Impacts (Bare, 2002; Bare *et al.*, 2003). It characterises impact for the following categories ozone depletion, global climate change, acidification, eutrophication, tropospheric ozone (smog) formation[81], ecotoxicity, human health effects (cancer and non-cancer), fossil fuel depletion, and land-use effects, see Table 3.1. Impact categories are characterised at the mid-point level for reasons including a higher level of societal consensus concerning the certainties of modelling at this point in the EM (Bare *et al.*, 2003). Suspended Particulate Matter (SPM), is explicitly used as category indicator. No normalisation or valuation processes is included. Explicit consideration of the United States conditions are used to calculate the impacts regarding: human cancer and non-cancer categories, acidification, eutrophication, ecotoxicity, land use and smog formation.

Impact 2002+ is proposed by Humbert *et al.* (2005) (IM02), which presents an implementation working both at mid-point and end-point levels; with 14 mid-point categories[82], and 4 end-point categories [83], see Table 3.1. It is a combination between IMPACT 2002 (Pennington *et al.*, 2005), Eco-indicator 99 (Goedkoop & Spriensma, 2001) using egalitarian factors, CML (Guinee *et al.*, 2001a) and IPCC considerations. For each elementary flow two CFs are proposed one at mid-point (Eq. 2.17) and one at end-point (normalised damage factor, Eq. 2.19), the latter allows evaluating a normalised damage score.

ReCiPe 2008 , proposed by Goedkoop *et al.* (2009) (ReC08) is a LCIA method that is harmonised in terms of modelling principles and choices, which offers results at both the mid-point and end-point level. Eighteen impact categories are addressed at the mid-point level[84] for use in Eq. 2.17, see Table 3.1, while at the end-point level, these mid-point impact categories are further converted and aggregated into three end-point categories: damage to human health (HH), damage to ecosystem diversity (ED) and damage to resource availability (RA) for use in Eq. 2.19. In particular, the focus was on the first part of a LCIA when impact categories and category indicators are chosen and characterisation models are selected or

[81] Smog-formation effects are kept independent and not aggregated with human health impacts.

[82] Human toxicity (HHC, HHNC), respiratory effects (inorganics HHRI, organics HHRO), ionising radiation (HHIR), ozone layer depletion (ODP), photochemical oxidation, aquatic ecotoxicity (AqE), terrestrial ecotoxicity (TeE), terrestrial acidification/nutrification (TeAN), aquatic acidification (AqA), aquatic eutrophication (AqEu), land occupation, global warming (GWP), non-renewable energy (ADener) and mineral extraction (ADmin)

[83] Human health, ecosystem quality, climate change and resources

[84] Climate change (CC), ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), human toxicity (HT), photochemical oxidant formation (POF), particulate matter formation (PMF), terrestrial ecotoxicity (TET), freshwater ecotoxicity (FET), marine ecotoxicity (MET), ionising radiation (IR), agricultural land occupation (ALO), urban land occupation (ULO), natural land transformation (NLT), water depletion (WD), mineral resource depletion (MRD) and fossil fuel depletion (FD)

developed to convert LCI results into category indicator results. Two main approaches were used the CML mid-point approach and the end-point based on EI99. Similarly to the case of IM02, two sets of CFs are available for each environmental intervention.

Discussion CMLv2 and EI99 both evolved in The Netherlands, while CML v2 tried to operationalise models and CFs in the second emphasis is put on weighting given for the purposes of "eco-design" (Guinee *et al.*, 2001a). Compared to CML, the EI99 method has several serious shortcomings, it includes fewer inventory items and provides limited coverage for human toxic impacts (only carcinogenicity) and the acidification and eutrophication models are based on the Dutch situation. The main advantage of the EI99 method is that indicators are defined at end level giving them environmental relevance. Comparing CMLv2 regarding the global warming characterisation model, EDIP97's is extended through the inclusion of indirect contributions from methane, NMVOCs and CO (Dreyer *et al.*, 2003; Wenzel *et al.*, 1997). In the case of ODP, the CFs for CMLv2 are more recent than the ones for EDIP97. The nutrient enrichment impact is expressed in equivalents of different reference substances (nitrate in EDIP97 while phosphate in CMLv2) even though the same EM is used by the two methods. A major difference between the two methods is that the contribution of COD is included in the CMLv2 method despite the fact that COD does not contribute to nutrient enrichment or eutrophication at the indicator point which defines the category. In the case of AP, the EDIP97 methodology includes more substances than CMLv2. In the case of Impact2002+, it includes new concepts and methods for the case of human toxicity and ecotoxicity impact assessment while for the remaining categories, methods have been transferred or adapted from the EI99 and the CMLv2.

Regarding the metrics used in each category, Table 3.2, summarises each method selection. For the case of AP, GWP, ODP and EP, the reviewed methodologies widely agree in the mid point indicators to be used: kg SO_2eq., kg CO_2eq., kg CFC-11eq. and kg PO_4^{3-}eq. respectively. For the case of Abiotic Depletion the trend is to subdivide this category in metals and fossil fuels as shown by the two latest category indicators ReC08 and IM02, and two indicators are found: MJ of surplus energy (EI99 and IM02), and measurement of kg of compound eq. (CMLv2 and ReC08). Both cases try to address the amount of extra effort that is required to extract virgin resources, but certain LCI considerations have to be considered as discussed in previous section. In the case of Ecotoxicity, most methodologies include different ecosystems, terrestrial and aquatic (marine and fresh water), the reference compound is 1,4DB or TEG. In the case of Human health impacts mid point categories are referred to 1,4-DB or C_2H_3Cl, which are transformed into DALYs in the end point assessment if the methodology proposes them.

Table 3.1: Summary of characteristics of different impact assessment methodologies (Ecoinvent, 2006, 2008; Frischknecht & Jungbluth, 2005; Pennington *et al.*, 2004)

Method	Mid points	Normalisation		Damage Assessment	End Points			Weighting	Single score units	Origin
	#		# of geo. scenarios		Add end-points allowed?	# of end-points	Areas of protection			
CML 1992	9	Yes	4	No	No	None		No		Netherlands
CML v2 (baseline 2000)	10	Yes	4	No	No	None		No		Netherlands
TRACI	14	No	None	No	No	None		No		USA
Eco-indicator 95	11	Yes	2	No	Yes	None		Yes	Pt	Netherlands
Eco-indicator 99	12	Yes	2	Yes	Yes (Expert panel)	3	Human Health/Ecosystem Quality/Resources	Yes	Pt	Netherlands
EDIP 97	16	Yes	1	No	Yes (Distance to target)	1		Yes	Pt	Denmark
EPS 2000	13	No	None	Yes	Yes (Monetisation)	5	Human Health/Ecosystem Production Capacity/Abiotic Stock Resource/Biodiversity/Cultural-Recreational values	Yes	Pt	Sweden
LIME	10	Yes	1	Yes	Yes (Monetisation)	4	Human life/Social welfare/Net primary production/Biodiversity	Yes	Yen	Japan
IMPACT 2002+	15	Yes	1	Yes	Yes (Expert panel)	4	Human Health/Ecosystem Quality/Climate Change/Resources	Yes	Pt	Switzerland
ReCiPe 2008	18	Yes	2	Yes	Yes (Expert panel)	3	Human Health/Ecosystem Diversity/Resource availability	Yes	Pt	Netherlands

Table 3.2: LCIA categories indicators for different methodologies (Ecoinvent, 2006, 2008).

Method	**CML 2 2000**		**Ecoindic. 99**		**EDIP 97**		**EPS 2000**		**Impact 2002**		**ReCipE 2008**		**TRACI**	
Category	Unit	Sinks	Unit	Sinks	Unit	Sinks	Unit	Sinks	Unit	Sinks	Unit	Sinks	Unit	Sinks
Abiotic Depletion Overall	kg Sb eq.	Raw			kg.	Raw	ELU	Raw						
AD Fossil Fuels consumption			MJ surplus	Raw					MJ primary	Raw	kg oil eq	Raw		
AD (Mineral consumption)			MJ surplus	Raw					MJ surplus	Raw	kg Fe eq.	Raw		
Water depletion											m^3			
Acidification Potential	kg SO_2 eq.	Air	PDF * m^2yr^a.	Air	g SO_2 eq.	Air	H^+ eq.	Air	kg SO_2 eq.	Air, Water, Soil			H^+ eq.	Air
Terrestrial AP									kg SO_2 eq.	Air	kg SO_2 eq.	Air		
Ecotoxicity			PAF * m^2yr^a	Air, Water, Soil			NEX	Air, Water, Soil, Raw					2,4-D eq.	Air, Water
Ecotoxicity Aquatic (EAq)	kg 1,4-DB eq.	Air, Water, Soil			$m3^b$	Air, Water, Soil			kg TEG eq.	Air, Water, Soil				
EAq Fresh Water	kg 1,4-DB eq.	Air, Water, Soil									kg 1,4-DB eq.	Air, Water, Soil		

Continued on next page

Table 3.2 – continued from previous page

Method	**CML 2 2000**		**Ecoindic. 99**		**EDIP 97**		**EPS 2000**		**Impact 2002**		**ReCipE 2008**		**TRACI**	
Category	Unit	Sinks	Unit	Sinks	Unit	Sinks	Unit	Sinks	Unit	Sinks	Unit	Sinks	Unit	Sinks
EAq Marine	kg 1,4-DB eq.	Air, Water, Soil									kg 1,4-DB eq.	Air, Water, Soil		
Ecotoxicity Terrestrial	kg 1,4-DB eq.	Air, Water, Soil			m^3	Air, Water, Soil			kg TEG eq.	Air, Water, Soil	kg 1,4-DB eq.	Air, Water, Soil		
Eutrophication Nutrification potential	kg PO_4^{3-} eq.	Air, Water, Soil	PDF * m^2yr[a]	Air	g NO3	Air, Water, Soil			kg PO_4^{3-} eq.	Air, Water, Soil	kg P eq-kg N eq	Air, Water, Soil	N eq.	Air, Water
Global warming, greenhouse, climate change	kg CO_2 eq.	Air	DALY	Air	g CO_2 eq.	Air			kg CO_2 eq.	Air	kg CO_2 eq.	Air, Water	CO_2 eq.	Air
Human Non toxicity[c]							PersonYr	Air, Soil						
Human Toxicity	kg 1,4-DB eq.	Air, Water, Soil	DALY	Air, Water, Soil	m^3	Air, Water, Soil					kg 1,4-DB. eq.	Air, Water, Soil	benzene eq.	Air, Water
Human Toxicity Carcinogenic			DALY	Air, Water, Soil					kg C_2H_3Cl eq.	Air, Water, Soil				
Human Toxicity - ionising radiation			DALY / kBq	Air, Water					Bq C14	Air, Water	kg U235 eq	Air, Water		
Human Toxicity Non Carcinogenic									kg C_2H_3Cl eq.	Air, Water, Soil				
Human Toxicity Soil					m^3	Air, Water, Soil								
Human Toxicity Soil Carcinogenic													g benzene eq.[d]	Soil
Human Toxicity Soil Non Carcinogenic													g toluene eq.[d]	Soil
Human Toxicity Water					m^3	Air, Water, Soil							g toluene eq.	Air, Water
Land Use			PDF * m^2yr [a]	Raw					m^2 organable	Raw	m^2a			
Ozone Layer depletion	kg CFC-11 eq.	Air	DALY	Air	g CFC-11 eq.	Air			kg CFC-11 eq.	Air	kg CFC-11 eq.	Air	kg CFC-11 eq.	Air
Photochemical Oxidation Potential	kg C_2H_4 eq.	Air			g C_2H_4 eq.	Air					kg NMVOC eq.	Air	NO_x eq.	Air
Production Capacity[e]							kg	Air						
SPM (HH Criteria Air-Mobile)													PM2.5 eq.	Air
SPM (winter smog) (direct addition)									kg PM2.5 eq.	Air	kg PM10 eq.	Air	PM2.5 eq.	Air
Solid waste generation[f]							kg	Soil						

[a] Potentially Disappeared Fraction of plant species.
[b] Acute and chronic effects.
[c] Non toxicity effects considered as: life expectancy, severe and non sever Morbidity and severe and non severe morbidity.
[d] Soil considers ground-surface and root-zone.
[e] Considers detriment to crop growth, drinking and irrigation water, wood growth and fish and meat.
[f] Considers the direct addition of kg of waste in different categories: pesticides, radioactive, solid (hazardous and non-hazardous) and slags/ashes.

3.4.4 Interpretation and improvement Assessment

According to ISO (1997) LC interpretation is the phase of an LCA in which findings of either the LCI or the LCIA, are combined consistent with the defined goal and scope in order to reach conclusions and recommendations, ISO (2000b) describes its methodology. LC interpretation occurs at every stage in an LCA, if two product alternatives are compared and one alternative shows higher consumption of every material and every resource, an interpretation purely based on the LCI can be conclusive (Rebitzer *et al.*, 2004). Within the ISO the following steps are identified and discussed: (i) identify significant issues, (ii) evaluate the completeness, sensitivity and consistency of data and (iii) draw conclusions and recommendations (Skone, 2000). In order to implement steps (i) or (ii), several analysis can be performed on the data obtained, some of them are classified by Baumann & Tillman (2004, Ch. 6) and Heijungs and Kleijn (2001) as follows:

- *Contribution analysis*: the idea is to decompose the aggregated results of inventory, characterisation, normalisation or weighting into a number of constituent elements. This approach, points out those elements that make the highest/least contribution to a certain emission or impact category[85].
- *Perturbation analysis*: the main interest in performing this analysis lies in pointing out the system's response to small changes of the economic flows between echelons, for this case the linearity assumption holds. It is a local sensitivity analysis of model input parameters[86].
- *Analysis of robustness of the results*: this is performed not only on the data used for calculations, but also in the alternative scenarios or products used as comparison. It can also consider the methodological alternatives in the case of allocation.
  - *Completeness check*: it checks for data gaps in LCI, completeness of impact assessment and to which extent it covers inventory results.
  - *Uncertainty/Sensitivity analysis*: Heijungs and Kleijn (2001), define them as the systematic study of the propagation of input uncertainties into output uncertainties. The most common result visualisation is a table with means and standard deviations calculated for all model outputs. In general uncertainty analysis refers only to model outputs. These analysis are further discussed in sections 3.2 and 2.4.3.
- *Comparative analysis*: this is nothing more than a systematic place to list the LCA results for different product alternatives simultaneously. Some other possibilities are:
  - *Break even analysis*: it is used to compare different alternatives, where a model parameter is varied aiming at generating the same environmental impact for both alternatives.
  - *DM analysis*: it classifies different parts of the model by the degree of influence that the company that undertakes the LCA has over other echelons[87].

[85] However false negatives due to the underestimated or missing flows cannot be identified with this analysis. The results are expressed in percentages that add up to 100%, which can be better visualised using stacked bars due to the appearance of negative contributions for some cases.

[86] In this sense if and increase of 1% of an input parameters leads to a 2% increase of the output, then the multiplier that connects those items is said to be 2. Multipliers can be calculated easily from the matrix formulation of the LCI/LCIA see Heijungs & Suh (2002, Ch. 6) and section 3.2.1. While the application of this analysis to LCI is possible, it is more convenient to approach such analysis as a contribution, while leaving the perturbation to the characterisation, normalisation, weighting or allocation levels.

[87] A basic analysis of this type will divide environmental interventions arising from foreground or background systems.

- *Discernibility analysis*: entails a comparative study taking into account the results from the uncertainty analysis[88].

Heijungs and Kleijn (2001) classify the analysis available during the interpretation phase as in table 3.3, considering uncertainty in LCI and LCIA. Many software vendors provide means for calculation of LCAs, by assisting with connection to LCI databases and the possibility of doing the former analysis easily. A registry of LCA related tools is available from the EC[89]. The following are a few examples of software capable of performing most calculations steps required in an LCA: SimaPro, GaBi, umberto, TEAM, **??**KCL-ECO and IdeMat. The implementation steps of LCI and LCIA is eased and simplified by the use of the former software. The user could focus on other problem aspects such as allocation or interpretation of results. Most LCA software also provides with means for graphical representation of results, by using charts or network flows (Sankey diagrams). In the case of Simapro, it allows for the use of mathematical formula in the definition of LCI flows which allows for fast alternative comparison. It also allows for the calculation of uncertainty analysis using a Monte Carlo approach.

3.5 Remarks

Process simulation Process simulation use considering multiple objectives is straight forward, given that most simulation software allows for calculating different metrics based on the simulation results. Consequently its application in a multiobjective setting is simple provided the simulation tool can be connected to a multiobjective algorithm. As discussed in section 3.1.2.1, the implementation of a SP algorithm is quite manageable if the connection between the simulation tool and a random number generator is done. This approach is the one used in the PA case study in section 5.1, for the generation of the emission profile. One possibility for the generation of Pareto Fronts is the use of SAs, which is explored in the RD case study in section 5.3.

The generation of reliable Pareto fronts is discussed in section 4.1.2.3, where an algorithm is proposed, and used in chapter 6, regarding the framework application to batch industries.

Regarding uncertainty operationalization, the use of the algorithms proposed (3.1 and 3.2) is done in sections 5.1.2.4 and 7.4.3, in both cases the objective pursued is the generation of global trends regarding model results and consequently check the overall model response to the uncertainty in input variables.

Limitations of LCA As it is shown in previous sections the conceptual framework for LCA is well developed, but many difficulties and limitations presently restrict the practical application of LCA. Practical application of LCA to design is ultimately controlled by methodological factors relating to goal definition and scoping, data collection, data analysis and communication of results. But above all, the main limitation in the application of LCA is the lack of reliable input data. In fact, most of the LCA studies that are found in the literature rely on estimated data (Ayres, 1995). In this context, the quality and validity of the conclusions and

Table 3.3: Possible analysis available towards LC interpretation (Heijungs & Kleijn, 2001).

Uncertainty estimates	One product	Two or more alternatives
No	contribution or perturbation	comparative
Yes	uncertainty	discernibility

[88] It seeks to test if product A is statistically discernible from product B, see section 2.4.4.
[89] http://lct.jrc.ec.europa.eu/

suggestions provided at the end of the analysis depend on the accuracy of the input parameters. Finnveden (2000), emphasises that in most LCAs not all relevant environmental impacts are considered, there are many uncertainties (present in data, methodology and system description), and the weighting element involves subjective values which can not be objectively determined. Then as a consequence of those issues the LCA results can not be used to show the overall environmental preference for any of the alternatives compared.

With regards to lack of site specificity, Sonnemann *et al.* (2000) have proposed a methodology which merges ERA and LCA, by providing site specific impacts of some part of the system boundary by means of an ERA while the other echelons are still modelled using LCA data. The selection of which echelons are more deeply modelled is done using a dominance analysis.

Other limitation is related to the analysis of closed loop systems, these systems reflect the behaviour of natural occurring ecosystems in three aspects (i) waste from one part of the system is raw material for another, (ii) use of solar energy and (iii) diversity of actors. The calculation methodology proposed by Heijungs & Suh (2002, Ch. 3) using Eqs. 3.43 to 3.46 is shown to cope easily with recycle and multi-functionality problems and consequently is the preferred methodology, when recycles and product multi-functionality appears. The evaluation of these systems using LCA is extremely extensive and the results strongly depend on the allocation rules defined (Kralish, 2009). However, in the case of simple non multifunctional or systems with recycles present, the use of PDF and ecovectors is simpler and straightforward.

With regards to uncertainty in data, it has been argued that the credibility of an LCA can be questioned if the results are not accompanied by adequate uncertainty analyses. Presenting results merely as point estimates without uncertainty distributions is an unreasonable overestimation of their exactness, on the other hand there is also risk that incomplete methods for uncertainty analysis may give a false sense of credibility (Bjorklund, 2002).

It has been already pointed out by some authors (Bovea & Gallardo, 2006; Dreyer *et al.*, 2003) that different impact assessment methods can easily produce different results. Results depend among other things on (i) the coverage of actual environmental interventions and their respective impact categories and (ii) on the chosen impact category indicators and the models chosen for CFs. Moreover each one of the former methods has a different coverage of the LCI results due to the absence of CFs for all the possible environmental interventions. When choosing a LCIA, the number of available CFs should match the number of environmental interventions calculated.

Despite the former mentioned drawbacks, LCA is the most widely used method to assess products and processes environmental impacts. LCA exhibits two main advantages, in first place, it covers the entire LC of the product, process or activity, encompassing extraction and processing of raw materials; manufacturing, transportation and distribution; re-use, maintenance recycling and final disposal (Burgess & Brennan, 2001)[90]. The second advantage is the explicit incorporation of an environmental damage model that allows the environmental interventions translation into a set of potential environmental impacts[91], instead of using emissions as indicators.

[90]The application of this systems-based approach avoids alternatives that decrease the impact locally at the expense of increasing the negative effects in other stages of the life cycle of the process, which may eventually lead to higher overall impacts (Azapagic, 1999).

[91]These impacts calculated through any impact assessment framework are potential, and not actual impacts, given that there is no spatial or time differentiation of the emissions. In essence, LCA is a holistic approach that brings the environmental impacts into one consistent framework, wherever and whenever these impacts have occurred or will occur (Guinee *et al.*, 2001b).

Part II

Framework

Chapter 4

Model based sustainability framework for decision making aid

The former chapters have provided with an introduction to problems associated to chemical process design. Several drawbacks and limitations of current methodologies have been identified, but most importantly, it has been found that a consistent framework is lacking for the incorporation of sustainability considerations into the chemical process design.

Reviewed frameworks point the design phase during the synthesis of processing alternatives as the most promising for the inclusion of SD considerations. There is no agreement in how many steps this framework should have nor in the metrics to be used in each stage, but the following trends are found: (i) the use of very simple models (and metrics) in earlier stages, followed by more complex models, e.g. the application of process simulation for checking the viability of simple model solutions; (ii) an iterative procedure where first estimations are done using simple models which are further improved with more complex models at later stages and (iii) the generation of Pareto efficient solutions which are subject of analysis using a Multiple Criteria Decision Analysis (MCDA) method.

The framework proposed in this thesis is based on LCt and uses the LCA methodology by coupling it to models of different type. It is aimed at supporting the design decision making procedure taking into account the uncertainty associated to parameters and values. In this sense special consideration is given to process simulation, general modelling programs and other multivariate statistical methods. All of which are the principal tools used.

4.1 Sustainability framework development

The emphasis of the methodology is put in the design of continuous process plants, due to the potential benefits of tackling with SD issues at this stage as discussed in chapter 1, but the framework is able to cope with decisions regarding the operational level in the selection of best scheduling policies and also for the design, retrofit and planning of the complete chemical supply chain (SC).

4.1.1 Objectives

The framework is conceived to help in the design procedure of new processing options or in aiding to the selection of appropriate process retrofit alternatives. It consists of four methodological steps, that resemble the LCA stages and it incorporates many of the LCA features and nomenclature. Besides its LCA resemblance, it is based on the use of models of different complexity, which is driven by goal definition and the model's ability to cope with uncertainty.

4.1.2 Framework development

4.1.2.1 Model requirements for sustainability frameworks

Within the chemical engineering community, the use of models to represent systems; namely process plants, equipment or products; behaviour is a common feature, and is part of what is commonly known as a "systems approach". Models may have different complexity, which is driven by the needs of representing different real world behaviour. Models in this sense are required to (i) accurate represent the reality being modelled, (ii) be computationally inexpensive, in terms of time and code ease, and (iii) be easy to implement and understand. Metrics can result from the direct calculation of a model, or they might require of extra calculation by the use of other modelling layer. This calculation procedure involves two sequential steps, i.e., generation of input data required by the model's metric and the actual metric calculation.

Due to the inherent multiobjectivity of sustainability problems, the modelling approach to be used has to be able to reproduce sustainability related metrics. If one dimensional metrics are used then, at least, three models are required:

- economic model: able to predict economic related metrics
- social model: able to predict social metrics
- environmental model: able to predict environmental metrics

The former three models are fed from results of the model which represents the problem being considered. This model could be a process simulation or a general mathematical program. Chemical process are generally modelled by two different types of models (i) unit operation, and (ii) thermodynamical properties, connected in an appropriate fashion, which involves the use of material and energy balances. Unit operation models interconnected by means of material and energy balances shape different flowsheets topologies that represent the overall plant behaviour. The former balances require of thermodynamic methods for the calculation of stream's composition and energy content.

Sections 2.2.5 and 3.4.3, regarding environmental models and indicators showed that they require of mass and energy flows to calculate environmental impacts. Economic indicators reviewed (see section 2.2.3), use flows information but converted to monetary units (using prices) to estimate cash flows, and they also require fixed investment estimations, for which the engineering literature has several methodologies. Social indicators generally require data regarding human resources used in a factory, income distribution and land use as reviewed in section 2.2.4[1].

Consequently the objective of the process model is to estimate:

- Mass flows that enter or leave the system boundary, representing raw material extraction, production of products and most importantly emission estimations.
- Energy flows in any form that enters or leaves the systems boundary, ranging from heat to electrical power have to be quantified.

[1] Information regarding contribution to macroeconomic indicators is also required.

- Economic data, raw material and product prices, investments, fixed costs, and operating cost entailing also emission and waste treatment costs.
- Social data, employees wages and distribution, macroeconomic data[2].

Process simulation can provide mass and energy flows, and also helps in designing equipment that can be further quantified in terms of cost. It also allows for easy process modelling providing with unit operation and thermodynamic models easily combinable. A review of process simulation software available was done in section 3.1, and the available algorithms used by those tools were revised in section 3.1.1. In this sense, the selection of process simulation to build models seems natural given the information requirements. But some specific points should be addressed as follows.

Most process models are generally non linear, thus the framework considers the inherent non linearity[3] of process industries by adopting process simulation as a tool. This issue goes above standards regarding LCA model practises that consider linearity and fixed steady state conditions. Using process models allows also for generating confidence intervals on model outputs (e.g. emission or energy consumption), coping with different scenarios and improving the allocation insights (e.g. assigning process environmental interventions or costs to the actual generators). Moreover, the use of process simulation is in line with the possibilities of coping with consequential LCAs where non linearity is required to assess the impacts of changes in production flows.

Emissions estimations from process models, as discussed previously (see section 2.2.5.2), are not directly matched to the actual emission flow into an environmental compartment. In some cases, such as air emissions no extra environmental model is required, but in the case of soil and water emissions an extra model to decide the distribution of chemicals between environmental compartments is required. The need of extra environmental model requirements is directly linked to the assumptions made in the LCIA method to be used.

Mainly in the case of product and raw material movement, it is important to model its transport. Transport considerations have to be made in order to assess its cost and environmental impact. While in some situations the network of flows is fixed, in other cases the model should explicitly account for different network configurations and its associated cost and impact. Commonly transport is measured in terms of tn·km, consequently different transportation networks will provide with different amounts of tn·km.

Different metrics calculated from the problem's model are the ones used for decision making. However, decision making using different metrics, requires of a set of rules or a given modelling approach. This set of rules will be referred as the sustainability-decision model, which is understood in its broadest sense, and it ranges from aggregating metrics, ranking different decisions appropriately, or providing with the appropriate set of Pareto solutions.

4.1.2.2 Uncertainty considerations

All models and metrics have an inherently sense of doubt, understood in its broadest sense, as the uncertainty associated to the accurate representation of the reality by the model. The adopted classification of uncertainty sources considers: (i) model adequacy, (ii) model parameters and (iii) subjectivity and bias (also called variability, see section 2.4.1). The first two items are directly linked to the model itself, while point (iii) is more related to the way in which model results are transformed into metrics. In this sense, all model results have a degree of uncertainty that has to be assessed, and is related to points (i) and (ii). While other important

[2] If the problem being modelled will not affect the overall enterprise structure then proxy metrics related to safety can be used see section 2.2.4.

[3] A common example of non linearity is found in emissions estimation.

issue with regards to uncertainty is related to preference modelling, former point (iii), which is also related to MCDA.

Two different questions are commonly risen: how does the processes alternatives rank change when changes in the alternatives results are introduced?, and how does the alternative rank changes with different preferences?. To this end, sensitivity analysis and uncertainty analysis have been proposed as tools for fulfilling this need.

With the aim of answering to questions related to points (i) and (ii), model input variables uncertainty treatment is performed using sampling methods described in section 3.2.2.

Commercial chemical simulation results do not have any uncertainty information associated to them. Sampling methods can be coupled to process simulation for data generation which can be further used in sensitivity analysis. In sampling methods random numbers are required, for these cases, pseudo random number are generated using Matlab[4], which provides with any desired pdf distribution. An implementation of a Monte Carlo Sampling method using commercial simulations is shown in Alg. C.1.

In the case of environmental information uncertainty, SimaPro allows for the calculation of environmental metrics (LCIA), considering the LCI input variables uncertainty (de Schryver *et al.*, 2006). The LCI information holds pdf parameters for generating the appropriate scenarios which are fed to the selected LCIA method. One important drawback of the used approach is that mass balances in the LCI will not match due to the use of independent pdfs.

Finally, uncertainty due to preferences (former point (iii)) is tackled in terms of pre-made weighting sets, compared to equally important indicators. The approach adopted in this thesis intends to check the alternatives rank under different methodologies and the decision outcome. In the case of environmental metrics the broad amount of different metrics allows for checking the point of view of different groups, by feeding the same model results to each metric and check the resulting rank. This is specially suited to the case of environmental metrics which can be easily calculated over the same LCI results.

4.1.2.3 Multicriteria considerations

In any decision making process, different alternatives will be generated. This generation of alternatives can be done using engineering heuristics, discussed in section 2.3.2, or mathematical programming as discussed in section 2.3.1. In both cases optimisation can be used to decide among these alternatives, (a brief review of current optimisation approaches used in chemical engineering is done in section 3.1.2). In this thesis both approaches are exemplified within the framework proposed, alternatives are generated using heuristics to produce case study flowsheets which are further studied[5], and multiobjective optimisation is used for other cases, such as operating decisions and supply chain design.

Considerations regarding multiple criteria are necessary due to the multiple metrics that are used to study the different sustainability aspects of each alternative. A review of possible methods for MCDA was done in section 3.1.3. All MCDA methods require of a given set of alternatives already measured using different metrics to work upon and some methodology to select/rank alternatives.

One serious drawback of current multiobjective techniques is the generation of reliable Pareto frontiers. In this sense, this thesis implements an improved version of Messac *et al.*

[4]It uses the using the Mersenne Twister algorithm which provides with uniformly distributed numbers, and provides with a method (`random`) for generating different distributions based on a label for describing the distribution required and the distribution parameters.

[5]The use of heuristics to generate different alternatives is based on the decision maker desire to explore such structures.

(2003)'s normalised constraint method, in which the ϵ_i values are set iteratively over hyperplanes of the constrained objectives, and the Pareto filter used is the one developed by Cao (2009). A key point in the proposed method is the number of solutions that should be generated to obtain Pareto solutions. Exploring a high number of points may lead to an expensive computational effort, whereas an inadequate number of solutions would result in a fictitious Pareto frontier that contains dominated solutions due to unexplored Pareto optimal solutions. Clearly a trade off has to be achieved. In some cases, the solution space is discrete and increasing the precision in the number of divisions asked for a constrained based strategy does not guarantee the generation of more Pareto solutions.

In the proposed approach, the number of divisions of the utopia hyperplane is incremented on each iteration and the points explored are added as new solutions. Hence, an iterative approach is applied in order to generate a reliable estimation of the Pareto frontier and two ending criteria are proposed. Specifically, a minimum of N_0 points is initially generated[6] and in the next iteration j at least N_j new different points are further studied. The first ending criteria consists in checking the Pareto frontier at the end of each iteration, if no changes (in terms of number of Pareto solutions and their location) are found in two consecutive iterations the last Pareto frontier is accepted as solution to the multiobjective problem. The latter ending criteria imposes the end of the iteration procedure, when the number of new Pareto solutions divided by the total number of explored solutions is lower than a specific percentage, for example 10%. The algorithm is shown next in Alg. 4.1.

Algorithm 4.1: Pareto frontier generation.

Data: Number of utopia line divisions (nd_0), tolerance (tol).
Result: A reliable Pareto frontier estimate PF^*
begin
  explore S_0 solutions using nd_0 and count $np_0^{explored}$;
  generate first Pareto frontier estimate PF_0 from S_0;
  count Pareto points np_0^{PF};
  $j \longleftarrow 1$;
  $np_j^{PF}, np_j^{explored} \longleftarrow np_0^{explored} + 1$;
  while $np_j^{PF} \neq np_{j-1}^{PF}$ *or* $\frac{np_j^{PF} - np_{j-1}^{PF}}{np_j^{explored}} \geq tol$ **do**
    select j-th number of utopia line divisions nd_j;
    explore j-th solutions S_j using nd_j;
    $S_j \longleftarrow [S_j, S_{j-1}]$;
    perform a Pareto filter of explored solutions PF_j from S_j;
    count Pareto points np_j^{PF};
    count total explored solutions $np_j^{explored}$ in S_j;
    $j \longleftarrow j + 1$;
  $PF^* \longleftarrow PF_j$

This thesis does not aim at proposing any new weighting strategy to cope with different criteria. If a single criteria is desired then the approach preferred in this thesis consist of one or more of the following considerations (i) analyse utopian and nadir extreme solutions and rank options according to its distance, or (ii) use already developed sets (e.g. monetisation or end-point approaches in the case of environmental metrics, see section 2.2.2), of weights to

[6] These N_0 points are associated to a given selection of nd_0 utopian hyperplane divisions.

aggregate indicators.

4.2 Sustainability framework architecture

Different tools have been used to build the different models that support the framework proposed.

- Commercial process simulation (AspenPlus, AspenHysys).
- General modelling environments (GAMS, Matlab).
- LCA software (SimaPro).
- LCI database (Ecoinvent).

The first three items support the Windows environment the Component object model (COM) interface for its possible interconnectivity.

4.2.1 Commercial software components

In this thesis different commercial tools have been selected to be used and consequently required to be integrated. General modelling tools such as Matlab and GAMS have been used, provided their ability to create custom models for different needs.

Matlab is used in this thesis as the client application which is served by all the other applications. It is also used for results analysis and due to its integrated developing environment and provides with the required environment for developing and testing software prototypes. Moreover its extensive library of already developed mathematical functions related to regression and multivariate analysis eases its customisation requirements. In a similar way MS Excel is also used.

GAMS is used to code different models, involving representation of binary or integer decisions, which are found in the case of scheduling or supply chain design. More importantly GAMS ability to use different state of the art optimisation solvers is also exploited by tackling with different type of problems (MI, MIL, MINL).

Commercial process simulation tools such as AspenPlus and AspenHysys, have been used to model overall flowsheets using already coded models different from their respective model libraries. Besides using commercial model libraries, in this thesis, different models have been coded to represent some unit operation behaviour that was no addressed by the software. In those cases, those models were coded in MS Visual Basic, and connected to the simulation environment by means of simulator proprietary interfaces.

Both GAMS and AspenPlus-AspenHysys are used as server applications that are connected to Matlab which requires from them different actions, but mainly: accept input data, run model, retrieve results.

4.2.2 Interfaces development

Matlab connectivity Matlab provides with a COM interface which can be used to communicate between MS Windows applications. AspenHysys and AspenPlus provide with a set of proprietary methods that implement internal methods but that can be accessed using the COM interface. In this sense, there is currently a Matlab-Hysys toolbox developed by Berglihn (1999), which allows for using AspenHysys as a server from Matlab through the COM interface.

In the same line as the Matlab-Hysys toolbox, a set of methods has been developed in this thesis for the use of AspenPlus as a server from Matlab. The methods developed are briefly outlined in Appendix C.

In the case of GAMS, it does not provide with a COM interface, but there is already a toolbox developed by Ferris (2005) which uses GAMS input and output files for the exchange of information between Matlab and GAMS.

The methods developed allow for different stochastic analysis to be performed with ease. The most simple is running and Monte Carlo Sampling, as shown in Algorithm C.1. However if the model being run in AspenPlus uses the SQP algorithm for the optimisation of some simulation variable, then any MCS using this simulation will be actually performing stochastic programming as shown in Figure 3.1(b).

Matlab already provides with optimisation codes, which can be used together with the former interface to run any AspenPlus simulation, under both possible stochastic approaches detailed in section 3.1.2.1. In this sense any optimisation algorithm that can be used on black box models is suitable to be used with this interface. Similarly to Alg. C.1, a MCS can be done using GAMS and AspenHysys; using their corresponding set of methods.

AspenHysys-AspenPlus connectivity AspenHysys has a proprietary interface which accepts COM objects called AspenHysys Extensions, while AspenPlus allows for user models, coded in Fortran to be directly linked to its model library.

In the case of the connection of AspenPlus-AspenHysys together, the approach proposed makes use of artificial neural networks (ANNs), briefly described in section 3.1.4. One possible situation that is considered in this thesis is the case of using AspenPlus results inside AspenHysys.

The implementation of this approach requires of three steps, (i) generating representative data in AspenPlus, (ii) training the ANN, and (iii) using the trained ANN in AspenHysys. Step (i) is carried out in AspenPlus using its sensitivity analysis tool or an algorithm similar to the one previously described (see Alg. C.1). Step (ii) which encompasses, the ANN training task was carried out using the ANN toolkit provided with Matlab, taking into consideration different sets for training and validation. Step (iii) requires of a model that uses the ANN results and provides with the appropriate results.

Algorithm 4.2: Implementation of ANN use inside AspenHysys.

Data: Trained ANN (**IW**, **LW**, b_1 and b_2), definition of input (X_{in}) and output variables (Y_{out}) in AspenHysys.
Result: ANN estimated values for output variable Y_{out}.
begin
  retrieve input values from different AspenHysys streams and blocks X_{in};
  scale input values $X_{s1} = \mathsf{scaleInputs}(X_{in})$;
  calculate first level $X_{s2} = \mathsf{tansig}(\mathbf{IW} \cdot X_{s1} + b_1)$;
  calculate output level $X_{s3} = \mathsf{purelin}(\mathbf{LW} \cdot X_{s2} + b_2)$;
  scale output values $Y_{out} = \mathsf{scaleOutputs}(X_{s3})$;
  set output values to corresponding AspenHysys streams and blocks Y_{out};

The algorithm has been implemented as a AspenHysys Unit Operation Extension (AspenTech), and it is shown in Alg. 4.2. The ANN structure used is shown in Figure 4.1. Initially, input values (X_{in}) are scaled to [-1;1] interval (X_{s0}). In the former algorithm 4.2, the first level of neurons response is obtained by performing the function evaluation of the first level over

the result of multiplying the input matrix **IW** and adding the corresponding bias ($b1$). This result is multiplied by a middle layer matrix **LW**, and other bias is added ($b2$) together with a last function evaluation. The number of neurons in the first level has been fixed to a given number $nNeu$[7]. Functions used are "tansig" for first level and "purelin" for the second level[8]. Results of the second function evaluation are scaled back to real values.

The use of ANNs instead of polynomials or other metamodelling techniques such as krigging, is based on the ANNs ability to cope with multi-output models straightforward, while other techniques require of one metamodel for each output variable.

4.2.3 Framework application procedure

The procedure proposed is derived from the ISO14040 implementation of LCA, which has been extended in this case to tackle with the use of process simulation and other general models.

4.2.3.1 Step 1 - Goal definition

In this step the study goal is defined, other aspects that have to be determined are:

a. Sustainability indicators to be assessed.
b. Functional Unit, service that the project is studying.
c. System boundaries and allocation procedure.
d. Uncertainty considerations.
e. Appropriate model complexity.

The selection of *sustainability indicators* has to be done in a iterative fashion, because an a priory assessment of sustainability problems can not be done. It is proposed to be as exhaustive as possible, selecting as many indicators as available for calculation, calculate them accordingly (see step 3), and check if alternative options (which could be related to process design or operation) reveal trade offs between objectives. This way also the requirements for some metrics are shown, and proper modelling can be done and modified accordingly.

The selection of the *functional unit* (FU) has to be performed following the guidelines of section 3.4.2, concerning the services provided by the product and not the product itself. In this sense, alternatives have to be considered provided they generate the same FU. In process industries the former can be simple, specially in the commodities or energy production where the product and service are pre-defined. However considerations of quality and market image for new products are difficult to quantify a priory. Commonly the FU will represent the annual (or the project's lifespan) production amount of a given commodity. The selection of FU serves for a priory normalisation of any calculated metric.

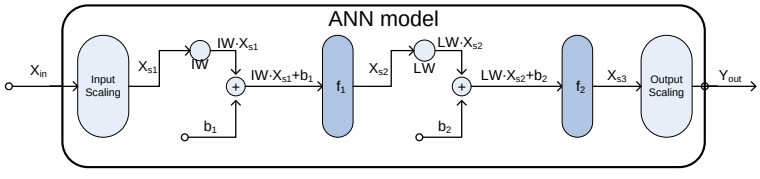


Figure 4.1: Artificial Neural Network employed in this work

[7]The number of neurons in the middle level fixes the sizes of all matrix and vectors used in the ANN, given that only one level is considered. **IW** is a matrix of $[nNeu, nIn]$, while **LW** is a matrix of $[nOut, nNeu]$

[8]tansig: $y = \frac{2}{1+e^{-2x}} - 1$, purelin: $y = x$

System boundaries are to be extended for explicit consideration of upstream and downstream echelons associated to the selected FU, given that they are important contributors in the case of process industries. This extension is susceptible of uncertainty related to cut-off criteria, i.e. where to draw the line that defines the systems limits. It has to be taken into account that, in most cases, process modifications should not alter the final product (i.e. a commodity has its properties fixed), so use and final disposal life cycle stages are usually the same for all considered options, provided that they generate exactly the same product[9]. Generally, the system boundary is set from cradle to gate, and common FUs are mass or energy flow rates. In the case of using pre-compiled LCI data considerations regarding process infrastructure should be checked and modified accordingly.

Multi-product manufacturing is a common characteristic in process industry, i.e. the same facility produces the studied product coupled with other different. In these cases, *allocation* has to represent the current plant case and consequently general assessments can not be done; the procedure will depend on each case. According to ISO standards, allocation should be avoided by the possibility of having a single product representation of the process. In some cases this is feasible if technical single by-product processes are available. However, this possibility can be also considered as a type of allocation. In all cases, uncertainty due to different allocation procedures has to be modelled following a value based method, by parameterizing it, and analysing the different resulting allocation scenarios.

Regarding *model complexity*, it has to be noted that not all models are able to modify the inputs of certain indicators[10]. Thus, the initial model complexity and the selected indicators should be assessed in tandem, if model complexity can not tackle the indicators requirements, then model improvements should be performed, or indicators should be simplified.

By analysing the former points, uncertainty has to be considered since the start of the analysis which prevents possible over or under confidence on the analysis results. It is meaningless to present results without including confidence intervals or that do no have into account the possible sensitivity to model parameters at least in a case study basis.

4.2.3.2 Step 2 - Model building and data gathering

No methodology that allows the use of unverifiable or erroneous data can be accepted as basis for comparing products or processes. In this sense, any model helps improving the verifiability and quality. This improvement is partially materialised in the provision of a means for traceability of model underlying hypothesis.

Two tasks are required at this step: (i) a model of the process is built and (ii) information required to calculate the process metrics under study is gathered in this step. Both task consider the objectives set in Step - 1. Special attention has to be given to the selected indicators information requirements and consequently model detail has to be defined accordingly.

This framework can be applied to the aid in decisions regarding process design, and short and log term operation and planning. Clearly the models required will be different due to the decisions that are considered.

Regarding process design, decisions are related to (i) process operating conditions (e.g. flows, temperature, pressure) and (ii) process topology (i.e. unit operations connectivity). These decisions have to consider also constraints related to product yield, production required, and

[9]Consideration of downstream process has to include waste treatment of residues produced during product manufacturing and it has to take into account plant decommission. The phases of use and final disposal of the product are difficult to quantify in the case of commodity products, given the wide variety of possible products where they maybe used.

[10]Measuring the impact of scheduling policies in the company contribution to gross domestic product (GDP) of a given country, could end in infeasibility.

quality (e.g. concentration). Process simulation is used for the case of continuous process design. Its selection is based on the following considerations: it provides with high detail unit operation and thermodynamic models which allow for modelling different process; it allows for connectivity with other tools for metrics calculation; and it permits to easily check underlying modelling hypothesis. Typically the use of process simulation adopts a hierarchical decomposition of decisions as shown in section 2.3.2, however the use of metamodels to replace the simulation model allows for using simulations in a mathematical programming context as discussed in section 3.1.

In the case of process scheduling, decisions are related to assignment and sequencing of different process tasks to available equipment. These decisions have to face constraints related to routing (i.e. product recipes), storage limits and waiting times, and possible task sequence dependence. The scheduling model used, coded using mathematical programming, allows for representing the former set of decisions and constraints with ease and is specially suited for the consideration of cleaning operations.

Related to the whole SC, the strategic decisions model has to consider: the SC structure in terms of nodes activities and nodes connectivity and simultaneously assess the material and cash flows associated to that structure.

In all cases special attention has been put to the estimation of emissions; in the process design context emission is explicitly considered in the simulation model, while in the scheduling model these considerations are part of the model input requirements.

Uncertainty considerations are taken into account by allowing the process variables and model parameters considered to match pdfs based on literature surveys or industrial field measurements. Tools such as the ones described in 3.2, and methodologies shown in section 2.4 can be used. In this thesis due to the shape that models have and the tools that implement them, a sampling approach is the one envisaged and applied. This approach allows for and aims at considering two sources of uncertainty (see section 4.2.2), (i) from model and model parameters, and (ii) due to choices made in building and using model results. Sensitivity analysis in this step tend to validate the model behaviour in terms of input-output behaviour.

Similarly to the case of a LCI, this step gathers all the sustainability interventions of the process being considered. These interventions will be: mass, energy and cash flows mainly. The connection between the different required models (i.e. different simulation models, or environmental models) is done at this step. All former models results are fed to a corresponding sustainability model which considers economic, social and environmental metrics, due to this fact, the former models, process simulation and mathematical programming based, can be easily changed by any other which provides the same information. This model interchangeability is feasible due to the modular approach proposed.

4.2.3.3 Step 3 - Metrics calculation

In this step, model results (process alternatives sustainability interventions, i.e LCIs and additional data) from Step 2 are used to calculate all criteria/metrics defined in Step 1. Sensitivity analysis techniques (see section 3.2) are used here to determine sources of variability in the results, aimed at increasing the model capabilities. If this is required iterations between steps 1, 2 and this step are made. These iterations take into consideration the model's capabilities and tend to enhance it in order to provide with the appropriate behaviour. The SAs performed at this step considers the relationships between the model input variables and the KPIs selected in step 1.

Independently of the way that decision alternatives are generated, namely by heuristics decisions/case studies or by the use of optimisation, metrics have to be calculated for all of them. In the case of the use of optimisation, this step involves the resolution of different single

objective optimisation and the use of a given algorithm (eg. Alg. 4.1), to generate the Pareto set of alternatives. While if the alternatives have been previously generated by heuristics the Pareto set can be easily generated provided all alternatives are measured along each metric.

Special attention is made during this step to value based scenarios and its possible distinguishability. Confidence intervals and multivariate techniques, briefly described in section 3.3, are used during this stage to test the differences present between modelled alternatives. This is aimed at showing which are the possible metrics in which the alternatives differ the most and which are the metrics that show the closest similarities.

4.2.3.4 Step 4 - Decision making aid

This final step provides assessment in the actual decision, being it the selection of a single alternative or the need for further modelling.

Regarding alternative selection, MCDA techniques can be used to elicit DM's preferences and consequently a ranking of options can be obtained, see section 3.1.3. However most MCDA methods are partially compensatory, which is in clear contrast to the articulation of preferences performed by DMs, which is non-compensatory in most cases. The selection of the MCDA technique used depends on each case, but the central question regarding sustainability is whether a compensatory or non compensatory approach should be used.

Instead of focussing the attention on one single alternative it is far more important to see the actual trade off among them. In this sense, the set of Pareto alternatives is more informative than a single alternative selected based on a given set of preferences. More importantly special attention has to be put during this step to value based scenarios and the ability to distinguish between them. Multivariate and classic statistical techniques are used during this step to elucidate such differences. Dominance, contribution, break even and other analysis are performed aiming at determining main indicator contributors.

Outputs of this step are the trade offs between modelled alternatives and a possible ranking/ordering of alternatives in terms of each criteria.

4.3 Remarks

In the first step special attention is put to the definition of typical LCA considerations (system boundaries, functional unit and allocation procedure) and metrics are selected. These two aspects define the granularity and complexity of models required. All the former considerations are directed by the study goal.

The second step consists of the most time consuming, given that it encompasses model building and its validation. Model building is performed using the commercial tools (AspenPlus, AspenHysys or GAMS) while the validation step is proposed to be done in Matlab, where a toolbox for sensitivity and uncertainty analysis is used.

The third step considers the calculation of different sustainability metrics based on the model results. In some cases the model already provides the metric's value, but in other cases this extra calculation is done in Matlab. In this step a second round of sensitivity and uncertainty analysis can be done.

The last fourth step consists of aid decision making, depending on the study goal, different approaches are proposed. All case studies require to assess the sustainability concerns of a discrete set of process alternatives. This set of alternatives could be generated using heuristics or using an optimisation algorithm. The first approach has been exemplified in the case studies of phosphoric acid production, where uncertainty is also considered, and in the IGCC plant operation. The other case studies couple alternatives generation and decision making.

In these cases the Pareto Front of generated alternatives is presented and possible trade-off decisions are proposed.

During model building, data gathering and metrics calculation, steps 2 and 3, special emphasis is put on the model's validity, which is checked by the use of SAs performed at two levels: (i) one considering model inputs and model outputs (step 2), and (ii) model inputs and final KPIs (step 3). More importantly decisions made at step 1 should be re-assessed under the results in step 4, checking for objectives completion and model's adequacy.

The use of models allow for a robust treatment of uncertainty present in models, which otherwise could not be addressed. This way the models can provide with a more accurate representation of the reality, by providing not only with crisp estimations, but with a value and its associated confidence interval (CI). These CI provide with more information to the decision maker, which has to assign certain probability thresholds for acceptance. Clearly this issues will affect the decision adopted if compared to deterministic decision making.

In general any decision making process usually involves three general stages (Azapagic & Perdan, 2005a,b); (i) problem structuring, (ii) problem analysis and (iii) problem resolution. This framework adopts for item (i) different models and metrics, in the case of process design, commercial simulation software is used, while in the case of operation and strategic decisions, mathematical programming tools are used to represent the problem. In all cases environmental, efficiency and economic metrics are used to measure the problem sustainability interventions. For item (ii), the framework uses heuristics for decisions or multiobjective optimisation to generate different alternatives. Point (iii) is addressed in cases where no preferences are elicited and no uncertainty is considered by providing with the Pareto set of alternatives or with single alternatives if these preferences stated. In the cases where uncertainty is considered, model/metric's parameter uncertainty effects in the alternative rankings is analysed.

Part III

Framework Application

Chapter 5

Continuous process industries design

Recalling the research needs that have been mentioned before, this chapter presents a novel approach for the explicit consideration of sustainability considerations at the design stage, making special emphasis on the environmental and social aspect, and using the framework proposed in chapter 4.

The process design aspects that are tackled in this chapter are related to the selection of process alternatives, and the consideration of process operating conditions applied to a fixed and given, process topology. For this type of design considerations the use of a superstructure representation is not required, and a hierarchical approach is better suited. Consequently this approach is the one used and by following the trends of the literature reviewed the use of process simulation is adopted.

One of key aspects presented here is the application of process models as backbone together with other models (related to emission and environmental impact estimation), for the estimation of the SD considerations. The linkage of process environmental interventions, in terms of raw material and utilities consumption is also addressed by coupling simulation results with LCI from databases. The former considerations have been already addressed in the literature reviewed by some authors, however its application in an integrated and systematic way is lacking.

In this sense three different case studies are proposed, one aimed at measuring the effect of uncertainty in model variables on environmental metrics (see section 5.1). For this case three different waste water treatment (WWT) options are analysed for its application in a phosphoric acid (PA) production plant. A model of a PA production plant is built using industrial data and validated using linear regression based metrics. Mid point and end point metrics are calculated using model results and decisions suggested by their values are assessed in the presence of uncertainty.

The other two case studies do not consider uncertainty in model variables and are proposed to address other aspects. On the one hand, the analysis of raw material selection effects in plant efficiency and environmental aspects is studied in section 5.2. The case study considers the operation of an IGCC power plant, which has been modelled and validated using industrial data. Different environmental impact (EI), efficiency and thermodynamic metrics (see section 2.2.6) are proposed to be used to aid decision making.

The last case analyses process design decisions at the conceptual stage in terms of economic and environmental SD aspects (see section 5.3). The production of isopropyl myristate by means of reactive distillation is used as case study. The process model is based on literature, its results are validated using local sensitivity analysis (SA). In this sense local SAs are also used for the selection of process variables for optimisation considering the former economic and environmental metrics.

5.1 Phosphoric acid production case study

Phosphoric acid (PA) is the second largest mineral acid produced worldwide considering its volume and value. Its production is performed through two different processing routes: a wet method and a thermal method. The thermal route involves electric-furnace smelting of the phosphate containing mineral (apatite) using coke and silica to produce elemental phosphorus, which is then converted to PA by first burning (oxidising) the phosphorus to P_2O_5 and then absorbing the P_2O_5 obtained in water. This process results in a expensive food-grade acid of high purity that has proven to be over specified for general fertiliser use (Gard, 1998; Schrödter *et al.*, 2002). The wet method process is based on sulphuric acid lixiviation of apatite rock ($Ca_{10}P_6O_{24}F_2$, fluoroapatite $Ca_{10}P_6O_{24}(OH)_2$, hidroxyapatite) followed by a filtration of the waste gypsum formed, known in this industry as phosphogypsum (PG). The subsequent concentration of the filtered solution yields PA in technical grade, also known as wet process phosphoric acid (WPPA) (Becker, 1989; EFMA, 2000).

PA production using the wet method is a widely known process, it was intensively developed since World War II and a large amount of experimental knowledge has been amassed. Despite the large amount of data, process reactor design is still an uncertain field, based on empirical principles and industrial proven solutions. According to Becker (1989, Ch. 2), inside the apatite rock dissolution reactor the following reactions occur:

- mineral acids dispersion in the aqueous solution:
  $H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$
  $H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$
- H^+ ions attack the phosphate rock[1]:
  $nH^+ + Ca_3(PO_4)_{2(s)} \longrightarrow 2H_3PO_4 + (n-6)H^+ + 3Ca^{2+}$
- Ca^{2+} ions precipitate with SO_4^{2-} as gypsum:
  $Ca^{2+} + SO_4^{2-} + 2H_2O \longrightarrow CaSO_4 \cdot 2H_2O_{(s)}$

During the mineral's lixiviation, by controlling reactor temperature and P_2O_5 concentration one can select which calcium sulfate hydrate is formed: dihydrate ($CaSO_4 \cdot 2H_2O_{(s)}$) at ≈ 70-80ºC for 26-32% P_2O_5 or hemihydrate ($CaSO_4 \cdot 0.5H_2O_{(s)}$) at ≈ 85-95ºC for 40-52% P_2O_5. The WPPA obtained through this method is suitable for fertiliser production, which is the destiny of 80% of its production in Europe (van-der Loo & Weeda, 2000; Wiesenberger, 2002).

According to EFMA (2000) fluorine is present in most phosphate rocks to an extent of 2-4% by weight. This element is emitted during reaction of rock in acidic media, initially as hydrogen fluoride (HF), but in the presence of silica, HF reacts to form fluosilicic acid (H_2SiF_6), according to the following set of reactions:

- $CaF_{2(s)} + 2H^+ \longrightarrow 2HF + Ca^{2+}$
- $4HF + SiO_{2(s)} \longrightarrow SiF_4 + 2H_2O$
- $3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_{2(s)}$

[1] Note that apatites can be considered a mixture of $Ca_3(PO_4)_2$, CaF_2 and $Ca(OH)_2$, in this set of reactions only the first specie is considered.

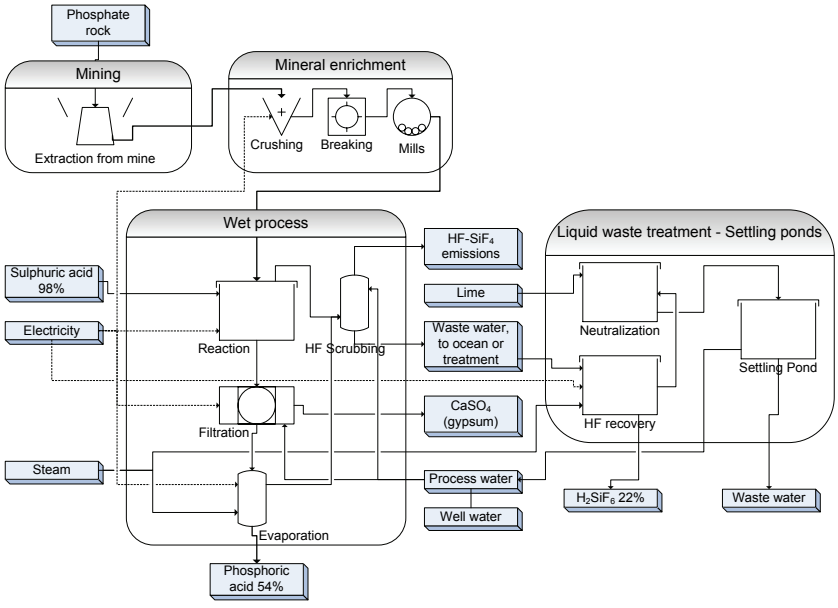


Figure 5.1: Processing stages considered for PA production using the wet method.

- $H_2SiF_6 \longrightarrow SiF_4 + 2HF$

A certain proportion of the fluorine evolves as vapour, depending on the reaction conditions while the rest remains in the solution leaving the process either with the product or with process water (Aigueperse *et al.*, 2002a). More volatile fluorine compounds appear in the vapours exhausted from the evaporators when the PA from the gypsum filter is concentrated. Fluosilicic acid may decompose under the influence of heat yielding volatile silicon tetrafluoride (SiF_4) and HF as shown in the last reaction (Aigueperse *et al.*, 2002b; Hocking, 2006; Yapijakis & Wang, 2006). The PA industrial facility studied uses mineral rock from different sources, while the sulphuric acid production facility is in the same site. The facility is located near Thesaloniki, Greece, and is operated by Phosphoric Fertilizers Industry S.A (PFI-S.A.). The plant has the following production facilities and capacities (PFI-S.A., Accessed 06/11/2007).

- Sulphuric acid, (two facilities) 385.000 tons/year.
- Oleum (fuming sulphuric acid), 13.000 tons/year.
- Dilute phosphoric acid, 110.000 tons/year.
- Concentrated phosphoric acid, 40.000 tons/year.
- Anhydrous hydrofluoric acid, 7.500 tons/year.
- Calcium phosphate, 60.000 tons/year.
- Facilities for storage, packing, palletizing, internal distribution and loading onto trains and trucks of fertilisers and chemical products.

Prior environmental studies related to the phosphorus fertilisers industry have shown that relevant environmental issues are those related to (EFMA, 2000; Kongshaug, 1998; Wiesenberger, 2002):

- green house gas (GHG) emissions,
- process emissions such as HF, PO_4^{3-} and SiF_4 mixtures into air and water,
- the management of the produced PG.

It is generally accepted that the biggest environmental problem in WPPA industry is the destiny of PG wastes and their lixiviates (EFMA, 2000; van-der Loo & Weeda, 2000). The destiny of PG is usually one of three possibilities: (i) discharge it into the ocean or other water basin, (ii) store produced PG in land into ditches and ponds or (iii) its use as a usable product (Schrödter *et al.*, 2002; Seijdel, 1999). In all three cases spent process water used to transport PG and PG itself contain trace metals found in the phosphate mineral and sulphuric acid used with other Si and F compounds. According to a screening LCA based analysis of the Dutch fertiliser industry (two industrial sites, Seijdel (1999)), the overall environmental performance of the gypsum reuse scenario is better than the landfill scenario, being both of them better than the discharge option, considering the Dutch and the Western European situations. Regardless of this finding in this work PG is assumed to be stockpiled on land, given that it is the current practise of the industrial site used as a case study.

Net emission of GHG from phosphate fertiliser manufacture is largely determined by the method of sulphuric acid production (Kongshaug, 1998). GHG emissions mainly consist of CO_2 emitted during consumption of fossil fuels. It is also reported that transport of raw materials, intermediates and products comprised a considerable proportion of the emissions budget which for some studies ranged from 20-33%. Other studies (Wood & Cowie, 2004), have indicated that overseas transport of raw phosphate rock was particularly important. Along these lines da Silva and Kulay (2003; 2005) highlighted that GHG are mainly caused by transportation in the case of the PA production in Brazil.

Regarding fluoride emissions Wiesenberger (2002) states that they can be reduced almost completely to zero if a water closed loop is accomplished, it is also reported (EFMA, 2000), that scrubber efficiency for their abatement is bigger than 99%. It has been described the possibility of generation of a H_2SiF_6, as a co-product up to 20-25% concentration, from the scrubbing liquors, which can be sold as a byproduct that can be used for the production of aluminium fluoride (EFMA, 2000; van-der Loo & Weeda, 2000). In the case of the PA production in Brazil it is reported that the main contributor to eutrophication are the losses of PO_4^{3-} during the PA production (da Silva & Kulay, 2003, 2005).

The studied industrial site has certain restrictions regarding PG reuse, being its disposal mandatory. However, the site has the ability to cope with different waste water treatment (WWT) options. These different WWT options are further studied following this thesis methodology proposed.

5.1.1 Step 1 - Goal and scope definition

Specifically, this analysis considers the impact of raw materials (phosphate rock and sulphuric acid) and PA production but neglects the product use and destiny (grave). Based on the former hypothesis a cradle to gate approach is adopted. Furthermore, it is important to highlight the following key points regarding the system boundaries:

- for PA production, the boundary lies just after the production of concentrated PA, considering that all produced low concentration acid (32%) is concentrated up to 54% (EFMA, 2000).
- with regards to PG, no production of usable product is analysed. Instead, it is considered to be stockpiled on settling ponds.

This system boundary setting is common for the case of mining related industries (Durucan *et al.*, 2006). Figure 5.1 summarises the four main processing steps considered in the inventory analysis of PA.

With regards to the indicators used, although the methodology allows for consideration of economic and social impacts, for the sake of simplicity, the analysis is restricted to the assess-

ment of certain environmental indicators. To asses the EI of each of the WWT options the CML mid-point (see section 3.4.3) impact categories are adopted (Guinee *et al.*, 2001b). Initially the selection of a mid point approach instead of an end point is due to the inherent uncertainty that end point category results have (see section 2.2.5.3). This fact allows for clearly identifying the WWT most significant differences in terms of EI. As a second step, different end point methodologies are also analysed. The end point categories to be analysed are: direct addition of CML v2 normalisation results, Environmental Priority System (EPS) (Steen, 1999a), the EcoIndicator 99 (EI99) method of Goedkoop and Spriensma (2001), and the Impact 2002+ proposed by Humbert *et al.* (2005). Further details on these methodologies is found in section 3.4.3.

Three possible process alternatives are analysed which are set according to how the liquid effluent from the plant and settling ponds is treated. This effluent comes mainly from the scrubbing liquors and the gypsum filter unit. The options considered in the analysis are the following:

- The first option considers that all waste water (WW) is dumped into the ocean. A very small amount of the process water is recycled back to the plant (1%). A pH of 8.2 is assumed for the calculation of the chemical species that are present in ocean water (Key *et al.*, 2004). This option is labelled as "**Option 1**: No waste water treatment (WWT) or ocean disposal".
- All WW is neutralised (a pH discharge of 7 is assumed) and then dumped into settling ponds. The plant recycles back part of the water required for processing; specifically, only 10% of the consumed water is disposed off, whereas the remaining 90% is recycled back to the plant, these percentages are based on current plant operating conditions (Kouloura, 2008). Water emission of these ponds is considered to contain the same composition of water plant effluents after neutralisation. These emissions enter ground-water compartment for the impact calculation. This option is denoted as "**Option 2**: Neutralisation only".
- All WW is treated to recover H_2SiF_6 (22%) and then neutralised in a second step prior to being disposed into settling ponds. In this case, the recirculation of spent water is done in a similar way as in the former option. This option is labelled as "**Option 3**: Neutralisation and HF recovery".

All the processing options are compared using as a FU: 1kg of produced PA. Regarding co-product allocation, for the case of option 3, the production of H_2SiF_6 is considered to prevent the EIs arising from its production from virgin materials. Boundaries for options 1 and 2 do not consider the systems boundary expansion needed for H_2SiF_6 co-production.

5.1.2 Step 2 - Model building and data gathering

In order to gather all required data, several models have been built and connected. The data that has been used in their development comes from a real industrial plant located Thessaloníki (Greece). Data regarding process modelling comes from literature. The whole model integrates three parts: (i) the PA production process model, (ii) a multimedia chemical fate model (for defining trace species destiny) and (iii) an environmental impact model (CML v2). The models are connected as shown in Fig. 5.2. Model building considerations related to PA production are discussed in section 5.1.2.1, while the multimedia fate model is discussed under section 5.1.2.2. Models uncertainty considerations are discussed in section 5.1.2.3, and the process model is validated under those considerations in section 5.1.2.4.

The electricity use for PA production, is based on the Greek power network, given that the industrial facility is located that region. The study assumes that a certain amount of electricity

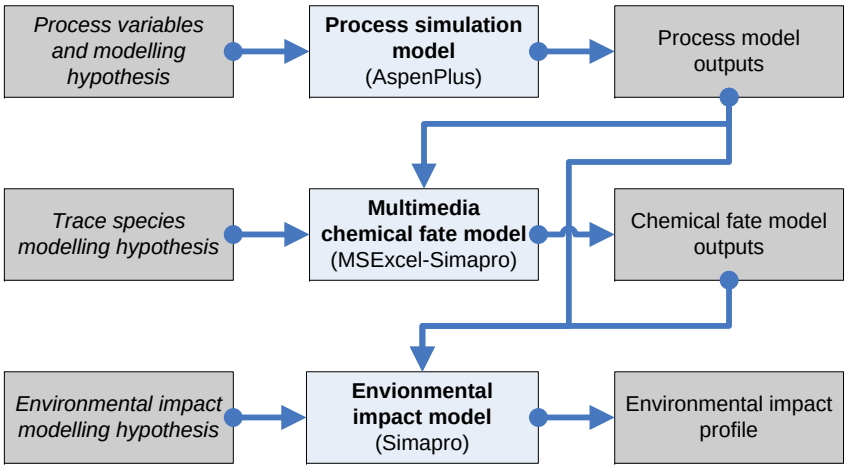


Figure 5.2: Used models and their interconnections.

is produced in site (20% of total), while for steam consumption, which is mainly used for PA concentration, it is supposed that its demand is mainly covered by steam generated from the H_2SO_4 production facility (80% comes from site-site integration), whereas the remaining amount is considered to be obtained from on site power production based on natural gas combustion. These assumptions are based on current plant operating conditions (Kouloura, 2008). The analysis also considers the use of chemicals (lime) for WWT control in the case of options 2 and 3 in which the effluent is neutralised. On the other hand, the transportation of the rock, sulphur and other materials is not included within the system boundaries. The emission of radionuclide's is not considered either, given that no industrial information is available. Finally, the processing infrastructure such as plant buildings or mines, is included in the analysis, using the same hypothesis that the Ecoinvent database does (Althaus *et al.*, 2007).

5.1.2.1 Wet Phosphoric Acid production plant simulation model

Four main processing steps can be identified for PA production. The first two involve phosphate rock raw material processing while the remaining two are the production of PA and the disposal of WW and solid effluents (see Figure 5.1). In this work these last two processing steps are modelled in AspenPlus. Note that the processing steps modelled in AspenPlus constitute the "forward system", for which process specific data is gathered. The rest of data concerning the "background system", comes from average processing technologies which is retrieved from an LCI database.

Modelling the PA process has been done by several authors in the past, and they have shown that it is not straightforward. The complexity of the model is caused by the diversity of processes that are occurring inside of it. The most simple reaction scheme involves two heterogeneous steps (Bechtloff *et al.*, 2001), dissolution of apatite and gypsum crystallisation. It also considers the superficial reaction and in the bulk solution the electrochemical equilibrium of different species. Given that the crystallisation step can occur over the rock or on gypsum particles, different models can be formulated. Basically, the model needs to cope with:

(1) Diffusion of reactive species towards the reaction zone, i.e. the apatite mineral particle's surface.

(2) Superficial reaction.
(3) Diffusion of product species towards the bulk solution.
(4) Formation of gypsum, over the mineral's particle or over gypsum particles.

Steps 1 and 3 can also include two diffusion steps, one due to fluid film resistance in the boundary layer that surrounds the particle and other due to possible formation of gypsum over the apatite particle. The model that most authors employ to visualise the process is based on a model proposed by Wen (1968) known as the "heterogeneous shrinking core" (HSC), which is further discussed in the literature mainly in the case of gas-solid reactions (Carberry, 2001; Froment & Bischoff, 1990; Levenspiel, 1999; Smith, 1981). The model's basic assumptions are:

- The particle is not porous.
- The "ash layer" moves slowly inside the particle and a pseudo stationary state can be achieved for the diffusion of reactive and products.
- The diffusion steps and the chemical reaction process take place in series.

The model is generally applied to the case of a chemical reaction as follows $a\ A_{(l)} + b\ B_{(s)} \longrightarrow c\ C_{(l)} + d\ D_{(s)}$, for this case and when none of the process (diffusion or reaction) is predominant, the equation that models the process is Eq. 5.1.

$$-\frac{1}{S_{part}}\frac{dN_B}{dt} = \frac{\frac{b}{a}C_A}{\frac{1}{k_L} + \frac{R(R-r_c)}{r_c D_e} + \frac{R^2}{r_c^2 k_s}} \tag{5.1}$$

N_B the dissolution rate is calculated given a boundary condition on the interface layer[2], and S_{part} is also related to the particle's core radius r_c. C_A is the bulk concentration in the reactor, while k_L is the liquid boundary layer mass transfer coefficient for component A, D_e is the component A specific diffusivity along the "ash" layer which has a thickness of $R - r_c$, while k_s is the superficial reaction constant. In the case of apatite rock dissolution, component A represents H^+ ions while B will be apatite mineral, and on the products side C will be Ca^{2+} while D gypsum.

The review of apatite dissolution mechanisms by Dorozhkin (2002), found that most of the models come from the current concern of natural apatite occurring in human and animal bones and the possible development of substitutes. The author cites eight possible mechanisms for apatite dissolution but all of them were elaborated for slight acidic conditions (pH=4-8), with relative small values of solution undersaturation and temperatures between 25-37ºC. Those models are valid within those experimental ranges, but nothing is know about their validity for apatite dissolution in strong inorganic acids, solutions of pH < 2 and temperatures above 70ºC. Other data available in the literature is based on laboratory experiments made in conditions similar to the industrial reactors. Some of these works are based on dissolution of apatite rock on other acids than sulphuric such as phosphoric and hydrochloric acid.

Dissolution of apatite rock in phosphoric acid van der Sluis *et al.* (1987) dissolved apatite rock with phosphoric acid in a batch reactor. The reaction scheme proposed is: (i) $Ca_{10}(PO_4)_6F_2 + 4H_3PO_4 \rightarrow 10CaHPO_4 + 2HF$ and (ii) $Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2HF$. The authors found that when concentration of P_2O_5 in the solution raises then, complete digestion time also rises, due to increase of solution's viscosity. This also implies an increase in the

[2]This side of the equation is formulated by considering the dissolution velocity of B as $\frac{dC_b}{dt} = -r_s\rho_B$, with r_s the superficial reaction rate.

diffusivity resistance of the boundary layer and not an expected increase of rate speed given by the increase of H^+ ions available in the solution. This is strong evidence against the hypothesis of a limiting step based on diffusion of H^+ ions towards the reaction zone. The authors also modified the reaction temperature and calculated its activation energy, arriving to a very small value: 13-23kJ/mol, independent of particle size and acid concentration. This implies that the dissolution is not controlled by the reaction step; the former would have required a higher activation energy values. They also assume that the reaction is so fast that the particle surface is at chemical equilibrium, and saturation concentration for $Ca(H_2PO_4)_2$ is reached. Considering that the dissolution is neither sensitive to H^+ concentration nor temperature the authors conclude that the rate determining step is the diffusion of Ca^{2+} ions from the particle to the bulk solution, calculating a value of $1.4{\cdot}10^{-8}$m/s for Ca^{2+} transport coefficient ($k_L^{Ca^{2+}}$). Ben-Brahim *et al.* (1999) found the same behaviour stated as by van-der Sluis *et al.* (1987), and found values of $k_L^{Ca^{2+}}$ in the range of $3\text{-}8{\cdot}10^{-3}$m/s, and activation energies around 14kJ/mol. According to Becker (1989, Ch. 2), porous ores reach 99% decomposition after 2 minutes, while non porous only 95% after 40 minutes, in this sense Mgaidi *et al.* (2003) paid attention to the surface changes during dissolution The authors fit rock dissolution data in low concentration H_3PO_4 acid to the following mathematical model: $m/m_0 = 1 - e^{-kt}$. Where m is the rock mass at time t and m_0 the final mass dissolved, k was found to be 0.21 min^{-1}. This value generates a rock's half life of 200s and a 99.99% dissolution after 43 minutes.

Dissolution of apatite rock in hydrochloric acid Calmanovici *et al.* (2006) applied the HSC model considering that Ca^{2+} ion diffusion is the controlling step. The reaction scheme that they use was: $Ca_{10}(PO_4)_6(OH)_2 + 20H^+ \rightarrow 10Ca^{2+} + 6H_3PO_4 + 2H_2O$, They found a $k_L^{Ca^{2+}}$ value of $4.2{\cdot}10^{-9}$m/s and a reaction's activation energy of 14kJ/mol. They also report an effective diffusivity, D_e, value of $8{\cdot}10^{-10}$ m^2/s.

Dissolution of apatite rock in sulphuric acid . According to Becker (1989, Ch. 2), gypsum can grow in two possible ways, regular crystal growth (RCG) and spontaneous nuclei formation (SNF). RCG occurs when concentration of Ca^{2+} and SO_4^{2-} stays between saturation and super-saturation (SS) lines, and SNF when concentration is over the SS threshold, in general the quantity of gypsum crystallised by RCG is given by: $Q = \Phi(K_{ss} - K_s)^3$. SNF is undesirable because it blinds the rock with the formation of gypsum over its surface. For dihydrate precipitation conditions, Becker (1989, Ch. 2) proposes $K_s = 0.83$ and $K_{ss} = 1.30$, consequently $G^* = K_s/K_{ss} = 1.57$, these values define three concentration regions as follows (i) $G < 1$: neither precipitation, nor nucleation occurs, (ii) $1 <= G < 1.57$: RCG occurs, and gypsum will precipitate over gypsum crystals preferably and (iii) $G >= 1.57$: spontaneous nuclei formation and precipitation occurs (SNF)[4].

Gioia *et al.* (1977) assumed a mineral dissolution in hemi-hydrate conditions. The reaction scheme used is the one proposed by Becker (1989). They assume that the process is controlled by diffusion of reactive (H^+) towards reaction plane. They propose two cases one for primary nucleation over the phosphate particle (blinding) and the other considering SNF over gypsum particles. They assume a value of G^*=2.5 for hemihydrate conditions. In the first case the mass transfer coefficient for H^+ ($k_L^{H^+}$) is calculated from a correlation for baffled agitated tanks, and gypsum formation/nucleation rate is proposed to be proportional to supersaturation. In the second case the authors assume that ash layer is the controlling resistance for diffusion and

[3]The Φ value represents the crystallisation mass transfer constant and is equivalent to 214kg/m^3 of gypsum when operating at 25% solids in 30% acid slurry at 75C (Becker, 1989).

[4]These values are reported considering SO_4 and CaO as % and not as molar concentrations, see Becker (1989, p. 91).

they adopt a D_e value for H^+ of $1.9{\cdot}10^{-11}m^2/s$. Dissolution rate of the mineral is set proportional to sulphuric acid bulk concentration. The authors use that model to simulate a series of consecutive CSTRs with recycle in RCG conditions, concluding that (i) the limiting step is the process of crystallisation requiring longer residence times than mineral dissolution; (ii) one reactor with 30min of residence time is enough for complete mineral dissolution and crystals of reasonable size and (iii) the supersaturation and gypsum precipitation mode are controlled by the recycle ratio.

Elnashaie *et al.*, (1990) studied batch dissolution of apatite rock in dihydrate formation conditions. They control the reaction conditions to ensure different gypsum formation behaviour (SNF or RCG). The reaction scheme used is similar to the one in Becker (1989) with slight modifications to cope with mineral calcite content ($CaCO_3$): $Ca_5(PO_4)_3F + CaCO_3 + nH^+ \rightarrow 3H_3PO_4 + CO_2 + H_2O + HF + (n-12)H^+ + 6Ca^{2+}$. They mention a simplification of the scheme which involves the formation of $Ca(H_2PO_4)_2$. Their model lumps in one parameter all possible diffusion and chemical reaction effects into one effective diffusion coefficient D_e. Using this model they found that (i) in conditions of RCG, D_e is $3.1{\cdot}10^{-10}m^2/s$ and a conversion of 75% is reached after 1min and 85% after 5min; moreover after 1min H_2SO_4 concentration is found to be almost zero; which provides clear evidence of the high reactivity of H^+ coming from H_3PO_4; (ii) in conditions of SNF they report three reaction periods: (a) from 0-t_1, high speed of reaction with high values of supersaturation, D_e during this period is in the order of 10^{-12}-10^{-13} m^2/s with t_1 around 18-25s; (b) from t_1-t_2, blinding of the particle is produced, D_e during this period is 10^{-15}-10^{-17} m^2/s with t_2 around 24-36min; (c) from t_2-t_3, due to continuous mixing the gypsum layer detaches from the particle. D_e reaches 10^{-15} m^2/s with t_3 around 2hours.

Elnashaie *et al.* (1990) states that conversion of 80% of the particle is reached after 1h, the dissolution rate is proportional to sulphuric and phosphoric acids concentration, using only sulphuric acid concentration in the model raises high discrepancies with experimental data. With regards to the effect of particle size in SNF conditions, the increase in specific surface for fine particles more than compensates the higher degree of coating. With regards to the effect of reaction temperature, higher temperatures yield higher dissolution rates; this could be the result of a synergistic effect based on decrease of viscosity and increase of gypsum solubility in the bulk solution. Moreover, if mixing agitation is increased the D_e increases in the first period, it remains constant in the second period and increases again in the third period. This could be explained recalling that mixing is related to diffusive bulk resistance.

Regarding the addition of gypsum crystals initially, it is observed that most gypsum grows over the added particles and not over the mineral, this gypsum particles are bigger than the ones that would grow if not gypsum is added initially. Elnashaie *et al.*, (1995) used the former data to model continuous reactors in different process conditions, using a pilot plant to compare the experimental results. They found that D_e in dihydrate conditions is $5.5{\cdot}10^{-13}$ m^2/s and in hemihydrate $8.3{\cdot}10^{-12}$ m^2/s. Abu-Eishah and Bu-Jabal (2001) modelled a continuous pilot plant with three CSTRs in series with recycle. The reaction scheme that they propose is: (i) $Ca_3(PO_4)_2 \cdot CaF_2 + 3H_2SO_4 + 3nH_2O \rightarrow Ca(H_2PO_4)_2 + 2HF + 3CaSO_4 \cdot nH_2O$, (ii) $Ca(H_2PO_4)_2 + H_2SO_4 + nH_2O \rightarrow 2H_3PO_4 + CaSO_4 \cdot nH_2O$[5]. They propose that the overall dissolution process is controlled by the diffusion of reactive (H^+) towards the particle. Since physical solubility of apatite rock in water is less than in sulphuric acid, dissolution rate of the particle is set proportional to sulphuric acid bulk concentration. Sevim *et al.*, (2003) fit experimental results using the Avrami model: $-\ln(1-X) = k\,t^m$. Where X is defined as (amount of P_2O_5 dissolved)/(total amount of P_2O_5). They found a value of m=0.7, and an expression

[5]In the paper $Ca(H_2PO_4)_2$, is only mentioned in the reaction scheme, no formation rate, nor formation constant are mentioned.

of the k value in terms of the initial particle size (r_0 [μ m]), the initial acid concentration (C [mol/dm^3]), the initial solid/liquid ratio (SL_r [g/dm^3])and the reaction temperature (T [K]), as follows: $k = k_0 r_0^{-0.52} C^{1.93} SL_r^{-0.27} e^{-3567.52/T}$. The authors calculated a reaction activation energy value of 29.66kJ/mol. This low value shows that the process could be controlled by solid film diffusion.

There is agreement between the authors regarding the controlling effect in apatite dissolution is diffusion or transport process. Activation energy for rock dissolution in H_3PO_4 and HCl acids (Ben-Brahim *et al.*, 1999; Calmanovici *et al.*, 2006; van-der Sluis *et al.*, 1987) was found in the range of 13-23kJ/mol and in the case of H_2SO_4 its value was near 30kJ/mol (Sevim *et al.*, 2003). This fact leads to the consideration of the reaction to occur fast by a proton transfer mechanism. However, there is no agreement between which diffusion effect is the controlling, if diffusion of H^+ towards the particle's surface or Ca^{2+} towards the bulk solution. In papers where no gypsum is formed, Ca^{2+} diffusion appears to be controlling, while in the other papers, H^+ diffusion through fluid and gypsum layer looks as the controlling step. None of the cited papers makes a difference in the fluid film resistance and the diffusion resistance of the gypsum layer. All authors lump them together, assuming that the gypsum layer is controlling or just disregard any possible difference. The surveyed literature agrees in that the H^+ reacts with the rock, however there are differences related to its source. In some cases it is assumed that H^+ comes from H_2SO_4 dissociation (Abu-Eishah & Bu-Jabal, 2001; Gioia *et al.*, 1977; Mathias *et al.*, 2000), while in others Elnashaie *et al.* (1990), it comes from both H_2SO_4 and H_3PO_4[6]. Most papers offer a reaction scheme that mentions calcium phosphate salts ($CaHPO_4$ or $Ca(H_2PO_4)_2$), that are formed as intermediary species, but none of them offers, reaction rates or kinetic constants to model the appearance of those species. Given that the controlling effect is a diffusion process this omission is of minor importance. Effective diffusion coefficient D_e for H^+, is in the order of 10^{-6} cm^2/s when gypsum does not cover the mineral particle and it decreases to the order of 10^{-11}-10^{-13} cm^2/s when gypsum blinds the particle (Abu-Eishah & Bu-Jabal, 2001; Elnashaie *et al.*, 1990). Ca^{2+} transport coefficient $k_L^{Ca^{2+}}$ is in the range of $1.4{\cdot}10^{-6}$-$4.2{\cdot}10^{-7}$ cm/s (Calmanovici *et al.*, 2006; van-der Sluis *et al.*, 1987).

Pondering the former findings, the high residence times that the industry under study uses[7], and the high reactivity of the rock towards its dissolution, it was decided that the approach used in this model is to consider rock dissolution occurring by a proton transfer mechanism. This hypothesis implies that all reactions considered in the simulation are forced to attain chemical equilibrium, a similar approach was already considered by Mathias *et al.* (2000). Phosphate rock dissolution can then be solved by a model that minimises the solution's Gibbs free energy or that considers the chemical equilibrium attainment for a set of reactions.

Model thermodynamic and kinetic considerations The simulation of the process chemistry requires the use of a complex thermodynamic model to deal with electrolyte species in solution. This issue is commonly addressed using an equilibrium approach that uses a model for estimation of the activity coefficients of all solution species and a simple equation of state to model the vapour phase. This approach is commonly known as a "gamma-phi" approach and there are several activity coefficient models are available (Chen & Mathias, 2002). However in order to model this system appropriately the following key points have to be properly addressed: (i) solution reactions and speciation, (ii) reaction equilibrium constants, and (iii) activity coefficients of ionic and solvent species (Liu & Watanasiri, 1999). Specifically, in this case the liquid phase makes use of Electrolyte-NRTL (non-random two liquid) model (Aspen-

[6]They showed experimental evidence of reactivity of H^+ after H_2SO_4 was consumed, however the relation proposed does not account for any difference in acid strengths, and just add up their concentrations.

[7]Becker (1989), reports total retention times in vessels of around 4-6h.

Tech, 2005b; Chen & Evans, 1986), which allows for considering the ionic species appearing in the mixture. This model is an extension of the NRTL model for estimation of activity coefficients, which can model the entire concentration range.

The ion species considered to be present are: Ca^{2+} - H_3O^+ - SO_4^{2-} - HSO_4^- - $H_2PO_4^-$ - H_3PO_4 - H_2SO_4 - H_2O. The selection of these species relies on several hypothesis considered for H_3PO_4 dissociation and OH^- presence already used in the literature (Messnaoui & Bounahmidi, 2005, 2006). Thermodynamic data for apatite rock was retrieved from the works of Bogach et al. (2001a; 2001b; 2001c), considering also the solubilities of other phosphates (Elmore & Farr, 1940). Vapour-liquid (VL) equilibrium for CO_2, air (O_2, N_2) and H_3PO_4, was modelled considering those species to follow Henry's gas solubility law. Henry gas constants (H_{ij}, see Eq. B.1) are retrieved from AspenProperties data library (AspenTech, 2005b), see Table B.1. For the case of HF VL equilibrium a special case of the Electrolyte NRTL equation is used, taking into account HF hexamerization ($6HF \longleftrightarrow HF_6$) in the vapour phase (Leeuw & Watanasiri, 1993; Liu & Watanasiri, 1999).

Unit operation model's considerations Following the assumption of chemical equilibrium, phosphate rock attack tanks are modelled using as a combination of AspenPlus' mixers (MIXER) and two phase flash (FLASH2) models, combined in such a way that they provide a similar set of outlet streams results as the ones in industry. The model reproduces a rock attack tank that is cooled by partial evaporation of its mixture, which is the technology currently implemented. The model considers two attack reactors working in series receiving fresh rock and acid mixed together with a recycled slurry returning from a filter. Specifically, the reactions that are taken into account in the reactors are the following:

- Solution ion equilibrium:
  - $CO_2 + 2H_2O \longleftrightarrow H_3O^+ + HCO_3^-$, $K1_{CO_2}$
  - $HCO_3^- + H_2O \longleftrightarrow H_3O^+ + CO_3^{2-}$, $K2_{CO_2}$
  - $H_2SO_4 + H_2O \longleftrightarrow H_3O^+ + HSO_4^-$, $K1_{H_2SO_4}$
  - $HSO_4^- + H_2O \longleftrightarrow H_3O^+ + SO_4^{2-}$, $K2_{H_2SO_4}$
  - $HF + H_2O \longleftrightarrow H_3O^+ + F^-$, K_{HF}
  - $H_3PO_4 + H_2O \longleftrightarrow H_3O^+ + H_2PO_4^-$, $K1_{H_3PO_4}$
  - $SiF_6^{2-} \longleftrightarrow SiF_4 + 2F^-$, $K_{H_2SiF_6}$
  - $H_2O \longleftrightarrow H^+ + OH^-$, K_{H_2O}
- Liquid-Solid (LS) equilibrium:
  - $CaF_{2(s)} \longleftrightarrow Ca^{2+} + 2F^-$
  - $CaCO_{3(s)} \longleftrightarrow Ca^{2+} + CO_3^{2-}$
  - $Ca_{10}P_6O_{24}F_{2(s)} + 12H_3O^+ \longleftrightarrow 2F^- + 10Ca^{2+} + 6H_2PO_4^- + 12H_2O$
  - $SiO_{2(s)} + 4H_3O^+ + 6F^- \longleftrightarrow 6H_2O + SiF_6^{2-}$

In the case of $K1_{CO_2}$, $K2_{CO_2}$ and K_{H_2O} their temperature relationship is considered by Eq. B.2 using data from Table B.2. The remaining equilibrium constants, except the ones related to gypsum formation (K_{Dihy} and K_{Hemy}), are calculated from Gibbs free energies of formation which are retrieved from AspenProperties data bank.

The phosphoric rock is modelled as a mixture of the following compounds: fluoroapatite ($Ca_{10}P_6O_{24}F_2$) 79.3%, calcite ($CaCO_3$) 11.1%, anhydrite ($CaSO_4$) 2.9% , CaF_2 4.0% and SiO_2 2.7% (Mathias *et al.* 2000; 1998). Gypsum LS behaviour considering possible hydrate states was modelled using data from the literature (Freyer & Voigt, 2003), (see Figure 5.3), fitted to the appropriate equilibrium constants see Table B.2[8].

[8]Properties fitting was performed using AspenProperties which uses the maximum likelihood as objective function. Maximum likelihood is a generalisation of the least-squares method, where each variable difference is divided by the standard deviation of the data.

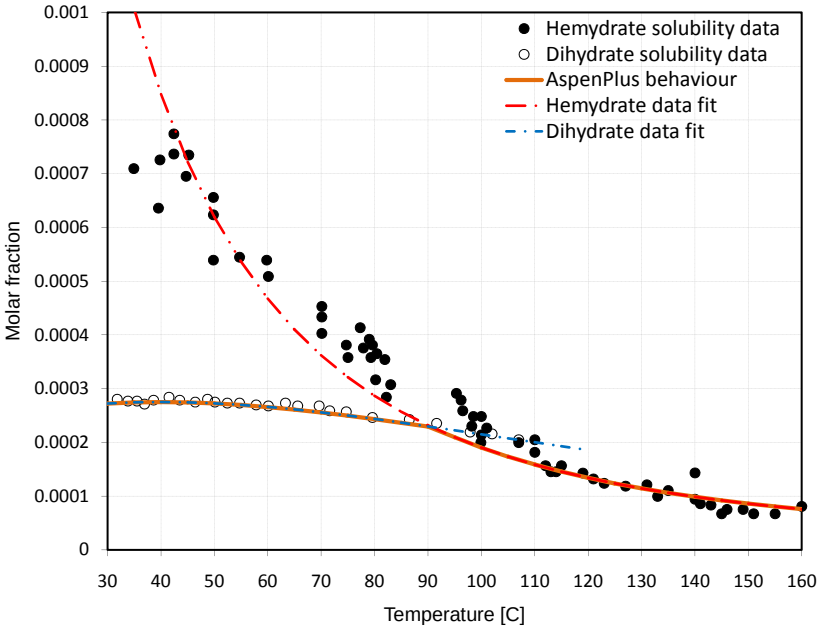


Figure 5.3: AspenPlus fitted data of hemyhidrate and dihydrate gypsum solubilities, data points from the review of Freyer and Voigt (2003).

- $CaSO_4 \cdot 2H_2O \longleftrightarrow 2H_2O + Ca2+ + SO_4^{2-}$, K_{Dihy}
- $CaSO_4 \cdot 0.5H_2O \longleftrightarrow 0.5H_2O + Ca2+ + SO_4^{2-}$, K_{Hemy}

Gypsum crystallisation is modelled by using a mixed suspension mixed product removal (MSMPR) crystalliser model (Dahlstrom *et al.*, 1999; Randolph & Maurice, 1988) . In this case the population balance for a well mixed crystalliser can be written as in Eq. 5.2.

$$\frac{d(nG)}{dt} + \frac{qn}{V} = 0 \tag{5.2}$$

where G is the crystals growth rate [m/s], n is the population density [no./m^3/m], V is the crystallizer volume [m^3] and q the volumetric discharge out flow [m^3/s][9]. If crystal growth rate is considered to be independent of crystal size then, Eq. 5.2, can be integrated as in Eq. 5.3.

$$n(L) = n^0 e^{\left(\frac{-L}{G\tau}\right)} \tag{5.3}$$

where n^0 is the population density of nuclei, and represents the value of $n(L)$ for $L = 0$, $n^0 = B^0/G^0$. The calculation of the amount of crystallised gypsum is based on equilibrium data, as the AspenPlus pre-built model used can not handle super saturation, so an overall nucleation rate B^0, and G are calculated as in Eqs. 5.4 and 5.5.

$$B^0 = k_b G^I M_T^J R^K \tag{5.4}$$

$$G = G_0(1 + \gamma_G L)^\alpha \tag{5.5}$$

[9] τ, the crystals residence time is calculated as $\tau = V/q$ [s].

The total mass of crystals (M_T) per unit of slurry volume [kg/m^3] can be calculated from the third moment of the particle size distribution (PSD)[10], as in Eq. 5.6.

$$M_T = \rho_c k_v \int_0^\infty L^3 n(L) dL = \rho_c k_v \int_0^\infty L^3 \frac{B^0}{G^0} e^{\left(\frac{-L}{G\tau}\right)} dL \tag{5.6}$$

Using Eqs. 5.4 and 5.5 to replace B^0 and G in 5.6 and considering that L is made discrete by the increments of the PSD, G^0 can be obtained from Eq. 5.6, which is the algorithm used in AspenTech (2005c, Ch. 8 Solids).

For this model in Eq. 5.4 the overall nucleation rate expression coefficient (k_b) is set to $1.0{\cdot}10^{15}$, and B^0 is considered to be linearly dependant on the crystals growth rate by setting $I = 1$, dependence on impeller rotation rate (R) and total mass of crystals (M_T) is dropped by setting J and K equal to 0. Moreover in this case, size independent growth rate was hypothesised by setting $\gamma_G = 0$.

The outlet of the second reactor is fed to an AspenPlus screen model (SCREEN) to mimic the filter behaviour. The model calculates the screen overflow (F_0) as in Eq. 5.7 and the selection function S_p which represents the fraction of feed particles in size range p that passes over the screen into the overflow product as in Eq. 5.8.

$$F_0 = \sum_p S_p F_p \tag{5.7}$$

$$S_p = \frac{1}{e^{A\left(1-\frac{dp_p}{S_0}\right)}} \forall\, dp_p < S_0 \tag{5.8}$$

Eq. 5.8 considers $S_p = 1 \;\forall\; dp_p \geq S_0$, where dp_p is the particles' diameter for size range p and S_0 the screen's opening. A is a function of the size of the screen opening as discussed in AspenTech (2005c, Ch. 8 Solids), while F_p are the mass flows related to each PSD size.

The kinetic and design parameters of the crystallizer and screen models have been effectively tuned to reproduce the process plant solids mass balance.

Fluorine air emissions of vapour effluents from rock attack reactors and the PA concentration unit are calculated considering a scrubbing efficiency of 99% on a mass basis. The efficiency value was based on BAT literature (EFMA, 2000; van-der Loo & Weeda, 2000; Wiesenberger, 2002). The PA concentrator unit and the HF scrubbers are modelled as single stage contactors that attain chemical equilibrium (AspenPlus' model FLASH2). H_2SiF_6 byproduct recovery from scrubbing liquors is calculated considering a fluorine compounds recovery of 90% mole basis EFMA (2000) and an outlet concentration of 22%. This separation unit is modelled using a component splitter, no rigorous treatment of this recovery stage is performed, due to the lack of industrial data available. This stage is the regarded as a "black box" model, that attains thermodynamical equilibrium.

5.1.2.2 Environmental model: trace species model

The trace component lixiviates are considered to be only 10% of the trace species released to the soil (van-der Loo & Weeda, 2000; Seijdel, 1999). For the sake of simplicity, trace species are treated separately; its chemical behaviour was not taken into account in the process simulation and only a mass balance is performed on them. The trace species considered in this

[10] AspenPlus calculates the j-th moment of the PSD as $m_p = \int_0^\infty L^p n(L) dL$; the PSD mean size ($\bar{L}$), is calculated as $\bar{L} = \frac{m_4}{m_3}$.

Table 5.1: Upper and lower values for trace species PG-WW partition coefficient value from Seijdel (1999). Trace specie flowing completely with gypsum are considered α_i^{up}=α_i^{low}=1, see Eqs. 5.11 and 5.12.

Trace specie (i)	α_i^{low}	α_i^{up}
As	0.00	0.05
Cd	0.00	0.05
Co	0.00	0.00
Cr	0.00	0.05
Cu	0.30	0.60
Hg	1.00	1.00
Mn	0.00	0.00
Ni	0.00	0.10
Pb	1.00	1.00
Ti	0.00	0.00
V	0.00	0.00
Zn	0.00	0.05

model are: As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Ti, V, and Zn. No distinction between different oxidation states is made, given that no information was available. The mass fraction compositions (w_i^r) of trace species in the phosphate rock and on sulphuric acid (w_i^r) are taken from the literature (Becker, 1989). A partition coefficient α_i, based on the work of Seijdel (1999) is considered for the split of each one of the i-th trace species between gypsum and filter liquor, see Table 5.1, where upper and lower values have been summarised.

Eqs. 5.9 and 5.10, correspond to a mass balance for each trace specie i; that combined with 5.11 and 5.12 provide the trace species distribution between outlet flow streams for each WWT option j.

$$total\ trace_{ij}^{in} = w_i^r rock\ flow_j^{in} + w_i^a acid\ flow_j^{in} \qquad \forall i,j \tag{5.9}$$

$$total\ trace_{ij}^{in} = gypsum\ trace_{ij}^{out} + total\ WW\ trace_{ij}^{out} \qquad \forall i,j \tag{5.10}$$

$$gypsum\ trace_{ij}^{out} = \alpha_i total\ trace_{ij}^{in} \qquad \forall i,j \tag{5.11}$$

$$total\ WW\ trace_{ij}^{out} = (1-\alpha_i) total\ trace_{ij}^{in} \qquad \forall i,j \tag{5.12}$$

Allocation of the traces amount in process outlet streams such as WW, PA product and HF recovered is based on the mass flows ratios given by the simulation (β_j and γ_j) for each option j[11]. Equations 5.13 and 5.14, allocate trace species between the PA product and the remaining streams. No emission from PA product is considered. Trace species in the other remaining streams are allocated using equations 5.15 and 5.16.

$$total\ WW\ trace_{ij}^{out} = PA\ traces_{ij}^{out} + WW\ trace_{ij}^{out} + HF\ traces_{ij}^{out} \qquad \forall i,j \tag{5.13}$$

$$PA\ traces_{ij}^{out} = \beta_j total\ WW\ trace_{ij}^{out} \qquad \forall i,j \tag{5.14}$$

$$WW\ trace_{ij}^{out} = (1-\beta_j)(1-\gamma_j) total\ WW\ trace_{ij}^{out} \qquad \forall i,j \tag{5.15}$$

$$HF\ traces_{ij}^{out} = (1-\beta_j)\gamma_j total\ WW\ trace_{ij}^{out} \qquad \forall i,j \tag{5.16}$$

Equations 5.9 to 5.16 account for the distribution of the trace species between all streams leaving the process. The emission to soil and water of the i-th trace species is modelled by considering an emission constant depending on the sink as follows as in Eqs. 5.17 and 5.18.

$$soil\ emission_{ij} = k_{GE} gypsum\ trace_{ij}^{out} \qquad \forall i,j \tag{5.17}$$

[11] Note that these ratios are independent of the trace species studied. In the case of γ_j for options 1 and 2, its value is zero, given that HF is not recovered as byproduct.

Table 5.2: Input variables ranges and pdfs used for MCS feed to AspenPlus.

Variable	Distribution	Range		Unit
		min	max	
Water inlet temperature	Uniform	25	33	ºC
Air inlet temperature	Uniform	20	30	ºC
Reactor 1 flash vessel temperature	Uniform	63	73	ºC
Reactor 2 flash vessel temperature	Uniform	63	73	ºC
Reactor 1 flash vessel pressure	Uniform	640	720	mmHg
Reactor 2 flash vessel pressure	Uniform	640	720	mmHg
Scrubber 1 pressure	Uniform	700	780	mmHg
Scrubber 2 pressure	Uniform	580	660	mmHg
Scrubber 3 pressure	Uniform	700	780	mmHg
Flash concentration unit pressure	Uniform	560	640	mmHg
Scrubber 4 pressure	Uniform	680	760	mmHg

$$water\ emission_{ij} = k_{WE} WW\ trace_{ij}^{out} \qquad \forall i,j \tag{5.18}$$

The previous formulation is a rigorous attempt to model trace species flow rates without considering the complex chemistry involved in such chemical system. The model presented contains species in very low concentrations (ppms and ppbs) and in different possible states of oxidation, and it is specially suited to the industrial data available. The value of k_{GE} was set to 10% for all the trace species that flow with gypsum in all WWT options (Seijdel, 1999). With regards to k_{WE}, it was considered that all the trace species in the water effluent are water emissions (100%). No emission of trace metals is considered to air.

5.1.2.3 Sources of models uncertainty

The uncertainty of the model rises from the industrial and literature data used. These data has a specific degree of accuracy and variability. Specifically, the uncertain parameters considered in this study can be separated into three different groups:

- *Process simulation model parameters*: simulation variables values and distribution functions are based on modelling hypothesis and available industrial data. Unit operation temperatures and pressures as well as temperatures of inlet streams are assumed to follow uniform pdfs (see Table 5.2).
- *Trace species model parameters*: distribution coefficients are taken from the literature Seijdel (1999) (w_i, α_i, k_{GE}, k_{WE}). The former variables uncertainty is taken into account using uniform pdfs (for the case of α_i see table 5.1). Others variables that are calculated from simulation results (see Table 5.3, for $rock\ Flow_j^{in}$, β_j, γ_j), are modelled considering normal or log normal pdfs.
- *Parameters from other production SC echelons*: these parameters are associated to production of sulphuric acid, phosphate rock and lime as well as electricity and heat generation. The pdfs used are normal or lognormal, and the pdf's parameters depend on the information available in the Ecoinvent database.

The first two items represent data that corresponds to foreground processes while the third item represents data that remains in the background system, where individual plants and operations cannot be identified. A Monte Carlo Sampling (MCS) scheme was used to treat the uncertainty rising from model parameters. The MCS was implemented in two consecutive stages. The first stage deals with the first group of uncertain parameters and is implemented in Matlab (MathWorks, 2005), which generates several equiprobable scenarios based on the pdfs proposed. These scenarios are fed to AspenPlus using the Windows COM interface. Here a simulation is run for every scenario and the associated results are compiled for the calculation of a partial LCI. This LCI corresponds to the simulated echelon of PA production associated with a waste treatment option. In a second stage the foreground information compiled

in the first stage is used in combination with information arising from the trace model and Ecoinvent databases to calculate the complete LCI, which covers the entire supply chain (SC) of the PA (see Fig. 5.4).

The selection of the process simulation variables that are regarded as stochastic, comes from a sensitivity analysis (SA) that identifies which variables have the highest influence on the emissions of HF into air and water. The stochastic variables and their selected pdf can be seen in table 5.2. A uniform pdf is used given that industrial information regarding most probable value was not available. Moreover, the use of a uniform pdf allows for the selection of operating parameters that allows for process simulation model to converge on all scenarios.

5.1.2.4 Process model validation and testing

The number of simulation runs, equal to the number of scenarios, was set to 1400. This number was fixed by gradually increasing the number of scenarios, in batches of 100 scenarios, and stopping whenever no significant changes were detected in the mean and standard deviation of the simulation results (as shown in Alg. 3.1). Matlab and AspenPlus inter connectivity is accomplished by using the interface described in section 4.2.2 and the algorithm shown in C.1. Table 5.3 summarises the results obtained by following the above mentioned procedure. In particular, it shows the mean value (Eq. 3.20) and standard deviation (Eq. 3.21) of the AspenPlus simulation results for each WWT option generated by MCS. These results are expressed per kg of PA produced.

The results show that the three options lead to similar outcomes in most of the calculated ratios. Nevertheless, the following differences in mean values are observed:

- *Lime consumption*: option 2 leads to a higher consumption compared to option 3. This is due to the fact that in option 3 the amount of acid being dumped to ponds is lower, requiring less neutralising agent.
- *HF emissions to water*: options 1 and 2, give similar values, while option 3 results in an order of magnitude lower. This is attributed to the recovering of HF as a byproduct.
- *Steam consumption*: in option 3 is slightly higher than in the other two options. This is mainly due to the steam consumption associated with the recovery of HF.

From the results shown in Table 5.3, it can be concluded that the steam consumption related to impacts of option 3 will be bigger than those corresponding to the other options, whereas water and air emission impacts of options 1 and 2 are larger than those in option 3. It is also found that all coefficients of variation (CV, see Eq. 3.23) values are small and lower than 5% for all results. The CI calculation reported in Table 5.3 assumes to have a random sample from a normally distributed population, see Eq. 3.24.

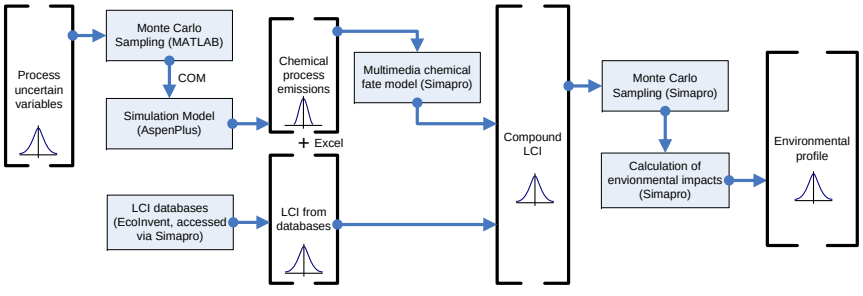


Figure 5.4: Used models and its interconnections when dealing with uncertainty in model parameters.

To analyse the MCS results and for providing a means for model validation two different techniques are applied: (i) linear correlation metrics (discussed in section 3.2.2), and (ii) principal components analysis (discussed in section 3.3.1).

Linear correlation metrics

The problem is studied from the input-output correlation point of view by calculating standardised regression coefficients (SRC, see Eq. 3.27) which are shown in Tables 5.4 to 5.6. Tables 5.7 to 5.9 summarise the partial correlation coefficients (PCC, see Eq. 3.28), while Tables 5.10 to 5.12 show the % of variance explained by each variable considering linear dependence, calculated using the algorithm 3.2.

With regards to SCR values, there is a strong correlation between reactor temperatures ($TempRC_1$, $TempRC_2$), and air emissions (HF_{air}^{OUT}, $CO_2{}_{air}^{OUT}$), the higher the temperature, higher the emission, it is interesting to note that this happens for both reactors and for all WWT options. This fact was expected given that chemical and phase equilibrium are attained, the correlation coefficient is larger for the second reactor, which is downstream of the first. Pressure in the concentration unit (PressEvaPA), is found to be related to CO_2 emission, higher the pressure lower the emission, this behaviour can be explained by the thermodynamic model used (ENRTL-activity coefficient and Henry's law) which increases the CO_2 solubility with pressure. In the case of water emissions (HF_{water}^{OUT}, $H_2SO_4{}_{water}^{OUT}$, $H_3PO_4{}_{water}^{OUT}$), reactor temperatures are also found to be correlated; in the case of options 1 and 2 a similar behaviour is found, higher temperatures increase H_2SO_4 water emissions, this could be due to an increase of gypsum solubility, while a decrease of HF emission could be due to its lower solubility in higher temperature and more acidic media. In the case of PCC results (see Tables 5.7 to 5.9), there is correlation between reactors temperatures and air emissions (HF and CO_2). The correlation is found for both reactors in all options, with higher PCCs in the case of the temperature of the 2nd reactor, meaning a bigger significance of that variable. In the case of water emissions, reactors temperature and pressure are found to be significantly correlated.

The values reported in the first row of Tables 5.7 to 5.9 represent the amount of variance which can not be explained by linear relationships. For some output variables, such as $Rock^{IN}$, $H_3PO_4{}_{water}^{OUT}$, the regression metrics are not suitable, given that they can only explain less that 5% of the output variance. For other output variables the most important input variable are the reactor temperatures ($TempRC_1$, $TempRC_2$) and the pressures associated to the concentration unit (PressEvaPA, $PressScrub_4$), which in most cases account for more than 60% of the model's output variance. In all cases the variance explained by $TempRC_2$ is higher than the amount explained by $TempRC_1$.

Table 5.3: MCS AspenPlus simulation results, mean values are expressed in kg/kg

Variable	Option 1				Option 2				Option 3			
	Mean	STD	CV	95% CI	Mean	STD	CV	95% CI	Mean	STD	CV	95% CI
$Rock^{IN}$	1.35E+00	7.40E-06	0.00%	3.32E-07	1.35E+00	6.93E-06	0.00%	2.56E-07	1.35E+00	6.79E-06	0.00%	3.50E-07
$H_2SO_4{}^{IN}$	1.83E+00	1.00E-05	0.00%	4.50E-07	1.83E+00	9.40E-06	0.00%	2.56E-07	1.83E+00	9.22E-06	0.00%	4.75E-07
STM^{IN}	5.14E-01	7.64E-03	1.49%	3.43E-04	5.51E-01	7.46E-03	1.35%	6.73E-04	**5.66E-01**	7.44E-03	1.32%	3.83E-04
$Lime^{IN}$	****	****	****	****	**4.45E-01**	6.36E-05	0.01%	7.11E-06	4.10E-01	2.16E-05	0.01%	1.11E-06
HF_{air}^{OUT}	**1.01E-05**	2.98E-07	2.96%	1.34E-08	1.00E-05	2.86E-07	2.84%	1.41E-03	1.00E-05	2.92E-07	2.91%	1.50E-08
$CO_2{}_{air}^{OUT}$	6.15E-02	9.80E-05	0.16%	4.40E-06	6.15E-02	9.55E-05	0.16%	7.72E-05	6.15E-02	9.69E-05	0.16%	4.99E-06
HF_{water}^{OUT}	**6.49E-02**	1.19E-04	0.18%	5.33E-06	6.15E-02	1.19E-04	0.19%	9.61E-05	6.80E-03	4.06E-05	0.60%	2.10E-06
$H_2SO_4{}_{water}^{OUT}$	9.78E-01	5.87E-03	0.60%	2.64E-04	9.78E-01	5.65E-03	0.58%	2.87E-04	9.78E-01	5.74E-03	0.59%	2.96E-04
$H_3PO_4{}_{water}^{OUT}$	3.34E-03	1.84E-08	0.00%	8.24E-10	3.34E-03	1.72E-08	0.00%	2.56E-07	3.34E-03	1.69E-08	0.00%	8.69E-10
$H_2SiF_6{}_{rec.}^{OUT}$	****	****	****	****	****	****	****	****	4.42E-02	7.99E-04	1.81%	4.12E-05
β_j	5.14E-01	9.80E-04	0.19%	4.40E-05	5.14E-01	9.51E-04	0.18%	9.19E-05	5.14E-01	9.81E-04	0.19%	5.05E-05
γ_j	****	****	****	****	****	****	****	****	1.95E-01	3.73E-04	0.19%	1.92E-05

Table 5.4: SRC values for input output variables in the case of Option 1

In vars \ Out vars	$Rock^{IN}$	$H_2SO_4{}^{IN}$	STM^{IN}	HF_{air}^{OUT}	$CO_2{}_{air}^{OUT}$	HF_{water}^{OUT}	$H_2SO_4{}_{water}^{OUT}$	$H_3PO_4{}_{water}^{OUT}$	β_j
$TempWater^{IN}$	0.038	0.038	0.000	-0.001	-0.001	0.000	0.001	0.038	0.000
$TempAir^{IN}$	-0.018	-0.018	-0.016	0.014	-0.007	-0.020	0.003	-0.018	-0.007
$TempRC_1$	-0.023	-0.023	**-0.241**	**0.521**	**-0.306**	**-0.291**	**0.382**	-0.023	**-0.323**
$TempRC_2$	-0.117	-0.117	**-0.865**	**0.793**	**-0.361**	**-0.937**	**0.863**	-0.116	**-0.812**
$PressRC_1$	0.026	0.026	0.057	0.023	-0.019	-0.052	-0.163	0.026	0.155
$PressRC_2$	-0.009	-0.009	0.041	-0.048	0.033	0.009	-0.088	-0.010	0.086
$PressScrub_1$	0.010	0.010	-0.020	0.015	-0.015	-0.009	0.004	0.010	-0.021
$PressScrub_2$	0.010	0.010	0.010	-0.005	0.005	0.005	-0.001	0.010	0.009
$PressScrub_3$	0.009	0.009	-0.007	0.003	-0.004	-0.002	-0.001	0.009	-0.009
$PressEvaPA$	0.028	0.028	0.188	0.086	**-0.838**	0.021	0.000	0.028	0.000
$PressScrub_4$	-0.018	-0.018	0.006	-0.015	0.004	0.003	-0.009	-0.018	0.004

Table 5.5: SRC values for input output variables in the case of Option 2

In vars \ Out vars	$Rock^{IN}$	$H_2SO_4{}^{IN}$	STM^{IN}	$Lime^{IN}$	HF_{air}^{OUT}	$CO_2{}_{air}^{OUT}$	HF_{water}^{OUT}	$H_2SO_4{}_{water}^{OUT}$	$H_3PO_4{}_{water}^{OUT}$	β_j
$TempWater^{IN}$	0.027	0.027	0.002	0.000	0.001	0.002	0.001	0.000	0.027	0.003
$TempAir^{IN}$	0.059	0.058	-0.010	-0.019	0.010	-0.008	-0.019	0.004	0.059	-0.001
$TempRC_1$	-0.011	-0.011	**-0.250**	**-0.357**	**0.534**	**-0.311**	**-0.289**	**0.389**	-0.011	**-0.342**
$TempRC_2$	-0.024	-0.023	**-0.919**	**-0.921**	**0.832**	**-0.384**	**-0.951**	**0.889**	-0.024	**-0.877**
$PressRC_1$	-0.001	-0.001	0.045	-0.071	0.014	-0.020	-0.053	-0.180	-0.001	0.139
$PressRC_2$	-0.070	-0.070	0.046	0.007	-0.056	0.036	0.011	-0.089	-0.070	0.093
$PressScrub_1$	0.001	0.001	-0.013	-0.032	0.002	-0.006	-0.002	-0.010	0.001	-0.016
$PressScrub_2$	0.018	0.018	-0.004	-0.003	0.004	-0.001	-0.001	-0.005	0.018	-0.006
$PressScrub_3$	-0.020	-0.019	0.008	0.002	-0.001	0.002	0.003	0.006	-0.019	0.009
$PressEvaPA$	0.020	0.021	0.183	0.080	0.085	**-0.853**	0.018	-0.006	0.020	-0.009
$PressScrub_4$	0.004	0.004	0.004	-0.018	-0.008	0.000	0.001	0.005	0.004	0.004

Table 5.6: SRC values for input output variables in the case of Option 3

In vars \ Out vars	$Rock^{IN}$	$H_2SO_4{}^{IN}$	STM^{IN}	$Lime^{IN}$	HF^{OUT}_{air}	$CO_2{}^{OUT}_{air}$	HF^{OUT}_{water}	$H_2SO_4{}^{OUT}_{water}$	$H_3PO_4{}^{OUT}_{water}$	$H_2SiF_6{}^{OUT}_{rec.}$	β_j	γ_j
$TempWater^{IN}$	-0.064	-0.064	-0.020	-0.022	0.002	-0.006	0.000	-0.014	-0.064	-0.005	-0.023	0.013
$TempAir^{IN}$	-0.023	-0.023	-0.009	-0.003	0.011	-0.003	0.005	0.004	-0.023	-0.020	-0.004	-0.008
$TempRC_1$	0.032	0.031	0.006	**-0.797**	**0.529**	**-0.306**	**0.430**	**0.389**	0.031	**-0.432**	**-0.326**	**0.515**
$TempRC_2$	-0.077	-0.076	**-0.890**	0.100	**0.794**	**-0.366**	**-0.525**	**0.859**	-0.076	**-0.847**	**-0.825**	**-0.673**
$PressRC_1$	-0.010	-0.010	0.077	-0.061	0.007	-0.014	0.146	-0.188	-0.010	-0.104	0.148	0.087
$PressRC_2$	0.030	0.030	0.026	0.064	-0.059	0.036	-0.060	-0.095	0.030	0.032	0.095	-0.027
$PressScrub_1$	-0.005	-0.004	-0.051	-0.081	0.007	-0.003	0.143	0.013	-0.004	-0.044	0.008	0.061
$PressScrub_2$	-0.006	-0.006	-0.005	0.005	0.009	-0.004	-0.016	0.007	-0.006	0.004	-0.002	-0.005
$PressScrub_3$	0.026	0.026	-0.005	0.000	0.009	-0.003	-0.003	0.001	0.026	-0.001	-0.005	-0.003
PressEvaPA	-0.013	-0.013	**0.203**	0.057	0.076	**-0.843**	0.020	-0.015	-0.013	0.023	0.005	-0.016
$PressScrub_4$	-0.011	-0.011	0.022	-0.044	-0.009	-0.004	**0.536**	-0.004	-0.011	-0.178	-0.008	0.030

Table 5.7: PCC values for input output variables in the case of Option 1

In vars \ Out vars	$Rock^{IN}$	$H_2SO_4{}^{IN}$	STM^{IN}	HF^{OUT}_{air}	$CO_2{}^{OUT}_{air}$	HF^{OUT}_{water}	$H_2SO_4{}^{OUT}_{water}$	$H_3PO_4{}^{OUT}_{water}$	β_j
$TempWater^{IN}$	0.038	0.038	0.001	0.004	0.007	0.002	0.002	0.038	0.001
$TempAir^{IN}$	0.018	0.018	0.040	0.054	0.032	0.124	0.013	0.018	0.017
$TempRC_1$	0.023	0.023	**0.525**	**0.892**	**0.817**	**0.880**	**0.845**	0.023	**0.595**
$TempRC_2$	0.117	0.117	**0.911**	**0.949**	**0.858**	**0.986**	**0.963**	0.116	**0.881**
$PressRC_1$	0.026	0.026	0.145	0.088	0.087	**0.314**	**0.561**	0.026	**0.335**
$PressRC_2$	0.009	0.009	0.104	0.177	0.151	0.060	**0.340**	0.010	0.192
$PressScrub_1$	0.010	0.010	0.052	0.059	0.070	0.056	0.017	0.010	0.047
$PressScrub_2$	0.010	0.011	0.026	0.018	0.025	0.029	0.003	0.010	0.021
$PressScrub_3$	0.009	0.009	0.019	0.011	0.017	0.012	0.002	0.009	0.021
PressEvaPA	0.028	0.028	**0.434**	**0.309**	**0.968**	0.133	0.001	0.028	0.001
$PressScrub_4$	0.018	0.018	0.015	0.057	0.020	0.018	0.039	0.018	0.008

Table 5.8: PCC values for input output variables in the case of Option 2

In vars \ Out vars	$Rock^{IN}$	$H_2SO_4{}^{IN}$	STM^{IN}	$Lime^{IN}$	HF^{OUT}_{air}	$CO_2{}^{OUT}_{air}$	HF^{OUT}_{water}	$H_2SO_4{}^{OUT}_{water}$	$H_3PO_4{}^{OUT}_{water}$	β_j
$TempWater^{IN}$	0.027	0.027	0.009	0.001	0.006	0.019	0.013	0.001	0.027	0.010
$TempAir^{IN}$	0.059	0.059	0.039	0.155	0.071	0.077	0.204	0.020	0.059	0.003
$TempRC_1$	0.011	0.011	**0.697**	**0.948**	**0.969**	**0.950**	**0.953**	**0.880**	0.011	**0.725**
$TempRC_2$	0.023	0.023	**0.963**	**0.992**	**0.987**	**0.966**	**0.995**	**0.973**	0.023	**0.937**
$PressRC_1$	0.001	0.001	0.171	**0.510**	0.105	0.192	**0.504**	**0.651**	0.001	**0.392**
$PressRC_2$	0.070	0.070	0.175	0.060	**0.381**	**0.337**	0.119	**0.391**	0.069	0.275
$PressScrub_1$	0.001	0.001	0.050	0.262	0.017	0.064	0.025	0.050	0.001	0.049
$PressScrub_2$	0.018	0.018	0.017	0.024	0.028	0.008	0.008	0.026	0.018	0.017
$PressScrub_3$	0.020	0.019	0.031	0.014	0.010	0.022	0.033	0.030	0.019	0.027
PressEvaPA	0.020	0.021	**0.580**	**0.560**	**0.531**	**0.993**	0.192	0.029	0.021	0.029
$PressScrub_4$	0.004	0.004	0.014	0.149	0.059	0.003	0.012	0.026	0.004	0.012

Table 5.9: PCC values for input output variables in the case of Option 3

In vars \ Out vars	$Rock^{IN}$	$H_2SO_4{}^{IN}$	STM^{IN}	$Lime^{IN}$	HF_{air}^{OUT}	$CO_2{}_{air}^{OUT}$	HF_{water}^{OUT}	$H_2SO_4{}_{water}^{OUT}$	$H_3PO_4{}_{water}^{OUT}$	$H_2SiF_6{}_{rec.}^{OUT}$	β_j	γ_j
$TempWater^{IN}$	0.064	0.064	0.048	0.038	0.009	0.029	0.001	0.058	0.064	0.022	0.054	0.026
$TempAir^{IN}$	0.023	0.023	0.022	0.005	0.044	0.013	0.011	0.016	0.023	0.094	0.009	0.016
$TempRC_1$	0.032	0.031	0.015	**0.812**	**0.897**	**0.838**	**0.686**	**0.844**	0.031	**0.896**	**0.610**	**0.703**
$TempRC_2$	0.077	0.076	**0.907**	0.172	**0.950**	**0.879**	**0.755**	**0.961**	0.076	**0.970**	**0.890**	**0.792**
$PressRC_1$	0.010	0.010	0.184	0.106	0.029	0.070	**0.305**	**0.606**	0.010	**0.438**	**0.330**	0.164
$PressRC_2$	0.030	0.030	0.063	0.110	0.219	0.177	0.130	**0.359**	0.030	0.148	0.219	0.051
$PressScrub_1$	0.005	0.004	0.122	0.141	0.027	0.014	0.299	0.051	0.005	0.201	0.019	0.117
$PressScrub_2$	0.006	0.006	0.011	0.009	0.035	0.020	0.036	0.030	0.006	0.018	0.005	0.010
$PressScrub_3$	0.026	0.026	0.012	0.000	0.033	0.016	0.007	0.002	0.026	0.004	0.012	0.006
PressEvaPA	0.013	0.013	**0.441**	0.100	0.279	**0.973**	0.043	0.062	0.013	0.108	0.012	0.030
$PressScrub_4$	0.011	0.011	0.054	0.077	0.036	0.018	**0.761**	0.015	0.011	**0.641**	0.019	0.058

Table 5.10: Input variables rank for all output variables in the case of Option 1

In vars \ Out vars	$Rock^{IN}$		STM^{IN}		β_j		HF_{air}^{OUT}		$CO_2{}_{air}^{OUT}$		HF_{water}^{OUT}		$H_2SO_4{}_{water}^{OUT}$		$H_3PO_4{}_{water}^{OUT}$	
	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var
Not explained	0	**98.416**	0	**15.182**	0	**19.003**	0	6.975	0	4.644	0	**20.398**	0	**23.048**	0	**98.828**
$TempRC_1$	4	0.063	2	5.559	2	**10.243**	2	**27.176**	3	**9.298**	2	7.618	2	**12.477**	3	0.039
$TempRC_2$	1	1.321	1	**75.230**	1	**67.513**	1	**64.779**	2	**13.495**	1	**71.376**	1	**61.644**	1	0.909
$PressRC_1$	3	0.067	4	0.336	3	2.467	5	0.055	5	0.035	3	0.407	3	1.848	6	0.010
$PressRC_2$	8	0.008	5	0.157	4	0.712	4	0.211	4	0.101	5	0.043	4	0.900	5	0.025
$PressScrub_1$	6	0.010	6	0.041	5	0.042	6	0.023	6	0.022	6	0.019	6	0.026	9	0.000
$PressScrub_2$	7	0.009	7	0.009	7	0.008	8	0.002	7	0.003	8	0.004	9	0.000	4	0.038
$PressScrub_3$	9	0.007	8	0.006	6	0.009	9	0.001	9	0.001	9	0.001	8	0.000	7	0.001
PressEvaPA	2	0.074	3	3.477	9	0.000	3	0.755	1	**72.399**	4	0.130	5	0.036	2	0.148
$PressScrub_4$	5	0.025	9	0.004	8	0.001	7	0.022	8	0.002	7	0.004	7	0.020	8	0.001

Table 5.11: Input variables rank for all output variables in the case of Option 2

In vars \ Out vars	$Rock^{IN}$		$Lime^{IN}$		STM^{IN}		β_j		HF_{air}^{OUT}		$CO_2{}_{air}^{OUT}$		HF_{water}^{OUT}		$H_2SO_4{}_{water}^{OUT}$		$H_3PO_4{}_{water}^{OUT}$	
	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var
Not explained	0	**99.325**	0	1.443	0	**6.558**	0	**10.505**	0	1.824	0	1.034	0	**99.483**	0	**99.483**	0	**99.483**
$TempRC_1$	6	0.012	2	**12.626**	2	5.812	2	**11.405**	2	**29.095**	3	**9.759**	6	0.006	6	0.007	6	0.007
$TempRC_2$	2	0.047	1	**84.648**	1	**83.952**	1	**75.225**	1	**67.981**	2	**14.507**	5	0.009	5	0.010	5	0.009
$PressRC_1$	8	0.000	4	0.498	5	0.207	3	1.935	5	0.019	5	0.039	3	0.121	3	0.121	3	0.121
$PressRC_2$	1	0.498	7	0.005	4	0.208	4	0.885	4	0.316	4	0.133	2	0.141	2	0.143	2	0.141
$PressScrub_1$	9	0.000	5	0.106	6	0.016	5	0.025	8	0.001	6	0.004	4	0.013	4	0.012	4	0.013
$PressScrub_2$	5	0.028	8	0.001	8	0.002	8	0.003	7	0.001	8	0.000	8	0.003	8	0.003	8	0.003
$PressScrub_3$	4	0.043	9	0.000	7	0.006	7	0.008	9	0.000	7	0.001	9	0.002	9	0.002	9	0.002
PressEvaPA	3	0.044	3	0.638	3	3.238	6	0.008	3	0.758	1	**74.522**	1	0.215	1	0.214	1	0.215
$PressScrub_4$	7	0.003	6	0.034	9	0.001	9	0.002	6	0.006	9	0.000	7	0.006	7	0.005	7	0.006

Table 5.12: Input variables rank for all output variables in the case of Option 3

In vars \ Out vars	$Rock^{IN}$		$Lime^{IN}$		$H_2SiF_6^{OUT}_{rec.}$		STM^{IN}		β_j		γ_j		HF^{OUT}_{air}		$CO_2^{OUT}_{air}$		HF^{OUT}_{water}		$H_2SO_4^{OUT}_{water}$		$H_3PO_4^{OUT}_{water}$	
	#	%	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var	#	%Var
Not explained	0	**99.137**	0	**32.704**	0	**4.584**	0	**16.956**	0	**17.917**	0	**26.931**	0	6.760	0	3.954	0	20.664	0	6.084	0	**99.142**
$TempRC_1$	2	0.108	1	**64.332**	2	**19.044**	7	0.005	2	**10.517**	2	**27.038**	2	**28.084**	3	**9.441**	3	**19.406**	2	**14.988**	2	0.107
$TempRC_2$	1	0.564	2	1.053	1	**71.843**	1	**78.004**	1	**68.353**	1	**44.738**	1	**64.184**	2	**13.545**	2	**26.849**	1	**74.391**	1	0.562
$PressRC_1$	7	0.006	5	0.343	4	1.087	3	0.596	3	2.297	3	0.738	8	0.006	5	0.018	4	2.213	3	3.593	7	0.006
$PressRC_2$	3	0.094	4	0.382	6	0.099	5	0.062	4	0.894	6	0.067	4	0.338	4	0.126	6	0.370	4	0.898	3	0.093
$PressScrub_1$	9	0.003	3	0.664	5	0.199	4	0.271	5	0.008	4	0.365	9	0.005	9	0.001	5	2.119	6	0.016	9	0.003
$PressScrub_2$	8	0.003	8	0.003	8	0.001	9	0.002	9	0.000	8	0.003	5	0.009	6	0.002	8	0.027	7	0.006	8	0.003
$PressScrub_3$	4	0.059	9	0.000	9	0.000	8	0.003	7	0.003	9	0.001	7	0.007	8	0.001	9	0.001	9	0.000	4	0.059
PressEvaPA	5	0.016	6	0.326	7	0.054	2	4.053	8	0.003	7	0.024	3	0.598	1	**72.912**	7	0.040	5	0.023	5	0.016
$PressScrub_4$	6	0.009	7	0.192	3	3.088	6	0.048	6	0.007	5	0.095	6	0.008	7	0.001	1	**28.310**	8	0.001	6	0.009

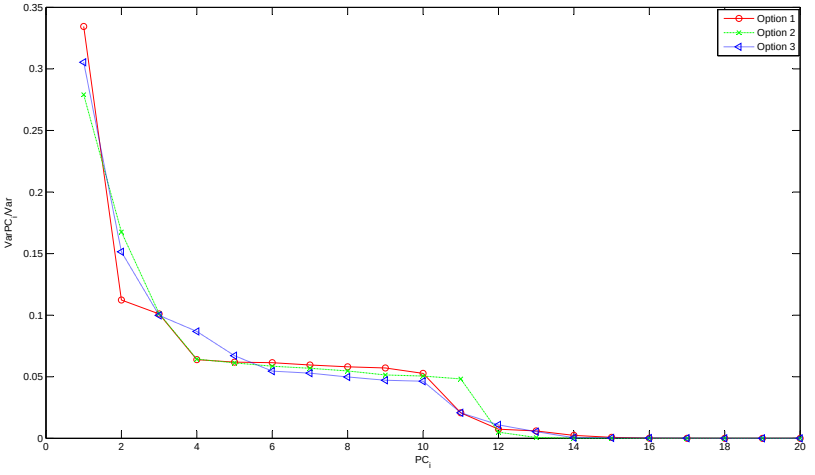


Figure 5.5: Variance explained by each PC for each of the WWT options

Principal component analysis

The principal component analysis (PCA) method, is applied to all output variables for each WWT option separately. The eigen values associated to each principal component (pc) were calculated for all three WWT options (see Fig. 5.5). Almost the same behaviour is found, most of the variance is explained by the 3 first pcs, and then an abrupt drop in explained variance is found for the remaining; however the amount of variance explained by these three pcs is nearly 55%. The number of pcs that can be selected varies depending on the variance explained, it is common practise to select pcs up to a variance explained of 75%. In the case of Option 1 the number of pcs selected would be 7 (see Fig. 5.6), in the case of Option 2 the number is 8 (see Fig. 5.7), while in the case of Option 3 the number is 6 (see Fig. 5.8).

In the case of Option 1 (see Fig 5.6), pc1 is mainly associated to $TempRC_2$, STM^{IN}, β_j, HF^{OUT}_{air}, HF^{OUT}_{water} and $H_2SO_4{}^{OUT}_{water}$, this combination explains nearly 33% of the variance. This pc1 is associated to the relationship of $TempRC_2$ with all output variables that were found important in Table 5.7. The pc2 is associated to PressEvaPA, $CO_2{}^{OUT}_{air}$ and $H_3PO_4{}^{OUT}_{water}$, clearly this pc2 extracts the relationship found in table 5.7 for the case of $CO_2{}^{OUT}_{air}$, and also includes the $H_3PO_4{}^{OUT}_{water}$. The pc3 in this processing option is associated to operating pressures ($PressRC_1$, $PressRC_2$, $PressScrub_3$ and PressEvaPA) and the emissions of $CO_2{}^{OUT}_{air}$ and $H_3PO_4{}^{OUT}_{water}$, this relationship was not discovered when analysing the variance as in the previous section.

In the case of Option 2, pc1 is associated to $TempRC_2$, $Lime^{IN}$, STM^{IN}, β_j, HF^{OUT}_{air}, and explains 28% of the total variance. The relationship between $TempRC_2$ and HF^{OUT}_{air} is maintained, but the correlations of HF^{OUT}_{water} and $H_2SO_4{}^{OUT}_{water}$ are better explained by pc2. It is interesting to note that in this WWT option pc1 is associated mostly to the variance of air emissions and its relation to reactor 2 temperature (similar results were found for pc1 in option 1 and in table 5.8), while pc2 to water emissions. In the case of pc3, it is defined by two large coefficients for PressEvaPA and $CO_2{}^{OUT}_{air}$, which clearly shows their relation (increases of the pressure lower the CO_2 emissions), this was already found in option 1 for pc2.

In the case of Option 3, pc1 explains nearly 30% of the output variance and is associated to $TempRC_2$ and HF related variables ($H_2SiF_6{}^{OUT}_{recovered}$, HF^{OUT}_{air} and HF^{OUT}_{water}), and also to variables such as the $H_2SO_4{}^{OUT}_{water}$, STM^{IN}, β_j and γ_j. Pc1 shows the expected behaviour with regards to HF, higher recovery is associated to lower HF air emissions, moreover it describes the relationship between changes in $TempRC_2$, similarly to options 1 and 2, this relationship can also

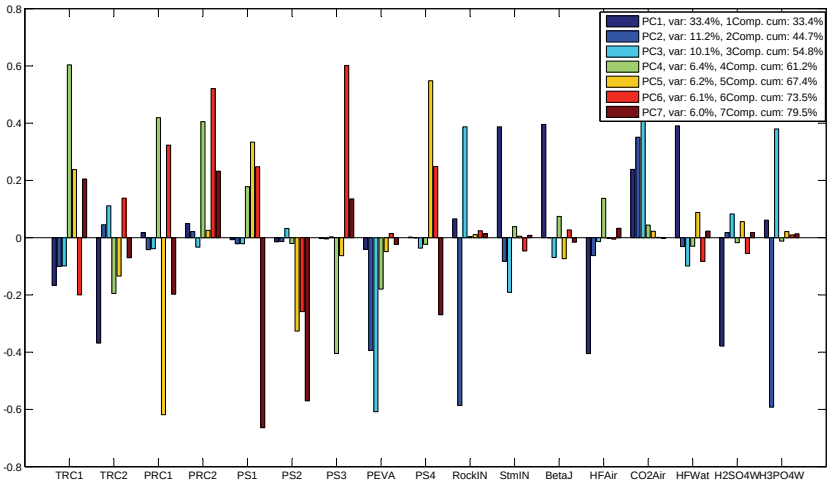


Figure 5.6: Principal component coefficients for WWT option 1

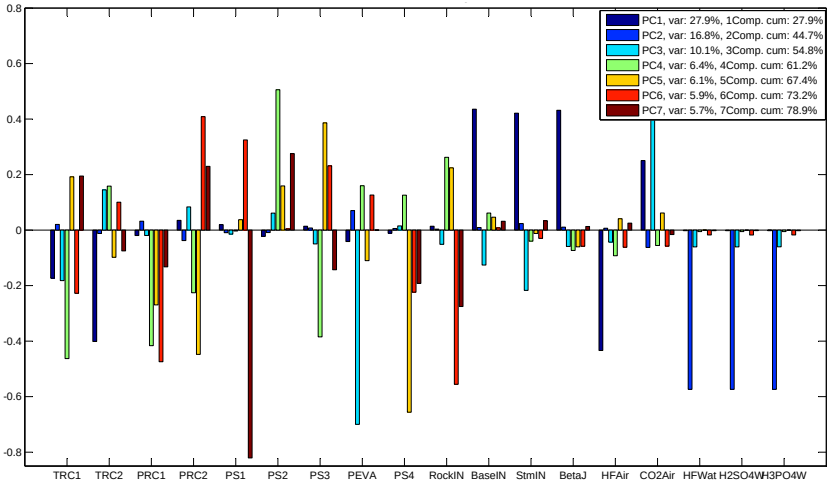


Figure 5.7: Principal component coefficients for WWT option 2

be grasped by looking at the values of Table 5.9, for this input variable. The pc2, explaining 15% of the variance, is associated only to 4 variables TempRC_1, Lime^{IN} $\text{HF}^{\text{OUT}}_{\text{water}}$ and γ_j, this can also be foreseen from the values reported in Table 5.9, for the case of TempRC_1. Pc3 of this WWT option represents the relationship between Rock^{IN} and $\text{H}_3\text{PO}_4{}^{\text{OUT}}_{\text{water}}$, which were found uncorrelated to all input variables, while pc4 records the relationship between PressEvaPA and $\text{CO}_2{}^{\text{OUT}}_{\text{air}}$, previously found in pc3 for options 1 and 2.

The sensitivity and principal component analysis have been applied to study input output variables relationships. SRCs and PCCs results pointed out some of the important relations, while variance decomposition using linear regression showed how much each input variable affects the behaviour of the output variable. In the case of PCA, it showed that not all information could be grasped using linear metrics, pointing out relations that the linear regression metrics missed. In all cases these results showed that the current model behaves as it is expected regarding emission estimation, and served as a validation of the process model.

The MCS applied to the process model provides with a picture of the uncertainty in emis-

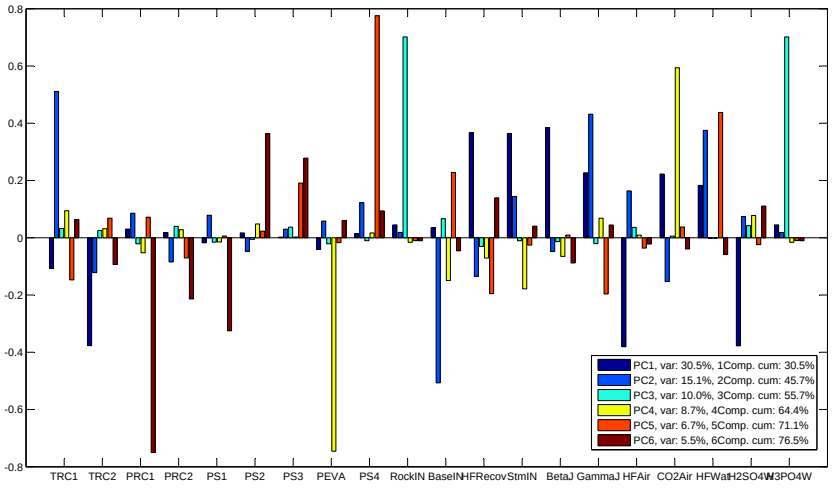


Figure 5.8: Principal component coefficients for WWT option 3

sions that is found related to only process conditions. It clearly shows the need for process simulation to cope with the non-linearity which is found in the estimation of process emissions.

5.1.3 Step 3 - Environmental metrics calculation

The quantification of the environmental performance of the PA production process requires the use of an impact model that allows for the translation of the process environmental interventions into EIs.

The EIs analysed in this case study are those corresponding to method CML v2 with the normalisation and weighting coefficients set for west Europe in 1995[12], see section 3.4.3.

The calculation of these impacts is carried out using SimaPro (de Schryver *et al.*, 2006), which is also used to access the Ecoinvent database (Ecoinvent, 2006), (see Figure 5.2). The latter source provides the inventory of emissions associated with the most widely used manufacturing technologies found in Europe. Consumption of raw materials (inlets) and outlets flows (emissions) of the PA process are taken from the simulation results, and are fitted to a probability distribution function (pdf)which is used in SimaPro. SimaPro also allows for simple mathematical relations such as the ones used in Eqs. 5.17 and 5.18 to be coded, and used for LCI calculation. This allows for coding the environmental emission model regarding trace species (Eqs. 5.9 to 5.18) to be coded inside SimaPro. Moreover the uncertainty associated to this model parameters can be handled together with the LCI uncertainty parameters.

The combined use of process simulation and standard data from the environmental database (Ecoinvent, 2006) allows for the calculation of the inventory of emissions required to determine the EI of each WWT option being analysed. With regard to Ecoinvent data used, it is considered that the sulphuric acid is produced in Europe using BAT. Other consumption's such as electricity and heating are taken from process simulation results (Table 5.3) and LCIs available in Ecoinvent database. Phosphate rock processing is considered to be carried out in a similar way as it is done in the United States (US). These processes take into account the following activities: mining process, transport to beneficiation plant, wet processing including

[12]The characterisation results are normalised according to the work of Huijbregts *et al.* (2003), which makes use of the cumulative EIs per year accounted for the whole Western Europe. The use of such normalisation scheme allows for comparison of emissions into the context of Europe.

screening, washing and flotation. It also considers land use for mining and reclamation however it does not take into account drying or calcination and considers energy consumption data related to mass of rock moved.

Regarding H_2SiF_6 byproduct recovery, its impact calculation has been carried out using an LCI which provided the environmental gain that is achieved when the product is recovered instead of being produced from virgin material. The data for the production of fluosilicic acid was taken from the literature (EFMA, 2000) and completed with information from Ecoinvent database. In this case it is produced from apatite rock treated with H_2SO_4.

5.1.3.1 Deterministic impact assessment approach

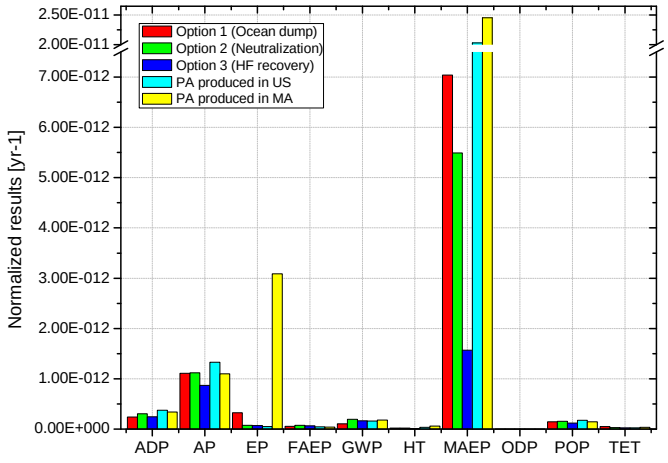
As a first step, the EI calculations were performed under the assumption that no dispersion in the input LCI data exists and using the mean value of the fitted distribution from the AspenPlus simulation results. Data consistency was checked through comparison with built in process units present in the Ecoinvent database. In this sense the PA US/U and PA MA/U LCIs are retrieved from Ecoinvent database and are taken as reference for comparison purposes. PA US/U, represents data of the production of PA in the United States while PA MA/U considers the production of PA in Morocco[13]. The goal of this consistency step is to check whether similar environmental profiles are found in the WWT cases and to compare them against previous data. Specifically, this EI profile is characterised by large impacts in Marine Aquatic Ecotoxicity Potential (MAEP), acidification potential (AP), eutrophication potential (EP) and abiotic depletion potential (ADP), see Figure 5.9(a). In this case, it has been found lower impacts than the ones reported in the database for the case of MAEP, but almost the same results for the case of AP, ADP and EP. In all options these differences can be due to the boundaries set for each of the systems (recall transport and energy integration), and in the case of option 3, for the consideration of H_2SiF_6 as a byproduct with a net gain. In order to compare results with very different scales (see ODP), the results of the different WWT options were normalised by taking the maximum value for each environmental category as reference for comparison purposes between alternatives, see Figure 5.9(b).

In Table 5.13 contains the LCI calculated by Simapro for the case of the different processes that are used for PA production. Similarly to the case of Table 5.3, it can be seen that rock consumption is the same for the three options, while limestone and sulphuric acid consumption are lower in the case of option 3, in the case of limestone its consumption its lower due to the lower plant requirements, while in the case of sulphuric acid its due to the effect of recovering HF which uses sulphuric acid for its production. In the case of steam (considered directly as heat) and electricity, options 1 and 2 show the same consumption per kg of PA produced, while option 3 shows negative values due to the recovery of HF as a byproduct, these values could already point out that option 3 is better, however the EI of this WWT option is not defined by its utilities consumption.

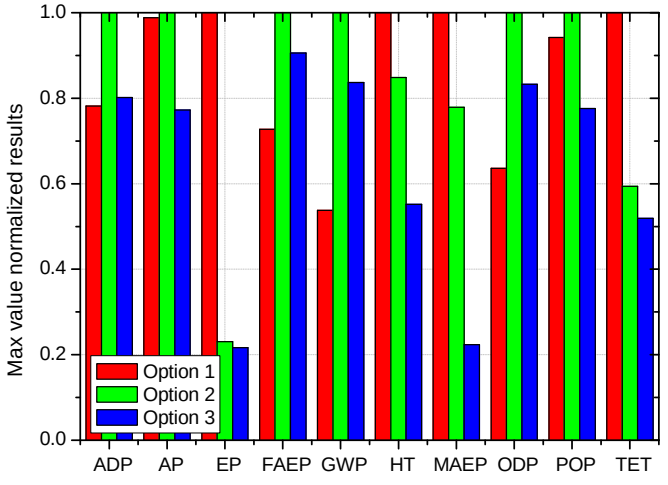
In Table 5.14 a deterministic rank of options is presented for each damage category, position 1st, refers to the best (less polluting or less resource depleting) option, while 3rd refers to the least environmentally friendly option (more polluting or more resource depleting). The WWT options that are in the first place are neutralisation with HF recovery and ocean dump (i.e. options 3 and 1 respectively) while Neutralisation (option 2) always occupies the 2nd or 3rd position. In this sense option 2, is a dominated solution in Pareto efficiency terms if compared to options 1 and 3.

Table 5.14 shows also the normalised (Huijbregts *et al.*, 2003) [yr^{-1}] results associated with the three WWT options. It can be observed how the highest impact corresponds to the MAEP

[13]The main difference between both processes lies in the way phosphate rock is processed and in the way that gypsum is disposed off.



(a) Comparison of normalised environmental impacts for different WWT options and other processing possibilities.



(b) Comparison of EIs, normalised to maximum value.

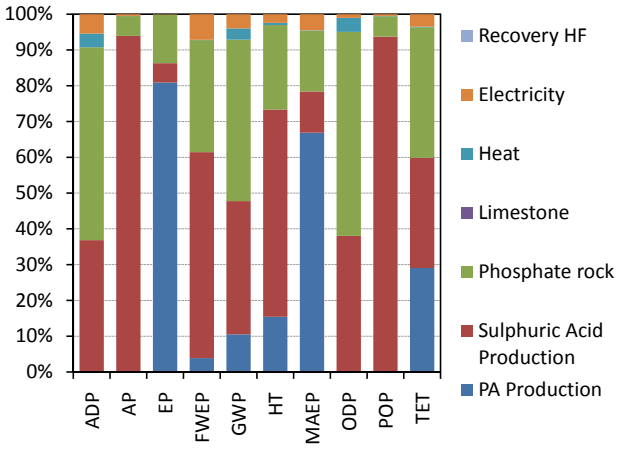
Figure 5.9: Deterministic impact assessment results, normalised to max value and using normalisation constants for Western Europe.

damage category. The first five most important environmental interventions considering its normalised contribution are found to be MAEP, AP, EP, ADP and GWP.

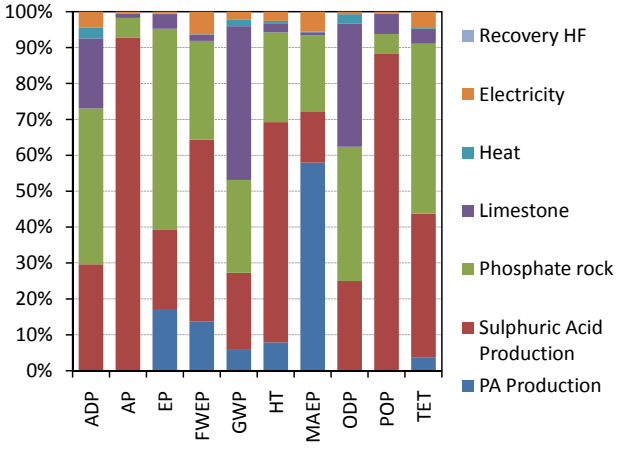
Figures 5.10 shows the contribution percentage for each of the echelons in the production of PA. Heat represents steam consumption that has to be generated and that is not able to be

Table 5.13: LCI data calculated for the production echelons considered.

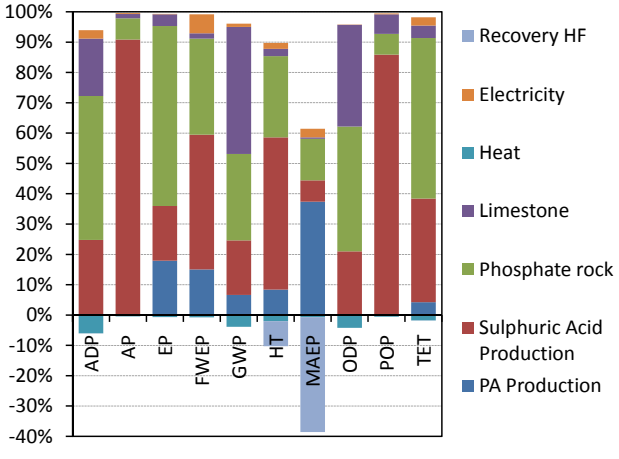
Process	Unit	Option 1	Option 2	Option 3
PA Production	kg	1.000	1.000	1.000
Sulphuric Acid Production	kg	1.826	1.826	1.393
Phosphate rock	kg	1.346	1.346	1.346
Limestone	g	0.0	444.9	394.0
Heat	kJ	258.0	258.0	*-432.4*
Electricity	kJ	77.9	77.9	*-18.9*
Recovery HF	g	0.0	0.0	*-194.8*



(a) Option 1

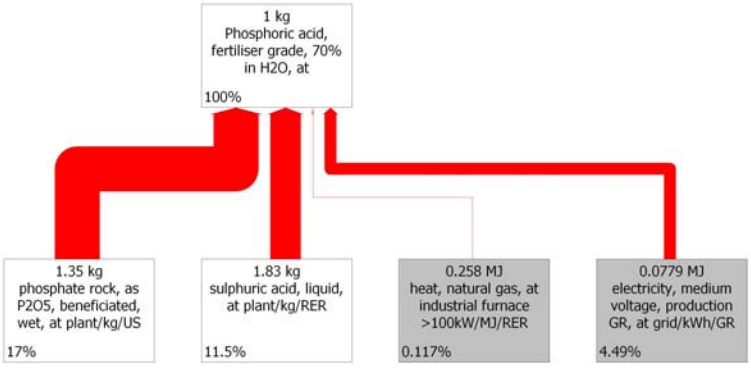


(b) Option 2

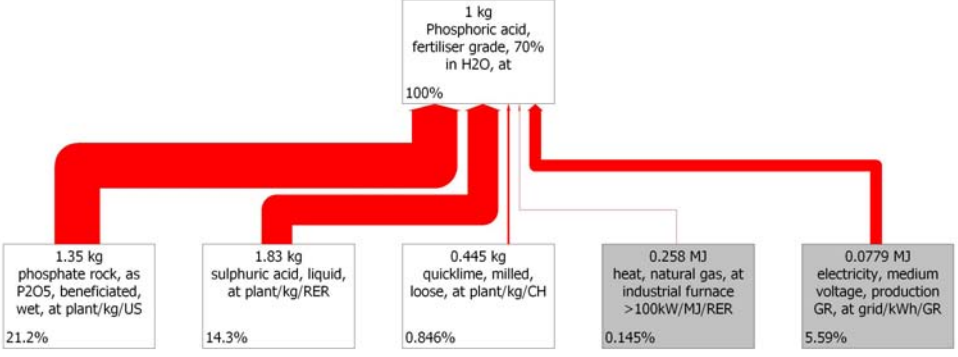


(c) Option 3

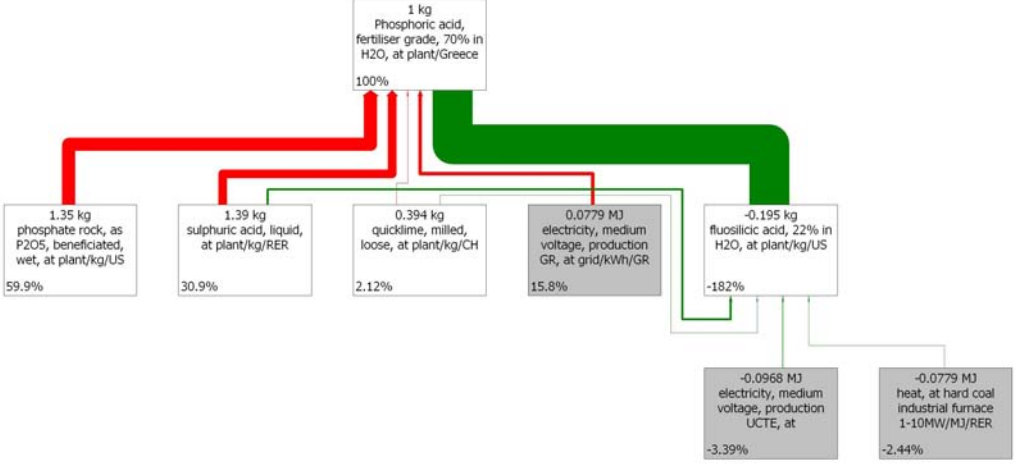
Figure 5.10: Distribution of EI along the different SC echelons. See Table 5.14 for characterisation results.



(a) Option 1, MAEP 7.99E+02 kg 1,4-DB eq.

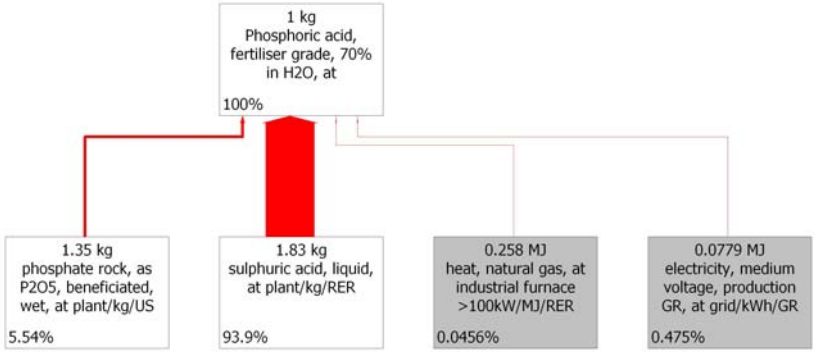


(b) Option 2, MAEP 6.23E+02 kg 1,4-DB eq.

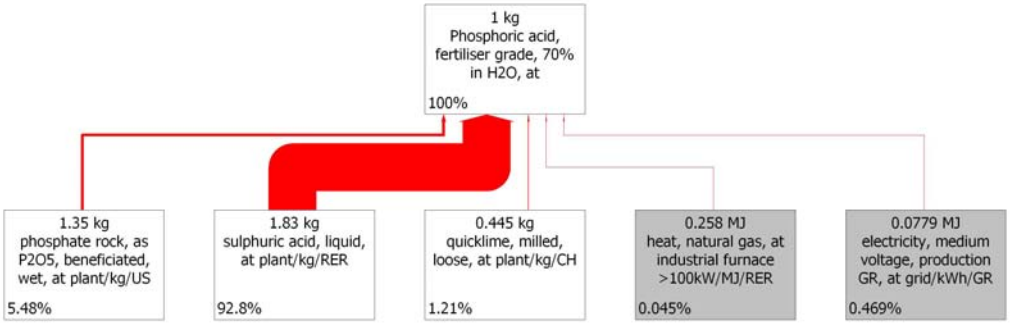


(c) Option 3, MAEP 1.79E+02 kg 1,4-DB eq.

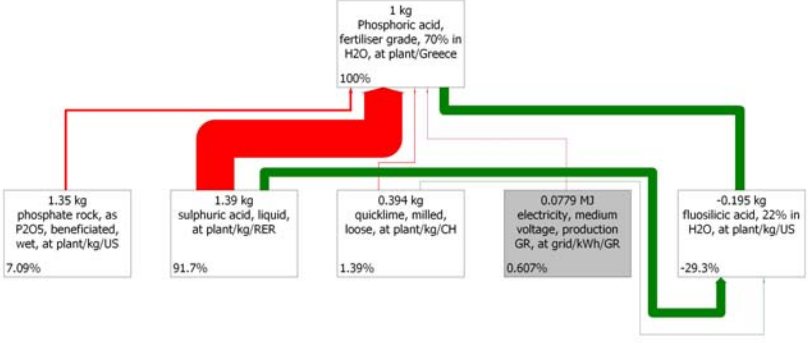
Figure 5.11: Networks of processes involved in the MAEP EI. See Table 5.14 for characterisation results.



(a) Option 1, AP 3.03E-02 kg SO_2eq.

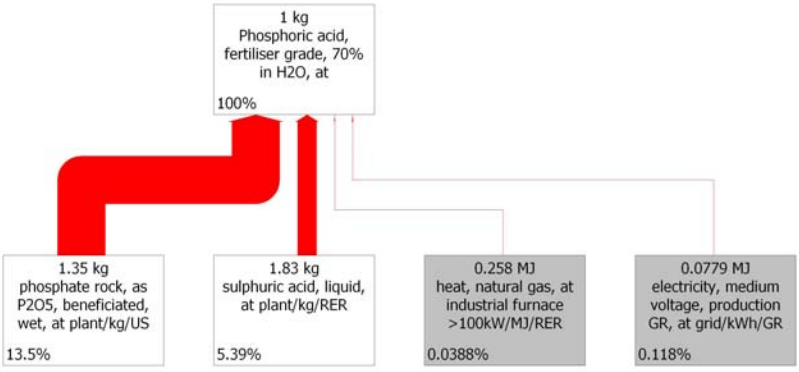


(b) Option 2, AP 3.07E-02 kg SO_2eq.

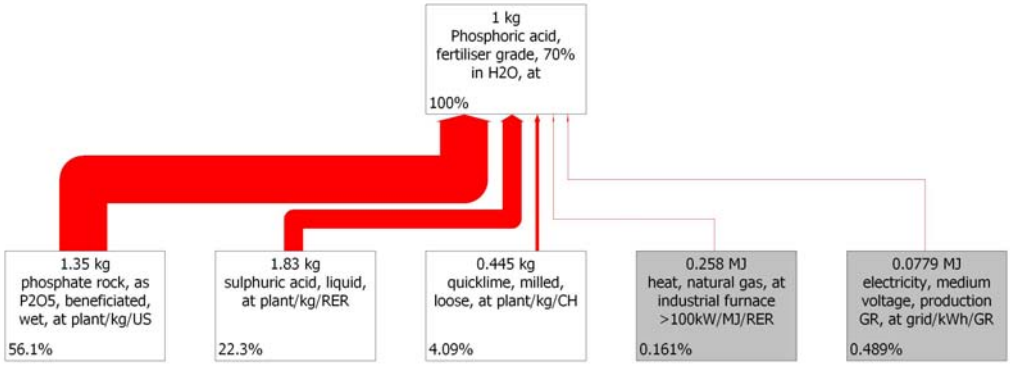


(c) Option 3, AP 2.37E-02 kg SO_2eq.

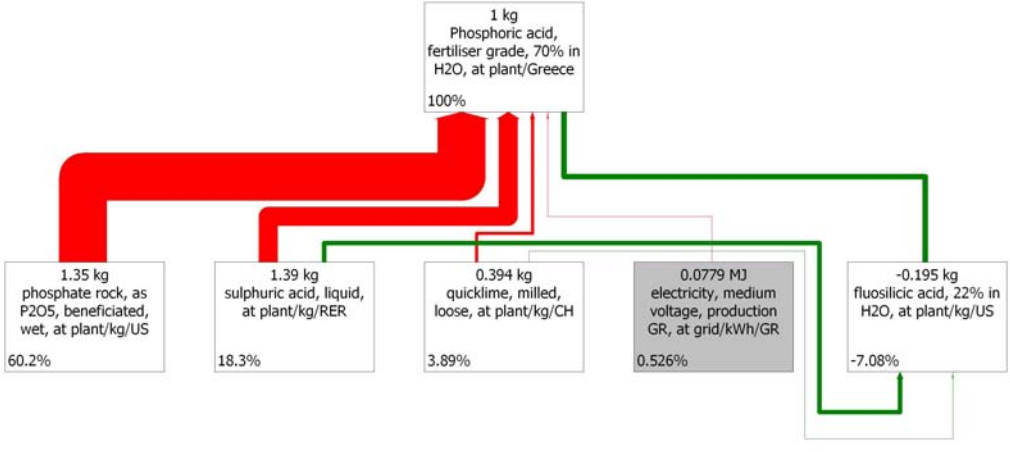
Figure 5.12: Networks of processes involved in the acidification (AP) EI. See Table 5.14 for characterisation results.



(a) Option 1, EP 4.03E-03 kgPO_4^{3-} eq.

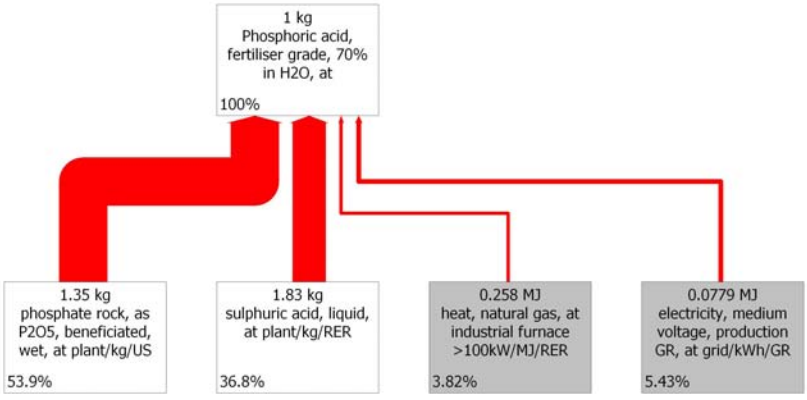


(b) Option 2, EP 9.31E-04 kgPO_4^{3-} eq.

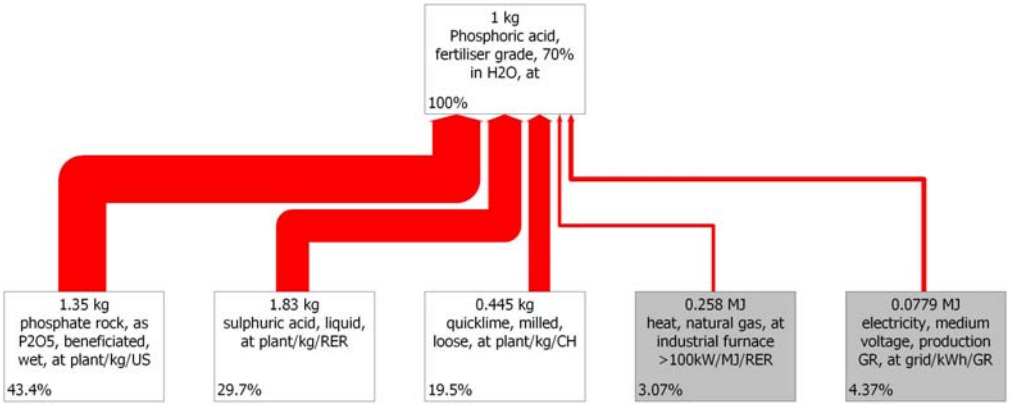


(c) Option 3, EP 8.73E-04 kgPO_4^{3-} eq.

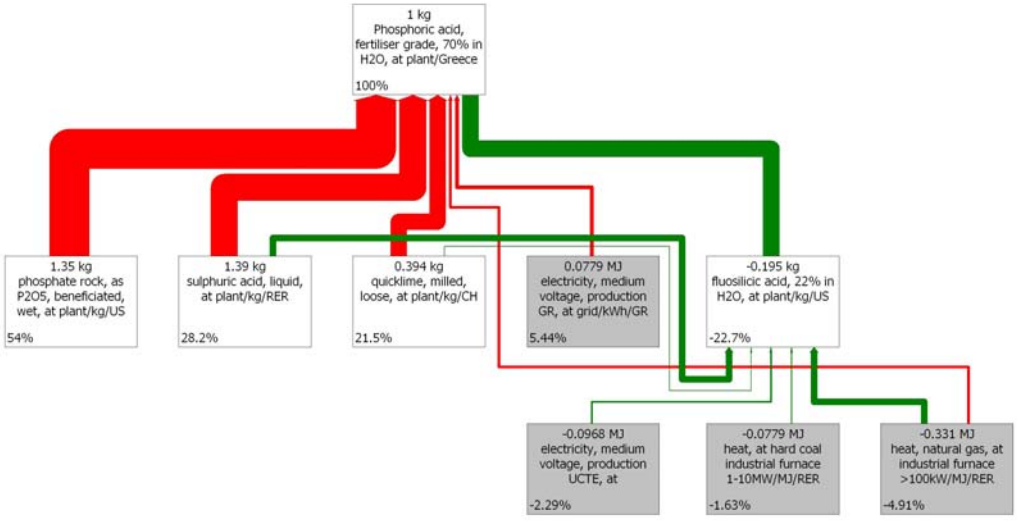
Figure 5.13: Networks of processes involved in the eutrophication (EP) EI. See Table 5.14 for characterisation results.



(a) Option 1, ADP 3.53E-03 kg Sb eq.

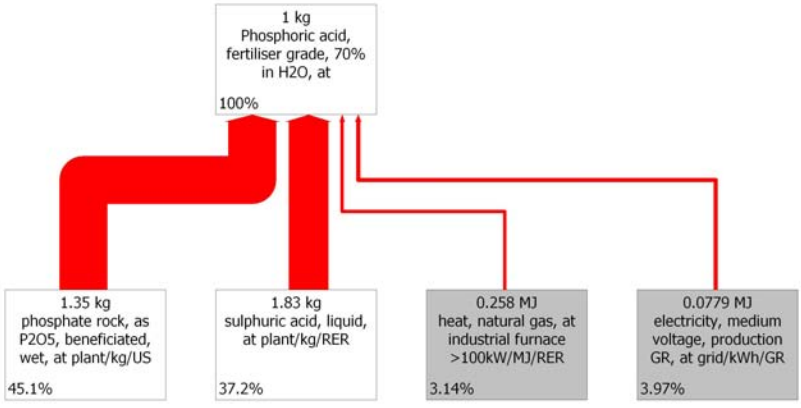


(b) Option 2, ADP 4.51E-03 kg Sb eq.

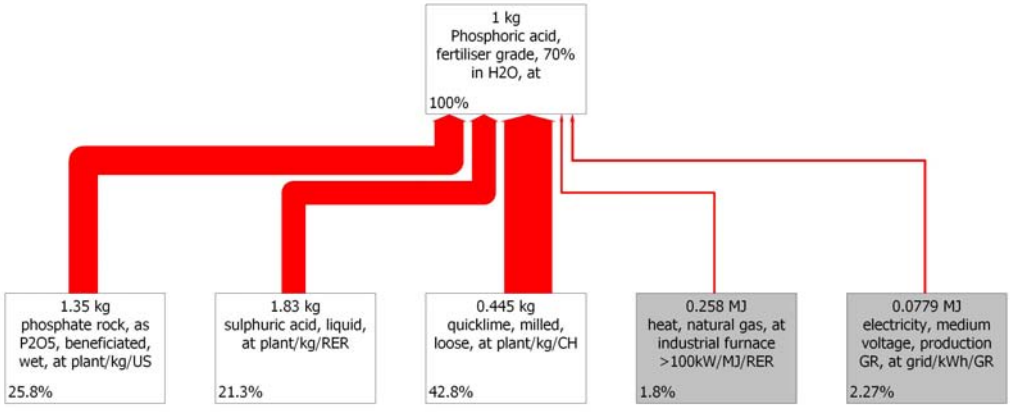


(c) Option 3, ADP 3.62E-03 kg Sb eq.

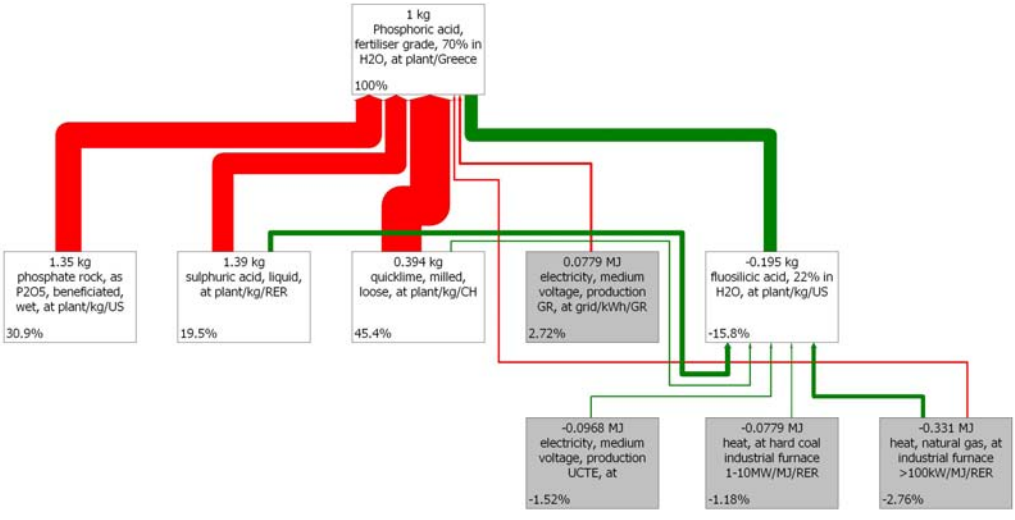
Figure 5.14: Networks of processes involved in the abiotic depletion (ADP) EI. See Table 5.14 for characterisation results.



(a) Option 1, GWP 5.07E-01 $kgCO_2eq$.



(b) Option 2, GWP 9.43E-01 $kgCO_2eq$.



(c) Option 3, GWP 7.89E-01 $kgCO_2eq$.

Figure 5.15: Networks of processes involved in the climate change (GWP) EI. See Table 5.14 for characterisation results.

Table 5.14: Deterministic EI assessment results, characterisation results are found under column Ch. val. while the normalised ones found under column Nor. val., used weights from Huijbregts *et al.* (2003) and are expressed in [yr^{-1}]; # indicates the ranking of the option regarding that EI category.

Impact category	Unit	Option 1			Option 2			Option 3		
		Ch. val.	Nor. val.	#	Ch. val.	Nor. val.	#	Ch. val.	Nor. val.	#
ADP	kg Sb eq.	3.53E-03	2.38E-13	1st	4.51E-03	3.043E-13	3rd	3.62E-03	2.44E-13	2nd
AP	kg SO_2 eq.	3.03E-02	1.11E-12	2nd	3.07E-02	1.124E-12	3rd	2.37E-02	8.68E-13	1st
EP	kg PO_4^{3-} eq.	4.03E-03	3.233E-13	3rd	9.31E-04	7.463E-14	2nd	8.73E-04	7E-14	1st
FAEP	kg 1,4-DB eq.	2.71E-02	5.373E-14	1st	3.73E-02	7.39E-14	3rd	3.38E-02	6.7E-14	2nd
GWP	kg CO_2 eq.	5.07E-01	1.055E-13	2nd	9.43E-01	1.962E-13	3rd	7.89E-01	1.64E-13	1st
HT	kg 1,4-DB eq.	1.64E-01	2.162E-14	1st	1.39E-01	1.834E-14	3rd	9.04E-02	1.19E-14	2nd
MAEP	kg 1,4-DB eq.	7.99E+02	7.041E-12	3rd	6.23E+02	5.485E-12	2nd	1.79E+02	1.57E-12	1st
ODP	kg CFC-11 eq.	5.24E-08	6.285E-16	3rd	8.23E-08	9.879E-16	2nd	6.86E-08	8.23E-16	1st
POP	kg C_2H_4 eq.	1.19E-03	1.446E-13	1st	1.27E-03	1.534E-13	3rd	9.84E-04	1.19E-13	2nd
TET	kg 1,4-DB eq.	2.28E-03	4.836E-14	3rd	1.35E-03	2.871E-14	2nd	1.18E-03	2.51E-14	1st

coped by integration with the sulphuric acid production. In the case of WWT option 1 (see Figure 5.10(a)), EP and MAEP are dominated by the PA production echelon while AP and POP are dominated by the sulphuric acid production, in the case of ADP and ODP phosphate rock production holds the dominating share. In the case of FWEP, GWP and HT impacts, sulphuric acid and rock production are the most important shares, in the case of TET the PA production and the two raw materials equally share the impact. It is worth noting that for this option steam and electricity impacts account for less than 10% in all the impact categories.

In the case of Figure 5.10(b) which shows the impacts associated to WWT option 2 the same behaviour than in the case of option 1 are found for categories AP, FWEP, HT, MAEP and POP. Differences in ADP, GWP and ODP are mostly due to the consumption of lime as a means for neutralisation, while in the case of EP and TET the difference is mainly due to the emission reduction of phosphates. Figure 5.10(c) summarises the results for WWT option 3. For the case of AP, EP, FWEP, POP and TET, small amounts of the each impact are avoided by the HF recovery and these categories show the same behaviour that WWT options 2 and 1. In the case of ADP, GWP, ODP a reduction of nearly 4% of each category impact is achieved by the avoidance of HF production which renders lower heat consumption. For the HT and MAEP categories the reduction is higher accounting for 13 and 35% in each case, however in this case the impact reduction in these categories is due to the reduction of avoided impacts associated directly to the HF production and not to echelons of that production chain, a clarifying image can be grasped in figure 5.11.

Figures 5.11, 5.12, 5.13, 5.14 and 5.15 show the contribution of each echelon of the production process to the most important EIs. Gray boxes represent energy related echelons such as steam (heat) and electricity, while white boxes represent material production echelons. In all cases red flows indicate actual consumption flows, while in the case of green flows are avoided consumption due to the production of a given product, see Figures related to Option 3. In all cases arrows width represent the activity impact amount associated to that flow.

Regarding marine aquatic ecotoxicity (MAEP), figure 5.11, in option 3 MAEP is mainly due to the phosphate rock and sulphuric acid production process itself (81.3% of the total impact), see figures 5.11(c). In the case of options 1 and 2 MAEP is mostly due to the PA production echelon, that accounts for nearly 67% and 59% respectively. In the case of neutralisation and HF recovery (option 3), it is observed how the recovery of HF, leads to a reduction in MAEP. Other process contributing to MAEP are found to be burning of lignite and coal, which are both used as raw materials for electricity generation. In all three options the substance flow with the highest contribution to MAEP is HF released to air, followed by trace species flows to water (Be, V and others).

Regarding AP, all options exhibit the same tendencies see Figure 5.12, i.e. AP is mainly due

to the sulphuric acid and sulphur production processes and consequently to the emission of SO_2 to air; in all cases more than 90% of the AP EI rises from those echelons. All options show similar mean consumption of H_2SO_4, see Table 5.3, consequently AP is similar among them, however for the case of option 3 a reduction of the net H_2SO_4 consumption is found from 1.83 in options 1 and 2 to 1.39 in the case of option 3 see reported values in figures 5.12 and Table 5.13.

In the case of Eutrophication impact (EP) for Option 1, it is mainly attributed to the PA production step (more than 80% see Figure 5.13(a)), while in options 2 and 3 rock production and sulphuric acid production are the most important, accounting for roughly 78% in both cases. All these processes contribute to the emission of phosphates and phosphorus to water. These results are in line with those shown by da Silva and Kulay (2005). The recovery of HF shows a small impact and accounts for 7% of EP impacts in the case of option 3.

ADP for all three options is mainly caused by the consumption of phosphate rock which accounts for 53.9, 43.4 and 54% of the total impact in each option, see Figure 5.14. The second most important is the consumption of sulphuric acid with a share of around 30% in all options. In options 2 and 3 the consumption of lime for neutralisation is the third most important producer of this impact. In the case of option 3 the recovery of HF helps in reducing the life cycle impact associated to sulphuric acid and the consumption of fossil fuels associated to heat production, see Figure 5.14(c).

Regarding climate change impacts (GWP), in the case of Options 2 and 3 the highest producer of this impact is the production of lime for neutralisation which accounts for more than 40% of this impact category (see Figures 5.15(b) and 5.15(c)). In second and third place comes the consumption of phosphate rock and sulphuric acid, which in the case of Option 1 have the first and second most important shares, see Figure 5.15(a).

In all cases the impacts associated to industrial utilities such as electricity and steam, are small and in most cases less than 5% of the total mid-point impact. The production of PA was found as the most important echelon for the EI associated to MAEP and EP, see in the case of options 1 and 2, see Figures 5.11(a), 5.11(b) and 5.13(a). For all the other categories and options the upstream process has the most contribution.

5.1.3.2 Stochastic impact assessment approach

Analysis of uncertainty sources This analysis focuses the attention on two sources of uncertainty: (i) the uncertainty associated to parameters of the AspenPlus simulation and trace species model, and (ii) uncertainty of the LCIs results given by the Ecoinvent database. In order to compare these sources three MCS runs considering different versions of the same WWT option were made. In each one of these runs certain sets of variables were fixed to its mean value while the others were regarded as stochastic. In order to perform this analysis one of the most important features of the Ecoinvent database was used, the provision of Ecoinvent Units and Ecoinvent Systems. Ecoinvent units provide with partial LCIs for each of the modelled production processes, in this sense the information is disaggregated along all the processing steps of the SC (e.g. flows of utilities and raw materials and some environmental interventions), while Ecoinvent Systems provide with aggregated results where only environmental interventions are inputs and outputs. In the case of Ecoinvent systems each flow does not have any uncertainty associated, while in the case of units uncertainty is associated to most of the considered flows. Table 5.15 summarises this information. It should be noted that when using no uncertain information from the database the total number of variables is drastically reduced. Version 1 considers all process to be modelled using Ecoinvent Systems, version 2 considers uncertainty in flows associated to raw materials and emissions from the PA production plant, but whose processing facilities do not have any uncertainty. Version 3

Table 5.15: Summarising information regarding different MC simulation versions of WWT Option 1.

	Version 1	Version 2	Version 3	Version 4
Uncertainty in simulation LCI	No	Yes	No	Yes
Uncertainty in database LCI	No	No	Yes	Yes
Total number of variables	4065	4065	52589	52589
# of uncertain variables	0	29	38597	38626
# of fixed value variables	4065	4036	13992	13963
% of uncertain variables	0.00	0.71	73.39	73.45

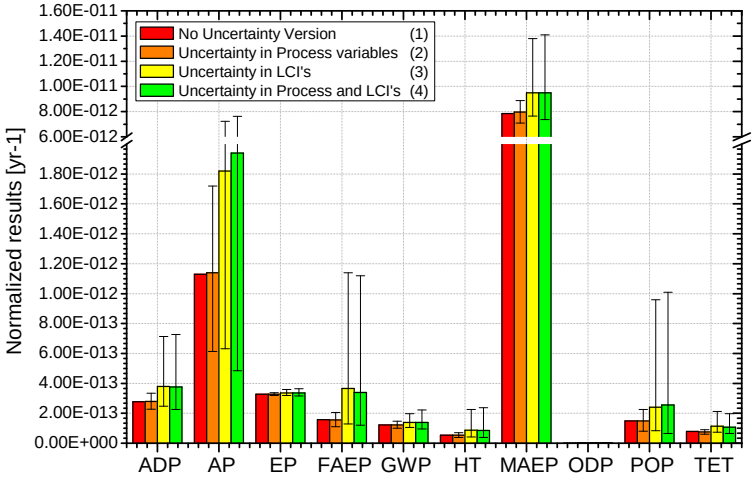


Figure 5.16: Comparison of confidence intervals for different sources of uncertainty, for the same treatment option 1. Error bar shows the 95% percentiles.

considers uncertainty in raw materials and utilities production echelons by using Ecoinvent Units whose flows are deterministic, while version 4 considers this flows as uncertain. The results of the three MC runs can be seen in Figure 5.16. Figure 5.16, shows that most of the results scattering is a consequence of uncertain information that comes from LCI data stored in the Ecoinvent database (by means of Ecoinvent Units). The confidence intervals (CI) shown is calculated from the MC simulation results 95% percentiles. Version 2 shows the smallest CI, given that it considers only simulation model uncertainty (i.e foreground system variables), while Versions 3 and 4 of the same WWT option show the largest CI. The former analysis was performed for the case of ocean disposal (option 1), but similar results are found for the other WWT options. It is clear from Table 5.15, that the CI for version 4 will be bigger than for all other versions, however the difference between version 3 and 4 is small, pointing out that despite the fact that foreground variables drive the mass flows of the system, these flows have more inherent uncertainty than the uncertainty associated to its flow value which is related to the process simulation.

In the case of Figure 5.16, it is important to note the error bars associated to categories EP and MAEP, which were completely dominated by the process interventions (see Figures 5.11(a) and 5.13(a)) and not by the background LCI. Surprisingly it is found that the CI associated to version 2 is smaller than for version 3. Figures 5.17 and 5.18, which show the same uncertainty analysis for WWT options 2 and 3, provided similar trends. It is worth mentioning that the CI for MAEP in WWT option 3 contains negative values. Please note that the results shown are for individual 1000 scenarios runs and that the mean and CI values are not exactly the same due to the fact that different amount of variables are considered to be stochastic see Table 5.15.

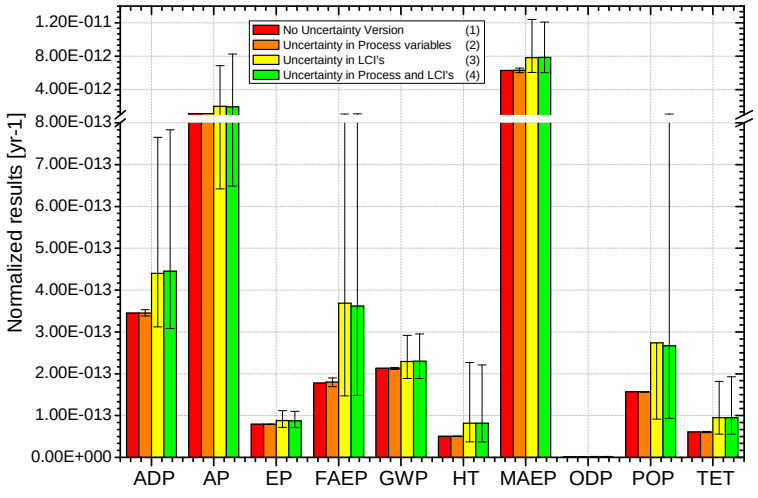


Figure 5.17: Comparison of confidence intervals for different sources of uncertainty, for the same treatment option 2. Error bar shows the 95% percentiles.

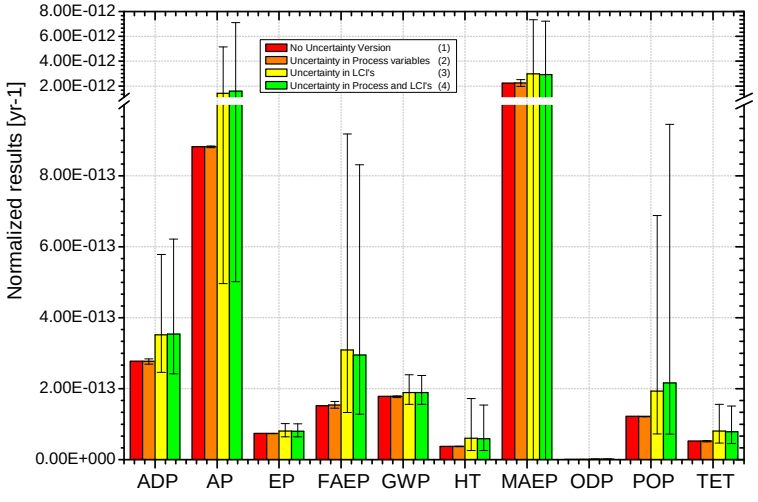


Figure 5.18: Comparison of confidence intervals for different sources of uncertainty, for the same treatment option 3. Error bar shows the 95% percentiles.

An uncertainty analysis of the impact assessment for each of the WWT options was next performed. All variables sets, related to simulation and LCI-database were considered to be stochastic. A MC simulation was carried out in SimaPro using 1000 equiprobable scenarios. The number of scenarios was set by gradually increasing it and stopping whenever no significant changes in the environmental interventions can be appreciated[14]. No uncertainty in the LCIA model was considered for the impact characterisation step, i.e. all the characterisation factors (CFs) used to transform emissions released into EIs are considered constant.

[14]SimaPro currently has a restriction on the random number generator, it can not guarantee that the same values are used if single MC runs are performed. It can only guarantee such behaviour if binary comparisons are done. Consequently in this case 3 binary comparisons of 1000 scenarios each were performed: option 1 vs option 2, option 1 vs option 3 and option 2 vs option 3.

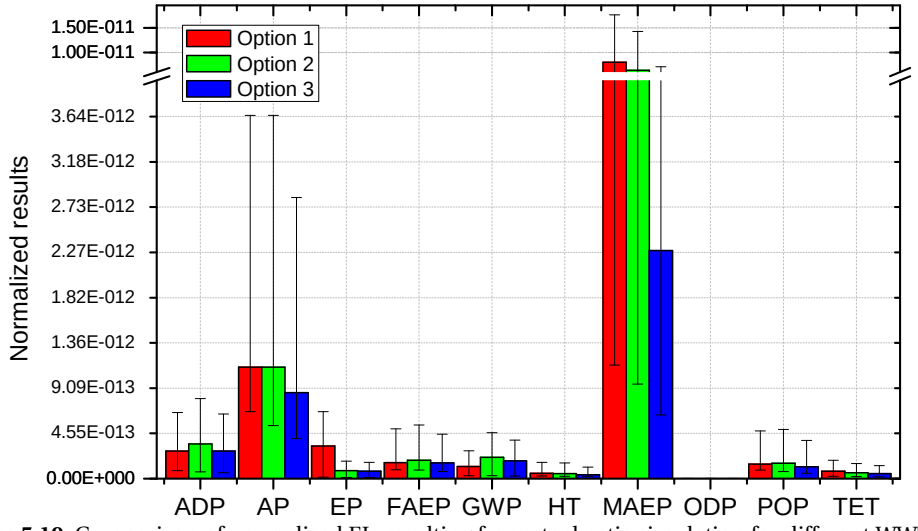


Figure 5.19: Comparison of normalised EIs resulting from stochastic simulation for different WWT options. Error bar shows the 95% percentiles.

This assumption is motivated by the lack of reliable information regarding the uncertainty affecting the aforementioned damage model parameters (de Schryver *et al.*, 2006). It should be remarked, that uncertainty comes only from inventory information, and not from impact assessment. In the case of the PA simulation variables, the values used are the stochastic ones obtained from the sampling stage performed in AspenPlus (see Table 5.3), while in the case of the trace species environmental model values are summarised in Table 5.1.

Results analysis using classical statistical tools Table 5.16 summarises the data available in Figure 5.19. As it can be observed, the uncertainty of the input data (simulation and database) drastically affects the values of several EI indicators. The degree of dispersion is reflected by the coefficient of variation (CV, see Eq. 3.23), which takes high values for some impact categories. Moreover it is also found that mean and median value of the results do not coincide, this is due to the uncertainty representation using the lognormal pdf for many of the variables present in the Ecoinvent database.

Regarding the biggest EIs, the categories that impact the most in terms of normalised results are: MAEP, AP, ADP, EP, POP, GWP. The first four coincide in order to the ones found in the deterministic case, while POP is bigger than GWP, which was fifth in the former case. However the stochastic results reveal that the hierarchy of environmental goodness established in the deterministic case (Table 5.14) does not hold true in the presence of uncertainty in parameters, see Table 5.18. A new ranking of alternatives is therefore obtained. This ranking is based on the mean value of the results over the entire range of scenarios from Table 5.16.

Table 5.18 shows that WWT option 2 still remains as a the 2nd or 3rd best option for all categories. This is the same result that is obtained in the deterministic case. In the case of EP, Fresh Water aquatic Ecotoxicity Potential (FWEP), MAEP and Terrestrial Ecotoxicity Potential (TEP) impacts, the deterministic and stochastic results are the same. While in the remaining categories (ADP, AP, GWP, HTP, OLDP and POP) they differ which leads to a different ranking.

Results analysis using probabilities The ordering obtained using mean values is not fair given that the CIs largely overlap, and under those circumstances the three WWT options seem to be indiscernible in the sense of showing no significant difference in some impact

categories, see Heijungs & Suh (2002, Ch. 8) and Basson and Petrie (2007b).

In general, the problem of elucidating if an option A is superior to B in terms of a given metric under uncertainty is equivalent to determine the probability of option A being better than option B. This information can be obtained by simply counting the number of scenarios in which A behaves better than B, and dividing that value by the total amount of scenarios (see section 2.4.4.1, and Eq. 2.36).The former analysis can be extended to more than two options, for the calculation of the probability of being the best option; which can be calculated by counting the number of times where each option scores best and dividing by the total number of scenarios. In Table 5.17 the values are reported for binary comparison ($p(j'^*|j)$, j' is better than j), and for comparisons against all other options ($p(j'^*|\forall j \neq j')$, j' is the best option, and $p(j'^0|\forall j \neq j')$, j' is the worst option). In the case of binary comparisons the probabilities calculated hold Eq. 5.19, while in the case of best and worst options Eq. 5.20.

$$p(j^*|j') + p(j'^*|j) = 1 \qquad j' \neq j \tag{5.19}$$

$$\sum_j p(j*|\forall j' \neq j) = 1 \tag{5.20}$$

If a probability of 0.90 or higher is considered for accepting an option as better than other or the best, then a new ranking for the WWT options proposed can be obtained for each impact category. The ordering obtained is summarised and compared to other orderings in Table 5.18. The following points can be highlighted:

- EP, MAEP and TEP: option 3 is the best followed by option 2 that shows a very high probability value when compared to 1.
- GWP and OLDP: for these indicators option 1 is clearly the best given its high probability values. Also option 3 is better than option 2. The order obtained is as follows: Option 1 better than Option 3 better than Option 2.
- ADP: No clear differentiation between options 1 and 3 is possible, being both of them better than option 2 (see p(1*|2) and p(3*|2)), that remains 3rd.
- HTP: option 3 is clearly the best, but no ordering of the remaining two options is possible given the low values of the binary comparison probabilities obtained.

For the remaining indicators (AP, FWEP, and POP), no possible general ordering can be made from the calculated probabilities. However, for all these indicators option 2 is always worst than option 3, see p(2*|3) and p(3*|2) values in Table 5.17, however the low values obtained for p(1*|2) make the ordering difficult between options 1 and 3. It is interesting to note that AP and POP showed the same EI structure regarding its source in all three options in the deterministic case (see Figure 5.10).

Basson and Petrie (2007b) calculate a discernibility index (DI) as in Eq. 2.39, however in that case it is based on the use of CI for the selection of non overlapping indicators, and is used only in binary comparisons. Here the DI definition has been extended, and is calculated for each option based on the probability value, where the number of non-overlapping attributes is counted if $p(j'|j) \geq 0.90$ and if $p(j'|j) \leq 0.10$ for the case of binary comparisons, while only the biggest than 0.90 in the case of comparisons against all other options. Following the former guidelines the DI has been calculated for all possible comparisons, and is reported in the last two rows of Table 5.17, from its value it can be seen that Option 1 is partially distinguishable from all other options (DI_1=0.6, compared to 2 and 3) while Options 2 and 3, are completely distinguishable between them. The DI value for the best and worst option requires the addition of the values obtained for all options, then the DI for best option is DI^*=0.2+0+0.4=0.6, while in the case of DI for worst is DI^0=0.4+0.4+0=0.8. In the case of DI^*=0.6, it can be affirmed that only in 6 out of 10 categories the best option can be identified, while for the case

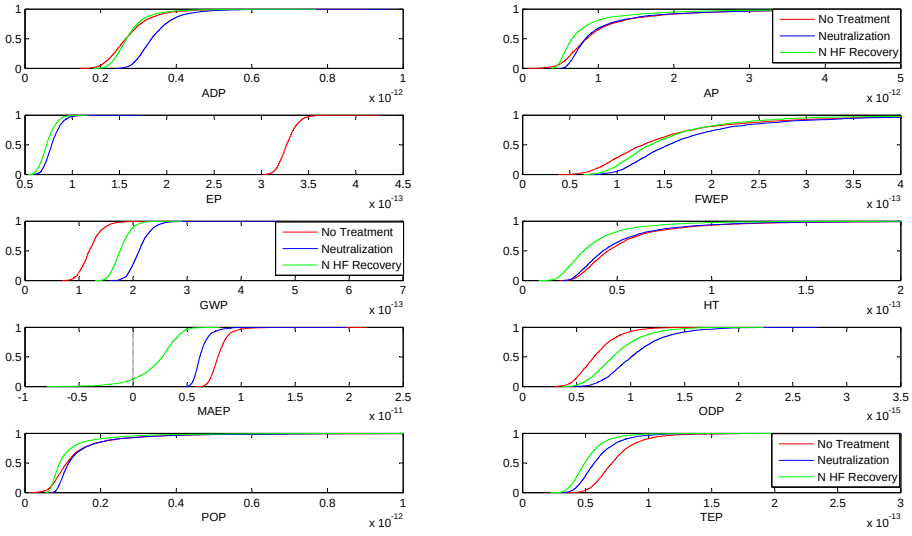


Figure 5.20: CDFs for all three WWT options for different EIs, based on 1000 scenarios using CRN, for the binary comparisons.

of DI^0=0.8, only in 8 of 10 the worst option is identified. Clearly none of the options can be said to be the worst or best.

The analysis of the cumulative probability distribution functions (CDFs) curve shapes draws similar conclusions as the one showed in Table 5.18 for the probability based ordering. Figure 5.20, shows the CDFs derived from the MC simulations realised. The impact categories that do not show CDFs crossings are: EP, GWP, MAEP, OLDP and TEP, and are the categories for which the probabilities allow for a clear ordering. In the case of EP it is clear how different from option 1 are options 2 and 3 due to the large found between the CDFs obtained. In the case of MAEP it is interesting to note that some MC simulation results show a negative value, in which a net environmental gain is obtained, for the case of option 3.

All impact categories for which no clear decision can be made based on probabilities show crossing of their respective CDFs curves, see the case of ADP, AP, FWEP, HTP, and POP in Figure 5.20. FWEP, POP and AP show the same behaviour, the CDFs for each option cross each other and do not allow for any option ordering. In the case of ADP, the CDFs of options 1 and 3 cross and prevent the distinguishability between them as best options, being both of them clearly better than option 2. The HTP CDFs curves for options 1 and 2 cross each other preventing selecting them as the worst option,

Table 5.16: Stochastic EI assessment normalised results [yr^{-1}]. Bold values in mean and median columns indicate smallest results for that EI category.

Impact category	Option 1				Option 2				Option 3			
	Mean	Median	STD	CV [%]	Mean	Median	STD	CV [%]	Mean	Median	STD	CV [%]
ADP	2.98E-13	2.74E-13	1.10E-13	36.8	3.55E-13	3.40E-13	7.19E-14	20.2	**2.86E-13**	**2.73E-13**	6.59E-14	23.0
AP	1.87E-12	1.17E-12	2.62E-12	*140.0*	1.69E-12	1.12E-12	1.81E-12	*107.0*	**1.56E-12**	**9.26E-13**	2.11E-12	*135.0*
EP	3.27E-13	3.26E-13	9.78E-15	3.0	7.86E-14	7.78E-14	8.26E-15	10.5	**7.34E-14**	**7.24E-14**	8.45E-15	11.5
FAEP	**8.62E-14**	**8.15E-14**	2.80E-14	32.5	1.12E-13	1.06E-13	3.10E-14	27.8	1.01E-13	9.46E-14	3.51E-14	34.8
GWP	**1.12E-13**	**1.10E-13**	1.76E-14	15.7	2.02E-13	2.01E-13	1.69E-14	8.4	1.70E-13	1.69E-13	1.64E-14	9.7
HT	2.79E-14	2.76E-14	3.87E-15	13.9	2.46E-14	2.41E-14	3.57E-15	14.5	**1.65E-14**	**1.65E-14**	4.26E-15	25.8
MAEP	7.74E-12	7.69E-12	6.82E-13	8.8	6.09E-12	5.98E-12	6.58E-13	10.8	**1.53E-12**	**2.04E-12**	2.48E-12	*162.0*
ODP	**7.64E-16**	**7.27E-16**	2.21E-16	29.0	1.20E-15	1.13E-15	3.51E-16	29.3	9.87E-16	9.31E-16	3.00E-16	30.4
POP	2.45E-13	1.53E-13	3.47E-13	*141.0*	2.29E-13	1.53E-13	2.40E-13	*105.0*	**2.11E-13**	**1.27E-13**	2.78E-13	*132.0*
TET	5.74E-14	5.45E-14	1.59E-14	27.8	4.15E-14	3.84E-14	1.46E-14	35.2	**3.57E-14**	**3.31E-14**	1.70E-14	47.6

Table 5.17: Probabilities of being better or best than for different WWT options. Bold values indicate probabilities higher than 0.9.

Impact category	**Option 1** No treatment				**Option 2** Neutralisation				**Option 3** HF recovery			
	$p(1^{*}\|2)$	$p(1^{*}\|3)$	$p(1^{*}\|2,3)$	$p(1^{U}\|2,3)$	$p(2^{*}\|1)$	$p(2^{*}\|3)$	$p(2^{*}\|1,3)$	$p(2^{U}\|1,3)$	$p(3^{*}\|1)$	$p(3^{*}\|2)$	$p(3^{*}\|1,2)$	$p(3^{U}\|1,2)$
ADP	**0.973**	0.517	0.510	0.000	0.027	0.000	0.000	**1.000**	0.483	**1.000**	0.490	0.000
AP	0.536	0.210	0.125	0.522	0.464	0.000	0.000	0.469	0.790	**1.000**	0.875	0.009
EP	0.000	0.000	0.000	**1.000**	**1.000**	0.000	0.000	0.000	**1.000**	**1.000**	**1.000**	0.000
FWEP	0.880	0.622	0.597	0.022	0.120	0.031	0.004	**0.978**	0.378	**0.969**	0.399	0.000
GWP	**1.000**	**0.999**	**0.999**	0.000	0.000	0.000	0.000	**1.000**	0.001	**1.000**	0.001	0.000
HTP	0.287	0.021	0.006	**0.997**	0.713	0.000	0.000	0.003	**0.979**	**1.000**	**0.994**	0.000
MAEP	0.002	0.000	0.000	**1.000**	**0.998**	0.000	0.000	0.000	**1.000**	**1.000**	**1.000**	0.000
OLDP	**0.994**	**0.916**	**0.916**	0.000	0.006	0.000	0.000	**1.000**	0.084	**1.000**	0.084	0.000
POP	0.650	0.274	0.197	0.082	0.350	0.000	0.000	0.891	0.726	**1.000**	0.803	0.027
TEP	0.042	0.003	0.000	**0.999**	**0.958**	0.001	0.001	0.001	**0.997**	**0.999**	**0.999**	0.000
DI Bin.	0.6	0.6	****	****	0.6	1	****	****	0.6	1	****	****
DI All	****	****	0.2	0.4	****	****	0	0.4	****	****	0.4	0

Table 5.18: Comparison of WWT options rankings by different approaches.

Impact category	**Option 1** No treatment			**Option 2** Neutralisation			**Option 3** HF recovery		
	Det pos.	**MC pos.**	**Prob pos.**	**Det pos.**	**MC pos.**	**Prob pos.**	**Det pos.**	**MC pos.**	**Prob pos.**
ADP	1st	1st	1st-2nd	3rd	3rd	3rd	2nd	2nd	1st-2nd
AP	2nd	3rd	No decision	3rd	2nd	No decision	1st	1st	No decision
EP	3rd	3rd	3rd	2nd	2nd	2nd	1st	1st	1st
FWEP	1st	2nd	No decision	3rd	3rd	No decision	2nd	1st	No decision
GWP	1st	1st	1st	3rd	3rd	3rd	2nd	2nd	2nd
HTP	3rd	3rd	2nd-3rd	2nd	2nd	2nd-3rd	1st	1st	1st
MAEP	3rd	3rd	3rd	2nd	2nd	2nd	1st	1st	1st
OLDP	1st	1st	1st	3rd	3rd	3rd	2nd	2nd	2nd
POP	2nd	2nd	No decision	3rd	3rd	No decision	1st	1st	No decision
TEP	3rd	3rd	3rd	2nd	2nd	2nd	1st	1st	1st

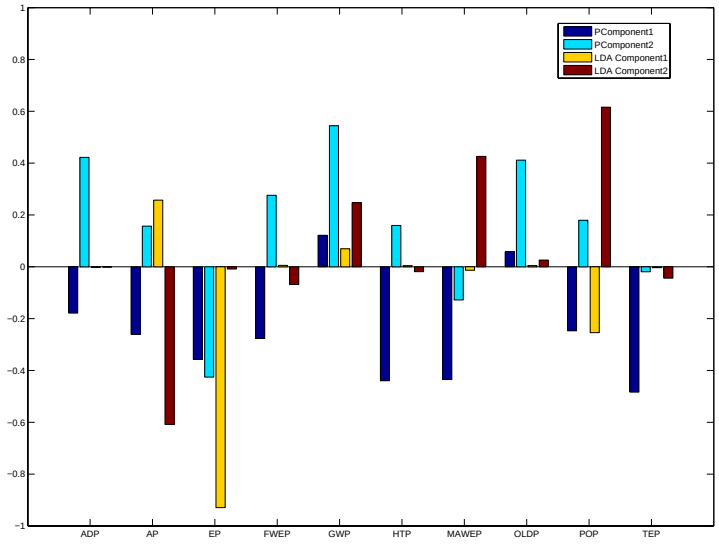


Figure 5.21: Principal and linear discriminant components for all three WWT options. Based on CML result categories.

Analysis using multivariate tools Other way of analysing the impact assessment results is the application of PCA and LDA. In the first case the first principal components (pc) will have associated most of the models output variability while in the case of LDA, the first components will have the combination of the largest mean differences between the classes, as discussed in sections 3.3.1 and 3.3.2. Figure 5.21 shows the results obtained.

The first component using PCA, has high values (>0.4) for TEP, MAWEP and HTP categories, and smaller values for all other categories while the 2nd has important coefficients for ADP, EP, GWP and OLDP categories. These results clearly show that toxicity related categories (TEP, MAWEP, HTP, and to a lesser extent FWEP), are the ones which have the highest variability and are selected in the first pc; while ADP, GWP and OLDP are ranked second most variable categories and are mostly related to consumption of raw materials specially ADP and GWP.

In the case of LDA components the first holds a very high value for the EP category while the second component shows relationships between AP, MAWEP and POP. This clearly shows that EP is the category that best differentiates options. Figure 5.22, shows the transformed values (z-values) for both multivariate techniques.

The application of both techniques sheds light in the relationships that different indicators have in the case of PCA, while LDA helps in devising which indicators help in differentiating options.

5.1.3.3 Results using aggregating LCIA methodologies

All former analysis were done considering the CML v2 mid points impact categories, as discussed in sections 2.2.5 and 3.4.3, these impact categories can be aggregated in different ways. One of such is the application of nadir-utopian point distances (as discussed in section 3.1.3, related to the TOPSIS methodology), while the other is related to the use of end point LCIA. SimaPro allows for calculating LCIA using different methodologies.

Utopian and Nadir points Other possible way of assessing which of the three options is better than the other is the calculation of distances towards nadir and utopian points as dis-

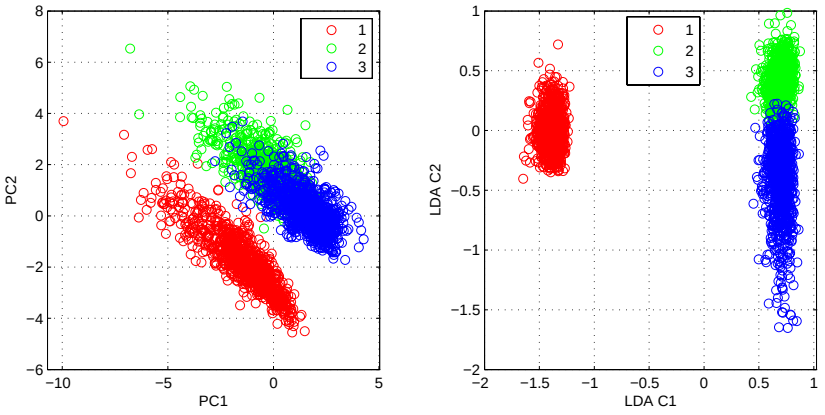


Figure 5.22: Principal and linear discriminant scores, colored by WWT option.

cussed in section 3.1.3. These points represent the worst and best single objective solutions combined irrespective of which alternative provides them. In the case of the deterministic assessment, these distances are calculated as in Eq. 3.9, while in the case of stochastic, these are calculated per scenario and the mean and CI values are summarised in Table 5.19. In the case of deterministic and stochastic impact assessment results, option 3 shows the shortest distance to the utopian point and the largest distance to the nadir point (see bold values in Table 5.19). Regarding options 1 and 2, the second remains the closest to nadir point in both approaches, while the results differ regarding the utopian point distance. The CI in all cases shows a great deal of overlapping, which prevents the selection of one of the options based on the utopian or nadir distances.

End point LCIA metrics results The Impact 2002+ (IM02), EcoIndicator99 (EI99) and EPS have been selected. These methods use different CFs for mid and end-point impacts, see section 3.4.3. End-point impacts, which a single scalar value, are aggregated by addition normalisation and weighting into a single metric. CML v2 does not provide with end-point CFs nor with a set of weights, however in this case weights have been set to 1 for all normalised mid-point indicators and the CML v2 overall impact is calculated as the addition of normalised mid-point impact categories. This will allow for comparison of this result with other end-point indicators, the result is indicated using cumCMLv2. Three different MC simulations, of 1000 scenarios each, were performed. Each of them using different end-point metrics. Figure 5.23 presents the box plots of end-point results, from this figure it could be foreseen that process options will be almost indistinguishable, however a clearer picture is drawn from Figure 5.24[15], where crossings between curves appear in some cases only, such is the case of the

Table 5.19: Nadir and Utopian point distances for each WWT option. Bold values represent shortest and largest distances to utopian and nadir points. CI intervals are calculated for the stochastic results. considering the 95% quantiles.

Approach	Deterministic		Stochastic			
Distance to	Nadir point	Utopian point	Nadir point	CI	Utopian point	CI
Option 1	4.069	5.449	4.134	[1.341,7.169]	4.915	[2.142,8.016]
Option 2	1.872	6.974	2.949	[0.920,6.614]	5.753	[2.276,8.797]
Option 3	**7.280**	**1.149**	**6.869**	[2.889,9.384]	**1.822**	[0.110,5.992]

[15]The box has lines at the lower quartile, median, and upper quartile values. Whiskers extend, 1.5 times the interquartile range, from each end of the box. Data outliers are considered for values beyond the ends of the whiskers and

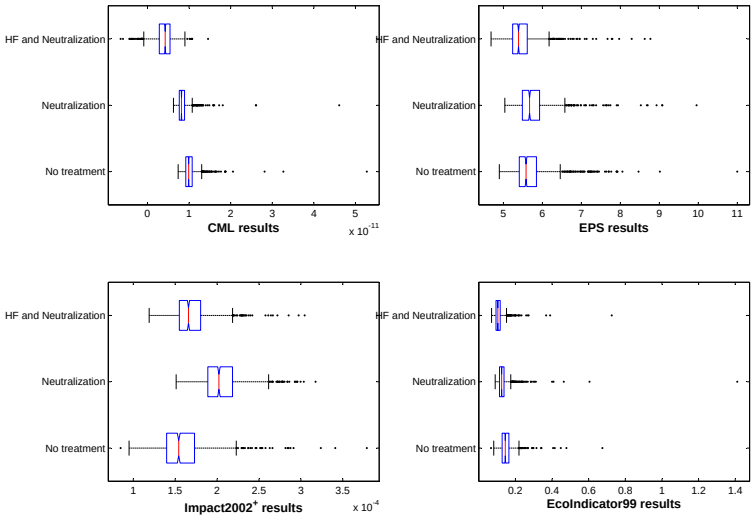


Figure 5.23: Box plots representing the MC simulation runs for different end-points.

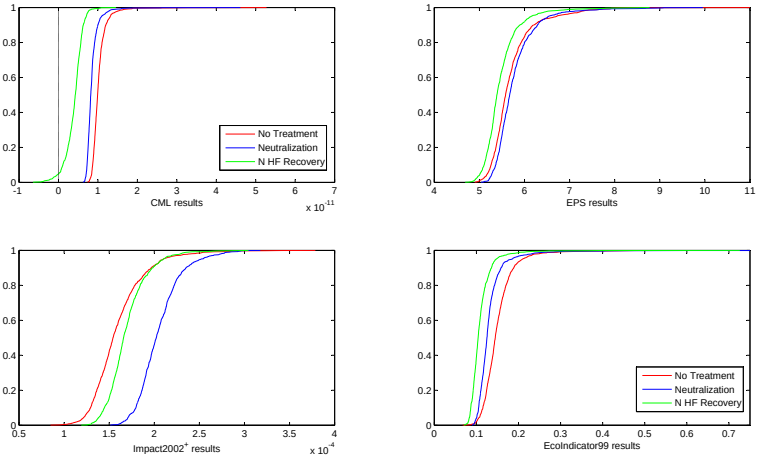


Figure 5.24: CDFs for all three WWT options for different end-point EIs.

EPS results for options 2 and 1; and for IM02 for options 1 and 3. Note that curve crossing's occur at high cumulative probability values. The probabilities of being the best and worst off all options have been calculated as in the case of mid-point metrics, using Eq. 5.20, results have been summarised in Table 5.20. In all cases the probabilities obtained of best and worst option are larger than 0.9 and it is possible to decide between different options and appropriately select one of the options. In the case of aggregated CML (cumCMLv2) it is found that the worst option is 1 while the best is 3, the same ordering result is obtained for EI99. In the case of EPS, the best option is 3 but the worst is 2, being the second best 1. For IM02 the best option is 1 while the worst is 2, being the second best the third option.

are displayed with a red + sign (Mathworks, 2009).

Table 5.20: Probabilities of being the best or worst for different options comparing end point metrics.

End point	Prob. of being	Option 1	Option 2	Option 3
cumCMLv2	best	0.000	0.000	**1.000**
cumCMLv2	worst	**1.000**	0.000	0.000
EI99	best	0.002	0.000	**0.998**
EI99	worst	**0.988**	0.012	0.000
EPS	best	0.000	0.000	**1.000**
EPS	worst	0.052	**0.948**	0.000
IM02	best	**0.952**	0.000	0.048
IM02	worst	0.003	**0.997**	0.000

5.1.4 Step 4 - Interpretation

Regarding LCI, results show that the three options lead to similar outcomes in most of the calculated environmental interventions, but there are differences in the case of lime and steam consumption which are inherent to the WWTs structure. Differences in the HF emissions to water were also found, and are attributed mainly to HF recovering as a byproduct. An important point risen from the LCI stage is that the consideration of the recovery of HF as H_2SiF_6 is important due to the savings in the overall consumption of raw materials and utilities from a LC perspective, as shown in Table 5.13, this point is completely missed if only the PA production echelon is analysed as shown in Table 5.3.

In the case of the impact assessment four different approaches were taken: the first considering all values as certain (deterministic), and the rest considering uncertainty in the model's parameters. The first two uncertain approaches analyse mid-point MC simulation results using classical statistics and probabilities, while the third analyses end-point results considering probabilities.

Deterministic conclusions The biggest normalised EIs were found for MAEP, Figure 5.11, shows the different process contributing to the overall value, which is found linked to the phosphate rock and sulphuric acid production process. AP is found to be due to the sulphuric acid and sulphur production processes. Regarding EP two trends are found in the case of Option 1 it is associated to the PA production step (more than 80% see Figure 5.13(a)), while for the other options the most important processes are rock production and sulphuric acid production. ADP for all three options is mainly caused by the consumption of phosphate rock, being sulphuric acid production the 2nd most important process. In the case of GWP, Options 2 and 3 score high due to the production of lime for neutralisation and in second and third place comes the consumption of phosphate rock and sulphuric acid, which in the case of Option 1 are the first and second most important process.

The former findings are in line with the LCI results, options that scores low values of HF emissions show low MAEP values see Tables 5.3 and 5.14. Similar results can be seen for the case of options consuming high amounts of lime (option 2) and scoring high values for the case of ADP and GWP. The effect of steam consumption (modelled considering heat production at industrial furnace) passes nearly unnoticed given that it's impact is very small compared to the other process.

One of the most important findings of this analysis is that neither of the three options scores better (smaller) in all 10 impact categories. Option 1 scores better in 4 out of 10 categories, while Option 3 is best for the remaining categories. Option 2 remains always as second or worst option and in this sense can be considered as dominated in Pareto efficiency terms. If all impact categories were regarded as equal in terms of normalised impact, the CML normalised results could be directly added together, Option 3 is better than 2 and option 1 is the last. Different impact categories weighting will most probably produce different ordering of options.

Mid point metrics stochastic considerations The inclusion of uncertainty in parameters associated to the process and environmental models and to other SC LCIs have shown influence on EI results. It was found that the set of parameters that affect the most to results is the one associated to the LCIs of process connected to the PA production echelon, see Figure 5.16. The MCS results, considering all parameters as uncertain, for the three WWT options show that there is overlap on their CI, see Figures 5.19 and 5.20. Two different options ordering were considered by taking into account the lower mean value and the probabilities of being the best/worst option.

In the case of the EP, GWP, MAEP, OLDP and TEP categories, the deterministic and both stochastic orderings are the same. Similarly to the deterministic case no option scores the best in all categories. If the decision maker considers these categories as the most important a deterministic analysis would have been sufficient, see Table 5.18. It is found that for the case of categories where no crossing of CDFs curves is found both stochastic methods provide the same ordering, which coincides with the deterministic approach.

In the case of ADP, no clear differentiation between options 1 and 3 is possible, being both of them better than option 2, that remains 3rd. For the HTP impact category option 3 is clearly the best, but no ordering of the remaining two options is possible given the low values of the binary comparison probabilities obtained. For the remaining indicators (AP, FWEP, and POP), no possible general ordering can be made from the calculated probabilities. For these five indicators the generation of an options ordering requires of more information regarding accepted values of each category impact. Based on such impact category value the probabilities of attaining it can be obtained from the CFDs and the ordering can be completed.

End point metrics stochastic considerations The use of nadir-utopian point distance concept provides with the same decision if the deterministic and the mean from the stochastic results are compared. These two approaches selected option 3 as the closest to the utopian point, while option 2 is the closest to the nadir point. However when the distances CIs are calculated, they show a great deal of overlapping, which prevents decision based on stochastic results.

In the case of the use of end point metrics, the results obtained show that cumCMLv2 and EI99 select as better option the one where recovery occurs (option 3), and as worst option 1; EPS coincides in the best option but selects as worst option 2, while IM02 selects option 1 (ocean disposal) as the most environmental friendly and option 2 as the worst.

5.2 Co-gasification case study

Integrated gasification combined cycle (IGCC) power production combines a gasification system with a Combined Cycle (CC) power system that integrates one or several gas turbines and/or one or several steam turbines including a Heat Recovery Steam Generator (HRSG) system. This makes it possible the use of multiple solid fuels, usually coal, to produce electricity. Biomass and of other low grade materials, such as petcoke or municipal solid wastes, can also be used and thereby reduce environmental and disposal costs. Co-gasification can be defined as the gasification of coal with other fuels, usually waste materials and/or biomass.

In the gasifier, fuel is converted into synthesis gas (syngas), which is a mixture of mainly H_2 and CO in different proportions. This synthesis gas requires to be cleaned in a train of purification units before being combusted. Gas cleaning before combustion leads to lower NOx and SO_2 emissions compared to conventional pulverised coal plants (Gasification-Technologies-Council, 2008). Typical byproducts are slag, arising from mineral material present in the feedstock and sulphur, both of which may be marketable. There are three different types of gasifier: (i) entrained bed, (ii) fluidised bed and (iii) moving bed. The use of coal/biomass combinations for IGCC applications is technically feasible up to 10% in an oxygen-blown entrained bed gasifier. The limitation is mainly due to the biomass pretreatment needs, as straw and/or sewage sludge need to be dried before entering the gasifier, and therefore efficiency decreases (Valero & Usón, 2006). A demonstration of the technical and economical feasibility of biomass to power conversion can be found in several works (Bridgwater, 1995, 2003).

Coal based IGCC plants are still not completely commercial, as all plants throughout the world are currently demonstration plants. Research and development of IGCC plant technology began in the 1970s. The eighteen gasification power plants currently operating around the world (Liu *et al.*, 2008), mainly in Europe and the USA, are demonstration plants with capacities of 50 to 600 MW. The aim of the research in this field is to improve the environmental performance and decrease marginal costs. However the current challenges in IGCC plants are capital cost and technology availability / reliability (Gasification-Technologies-Council, 2008). According to Gasification-Technologies-Council (2008) and Maurstad (2005), it is possible to recognise certain environmental pros and cons of IGCC plants:

- Advantages
  - The IGCC process can reduce their emissions due to fuel gas clean up, instead of flue gas clean up; Yuehong *et al.* (2006) and Valero and Usón (2006) studied coal co-gasification and found it to be a promising technology for reducing emissions.
  - Due to high partial operating pressures, impurities can be removed more effectively than in a conventional coal flue gas cleaning system;
  - IGCC technology leads to lower emissions of SOx, NOx and particulate matter;
  - Sulphur can be efficiently removed using currently available technologies;
  - Ideally, all gasified solids are converted into gas, but mineral material (ashes and other inert species), is transformed into slag which can be used in construction and building applications;
  - CO_2 can be captured using commercially available technologies, for instance by using water-gas shift reactors to transform CO into CO_2.
- Disadvantages
  - Biomass and wastes produce more CO_2 than coal during an electricity generation process;
  - The release of NOx depends mainly on the gas to electricity conversion stage and consequently gas cleaning to a high standard before the combustion stage is not the optimal approach.

- To achieve high environmental standards, a large economic investment in the operation and maintenance of the gas cleaning system is necessary. For instance, the costs of IGCC plants are between 10 and 20% higher than a natural gas fired CC plant (Ansolabehere *et al.*, 2007; Katzer, 2008).
- Plant reliability is a problem due to long construction periods and few real experiences.

As Jiang *et al.* (2002) points out, in order to increase the efficiency of an IGCC plant, integration is a key parameter. The gas system is composed of a GT, an air separation unit (ASU) and the gasification unit. The GT supplies part of its work as compressed air to the ASU, which supplies O_2 to the gasifier and N_2 for the syngas dilution and cooling before combustion in order to reduce NOx emissions. The flowsheet of a typical IGCC is shown in Fig. 5.25, which includes a gasifier and a series of gas purification units, and the GT and ST coupled to the HRSG. Heat is recovered by producing steam in the HRSG unit. Further downstream, this steam is used in a Steam Turbine (ST) to produce electricity.

The ASU is used to obtain enriched O_2 air at a purity of 85%wt. Steam, O_2 and fuel raw materials enter the gasifier and are converted into synthesis gas (syngas), which is cooled before it enters the purification units. Non-combustible materials (ashes) are removed efficiently as slag in the gasification reactor due to high pressure and temperature conditions, and the remaining dust particles are extracted from the synthesis gas by means of ceramic filters. Downstream of the ceramic filter other syngas purification units are: a Venturi Scrubber (VS), a carbonyl sulphide (COS) hydrolysis reactor, a Sour Water Steam stripper (SWS), an amines[16] absorber and a sulphur recovery Claus plant.

In the VS, syngas is placed in contact with a water stream that absorbs and removes acid (mainly H_2S) and basic (mainly NH_3) pollutants. Polluted water is treated in the SWS stripper and recycled back to the VS, which closes a water loop and decreases the overall plant-wide water consumption. The SWS stripper unit needs to be purged due to the build up of pollutants. The purged water is treated in a WWT plant and disposed of. Syngas is further purified through the COS hydrolysis reactor. This unit converts COS into H_2S, which is removed in the amines absorber. Thus, SO_2 emissions are controlled due to the removal of sulphur species (COS and H_2S), from the syngas before combustion in the GT. Polluted gas streams from the SWS stripper, COS hydrolysis section and amines absorber are sent to a Claus plant, where sulphur, mainly from H_2S, is recovered in liquid form. The clean gas obtained, after the amines absorber, is sent to the GT. NOx emissions are controlled partially considering different aspects: (i) using a combustor geometry which is specifically designed for its control, (ii) decreasing the relation oxidising agent/air, (iii) diminishing the flame temperature and the residence time at top temperatures. The later is achieved with clean gas saturation with water vapour and N_2 addition from the ASU. Heat from the exhaust gas after the GT is recovered in the HRSG system. CO_2 emissions are produced in the GT, while CO emissions are minimised as they are oxidised completely in the GT. Furthermore, according to (Ansolabehere *et al.*, 2007; Frey & Zhu, 2006) the integration that can be achieved on ASU-CC has three possible levels of integration: (i) a non-integrated ASU - with no N_2 injection or air extraction; (ii) a partially integrated ASU - with N_2 injection; and (iii) a totally integrated ASU, which combines N_2 injection and air extraction. The ST system, is based on heat recovery from several streams, by producing steam. All former integration possibilities can be used in coal gasification power stations and they can also be used for coal co-gasification.

With the aim of reducing the disadvantages of the current technology and knowing that coal is a worldwide abundant source with stable price, research is focused on new coal feeding systems, liquid CO_2 for feed transportation, and the use of air instead of O_2 as gasifier

[16]Several other amines can be used, in this case: N-MethylDiethanol Amine is selected, see section 5.2.2.1.

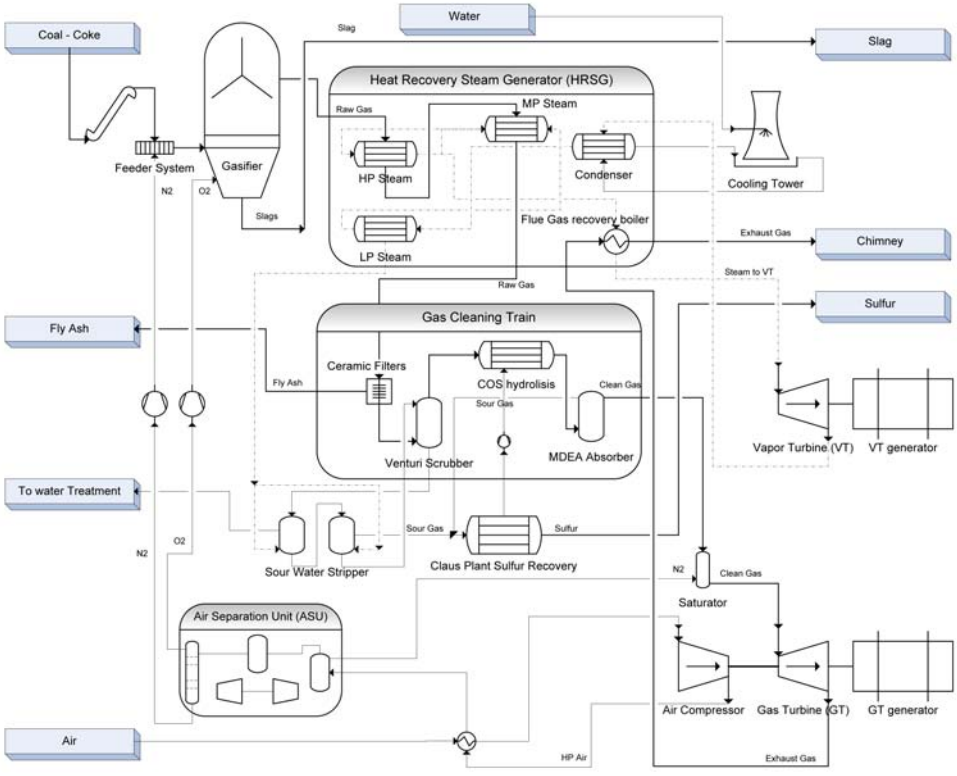


Figure 5.25: Typical IGCC plant layout

agent. In this sense, IGCC power plants current challenges include: CO_2 management and H_2 production-purification, possible integration (heat and power) between operating units and the co-gasification of different feedstocks.

5.2.1 Step 1 - Goal and scope definition

It is clear that the current challenges for IGCC power plants include: the co-gasification of different feedstocks, the H_2 production-purification, and the CO_2 management.

The study is focused on studying the environmental contributions changes obtained by the use of different raw material composition feeds in a IGCC plant. The ELCOGAS Puertollano power plant is used as case study, to this end, a system boundary and a functional unit (FU) have to be defined.

A model of a co-gasification plant is required, considering extraction and processing of raw materials, all of which will constitute the system. This boundary setting fits a "cradle to gate" approach, being the gate at the .

It is worth mentioning that the waste water treatment (WWT) plants are not included. The sulphur obtained from Claus plant is analysed specially to see which impacts are associated to it, in this case it is considered to be a credit and negative EIs are associated to it, while in other cases is disregarded.

Regarding the FU, a 1MJ-capacity of electricity production FU has been chosen. The objective of this analysis is to look specifically at co-gasification of different feedstocks, namely coal and petcoke, using an IGCC conceptual model for assessing the electricity production and its associated emissions.

5.2.2 Step 2 - Model building and data gathering

IGCC operation mainly requires fuels (coal, petcoke and others) and other components for the gas cleaning train. The former materials require to be produced and its emissions accounted for. For the SC echelons which encompass the production and extraction of raw materials, LCI of emissions are retrieved from the Ecoinvent database (Ecoinvent, 2006). In the current case, data regarding production of coal, petcoke, sulphuric acid and sodium hydroxide is required given their consumption for electricity generation.

Emission estimation and raw material consumption of the IGCC is calculated using a simulation model. IGCC models that can be found in the literature are usually validated with data from existing plants. Table 5.21 provides a summary of the most recent works on IGCC models. As it can be seen, most of the published work has focused on coal as raw material, and on an entrained bed gasifier as the most extended gasifier technology. However, in (Yuehong *et al.*, 2006) a new type of gasifier (based on a shaft furnace reactor) is developed and modelled for IGCC power plants. Table 5.21 shows that AspenPlus is the most common software used for modelling purposes, but no exhaustive model for the entire plant is reported in published articles, which generally focus on the gasifier plant section. All reported models have oxygen-blown gasifiers. Costs for design purposes, which are an important feature to be included in this type of work, are reported in only 9 of the 14 reviewed works.

The work based on the Texaco IGCC (Frey & Akunuri, 2001) is one of the most exhaustive models found in the literature. Other works that enhance the flowsheet have been based on it such as (Frey & Zhu, 2006), which analyses different levels of integration within ASU-CC, and Ordorica-Garcia *et al.* (2006), which incorporates CO_2 removal technology. The ELCOGAS Puertollano power plant, which is the basis of case study considered model, has been used in other works (Campbell *et al.*, 2000; Kanniche & Bouallou, 2007), in which the authors evaluated whether to include a CO_2 removal train. Arienti *et al.* (2006), model different plant configuration scenarios, taking into account a fix demand of H_2 to be accomplished, and also consider that the remaining gas is converted into power. Other papers study the efficiency of the whole plant (Descamps *et al.*, 2008; Desideri & Paolucci, 1999) including H_2 purification units. Desideri and Paolucci (1999) modelled a CO_2 removal train in AspenPlus, comparing it with literature data and performing a cost evaluation. Descamps *et al.* (2008) studies the integration of CO_2 capture in a complete and detailed IGCC power station, a simulation model is used in order to calculate the efficiency of the whole plant.

In previous works, the main focus has been the gasifier model and/or possible integration with other flowsheet units and not on the gas purification units. In order to generate reliable estimates of emissions and syngas composition, special attention has to be paid to the gasifier and gas purification sections. This is a step forward compared to previous works in which and is required for the estimation of EIs.

Table 5.21: Summary of current state of the art regarding IGCC modelling

Source	Software	Raw material	Data for validation	Technologies
Desideri and Paolucci (1999)	AspenPlus	Coal	Data from the literature	CO_2 removal configurations (methanol and Selexol solvents and activated MDEA with a CO shift conversion unit) added to Puertollano IGCC power plant scheme
Campbell *et al.* (2000)	ECLIPSE	Coal and Coal + petcoke	Puertollano IGCC power plant	FpT, ASU, filter, HRSG, venturi scrubber, COS hydrolyser, MDEA absorber, Claus plant
Frey and Akunuri (2001)	AspenPlus	Coal		FpT, ASU, gas cooling, filter, venturi scrubber, process condensate treatment, selexol absorber, Claus plant, Beavon-Stretford unit, HRSG
Zheng and Furinsky (2005)	AspenPlus	Coal	Bilbiography and suppliers	FpT, gas cooling, filter, venturi scrubber, COS hydrolyser, Selexol/Purisol absorber, Claus plant, SCOT tail gas, HRSG
Ordorica-Garcia *et al.* (2006)	Aspen Plus	Coal	Texaco-gasifier based IGCC	FpT, ASU, HRSG, cold gas clean up section, Selexol adsorber, Claus/SCOT sulphur recovery section, with or without CO shift conversion unit, and a glycol plant, with or without an acid gas stripper
Yuehong *et al.* (2006)	AspenPlus	Coal with low carbon containing fuels	Experimental studies	Gasifier
Frey and Zhu (2006)	AspenPlus	Coal	Texaco-gasifier based IGCC	FpT, ASU, gas cooling, filter, venturi scrubber, process condensate treatment, selexol absorber, Claus plant, Beavon-Stretford unit, HRSG
Arienti *et al.* (2006)		Asphalt and petcoke		FpT, ASU, syngas treatment (including acid gas removal and Claus plant), hydrogen production (CO shift reaction, PSA)
Martinez *et al.* (2006)	Matlab	Petcoke	Shell and Texaco operation plants	Filter, wateri scrubber, water treater, gas cooling, COS hydrolyser, Rectisol absorber, Claus plant, ASU
Kanniche and Bouallou (2007)	AspenPlus	Coal + petcoke	IGCC unit of Puertollano, revaluated under ISO conditions	CO_2 removal configurations (methanol and Selexol solvents and activated MDEA with a CO shift conversion unit) added to Puertollano IGCC power plant scheme
Koukouzas *et al.* (2008)	AspenPlus	Solid waste and lignite	SVZ Schwarza Pumpe	FpT, filter, ASU, HRSG, COS hydrolyser, MDEA absorber, SCOT unit, Claus plant
Zhao *et al.* (2008)		Coal	Academia, power companies, manufacturers and coal companies	FpT, ASU, HRSG, filter, water scrubber/candle filter, sulphur removal unit (with COS hydrolyser), sulphur recovery unit
Nathen *et al.* (2008)	AspenPlus	Coal	US Department of Energy base cases	ASU, CC
Descamps *et al.* (2008)		Coal	EDF (Electricité de France) IGCC existing plant model. CO_2 removal unit, validated with published data	FpT, ASU, filter, HRSG, venturi scrubber, MDEA absorber, Claus plant, CO shift conversion unit, CO_2 removal with a physical absorption process with methanol

Table 5.22: Summary of current state of the art regarding gasifier modelling.

Source	Software	Raw material	Type of gasifier	Supplier	Time model State	Brief description
Wen and Chaung (1979)	Fortran	coal liquefaction residues and coal-water slurries	Entrained	Texaco	Steady	Gasification kinetics, transport rates and hydrodynamics. Gasifier divided conceptually into three areas: pyrolysis and volatiles combustion, gasification and combustion (gas-solid reactions), and gasification (gas-solid reactions). Heat produced in combustion supports the gasification endothermic process. Unreacted-core shrinking model is used for estimating reaction rates in heterogeneous kinetic reactions.
Govind and Shah (1984)	Fortran	coal liquefaction residues and coal-water slurries	Entrained	Texaco	Steady	Analogous to Wen and Chaung (1979), reporting velocities along the gasifier height.
Chen *et al.* (2000)	Not specified	Coal	Entrained	Pilot plant	Dynamic	It solves the mass, momentum and energy conservation equations in three dimensions. Three zones can be distinguished: devolatilization, combustion and gasification zones. It uses a Multi-Solids Progress Variables method, that allows an arbitrary number of coal-to-gas components. Consideration of turbulent flow. It can supply profiles of gas temperature and compositions along the gasifier.
Frey and Akunuri (2001)	Aspen Plus	Coal	Entrained	Texaco	Steady	Based on minimizing Gibb's free energy
Higman and van-der Burgt (2003)	Not specified	Solid carbon	General	Bibliography	Steady - Dynamic	Based on thermodynamic equilibrium (for a set of specific reactions) and mass and energy balances. Distinction between three different temperature zones in the reactor.
Usón *et al.* (2004) Valero and Usón (2006)	Engineering Equation Solver (EES)	Coal + petcoke + up to 10% biomass	Entrained	Krupp Koppers	Steady	Analogous to Wen and Chaung (1979), considering two isothermal zones along the gasifier. Introduction of contaminants formation.
Petersen and Werther (2005)	C	Sewage sludge	Circulating fluidised	Pilot plant	Dynamic	Fluid dynamics and a complete reaction network of the gasification: kinetic expressions for the pilot plant-sewage sludge have been found. Kinetic parameters from the literature, and adjusted to sewage sludge. Three dimensions model.
Brown *et al.* (2005)	Not specified	Biomass	Fluidised	Experimental data from bibliography	Steady	A non stoichiometric equilibrium model based on total tar measurements, is used to estimate the distribution of tars. Then, the product is formulated as a stoichiometric equilibrium model with reaction equilibrium temperatures differences. Adjustment (parametrisation) of these temperature differences by means of ANN: relationship with independent variables, such as T.
Martinez *et al.* (2006)	Matlab	Petcoke	Entrained	Shell / Texaco	Steady	Based on minimizing Gibb's free energy
Nathen *et al.* (2008)	AspenHysys	Coal	Entrained	Shell	Steady	Based on minimizing Gibb's free energy
Robinson and Luyben (2008)	AspenDynamics	Biomass and coal	Fluidised	General Electric (GE)	Dynamic	Based on a gasifier model in AspenPlus that is exported to AspenDynamics. Kinetic reactor in AspenPlus

5.2.2.1 Overall plant modelling approach

The model is implemented using two main chemical flow-sheeting environments, AspenHysys and AspenPlus.AspenHysys has been chosen as the platform for the overall process simulation because it is able to accept custom models as extensions with ease of coding. These extensions can be coded using Visual Basic, which is the case in this section. These models can range from complex chemical reactions (COS hydrolysis) or partial gasification steps (pyrolysis, combustion and gasification). AspenHysys also allows new chemical components not included in its database to be created, such as the non-stoichiometric solids required for defining fuel raw material and char. The contribution of the model proposed is two-folded: on the one hand, the use of currently available models together which brings a new model altogether and, on the other hand, the specific developments performed in the shape of user models and compounds.

Alternatively, AspenPlus is used for calculations involving water systems and electrolytes. These ionic models are required for solving phase equilibrium problems for unit operation systems, such as VS, SWS stripper and amines absorbers. In the ELCOGAS power plant a water-MDEA is used. The aforementioned models have been integrated in AspenHysys by means of Artificial Neural Network (ANN) extensions. ANNs have mainly been used by the scientific community as data based models in function approximation problems, see section 3.1.4.

Data required for training each ANN come from a design of experiments, performed using the AspenPlus sensitivity analysis (SA) tool. The SA is performed by varying model inputs around typical plant operating conditions, which were varied by a 10% and collecting model results. It has to be noted that not all possible input variable combinations were calculated[17], consequently some variables were fixed in some of the SA runs. Sixty percent of the AspenPlus sensitivity analysis results were used for ANN training while the rest were used for ANN model validation and testing.

For unit operations modelled in AspenPlus, the MDEA absorber and the SWS stripper, the number of input variables selected was 7, in each case. These variables were studied at three levels, requiring a total of $3^7 = 2187$ scenarios, but only 1458 were realised (66%). In both cases all output stream information was gathered and used as outputs of the ANN, in the case of the MDEA this represented 24 variables and in the SWS 23. Two instances of the algorithm 4.2 have been coded in two AspenHysys user unit extensions: NN-MDEA and NN-Stripper.

Gasifier modelling approach Although different gasifier models have been developed in the past its appropriate modelling continues to be a challenge. Selecting a gasifier model depends on the accuracy and robustness desired for the model. Zheng and Furinsky (2005) compared different gasifier models in AspenPlus and concluded that the overall performance of an IGCC plant is significantly influenced by the gasifier type and feedstock characteristics. Jurado *et al.* (2003) and Faaij *et al.* (1997), have worked with Matlab and AspenPlus in order to appropriately model biomass gasification in an IGCC. In Table 5.22 a brief summary of the different approaches for gasifier modelling are presented. There are three main possibilities:

- Equilibrium models, such as those found in (Brown *et al.*, 2005; Robinson & Luyben, 2008), which use a predefined set of equilibrium reactions is used.
- Gibb's equilibrium models, such as those found in (Frey & Akunuri, 2001; Martinez *et al.*, 2006; Nathen *et al.*, 2008), which use a general equilibrium model, without pre-specified reactions.

[17]This calculation will require the computation of 3^{nVars} scenarios, given that each variable is studied at 3 levels: [-10%, default value, +10%].

- Kinetic and mass transfer models, the most relevant is described by Wen and Chaung (1979) and Govind and Shah (1984); which is the source of all later works (Chen *et al.*, 2000; Higman & van-der Burgt, 2003; Petersen & Werther, 2005; Usón *et al.*, 2004; Valero & Usón, 2006).

The two first models are able to predict final gas compositions, and are mainly suitable for lumped parameter models, while the third model is also able to predict reactor temperature, composition and other profiles. The third option is the best choice if dynamic aspects are of concern. In the Gibbs reactor the reaction products are calculated based on a minimisation of Gibbs free energy for all possible species[18], while in equilibrium models only a set of proposed reactions are taken into account.

A conceptual model of the ELCOGAS Pressurised Entrained Flow gasifier is considered. The gasification process encompasses a sequence of four main steps (i) pyrolysis, (ii) combustion, (iii) gasification and (iv) gas equilibrium. The model assumes that the gasifier is a non-isothermal reactor with adiabatic behaviour. It also considers that feedstock enters the reactor with a maximum of 2%wt of moisture. Around 90% of the char is converted.

Pyrolysis is modelled using a series of experimental correlations from the specialised literature (Balzioc & Hawsley, 1970; Loison & Chauvin, 1964). It is considered that fuel raw material represented as: $C_aH_bO_cN_dS_e \cdot (H_2O)_wA$, is converted into char, which is represented as: $C_\alpha H_\beta O_\gamma N_\delta S_\epsilon A$. In both cases A represents the mineral matter (ashes) content. Stoichiometric coefficients (a, b, c, d, e and w) are based on the composition each fuel while (α, β, γ, δ and ϵ) are stoichiometric coefficients calculated based on reactor temperature and raw material volatile matter content (Balzioc & Hawsley, 1970; Loison & Chauvin, 1964). Volatile species are modelled considering methane formation, while tars are represented by benzene production. Production of pollutant species (H_2S, COS, NH_3 and HCN) is represented by the correlations taken from previous works (García-Labiano & Adánez, 1996; Kambara & Takarada, 1993) and industrial data. Every set of correlations is inferred from different coal types and analysis. Equation 5.21 represents the pyrolysis step considered in the gasifier.

$$C_aH_bO_cN_dS_e(H_2O)_wA \longrightarrow C_\alpha H_\beta O_\gamma N_\delta S_\epsilon A + volatiles + tars + wH_2O \tag{5.21}$$

In Eq. 5.21, stoichiometric coefficients are based on each fuel composition. Volatile species are modelled considering methane formation, while tars are represented by benzene production. Pyrolysis is implemented and simulated using an AspenHysys reaction extension with experimental correlations, which transform coal-coke-biomass mixture into char.

In the case of the combustion of volatiles produced by raw material pyrolysis, they are considered to be consumed completely by combustion to produce CO_2 and H_2O. The kinetics of the main reactions of char combustion were taken from Wen and Chaung (1979) and Govind and Shah (1984). This step considers total O_2 consumption, which provides a reductive atmosphere for the next step. The main reactions involve the combustion of volatiles as in Eqs. 5.22, 5.23 and 5.24.

$$2CO + O_2 \longrightarrow 2CO_2 \tag{5.22}$$

$$2H_2 + O_2 \longrightarrow 2H_2O \tag{5.23}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \tag{5.24}$$

[18]The species present in equilibrium are calculated considering that all of them can be products, consequently the number of linearly independent chemical reactions taking place ($N_{RQ}^{LI} = N_p - N_a$) is the number of products (N_p) minus the number of different atoms occurring in all species (N_a).

Char combustion is represented by Eqs. 5.25, 5.26 and 5.27. While char gasification comprises Eqs. 5.26, 5.27 and 5.28.

$$C_\alpha H_\beta O_\gamma N_\delta S_\epsilon A + (\alpha/2 - \gamma/2 + \beta/4 - \epsilon/2) O_2 \longrightarrow \alpha CO + (\beta/2 - \epsilon) H_2O + \epsilon H_2S + \delta/2 N_2 + A \quad (5.25)$$

$$C_\alpha H_\beta O_\gamma N_\delta S_\epsilon A + (\alpha - \gamma) H_2O \longrightarrow \alpha CO + (\alpha - \gamma + \beta/2 - \epsilon) H_2 + \epsilon H_2S + \delta/2 N_2 + A \quad (5.26)$$

$$C_\alpha H_\beta O_\gamma N_\delta S_\epsilon A + \alpha CO_2 \longrightarrow 2\alpha CO + \gamma H_2O + (\beta/2 - \epsilon - \gamma) H_2 + \epsilon H_2S + \delta/2 N_2 + A \quad (5.27)$$

$$C_\alpha H_\beta O_\gamma N_\delta S_\epsilon A + (2\alpha + \gamma + \epsilon - \beta/2) H_2 \longrightarrow \alpha CH_4 + \gamma H_2O + \epsilon H_2S + \delta/2 N_2 + A \quad (5.28)$$

Chemical reactions represented in Eqs. 5.25 to 5.28 are modelled in AspenHysys, using chemical reaction extensions developed specially for these reactions. These extensions make possible to model the char composition, which is a general function of temperature.

Volatiles and char combustion is modelled using a Continuously Stirred Tank Reactor (CSTR) with custom-made kinetic equations that represent reactions 5.22 to 5.25. Char gasification, is simulated with other CSTR model that takes into account reactions 5.26 to 5.28. Gasifier outlet gases (syngas) are considered to be in chemical equilibrium, which is accomplished using an AspenHysys Gibbs reactor model. After this last step, syngas is obtained. Synthesis gas is sent to an ashes distribution model, which splits the solid stream into slag and fly ash, based on industrial data. Raw material, char and ash components have been introduced as Hypo-Components.

Purification units modelling approach The model considers the existing units in the ELCOGAS power plant. All gas purification units work at high pressure (22 bar). The Venturi scrubber (VS) and sour water steam stripper (SWS) reduce the emissions of polluting compounds, mainly H_2S, NH_3 and HCN, by absorbing them in water. Later on, this water is cleaned in the SWS stripper using steam and two columns: one for acid pollutants abatement, and one for basic pollutants abatement. The aforementioned units are simulated in AspenPlus using the electrolyte properties package (ENRTL), which allows the complex chemical equilibrium found in this solution system to be taken into account. Chemical equilibrium constants (using Eq. B.2), for selected reactions are calculated using data from AspenProperties (see Table B.2), while the remaining are calculated using Gibbs free energy temperature correlations. In all cases VLE is modelled using the Henry law (see Eq. B.1) and using data from AspenProperties data bank (see Tables B.1). The VS is modelled using an AspenPlus two phase flash vessel with the main objective of reducing the high pressure of the water stream (from 22 to 1.5 bar) in order to ease the acid stripper column working conditions. Solutions of H_2SO_4 and NaOH are introduced into the SWS stripper to control the pH. The SWS stripper steam required is generated by vapourising a portion of treated water. The sour gas streamthat leaves these units is the mixture of the outlet gases from the stripper columns and it is sent to the Claus plant. Pre-treated water is sent to the WWT unit in order to adapt its pollutant concentrations to environmental law limits. The reactions considered for the SWS are shown bellow, see Eqs. 5.30

to 5.40.

$$2H_2O \longleftrightarrow H_3O^+ + OH^- \tag{5.29}$$
$$H_2S + H_2O \longleftrightarrow H_3O^+ + HS^- \tag{5.30}$$
$$HS^- + H_2O \longleftrightarrow H_3O^+ + S^{2-} \tag{5.31}$$
$$CO_2 + 2H_2O \longleftrightarrow H_3O^+ + HCO_3^- \tag{5.32}$$
$$HCO_3^- + H_2O \longleftrightarrow H_3O^+ + CO_3^{2-} \tag{5.33}$$
$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^- \tag{5.34}$$
$$NH_3 + HCO_3^- \longleftrightarrow NH_2COO^- + H_2O \tag{5.35}$$
$$H_2SO_4 + H_2O \longleftrightarrow H_3O^+ + HSO_4^- \tag{5.36}$$
$$HSO_4^- + H_2O \longleftrightarrow H_3O^+ + SO_4^{2-} \tag{5.37}$$
$$HCl + H_2O \longleftrightarrow H_3O^+ + Cl^- \tag{5.38}$$
$$HF + H_2O \longleftrightarrow H_3O^+ + F^- \tag{5.39}$$
$$HCN + H_2O \longleftrightarrow H_3O^+ + CN^- \tag{5.40}$$

Both absorption and stripping columns are modelled using the AspenPlus' RadFrac model, and it is assumed that the column stages attain chemical equilibrium. The AspenPlus simulation results are mimicked within AspenHysys by means of an ANN unit extension.

Regarding COS hydrolysis, the main reaction taking place in this unit is the COS hydrolysis reaction into H_2S which is commonly catalysed using alumina as a catalyst, see Eq. 5.41.

$$COS + H_2O \longleftrightarrow H_2S + CO_2 \tag{5.41}$$

The main objective of this unit is to contribute to desulphurisation by transforming COS into H_2S in order to maximise the sulphur retention in the MDEA absorber. It is assumed that the hydrolysis reaction follows a first order kinetic reaction for COS and for H_2O has a zero-order behaviour (Huang *et al.*, 2005; Rhodes *et al.*, 2000). The reaction rate constant follows an Arrhenius relation, see Eq. 5.42, pre-exponential factor (Ak_{COS}) and activation energy (E_{aCOS}) reported by Rhodes *et al.* (2000).

$$r = Ak_{COS} e^{-\frac{E_{aCOS}}{RT}} \rho_{cat} X_{COS} \tag{5.42}$$

The previously scrubbed syngas from VS and SWS stripper passes through a heat exchanger whose main objective is to heat the stream above COS dew point. After the COS reactor, this gas stream is cooled down by pre-heating clean gas from the MDEA absorber, just before it enters this unit. This reactor is modelled in Aspen Hysys by means of a Plug Flow Reactor (PFR). The kinetics within the PFR are modelled using a custom made reaction extension which takes into account the catalysed kinetic reaction information from Rhodes *et al.* (2000) and Huang *et al.* (2005).

Syngas acid species are partially removed by means of a basic water solution absorption, several different components can be used to fulfil such removal: MEA (Methyl ethanol amine), MDEA (N-MethylDiethanol Amine $C_5H_{13}O_2N$), TEA (Tri ethanol amine) and AMP (2-amino-2-methyl-1-propanol)[19]. A water and MDEA (50% w/w) solution is used as the liquid washing agent given that H_2S is highly soluble in it. Eqs. 5.43 to 5.48 summarise the solution chemistry modelled in this unit, chemical equilibrium constants where retrieved from AspenPlus, see

[19] In the case of CO_2 removal amines can be used for its removal, as well as other chemicals such as: DEPG (a mixture of the dimethyl ethers of polyethylene glycol with formula $CH_3O(C_2H_4O)_nCH_3$ where n ranges from 2 to 9) and DGA, (diglycolamine).

Table B.2. ENRTL parameter values where gathered from AspenPlus database and from Posey and Rochelle (1997). A similar approach was used by Liu *et al.* (1999), to model CO_2 absorption in MEA-water solutions.

$$CH_3-NH^+=(C_4H_4-OH)+H_2O \longleftrightarrow CH_3-N=(C_4H_4-OH)+H_3O^+ \quad (5.43)$$

$$CO_2+2H_2O \longleftrightarrow H_3O^+ + HCO_3^- \quad (5.44)$$

$$HCO_3^- + H_2O \longleftrightarrow H_3O^+ + CO_3^{2-} \quad (5.45)$$

$$2H_2O \longleftrightarrow H_3O^+ + OH^- \quad (5.46)$$

$$H_2O+H_2S \longleftrightarrow HS^- + H_3O^+ \quad (5.47)$$

$$H_2O+HS^- \longleftrightarrow S^{2-} + H_3O^+ \quad (5.48)$$

The polluted MDEA solution stream is decompressed before it enters the desorption column and it is assumed that MDEA is completely recovered. The inlet gas comes from the COS hydrolysis reactor and the outlet gas goes to the Claus plant. Absorption columns are modelled with AspenPlus's RadFrac model, assuming all stages attain chemical equilibrium. The simulated unit is introduced into AspenHysys by means of an ANN extension similar to the one developed for the VS-SWS units.

Sulphur recovery is achieved using the Claus process by, producing liquid sulphur while venting innocuous N_2. This process consists of two parallel thermal stages and two catalytic stages with alumina as catalyst. The last step is hydrogenation, which is also catalysed, and is used to increase overall sulphur recovery. The reactions for the Claus process are shown in Eqs. 5.49 to 5.59.

$$H_2S+1.5O_2 \longrightarrow SO_2+H_2O \quad (5.49)$$

$$2H_2S+SO_2 \rightleftharpoons 1.5S_2+2H_2O \quad (5.50)$$

$$H_2S \rightleftharpoons 0.5S_2+H_2 \quad (5.51)$$

$$2NH_3 \longrightarrow N_2+3H_2 \quad (5.52)$$

$$2NH_3+1.5O_2 \longrightarrow N_2+3H_2O \quad (5.53)$$

$$2CO+S_2 \rightleftharpoons 2COS \quad (5.54)$$

$$CH_4+2S_2 \longrightarrow CS_2+2H_2S \quad (5.55)$$

$$COS+H_2O \longrightarrow CO_2+H_2S \quad (5.56)$$

$$CS_2+H_2O \longrightarrow COS+H_2S \quad (5.57)$$

$$S_2+2H_2 \longrightarrow 2H_2S \quad (5.58)$$

$$SO_2+3H_2 \longrightarrow H_2S+2H_2O \quad (5.59)$$

Sour gas is fed to two parallel kilns modelled using two heat exchangers, which are used to adjust the desired inlet temperature, and two AspenHysys CSTR models. The reactions that take place in these CSTR units are represented by Eqs. 5.49 to 5.55. Liquid sulphur is recovered from reactor outlets using two phase flash units to model the liquid vapour separations. Gas reactor outlets are fed to a series of two equilibrium reactors, which constitute the catalytic stages represented by the chemical reactions 5.50 catalysed, 5.56 and 5.57. The hydrogenation step takes place in a conversion reactor that considers S_2 and SO_2 conversion into H_2S (see Eqs. 5.58 and 5.59). Liquid sulphur is modelled in AspenHysys as a Hypo-Component. In each stage, condensation process recovers the maximum possible liquid sulphur, which is collected in a sulphur pit. A recycle gas is obtained which is mixed with the VS's outlet gas and is sent to the COS hydrolysis reactor inlet. It is important to mention that it is assumed that the catalytic stages are considered as equilibrium reactors and that the kinetic reaction expressions and parameters are retrieved from Hawboldt (1998) and Monnery *et al.* (2000). No

custom made reaction extensions were necessary in this step, and data from literature was used in all AspenHysys models without further modifications.

HRSG and power generation modelling approach Within the model developed it is considered that the HRSG system provides steam at three pressures: High Pressure (HP, 127 bar), Intermediate Pressure (IP, 35 bar) and Low Pressure (LP, 6.5 bar). HP, IP and LP steam streams are produced when heat is recovered from the GT exhaust gases (at 535º C). Moreover, in the HP and IP water steam circuits, heat is provided from two sources (i) GT flue exhaust gasses and (ii) cooling down of the gasifier outlet synthesis gas (from 800º C to 240º C). The LP steam circuit uses only one the GT flue exhaust gasses.

Given that no detailed information regarding heat exchanger geometry was required or available; all heat exchangers (boilers or others) were modelled using a simplified heat transfer model. The model calculates a heat flow based on the mass stream enthalpy change. This heat flow is used to heat up water streams to produce steam. The heater model is part of the AspenHysys model library.

In all CC power plants, the final power is the addition of the power obtained from the GT and ST cycles. The CC term comes from the integration of the two cycles that use the exhaust gas from the Brayton cycle heat for steam heating. In the developed model, the GT's compressed air is divided into two streams: one stream that continues to the combustor and one that goes into the ASU. The combustor is simulated in AspenHysys using a Gibbs equilibrium reactor. The clean gas enters after saturation, dilution and cooling processes which are performed by adding cool N_2 and steam. The gas expansion is used in the GT and the exhaust gas is cooled before being let out into the atmosphere. In the Rankine cycle, after the expansion, the exhaust steam is condensed by cooling water in a closed circuit. The condensate is pumped back to the HRSG system. Steam and gas turbines are modelled using the isentropic turbine AspenHysys model. The isentropic assumption is not very stringent and the model can tackle with mechanical and thermodynamical efficiencies if more industrial information is available. However, due to the conceptual level that this model claims to have, this assumption is accepted.

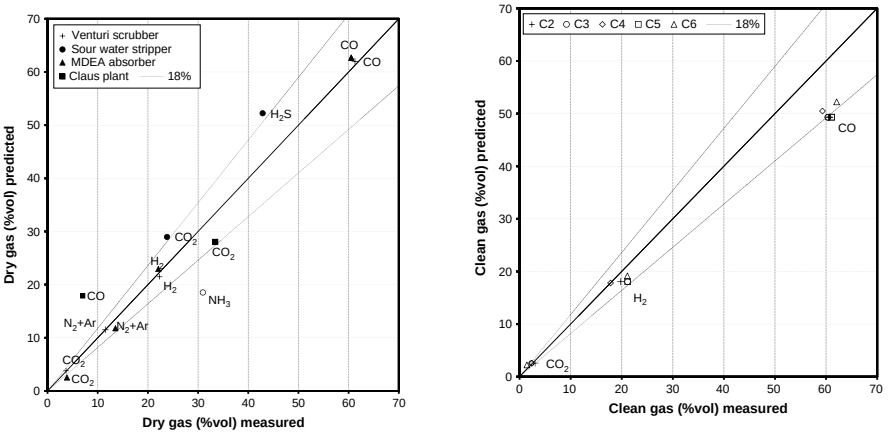
Table 5.23 summarises the different raw materials used in this section for the analysis of co-gasification options in an IGCC plant. These are different mixtures of solid fuels with different coal and petcoke ratios (C1 to C7). The last case C8 is a mixture of coal and petcoke with olive pomace (orujillo), a residual biomass. Operating conditions are the same in all the cases:

- Feedstock: 2600 t/day
- Working hours: 7200 h/year
- Gasification temperature: 1600º C
- Gasification pressure: 25 bar
- O_2/feedstock ratio (in mass basis): 0.715
- H_2O/feedstock ration (in mass basis): 0.13

5.2.2.2 IGCC model validation

The model required to be tested in terms of gas composition along the gas cleaning train and due to feed stock changes. To this end, model results were compared to the industrial available data. Inlet information from the ELCOGAS power plant is summarised in Table 5.23. Model results were compared with the industrial data as shown in Fig. 5.26.

The gas purification units were evaluated individually for the base case (50/50% coal and coke, see case C4 from Table 5.23), the results are shown in Fig. 5.26(a). All gas species having



(a) Results for each gas purification stage.

(b) Results for different feedstocks.

Figure 5.26: Comparison of gas composition results for different feedstocks and purification stage.

a volume composition larger than 3% considered. The VS unit model predicts quite accurate values for all the components, while the SWS unit model produces values slightly higher than the industrial data for CO_2 and H_2S, and lower for NH_3. The SWS is the unit which has the higher discrepancies, when compared to plant measurements. The largest model-industrial data discrepancy in the Claus plant is the CO gas composition, while the amount of liquid sulphur removed is quite similar (data 3113 and model 2810 kg/h). There is a remarkable agreement between the industrial and model predicted composition of the clean gas for the MDEA absorber. The former comparison shows that models allow for a good estimation of most important flowsheet streams in terms of flow-rates and compositions.

The model was also tested considering changes in the feedstock, which required the gasification and purification steps to be considered together. In Fig. 5.26(b) model results for different feedstock compositions (cases C2 to C6 from Table 5.23) are plotted against the corresponding industrial data. The final clean gas composition for the selected feedstock compositions shows again a good agreement with industrial data. The model predicts lower than measured gas concentrations for the main components H_2 and CO, being CO the component with the largest differences. Moreover, the model shows good agreement, a maximum error of 18%, between the simulated results and industrial data for outlet streams from the gasifier, venturi scrubber, sour water stripper, Claus plant and MDEA absorber. This maximum percentage in streams components amount is acceptable since an approximation of 15-20% is enough precision to take decisions concerning the process layout alternatives at the synthesis stage in preliminary (conceptual) design (Wells & Rose, 1986).

It has to be emphasised that a better adjustment to the specific data set of ELCOGAS power plant would imply data over fitting that could eventually lead to bigger discrepancies with other plant data sets. It can be added that, the model provided is general enough to accept other plant configurations. In this sense, other advanced models for gas purification, could be also incorporated and analysed for their eventual implementation in practise.

The model is also used considering the plant using only natural gas (NG) as fuel. In essence, the CC for syngas production from coal gasification or NG is the same. Main difference is found in terms of fluxes, inlet air and fuel flows. For natural gas combined cycle (NGCC) the difference in mass flow of raw material remains three times higher for the IGCC mode. NG is directly introduced into the GT combustion chamber together with pressurised air, while gasification requires enriched oxygen (85%) that comes from the ASU, which is fed from pres-

Table 5.23: Different feedstocks used for each of the studied scenarios.

Composition	C1	C2	C3	C4	C5	C6	C7	C8[a]
Coal (%)	100	58	54	50	45	39	0	*50*
Coke (%)	0	42	46	50	55	61	100	*40*
Carbon (% ar)	40.30	59.76	61.61	63.46	65.78	68.56	86.63	59.7
Hydrogen (% ar)	2.76	2.97	3.00	3.02	3.04	3.07	3.28	3.32
Oxygen (% ar)	7.36	4.28	3.98	3.69	3.32	2.88	0.02	7.24
Nitrogen (% ar)	0.90	1.36	1.41	1.45	1.51	1.57	2.00	1.33
Sulphur (% ar)	1.03	3.03	3.22	3.41	3.65	3.94	5.80	2.84
Moisture (% ar)	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Ashes (% ar)	45.67	26.60	24.78	22.97	20.70	17.97	0.27	23.56
Volatile Matter	23.13	18.10	17.62	17.15	16.55	15.83	11.16	22.72
LHV_{dry} (MJ/kg)	15.745	23.103	23.804	24.505	25.380	26.431	33.264	23.104

[a] 10% of olive pomace is also feed.

Table 5.24: Raw materials consumption for different feedstock scenarios in [kg/FU].

Flow	C1	C2	C3	C4	C5	C6	C7	C8	*NG*
Fuel	0.115	0.110	0.111	0.109	0.110	0.107	0.101	0.108	0.051
H_2O	0.0256	0.0244	0.0247	0.0243	0.0244	0.0239	0.0226	0.0240	0.7388
NaOH	0.00058	0.00055	0.00056	0.00055	0.00055	0.00054	0.00051	0.00054	0.00007
H_2SO_4	4.87E-06	4.64E-06	4.69E-06	4.62E-06	4.63E-06	4.54E-06	4.29E-06	4.57E-06	4.61E-06
CO_2	0.217	0.207	0.209	0.213	0.208	0.208	0.191	0.204	0.137
SO_2	7.37E-06	2.86E-05	2.93E-05	3.08E-05	2.92E-05	3.02E-05	2.65E-05	2.59E-05	7.08E-06
NO	0.00171	0.00163	0.00164	0.00167	0.00164	0.00164	0.00151	0.00160	0.00018
NO_2	4.91E-05	4.66E-05	4.71E-05	4.82E-05	4.70E-05	4.72E-05	4.33E-05	4.59E-05	4.68E-05

surised air that goes into this unit is from the GT compressor. In IGCC, the HRSG is enhanced with the using waste heat boiler from the gasifier that profits the waste heat of the syngas before entering the syngas cleaning units.

Fuel consumption, reported in Table 5.24, is the total amount of coal and coke, the percentage of each one of them is reported in Table 5.23. For the case of the coal production the Ecoinvent LCI used is "Hard coal supply mix/ES U", which corresponds to the coal mix used for electricity generation in Spain. In the case of coke production, it was assumed that the Ecoinvent LCI "Petroleum coke, at refinery/RER U" mimics the coke used in the ELCOGAS plant. Other raw material consumption such as H_2SO_4 and NaOH were considered to be represented by the Ecoinvent units for its production in the EU. Water consumption has been considered to require decarbonisation, and consequently the Ecoinvent LCI "Water, decarbonised, at plant/RER U", was used. Table 5.24, summarises the IGCC main LCI flows.

5.2.3 Step 3 - Efficiency and environmental metrics calculation

Two different sets of Key Performance Indicators (KPIs) are used in this section. First eco-efficiency based metrics related to the consumption of raw materials and energy production were calculated and as a second step LCIA metrics compared to aggregated thermodynamic metrics (CED, CExD and EF).

Raw material efficiency use metrics The KPIs calculated from the simulation output results are the net power, flue gas emissions (CO_2, NOx and SO_2) and raw material to power efficiency (Eff), which is based on raw material Low Heating Value (LHV)[20] and net obtained power ($NetPower$), see Eq. 5.60.

$$Eff = \frac{NetPower}{LHV_{RawMat}}\% \tag{5.60}$$

These metrics are used as eco-efficiency metrics, given that they relate the plant's production to its resource use. In order to compare different scenarios, all KPIs are normalised consid-

[20]The LHV has been calculated using the algorithm proposed by the Energy research Centre of the Netherlands (ECN).

ering the total inlet carbon flow. Net power which considers all turbines outlet power and compression work is compared for scenarios C1-C7. In Fig. 5.27, net power per kg of inlet carbon (C_{in}) is represented for each scenario. Efficiencies are shown in Fig. 5.27, and follow the same trend as net power: as the proportion of petcoke increases, the efficiency decreases.

Exhaust gas most important emissions (NOx, SO_2 and CO_2), per kg of total inlet carbon are represented in Figs. 5.28 and 5.29.

It has been found that net power decreases as the proportion of coal in fuel decreases. NOx emissions decrease as the proportion of petcoke increases, which is related to NOx forming in the GT, which holds the same amount of N_2 feed for all scenarios. No clear tendency is observed between feedstock changes and SO_2 emissions, which is mainly due to model inaccuracies. Nevertheless, the C1 scenario in which only coal is used is the scenario with less SO_2/kg C_{in} sent to the atmosphere. This is mainly due to the lower sulphur contents present in coal when compared to petcoke.

Fig. 5.29 shows the CO_2 emissions and kWh produced per kg of inlet carbon for all the considered feedstocks. The relationship between CO_2 emissions and kWh produced per kg of inlet carbon is quite linear for the set of studied scenarios, showing, as expected, that higher values of emissions per kg of inlet carbon when increasing the specific power production. Scenario C8 (with olive pomace) falls outside this possible linear relationship; in C8 a larger amount of kWh is produced per kg of inlet carbon compared to the petcoke and coal mixtures.

LCA related metrics A LCIA is performed based on the obtained LCI considering the previously defined FU and system boundaries. For the case of electricity generation broadly used impacts are Global Warming impact calculated using global warming potentials (GWP), acidification impacts using Acidification Potentials (AP), and resources use using Abiotic Depletion Potential (ADP). The Impact2002+ methodology for LCIA and the CED are used (Frischknecht & Jungbluth, 2005). The Impact2002+ (IM02) methodology uses the following mid point impact categories: human health carcinogens (HHC), human health non-carcinogens (HHNC), human health respiratory inorganics (HHRI), human health respiratory organics (HHRO), human health ioinising radiation (HHIR), ozone layer depletion (ODP), aquatic ecotoxicity (AqE), Terrestrial ecotoxicity (TeE), Terrestrial acidification and nutrification (TeAN), land ocupation (Land), global warming (GWP), non renewable energy (ADener) and mineral extraction resources (ADmin). Results are shown in Table 5.25. In Fig. 5.30 the EI results distributed according to different SC echelons are shown. Clearly raw material consumption is the biggest

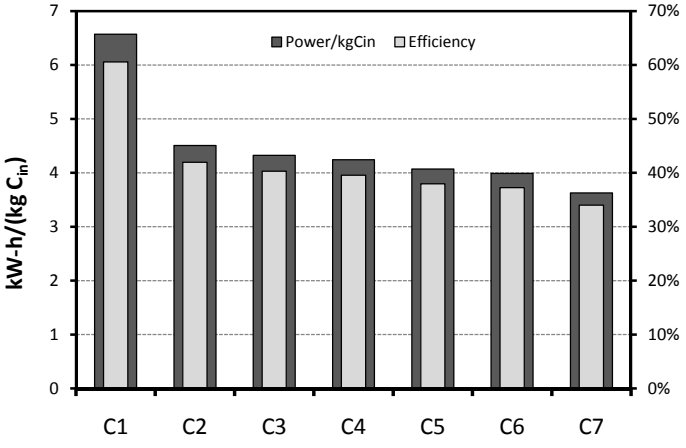


Figure 5.27: Net power and plant efficiencies between feedstock scenarios.

Table 5.25: EI and CED for the studied scenarios.

Scenario	Impact2002 [Pts] $\cdot 10^5$	CED [MJ-Eq]
C1	7.427	3.378
C2	8.486	4.708
C3	8.702	4.897
C4	8.857	4.964
C5	8.937	5.158
C6	9.040	5.266
C7	9.633	6.253

contributor to EI, while the IGCC plant stage ranks as the second, auxiliaries consumption (NaOH, H_2SO_4 and water), are nearly negligible. C1 and C7 bars clearly show that consumption of coal is more environmentally friendly than coke's. IGCC impact remains nearly the same for all scenarios, which was expected due to the nearly similar emission flows for all scenarios (see emissions of CO_2, NO, NO_2 and SO_2 in Table 5.24). On the other hand, Fig. 5.30, shows the EI of each raw material scenario distributed according to the different Impact2002+ mid point categories. Three impact categories clearly are the dominant ones: global warming, respiratory inorganic's impacts and non-renewable energy consumption. The first is mainly due to the emissions of CO_2 in the IGCC, respiratory inorganics (which are measured in kgPM 2.5), are due to consumption of raw materials and the IGCC emissions, while non-renewable impacts are related to the consumption of coke and coal.

Fig. 5.31, shows the distribution of energy demanded for the resources considered, clearly in this case more than 97% is from the consumption of non renewable, fossil sources, while other sources are negligible. It is important to remark that in this case the production of 1MJ of electricity (which is the FU defined), required the consumption of nearly 3 times that amount of energy in the case of coal based while roughly 6 in the case of coke.

In the case of comparing NGCC operation with IGCC, Tables 5.26 and 5.27, show the results for different indicators. In the case of hard coal and natural gas, they represent typical values for electricity generation in Spain using those raw materials, while high voltage at grid represents the electricity production and import mix found in Spain.

Table 5.26 shows the results for CED, CExD, EF and CO_2-eq emission. In all cases the lowest impacts are found for the case of NGCC followed by IGCC which also uses olive pomace as feedstock. Figure 5.32 shows the results of Impact 2002+ impact assessment methodology

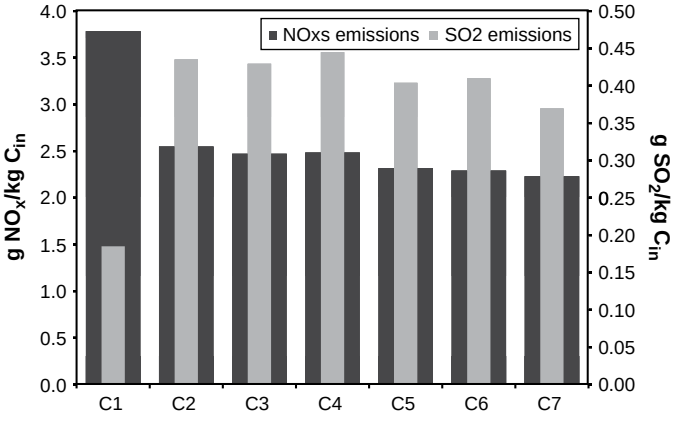


Figure 5.28: Comparison of NOx and SO_2 emissions in the different feedstock scenarios.

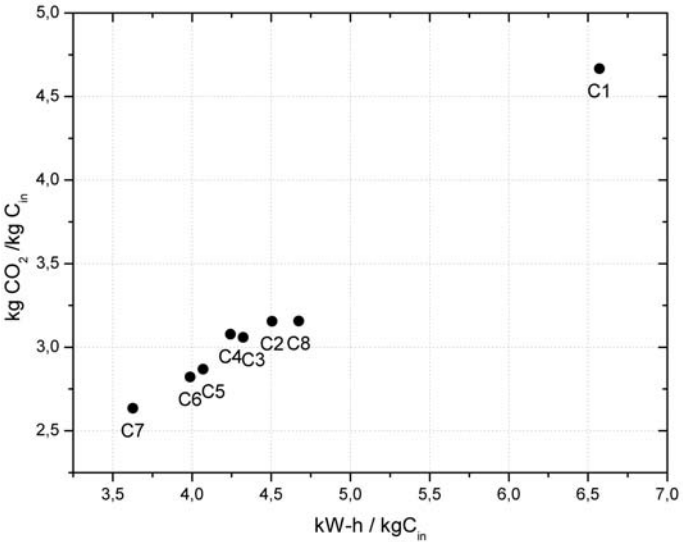


Figure 5.29: Emissions and power produced per kg C_{in} for all simulated scenarios.

at mid point and endpoint levels. The same trend is found with lowest impacts associated to NGCC and IGCC with olive pomace. In the case of mid-point categories the largest impacts are associated to: non renewable energy and global warming, which are mimicked by end-point categories: resources and climate change. Small differences are found for the end-point categories human health and ecosystem quality, which can not be traced directly to a single mid-point impact. Regarding end-point impacts, in the IGCC, IGCC w/olive pomace and NGCC electricity production cases, human health impact and ecosystem quality accounted for less than 13% of the total impact, while the remaining impact is partitioned evenly between resource use and climate change impacts. Hard coal, has bigger EIs than all the other options clearly showing the effect of gasification and CC. In the case of NG production the im-

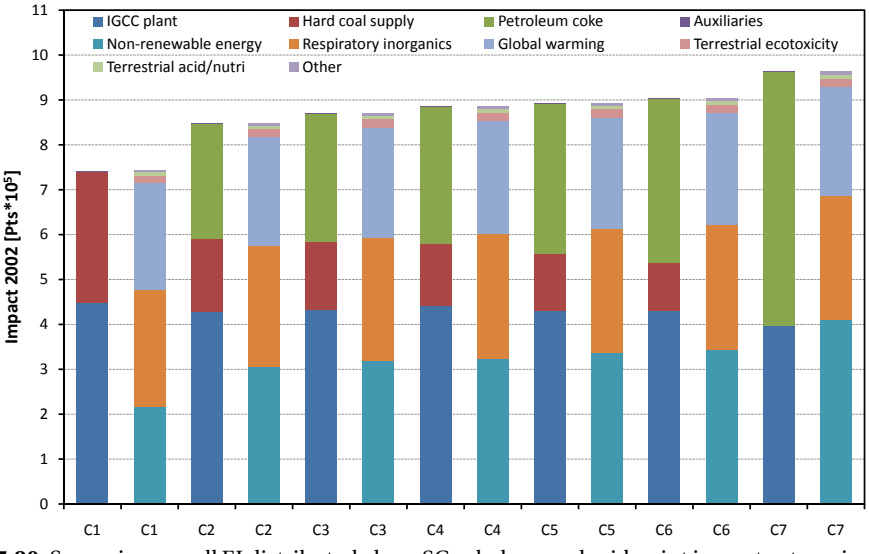


Figure 5.30: Scenarios overall EI distributed along SC echelons and mid point impact categories, in [Impact2002+ Pts].

pacts are nearly the same than for NGCC, this differences might be due to different allocation and system boundaries.

In all the former environmental metrics, the SC stages associated to most impact are: raw materials production (coal, coke and NG respectively for each scenario), for the case for resources, while most impact related to climate change is due to the IGCC/NGCC echelon where CO_2 emissions occur the most. Sulphur recovery studied in the case of IGCC operation, it is found that it allows for saving nearly 10% of the human health impact, in the other categories the effect is not appreciable, see Fig. 5.33.

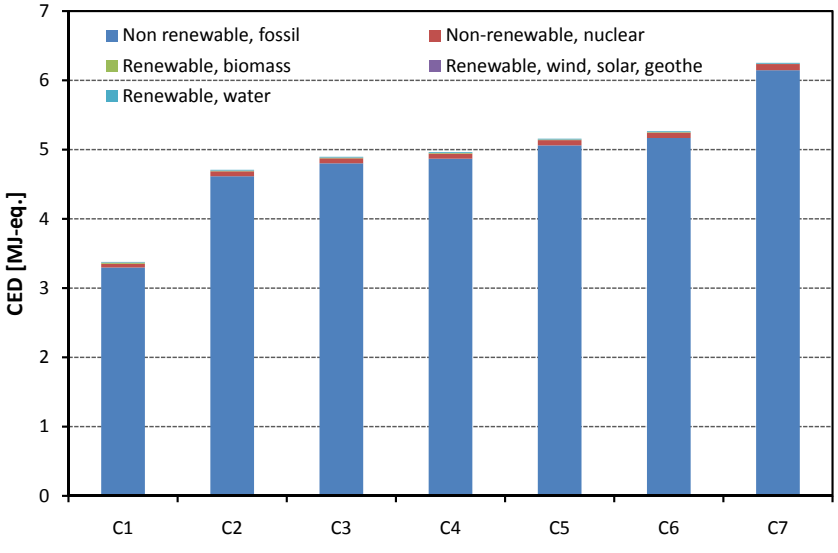


Figure 5.31: Comparison of overall plant efficiencies in the different scenarios.

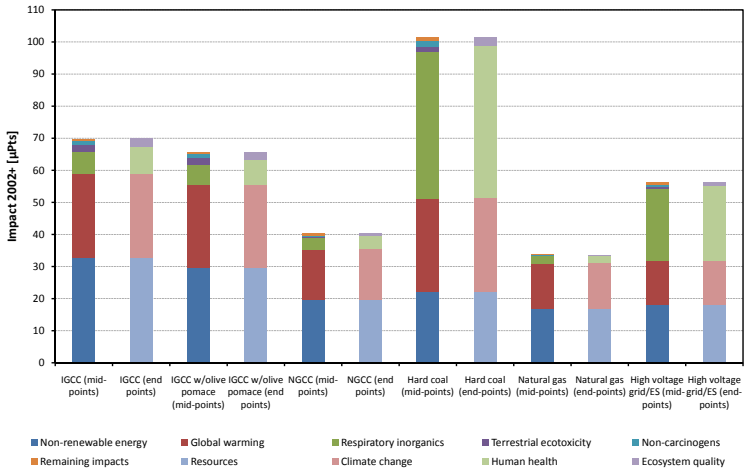


Figure 5.32: Comparison of end-point and mid-point impact indicators for different electricity production systems.

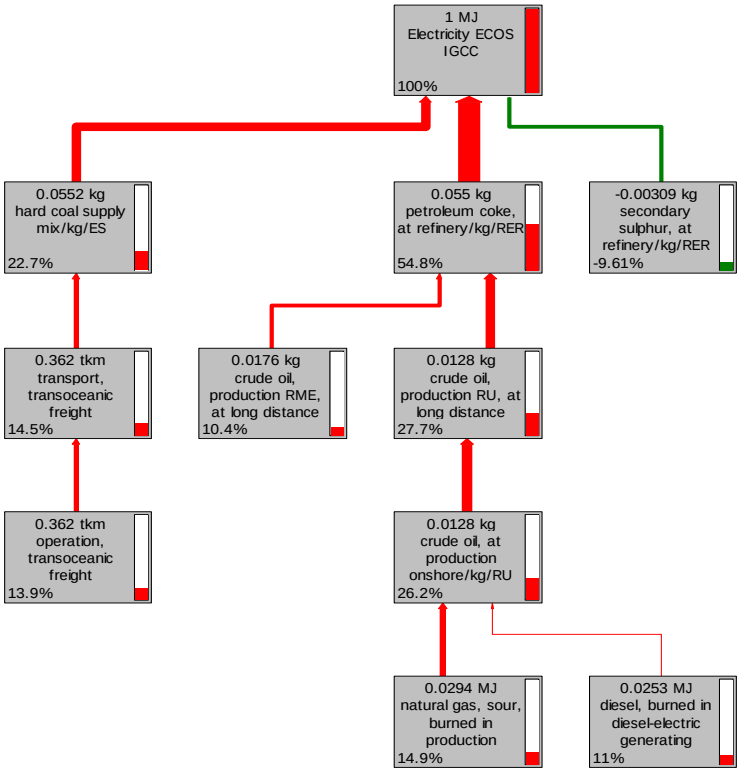


Figure 5.33: Human Health impact network for the case of IGCC electricity production considering sulphur production as credit. 100% represents 8.31μPts, see Table 5.27.

Table 5.26: Performance comparison between NGCC and IGCC operation. FU=1MJ.

Method	Unit	IGCC (C4)	IGCC w/olive pomace (C8)	NGCC	Hard coal	Natural gas	High voltage at grid
CED	MJ-eq	**5.0**	**4.5**	2.8	3.4	2.4	2.8
CExD	MJ-eq	**9.2**	**8.3**	3.1	6.9	2.8	**75.7**
EF	m^2a	0.70	0.69	0.41	**0.78**	0.37	0.59
IM02	μPts	69.8	65.7	40.3	101.5	56.3	33.7
GWP 100a	$kgCO_2eq$	0.27	0.27	0.16	**0.31**	0.14	0.14

Table 5.27: EI for IGCC and NGCC operation compared to other electricity production schemes in Spain. Values are reported in [Impact 2002 μPts].

Impact category	IGCC (C4)	IGCC w/olive pomace (C8)	NGCC	Hard coal	Natural gas	High voltage grid
HHC	1.77E-01	1.62E-01	5.51E-01	2.27E-01	1.37E-01	6.64E-02
HHNC	1.21E+00	1.19E+00	9.10E-02	1.82E+00	5.25E-01	4.69E-02
HHRI	6.87E+00	6.31E+00	3.54E+00	4.56E+01	2.25E+01	2.30E+00
HHIR	2.25E-02	2.05E-02	1.69E-03	1.62E-02	3.56E-01	2.53E-03
ODP	4.37E-03	3.97E-03	3.00E-03	2.20E-04	6.87E-04	2.89E-03
HHRO	1.73E-02	1.57E-02	1.08E-01	4.84E-03	3.69E-03	3.38E-03
AqE	1.53E-01	1.49E-01	1.42E-02	5.14E-02	2.65E-02	6.69E-03
TeE	2.25E+00	2.08E+00	5.12E-01	1.74E+00	6.23E-01	1.95E-01
TeAN	1.45E-01	1.35E-01	1.01E-01	6.68E-01	3.11E-01	6.51E-02
Land	5.99E-02	5.45E-02	2.28E-03	9.63E-02	3.04E-02	3.37E-03
GWP	2.62E+01	2.59E+01	1.58E+01	2.92E+01	1.38E+01	1.41E+01
ADener	3.27E+01	2.97E+01	1.96E+01	2.21E+01	1.81E+01	1.69E+01
ADmin	1.70E-03	1.58E-03	7.74E-04	1.28E-03	1.88E-03	6.50E-04
Total	6.98E+01	6.57E+01	4.03E+01	1.01E+02	5.63E+01	3.37E+01

5.2.4 Step 4 - Interpretation

The model proposed has proven to be useful for evaluating different IGCC operating conditions, as it is able to produce accurate results for this type of power plants. Nevertheless, differences between real and simulated results may rely on several simplifications or hypothesis that have been taken in this work.

- The pyrolysis model estimates the production of char, nitrogen and sulphur compounds based on experimental correlations for 100% coal feedstock, and the authors have assumed that feedstock mixtures behave similarly. Consequently, these correlations do not correspond exactly to the actual raw material mixtures considered in this case study. Char combustion and gasification reaction parameters are also based on experimental data.
- ANN models are limited to an interval of variation of gas composition, from which sensitivity analyses in AspenPlus were performed.
- The clean gas combustion, in the Brayton cycle, is modelled considering a Gibbs equilibrium reactor, and turbines are considered to be isentropic.

Despite of these drawbacks, this model allows different key performance parameters to be calculated, which can be used to test different trade-off situations. This is shown in the C1 scenario, in which using 100% coal use results in better efficiency and higher power output; however, this case is the worst scenario in terms of NOx emissions. In this case NOx emissions are in clear conflict with a higher power output or higher plant efficiency. This last point shows that analysing power production with a single criterion can lead to options where emissions are higher, and therefore it is necessary to take into account various performance indicators. Moreover, the model proposed can be used as a design tool for IGCC plants that allows the possibility of changing input parameters, such as feedstock composition and operating parameters (temperatures, pressures), as well as the possibility of adding new purification units to adapt the process layout to the end user needs.

With regards to the LCIA it is found that raw material consumption drives the EI of the energy production in this case. In this sense, coke which is commonly considered a residue of refineries has been assigned 3% of emissions associated to overall refinery crude oil consumption, and consequently its energy and exergy demands are high (Jungbluth, 2007). The consumption of (hard) coal has been shown to be more environmental friendly than coke consumption. Moreover, coal is also more efficient in terms on the amount of energy required, given that the production of 1MJ of electricity based on coke requires 1.85 times more energy (in CED terms). LCA results show that the co-gasification of biomass also reduces the overall EI.

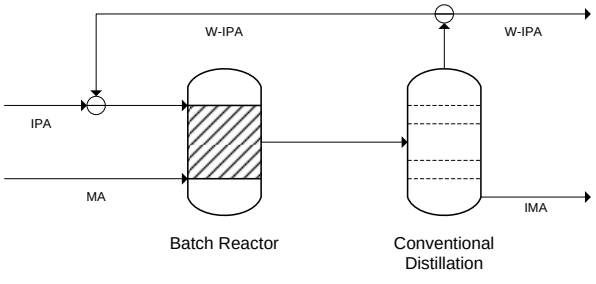
CED and EF are found to be good EI proxy metrics for the case of electricity generation. In this case raw material use and climate change impacts are most important and are the base for the calculation of those metrics, consequently its use can be done instead of more complex metrics as the Impact+ 2002 metric. However it has to be emphasised that this result is only possible in this case study, where toxicological effects (human health or ecosystem quality) are small.

5.3 Reactive distillation case study

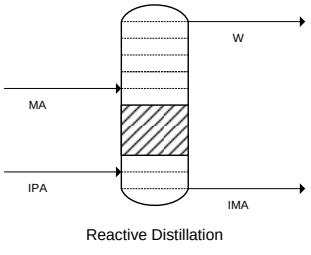
Process intensification (PI) leads to a higher process flexibility, improved inherent safety and energy efficiency, distributed manufacturing capability, and ability to use reactants at higher concentrations (Keil, 2007). These goals can be achieved using multifunctional reactors, thus one of the PI possibilities is the combination of chemical reaction with chemicals separation. This combination has been recognised by the chemical process industries as having favourable economics of carrying out reaction simultaneously with separation for certain classes of reacting systems, and many new processes (called reactive separations) have been invented based on this technology. One of the most interesting possibilities of these reactive separations is the combination of reaction and distillation i.e. reactive distillation (RD).

Optimal functioning of RD depends largely on relevant process design, properly selected column internals, feed locations, and placement of catalyst as well as on sufficient understanding of the process behaviour. All this unavoidably necessitates application of well-working, reliable and adequate process models (Kenig & Górak, 2007). Among the attractive features of RD, Kenig and Górak (2007) emphasise the following: increased yield due to overcoming of chemical and thermodynamic equilibrium limitations; increased selectivity through suppression of undesired consecutive reactions; reduced energy consumption through direct heat integration in case of exothermic reactions; avoidance of hot spots by simultaneous liquid evaporation; and separation of close boiling components.

In the case of the study of the sustainability of process systems which incorporate RD there are few examples in the literature available. In this sense Malone *et al.* (2003) discuss the implications of RD in terms of the 12 principles of green engineering Anastas and Zimmerman (2003), the authors qualitatively emphasise some advantages of RD such as the use of reduced number of units, but these units require further specialisation, showing that there is opportunity for trade offs. The RD case study selected involves the production of fatty acid esters. Different production schemes for these compounds have been studied using RD (Bock *et al.*, 1997; Omota *et al.*, 2003a,b). Nowadays the fatty acid esters are produced in batch reactors using strong acids like sulphuric acid, see Fig. 5.34(a). Moreover, their production processes encompasses costly separations, large energy consumption and the production of polluting by-products, which in this case are mixtures of water and un-reacted alcohol. Because of equilibrium limitations, high conversions can be only obtained by using a large excess of reactives (Dimian *et al.*, 2004). The synthesis of isopropyl myristate was selected as a case study. Isopropyl myristate is used in cosmetics as the oil component and is one of the most common used fatty esters. The flowsheet proposed encompasses the use of a RD unit as in Figure 5.34(b).



(a) Conventional process flowsheet for the production of esters.



(b) Reactive distillation process flowsheet for the production of esters.

Figure 5.34: Comparison of isopropyl myristate (IMA) production processes.

Table 5.28: Reaction constants for the production of isopropyl myristate (IMA) from myristic acid (MA) and isopropanol (IPA) (de Jong *et al.*, 2009a).

	Ea [KJ/Kmol]	k [molarity] (k_l)
RQ 1 (direct)	58900	333000
RQ 2 (reverse)	45900	2180

5.3.1 Step 1 Goal definition

This case study aims at analysis the effect of design considerations in SD terms. Two different metrics will be assessed, economic metrics, by calculating the total annual cost (TAC), and environmental metrics by applying the Impact 2002+ methodology (Humbert *et al.*, 2005)(IM02). Social aspects are not considered to be important given that the overall enterprise structure is not modified by the decisions considered at this level.

The selection of TAC instead of NPV, is based on the short project lifespan that is considered. The system boundaries are considered as cradle to gate, considering a lifespan of the project infrastructure of 3 years. To be coherent with the economic metric selected, the functional unit considered is the total production of isopropyl myristate (IMA), with a purity above 99% w/w, along 1 year.

5.3.2 Step 2 Model development and data gathering

Ir order to gather the economic and environmental data required to calculate the former metrics, a plant model is required. The model is developed in AspenPlus and Matlab, which are connected together using the COM interface. Economic and environmental metrics were coded in Matlab while AspenPlus is used for thermodynamic and unit operation models.

5.3.2.1 Reactive distillation model

Thermodynamic and kinetic considerations The chemical reactions consider the esterification of myristic acid (MA) with isopropanol (IPA) which produces isopropyl myristate (IMA) and water. The catalyst used for the ester synthesis is para-toluene sulfonic acid (pTSA).

- RQ 1 (direct): MA + IPA $\longrightarrow$ IMA + WATER
- RQ 2 (reverse): IMA + WATER $\longrightarrow$ MA + IPA

Reaction data was retrieved from de Jong *et al.* (2009a) and is summarised in Table 5.28. The reaction is first order on each of the reactive species and based on molarity concentrations. In both reactions the AspenPlus pre-exponential constant was calculated based on a given molar concentration of catalyst (see Eqs. 5.62 and 5.63). Thermodynamic and transport data from the Aspen Properties database was retrieved and used for all five components. All species were consider to participate on the L-V equilibrium except for pTSA which was assumed to be non-volatile, i.e. only present in liquid phases, the vapour pressure values gathered from the database were modified accordingly[21]. In the case of phase separation data there was only available for the V-L equilibrium of isopropanol and water. The L-L equilibrium present between myristic acid and water was regressed from the literature using the data available from Maeda *et al.* (1997). It was assumed that the isopropyl myristate presents an identical behaviour to myristic acid in terms of L-L equilibrium with water. All remaining binary interaction coefficients were estimated using UNIFAC. The liquid phase equilibrium was calculated with the NRTL activity coefficient model, while the vapour phase is considered to be ideal gas. Table 5.29 shows the AspenSplit results for the four components of the system under study,

[21] Aspenplus allows for the treatment of liquid only species by considering the liquid vapour pressure expression of Antoine (PLXANT) as C_1=1·10^{-20}.

Table 5.29: Phase equilibrium considerations for the system: myristic acid (MA) - isopropanol (IPA) - isopropyl myristate (IMA) - water (WA).

Temp. [C]	Classification	Type	No. Comp.	MA	IPA	IMA	WA
80.37	Unstable Node	Homogeneous	2	0.000	0.666	0.000	0.334
82.35	**Saddle**	**Homogeneous**	**1**	**0.000**	**1.000**	**0.000**	**0.000**
99.58	Saddle	Homogeneous	2	0.000	0.000	0.005	0.995
100	Saddle	Homogeneous	2	0.002	0.000	0.000	0.998
100.02	**Stable node**	**Homogeneous**	**1**	**0.000**	**0.000**	**0.000**	**1.000**
315.3	Saddle	Homogeneous	2	0.041	0.000	0.959	0.000
315.32	**Stable node**	**Homogeneous**	**1**	**0.000**	**0.000**	**1.000**	**0.000**
325.83	**Stable node**	**Homogeneous**	**1**	**1.000**	**0.000**	**0.000**	**0.000**

using the NRTL-ideal gas thermodynamic model. Analysing the boiling temperatures of the components it can be seen that reaction products are not the most and least volatile species in the system. In this case the homogeneous azeotrope between isopropanol and water (T = 82.3C) is the most volatile mixture while myristic acid is the least volatile (T = 325.8C). The appearance of the homogeneous water-IPA azeotrope is one of the reasons for the study of entrained reactive distillation, these studies were performed by several authors (Dimian *et al.*, 2004; de Jong *et al.*, 2009b), showing the feasibility of these flowsheets. In this study a different approach is taken, RD column works at higher pressure that the conventional distillation column.

Unit operations model The main model block is the reactive distillation (RD) column, it is a modelled using a Radfrac model (RDCOL). This model calculates QCOND and QREB which are fed to two HEATER models to represent the column condenser and reboiler. As can be seen from Figure 5.35, streams MYRIN2 and ISOIN2 represent the inlet flows of MA and IPA while the WAT-ISO and PRODUCT streams represent the outlet flows of the water and esterification reaction products from the RD column (block RDCOL). PRODUCT stream is feed to a falling film evaporator, modelled as a two phase flash model (FLASH2), where feed pressure is decreased 0.5bar, and a certain amount of heat is added to allow further separation of isopropanol from the ester stream. The ester stream (TOWWASH) is sent to a water contactor, modelled as a liquid-liquid DECANTER block, in which a certain amount of water is added, by means of stream WWASHIN, to remove catalyst present in the ester. The product stream cleaned from catalyst is FINPROD, while the water used for washing is PTSAW. To set the amount of water for catalyst washing a design specification is used (WWASHD), which enforces a recovery of pTSA of 99% from the product stream. The ISOREC stream which is mainly IPA at the bottoms RD temperature and pressure is recycled back to the column. To set correctly the MA/IPA ratio a calculator block (FEEDRAT) is used which takes into account the available IPA flow in the recycle streams to set the fresh IPA flow (ISOIN).

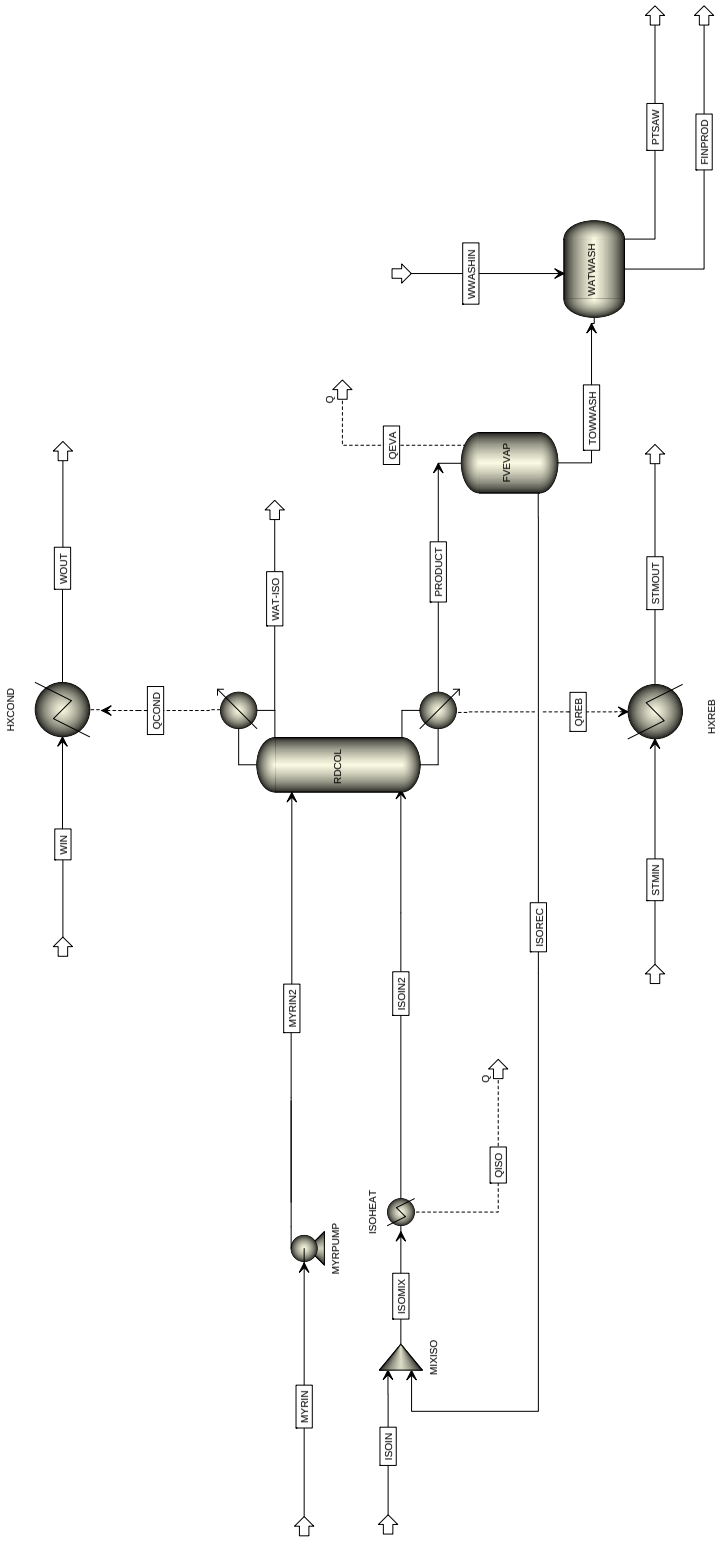


Figure 5.35: Reactive distillation flowsheet, showing AspenPlus models connectivity.

Reaction is supposed to take place in the liquid phase only and within the RD no L-L behaviour is assumed to occur. The IPA feed stream to the RD is assumed to be a vapour stream of a mixture of isopropanol and water which is fed at the columns bottom section. This isopropanol-water stream is vapourised to meet the RD bottoms temperature and pressure, a HEATER model (ISOHEAT block), is used to calculate duty requirements. Myristic acid (MA) is fed at the RD columns top in liquid state at condenser pressure; a pump model (MYRPUMP block), is used to calculate the pumping requirements. The RD condenser is considered to be total and the reboiler is a kettle, QCOND and QREB are the energy flows that model the condenser and reboiler duties.

It is considered that the column consists of a single vessel with the same diameter for its whole length and it is also assumed that tray liquid holdup ($TrayVol$) is the same on all trays. The volume holdup for the trays is calculated as in Eq. 5.61.

$$TrayVol = \frac{\pi}{4} CD^2 (1 - DC_{area}) h \tag{5.61}$$

where CD is the column diameter, which is calculated by AspenPlus, the DC_{area} is the down comer area fraction, and h is the weir height, which has been set to be 65mm. AspenPlus provides a stage design utility which is used for tray sizing; the input parameters selected for this utility were:

- Tray type: Sieve trays were selected
- Fractional approach to flooding: 0.8, (AspenPlus default value, the higher the closer the column operates to flooding conditions)
- Minimum downcomer area (DC_{area}): 0.1, (AspenPlus default value, as fraction of total tray area).
- System foaming factor: 1, (AspenPlus default value, non-foaming systems)
- Over design factor: 1, (AspenPlus default value)
- Approach to flooding calculation method: Fair, in this case is the method proposed in the Perry's Chemical Engineer's Handbook

A design specification block (DIAMSET), has been added to the flowsheet, which calculates the tray volume using Eq. 5.61, and sets that value in the column for a new calculation until the new value proposed and the previous are within the tolerance value. The previous algorithm shows convergence in 6 to 7 extra model runs, the initial estimate for the tray volume holdup has been set to be 25lts.

Catalyst molar concentration within the RD column is calculated by using the total mole (m^j_{total}, [mol/s]) and liquid volumetric (v^j_{total}, [m^3/s]) flows together with the pTSA mole fraction (x^j_{pTSA}), at a the j-th tray using Eq. 5.62. It is found that x^j_{pTSA} remains almost constant along the column.

$$M^j_{pTSA} = \frac{m^j_{total} x^j_{pTSA}}{v^j_{total}} \frac{1m^3}{1000lt} \qquad \forall i \tag{5.62}$$

This catalyst molar concentration M^j_{pTSA} [mol/lt] is used to correct the pre-exponential value for the lth-chemical reaction, by using Eq. 5.63.

$$k^{Aspen+}_l = M^j_{pTSA} k_l \tag{5.63}$$

The catalyst molarity calculation is implemented in a calculator block (REAKTION). The values required by this block use the results of the hydraulics of the column; consequently a first guess is required. Both DIAMSET and REAKTION calculation blocks are solved iteratively by AspenPlus when solving the RD model (RDCOL block).

Regarding pressure, the column pressure drop is calculated based on the number of stages (N_{st}), and a given pressure drop for each stage (Δp_{stage}). Inlet streams pressure depend on the condenser pressure (p^{Cond}), and the number of stages, consequently a calculator block (RDPRESS), was added to equalise pressures. MA pump outlet pressure is identical to the condenser pressure, and isopropanol pump output pressure (p_{IN}^{IPA}) is set according to Eq. 5.64.

$$p_{IN}^{IPA} = p^{Cond} + N_{st}\Delta p_{stage} \tag{5.64}$$

If the composition of the inlet streams and their state are fixed, the RD column degrees of freedom (DOF) are:

- *Continuous variables*: associated to the column, its reflux ratio (RR), distillate flowrate (D), condenser pressure (p^{Cond}) and associated to the whole flowsheet the molar feeds ratio ($Rat = (molIPA)/(molMA)$) and the inlet flow of pTSA, which controls the RD column's (M_{pTSA}^{j}).
- *Integer variables*: total number of stages (N_{st}), number of reactive stages (N_{rst}), position of reactive stages in the column, feed stage for myristic acid (F_j^{MA}) and isopropanol (F_j^{IPA}).

With regard to the number of reactive stages (N_{rst}) and their position in the column, in this case study they could be disregarded, given that the reaction proposed occurs homogeneously where the catalyst is present. Consequently, it will be considered that all stages below the MA feed stage are reactive (F_j^{MA}), given that pTSA is feed together with MA.

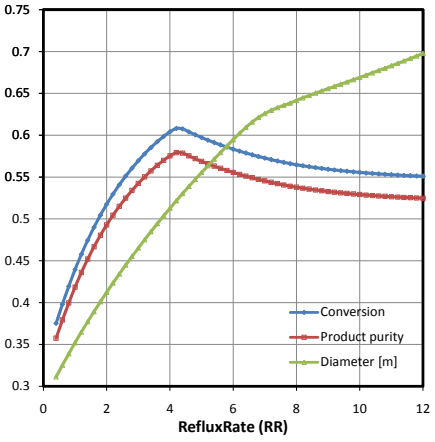
5.3.2.2 RD model validation

To test RD model capabilities in terms of convergence and solution appropriateness regarding the different input variables a series of local sensitivity analysis (SA) were performed. Different model output variables were taken into consideration, composition and temperature profiles within the RD column, MA and IMA purity in product streams and the overall conversion of MA as calculated in Eq. 5.65.

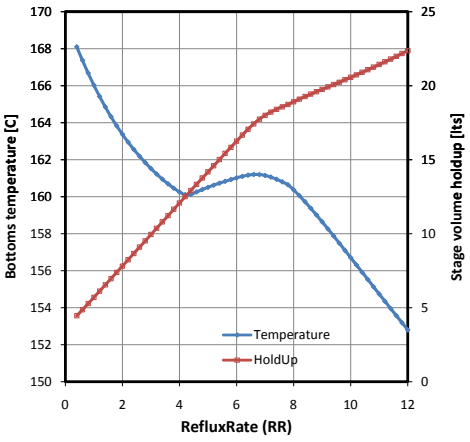
$$\eta^{MA} = \frac{(total_{IN}^{MA} - total_{OUT}^{MA})}{total_{IN}^{MA}} 100 \tag{5.65}$$

Analysis of RD distillate flow rate and ratio of inlet streams The column was considered to have 32 stages, with 30 reactive stages from stage 2 to 31. The RD column is fed at stages 2 (MA) and at 31 (IPA). The stage liquid volume holdup is considered to be constant and equal to 25lts, the catalyst concentration is constant and equal to 0.1M, disregarding actual pTSA flow. The condenser pressure was set to be 760mmHg, and a small pressure drop of 0.01psi per stage is assumed, no IPA is recycled back to the column which is feed with fresh IPA.

MA flow was fixed at 1mol/s, while the IPA flow rate range was varied in the range of 0.8-1.2mol/s. The distillate flow D rate was tested between 0.8-1.2mol/s and RR was defined as optimisation variable by maximising (η^{MA}), considering the following bounds: 0.1 to 10. In total 81 points were tested, from these 81 possible scenarios only 71 scenarios converged (87.6%), the RR was taken to its lower boundary (0.1) in most of the cases. The maximum conversion found is nearly 0.6, with a similar purity, showing that IMA split in the column is quite high, flowing completely with the bottoms product. The bottoms temperature was between two clusters of values: 29 scenarios converged to temperatures lower than 300C, while the rest was above that temperature. Considering that the boiling temperatures of the MA and IMA are 326.2C and 314.8C respectively (see Table 5.29), indicating the presence of these two



(a) Conversion, product purity and column diameter



(b) Bottoms temperature and stage holdup volume.

Figure 5.36: RD model results as a function of column's RR.

species in the vapour phase in the bottoms section of the column, while in the other cases the vapour phase will be mainly formed by water and isopropanol (boiling points of: 100C and 82.3C respectively).

The solutions of lower bottoms temperature are modeling a reactive vapour absorber where IPA and water are sorbed in the liquid phase where reaction occurs. The solutions of high reboiler temperature are vapourising part of MA or IMA to meet the distillate flow requirements which are not met by the top products flow (IPA-Water). Given that the objective of the column is to separate IMA from IPA the use of higher distillate flows than the IPA flow does not make any sense. Moreover higher conversions are found lying on the line where isopropanol flow equals the distillate flow. Consequently it has been adopted to restrict solutions where $Iso_{IN} \leq D$[22].

Analysis of RD column RR effects In this case D and isopropanol flow (Iso_{IN}) were fixed to 1.45 and 1.5 respectively[23]. N_{st} is considered to be 70, the feed stages for IPA and MA were 71 and 2 respectively, and all stages below the condenser were considered to be reactive. Holdup volume per stage was variable and dependant of the selected RR value. It can be seen from Figure 5.36(a) that there is a clear maximum conversion as a function of the column's RR which is found to be 4.3, see Table 5.30. The same trend is found for the bottoms product purity which shows the maximum for the same RR value. In the case of column diameter (CD) and liquid volume hold up ($TrayVol$), the relationship is almost linear with a break at around $RR = 7$ (see Figure 5.36). The bottoms temperature shows a "S-shape" behaviour (see Figure 5.36(b)), with respect to RR, a minimum is found at $RR = 4$ while a maximum at $RR = 7$, this behaviour could be the reason for the other curve's shape. It was found as expected that as the RR increases both utilities (steam and cooling water) consumption increase. The composition of liquid and vapour phase along the column has been studied for four values of RR that lie in the three regions found by the former analysis. In the case of $RR < 4$ ($RR = 2$), the IPA liquid and vapour compositions show a decrease along the column being the decrease more

[22] Given that the equality brings some convergence issues it has been implemented in AspenPlus as $D + 0.05 mol/s \leq Iso_{IN}$.

[23] In this case the bottoms temperature is found to be around 150C (for a condenser p=760mmHg), and the top stage will be around the isopropanol-water azeotrope boiling temperature (80C, see Table 5.29), these values were added as an estimation to the RD column block to ease the convergence.

Table 5.30: Conversion and tray volume for different column's RR values.

Variable \ Case study	Unit	1	2	3	Optimal
RR	[1]	2	6	8	4.3
η^{MA}	[1]	51.7	58.3	56.3	60.9
$TrayVol$	[lt]	7.81	16.25	18.91	12.71

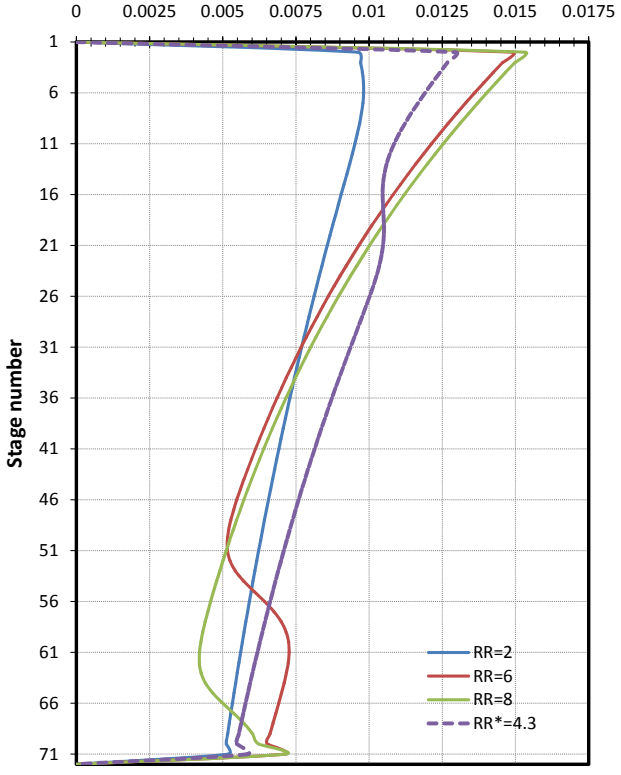


Figure 5.37: IMA generation amount per stage [mol].

important close to the column's top, probably due to the high concentration of MA. In the case of $4 < RR < 7$ ($RR = 6$) a large IPA concentration change is found between stages 51-61, while in the case of $RR > 7$ ($RR = 8$), this change is found between stages 65-71. In the $RR = 6$ and $RR = 8$ cases, the column's liquid composition is almost constant at the azeotrope water-isopropanol, which provides a low IPA concentration for the esterification reaction. Comparing the composition profiles of $RR = 6$ and $RR = 8$ with the one obtained at RR^*=4.3, it is observed that the IPA composition in the case of RR^* is higher, and that the azeotrope composition is only found around stages 1-10. Figure 5.37 shows the IMA generation amount per stage. It can be observed that the optimal RR, shows an almost constant generation amount along the column, this constant value is in most cases higher than the amount obtained using high reflux ratios. The decrease in the IMA generation per stage is due to the decrease in the MA composition. To allow for the consideration of the former effects, in all cases RR is optimised or set as a design specification (to reach a certain MA conversion), using the following boundaries: RR^{LB}=0.1 to RR^{UB}=10.

Table 5.31: MA conversion and column's RR values for different tray volumes not considering flooding calculations.

Variable	Flooding	Case study (2)	Case study (3)
$TrayVol$ [lts]	5.73	10.00	15.00
$TotalVol^a$ [lts]	2854	4980	7470
Conversion (η_{MA})	0.9315	0.9893	0.9988
Purity ($x_{MA}^{PRODUCT}$)	0.8872	0.9422	0.9512
RR [mol/mol]	0.9330	0.6238	0.6616

^{a} $TotalVol = TrayVol \cdot N_{st}$

Analysis of the effect of N_{st} and $TrayVol$ N_{st} was gradually increased considering the optimisation of MA conversion, by modifying the RR value while taking into account volume holdup changes. Increasing the N_{st} increases the conversion of MA into IMA. The optimal RR decreases to an almost non changing value close to 1. A value of RR almost constant (for values of N_{st} from 200-500[24]), makes the boil-up ratio also constant and consequently the column diameter to be almost constant at around 0.36m. According to Luyben (2006, Ch. 3), by increasing the number of trays until there is no further reduction in the RR is found allows, to calculate the minimum reflux ratio (RR_{min}). In this case the RR_{min} value is found to be 1.07. The maximum conversion is attained for the maximum amount of stages (498). The MA conversion for this case is 0.931 with a 0.887 liquid fraction composition of IMA. The liquid holdup in each stage is 5.73lts making a total volume hold up of 498*5.73=2851lts[25]. By analysing the column composition profiles it can be seen that two regions of high conversion are found, between stages 2-4 and around stages 130-200. Both sections corresponds to high molar liquid fractions of reactive components, in the first case is myristic acid (x_{MA}=0.31) while the second corresponds to isopropanol (x_{IPA}=0.33-0.57).

If the $TrayVol$ is fixed and is not longer calculated based on a flooding calculation, it is found that higher stage holdup volumes produce higher conversions and purity of the product which also render lower consumption of utilities, see Table 5.31.

Analysis of the catalyst concentration (x_{pTSA}) within the column In this case the molar flow of pTSA was gradually increased for a 90 stages column working a 760mmHg. The optimisation of RR was considered, maximising η^{MA}. MA flow is 1mol/sec and isopropanol ratio is 1.5, D was set at 1.45mol/s. Figure 5.38 shows that conversion increases steadily as pTSA concentration in the column increases, however purity (measured as x_{IMA}) drops, mainly due to the presence of pTSA in the IMA outlet flow[26]. Note than in the case of a concentration of pTSA 0.2M the inlet flow required is 0.1mol/s, and it increases linearly given that no holdup changes are found due to almost constant RR.

Analysis of the effect of condenser pressure changes The top column pressure was changed from p=1000-10000mmHg. The analysis was performed calculating a RR based on maximum conversion for a set of fixed inlet flows of catalyst and raw materials. It was found that the increase of pressure increases the MA conversion (see Fig. 5.39(a)), the reason for that is the increase of IMA conversion per stage as shown in Figure 5.39(b). This increase of conversion can also be seen in the overall temperature increase within the whole column. Figure 5.40 shows the condenser and reboiler temperatures for different condenser pressures. Note that

[24] This is the maximum possible number of stages that RADFRAC model in AspenPlus allows, please note that 2 stages are considered for condenser and reboiler.

[25] This result considers a weir height (h) of 65mm in Eq. 5.61

[26] pTSA has been considered a non volatile specie and consequently is only present in the liquid phase along the whole column.

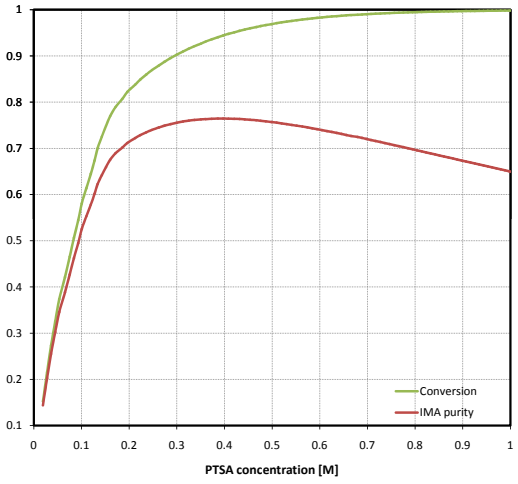
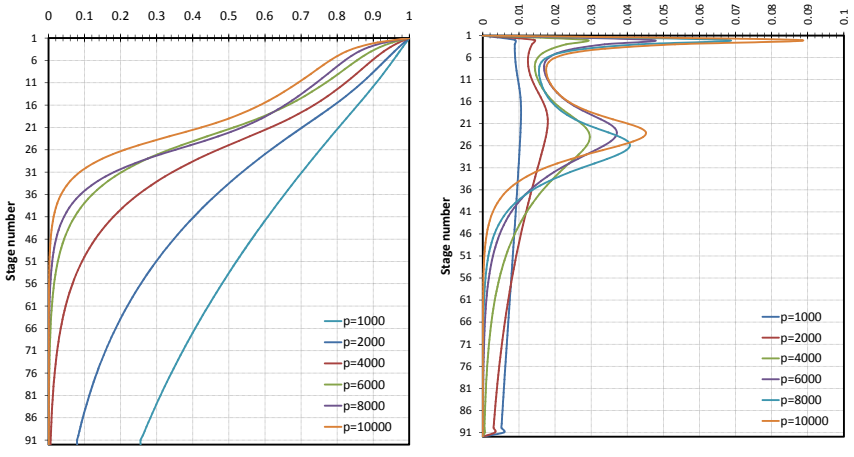


Figure 5.38: MA conversion and IMA purity for different pTSA concentration within the column



(a) MA consumption per stage

(b) IMA generation per stage

Figure 5.39: Changes in MA and IMA due to different RD column condenser pressures [mmHg].

in all cases no MA nor IMA is found in the vapour phase in the reboiler and the temperature increase is due only to the increase of bottoms pressure. It is also found that conversion is above 0.995 for condenser pressures higher than 4000mmHg. Pressure changes impact heavily on the reboiler and condenser temperatures and consequently on the amount of steam and cooling water requirements. In the case of the steam flow an abrupt increase is found, this is due to the fact that the steam does not condense. The steam outlet temperature at 6000mmHg has to be 355.1C, given that the reboiler works at 325.1C[27], while in the case of 7000mmHg the reboiler temperature is 336.9C and then the steam outlet temperature is set to be 366.9C. In the case of p^{Cond}=6000 steam available at 82000mmHg, can still condense at 355.1C while for the case of 7000mmHg it can not. Consequently it has been adopted that as operative requirement condenser pressure can not be greater than 6000mmHg. The column could operate at higher pressures provided there is a heating element for supplying the

[27] A fixed ΔT of 30C has been set for the reboiler outlet streams.

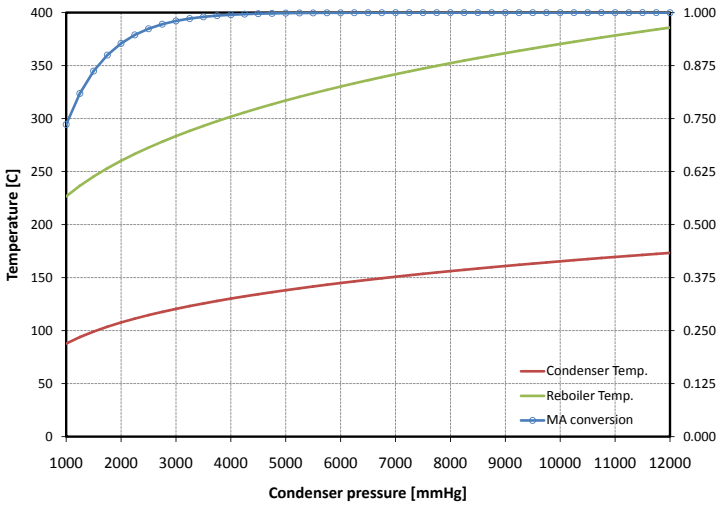


Figure 5.40: Condenser and reboiler temperatures for different condenser pressures. Conversion is shown as reference.

amount of heat to the reboiler at the nearly.

Remarks The former SAs served as validation of the overall model, in this sense input-output variable relationship were tested and appropriate model behaviour was found for all cases. It was found that:

- The columns distillate flow and the condenser pressure are determinant to set the bottoms temperature. The columns distillate flow (D) has to be as close to the IPA inlet flow in order to minimise MA flow along with the distillate. Values of distillate flow higher than the IPA inlet flow require vapourising MA or IMA from the bottoms which increase the overall column temperature profile.
- Increases in the catalyst concentration, stage liquid volume hold up ($Tray\ Vol$), number of stages (N_{st}) and condenser pressure (p^{Cond}) monotonically increase the MA conversion. In the case of the catalyst concentration, this is due to an increase in the reaction constant values, (see Eqs. 5.62 and 5.63), while $Tray\,Vol$ and N_{st} increase the overall residence time within the column. Pressure effects are due to the overall increase of column's temperature profile.
- The column's RR shows an optimal value not bounded for which maximum conversion is observed. This has been shown to be related to changes in the stage holdup and in the concentration profile.

5.3.2.3 Economic considerations and metrics

The TAC considers operative costs associated to the consumption of utilities such as water and steam, the consumption of raw materials and the product sales. TAC also requires an estimation of the equipment investment as in Eq. 5.66.

$$TAC = prodSales - opCost - \frac{Invest}{nYears} \tag{5.66}$$

The RD operative costs ($opCost$) are calculated using Eq. 5.67, while the investment ($Invest$) is estimated using Eq. 5.69. Note that for the TAC calculation the investment is considered

to be depreciated using the straight line method over the project's lifespan ($nYears$). If investment is disregarded then annual benefits are calculated as: $Benefits = prodSales - opCost$.

$$opCost = UCost + RMCost + WWTCosts \tag{5.67}$$

$$opCost = \sum_{k}^{utilities} \rho_k Fu_k + \sum_{k}^{RM} \rho_k FRM_k + \sum_{k}^{WWT} \rho_k FWWT_k \tag{5.68}$$

In Eq. 5.67, $UCost$, $RMCost$ and $WWTCosts$ represent the utilities (steam and electricity), raw materials (MA, IPA and PTSA) and the waste water treatment (WWT) costs respectively. Eq. 5.68 is used costs calculation, where flows are multiplied by their corresponding prices or costs. Table 5.32, summarise the prices and costs used.

Table 5.32: Summary of different material prices and utilities costs for IMA production.

Material	[€/ton]	[€/mol]
MA	1076	246
IPA	737	44
pTSA	24133	4591
IMA	4145	1121

Utilities	Value
Steam [€/ton]	6.32
Industrial water [€/m^3]	1.10
Electricity [€/KW-h]	0.08
WWT [€/m^3]	0.54

WWT costs are consider for the treatment of all liquid flows that exit the plant. The catalyst cost has been included by considering that no recovery of it is possible and that it's washed out from the product stream at a 99%.

Investment expenditures are associated to the RD column and its associated heat exchangers, as in Eq. 5.69.

$$Invest = InvCol_{vessel} + InvCol_{internals} + InvHX_{reb.} + InvHX_{cond.} \tag{5.69}$$

In Eq. 5.69, $InvCol$ represent the investment required for the column vessel and column internals while $InvHX$ is the investment associated to heat exchangers (reboiler and condenser). The investment estimation algorithm is based on Biegler *et al.* (1997, Chs. 4-5) and Doherty & Malone (2001, Ch. 6). Column stages are considered to be sieve trays. The procedure implemented does consider changes in the investment due to internal vessel pressure changes, an increase considering a cost factor F_p factor[28].

5.3.2.4 Environmental model and metrics

The environmental impacts considered in this case are the ones associated to a cradle-gate system boundary. No analysis of product environmental impacts was studied due to the large amount of possible products where IMA can be found. Given that in an LCA, environmental impacts are proportional to the consumed amount of raw material or service used, there is no point in retrieving the whole Life Cycle Inventory (LCI) of emissions for each raw material. A straight forward approach consists on retrieving the actual environmental impact of its consumption and use those figures instead. The environmental metric used is the overall Impact 2002+, which measures environmental impact in Pts.

The impacts considered can be separated into the following:

- Raw materials consumption: in the case of IPA and MA, appropriate environmental information was available in the ecoinvent database. For IPA the ecoinvent unit "Isopropanol, at plant/RER" was selected while for MA, the LCI of "Fatty acids, from vegetable oil, at plant/RER" is used. In the case of pTSA, no information of its production

[28]Further details are found in Doherty & Malone (2001, Ch. 6). This factor increases if column's pressure is higher than 4.5bar.

Table 5.33: Summary of raw material production environmental impacts. Total impact is reported in Impact 2002+ points [Pts].

Raw material	Env. Impact [Pts/Kg]	Env. Impact [Pts/mol]
IPA	0.000747	0.000045
MA	0.000778	0.000178
pTSA	0.000552	0.000095

Table 5.34: Summary of utilities use and equipment related environmental impacts.

Utilities	Env. Impact [Pts/Kg]
Steam, at plant/RER U	0.00006
Water, decarbonised, at plant/RER U	2.0E-09
Heat carrier liquid to WWT class 2/CH U	0.000099
Electricity (per kWh) UECT	4.43E-11
Pig iron, at plant/GLO U	0.000512

was available and a mixture of two processes was used. It is considered that pTSA is produced by the reaction of toluene and oleum (SO_3), these raw materials were considered as feedstocks for its production considering that 100kg of PTSA requires 53.4kg of toluene and 46.6kg of SO_3[29]. Table 5.33 summarises the values used.

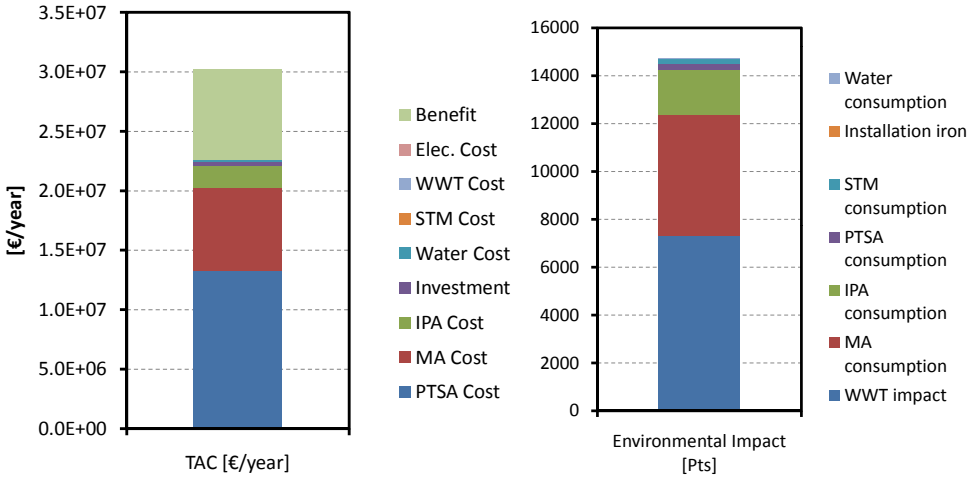
- Utilities consumption: water for product washing and condenser cooling is considered to come from the same source. Column distillate flow, which is a water and IPA stream, and product washing outlet stream are considered to be mixed together and sent to a WWT facility. Table 5.34 summarises the values used.
  - Water consumption: it is considered that decarbonised water is necessary and that 50% of it is recycled. The ecoinvent LCI data: "Water, decarbonised, at plant/RER U" unit is used.
  - WWT for distillate and washing agent: the column's distillate flow and washing water stream, used for product's pTSA removal, are considered to be sent to an industrial WWT facility. The ecoinvent data considered for this unit is "Treatment, heat carrier liquid, 40% $C_3H_8O_2$, to WWT class 2/CH". This LCI data was used due to the composition and chemical similarity.
  - Steam consumption: the environmental impact is gathered from ecoinvent data base (Steam, for chemical processes, at plant/RER U).
  - electricity use: the environmental impact is gathered from ecoinvent data base (Electricity European mix/ UECT U).
- Infrastructure: in this case the vessel and heat exchangers are considered to be part of the system boundary disregarding other installations. Distillation column, considering its internals, and heat exchangers are considered to be built from pig iron. The ecoinvent data from Pig iron, at plant/GLO U unit is used, to calculate the impact considering only iron consumption.

The environmental impact from the production of 1kg of MA (EI^{IMA}_{total}) is calculated as in Eq. 5.70.

$$EI_{total} = \sum_{k}^{RM,Utility,WWT} EI_k Fu_k + EI^{IMA}_{infr} \tag{5.70}$$

EI^{IMA}_k is the environmental impact per kg of raw material or utility k used and is reported in tables 5.33 and 5.34, while F^{IMA}_k is the flow of raw material or utility k per kg of IMA produced.

[29]These factors are calculated using the pTSA, toluene and SO_3 molecular weights.



(a) Contribution to TAC

(b) Contribution to EI

Figure 5.41: Distribution of different contributions to TAC and EI for the base case.

The environmental impact from the infrastructure (EI_{infr}^{IMA}) has to consider the project's lifespan and the operation constraints of the factory. In this case it is considered that the FU is the production of 1kg of IMA, consequently the total IMA production of the plant along the project lifespan has to be calculated and the infrastructure impact has to be divided by that value as in Eq. 5.71.

$$EI_{infr}^{IMA} = \frac{EI_{infr}}{totProd^{IMA}} \tag{5.71}$$

A service factor (SF), based onBiegler *et al.* (1997, Ch. 4-5), of 0.904 for the number of days worked along a year is considered for the calculation of IMA's total production ($totProd^{IMA}$). Fugitive emissions of IPA, MA and IMA are disregarded.

5.3.3 Step 3 Economic and environmental metrics calculation

As a preliminary analysis the analysis of how each variable affects the optimisation will be performed using the parameters defined by Fisher *et al.* (1985), see section 3.2.1.

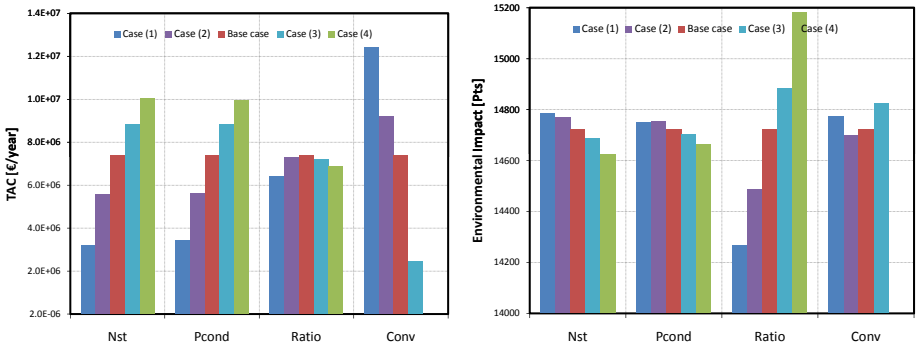
The selected base case considers a column with N_{st}=50 working at a p^{Cond} of 5000mmHg, a raw materials inlet ratio of Rat=1.5 [mole IPA/mole MA] and a fixed MA conversion of 0.995, which is attained by modifying the pTSA inlet flow. The base case TAC and EI is shown in Figure 5.41. In the case of TAC, see Figure 5.41(a), the greatest contribution is from the consumption of raw materials (pTSA, MA and IPA), the remaining cost items account for less than 2% of the TAC, including the investment which is associated to 1% of the TAC[30]. Clearly any attempt at reducing TAC should be aimed at reducing raw materials consumption.

In the case of the environmental impact (EI), see Figure 5.41(b), WWT nearly accounts for 50% of it while the remaining is due to MA and IPA consumption. PTSA, steam (STM), installation infrastructure and water consumption account for 3% of the total EI. In this sense any EI reduction attempt should aim at decreasing the use of WWT and to lower the consumption of raw materials. PTSA impacts are small compared to all the former, being the third most important the steam consumption. Table 5.35, contains the different values for the base case and the required designs for the calculation of rank and proximity parameters. The results from

[30]Investment is mainly due to vessel installation and trays, accounting for 63% and 25% respectively. In the case of the heat exchangers, they are roughly the same size and consequently their investment cost is similar.

Table 5.35: Summary of simulation runs for RD case. Base case values are in bold.

	N_{st}	p^{Cond}	Ratio	Conv.
Case (1)	40	4000	1.2	0.927
Case (2)	45	4500	1.35	0.990
Base	**50**	**5000**	**1.5**	**0.995**
Case (3)	55	5500	1.65	0.999
Case (4)	60	6000	1.8	



(a) TAC results (b) EI results

Figure 5.42: Simulation results for TAC and environmental impact for base case and other designs.

the 16 simulations proposed are summarised in Figure 5.42. N_{st} and p^{Cond} increments and decrements monotonically increase or decrease the TAC value. A non monotonic behaviour is found for the case of Ratio that presents a maximum at the base case value, and in the case of conversion, increments of its value decrease the TAC, see Figure 5.42(a), which summarises these results. Regarding the EI N_{st} and p^{Cond} increments generate lower EIs values while increases in the ratio of inlet raw materials generate higher EI. With regards to the conversion, a non monotonic behaviour is found with a minimum for the case (2), see Figure 5.42(b).

The results of the calculation of the rank and proximity values based on the former simulation runs are shown in Tables 5.36. In the case of rank parameters these are normalised using the base case objective function value and the reported value is the maximum found, while in the case of the proximity is the smallest found.

Regarding TAC rank results, it can be appreciated that conversion changes affect more than changes in the other variables. This was an expected result, given that conversion is fixed at a value by changing the input pTSA flow (which is the most important part of the TAC, see Figure 5.42(a)), and any change on the raw materials consumption will impact the most to TAC. The effect of input variables can be ranked as follows: Conv $>$ $p^{Cond} \approxeq N_{st} >$ Ratio. In the case of the EI a different ranking is found as follows: Conv $>$ Ratio $\approxeq$ $p^{Cond} \approxeq N_{st}$. For the case of the proximity parameter all variables are found to be far from the optimal value.

To draw a more complete view of the behaviour of the system a set of simulations was run to analyse the relationships between the former four variables. Due to the difficulties of

Table 5.36: Rank order parameter ROP_{jk}, see Eq. 3.14, and Proximity parameter PP_{jk}, see Eq. 3.15, for both objective functions considering the input parameters

ROP_{jk}	TAC	EI
p^{Cond}	1.108	0.0279
N_{st}	1.169	0.0261
Ratio	0.509	0.0703
Conv.	11.397	0.1250

PP_{jk}	TAC	EI
p^{Cond}	0.9684	0.1617
N_{st}	0.9559	0.3194
Ratio	0.1551	0.8867
Conv.	0.5694	0.1631

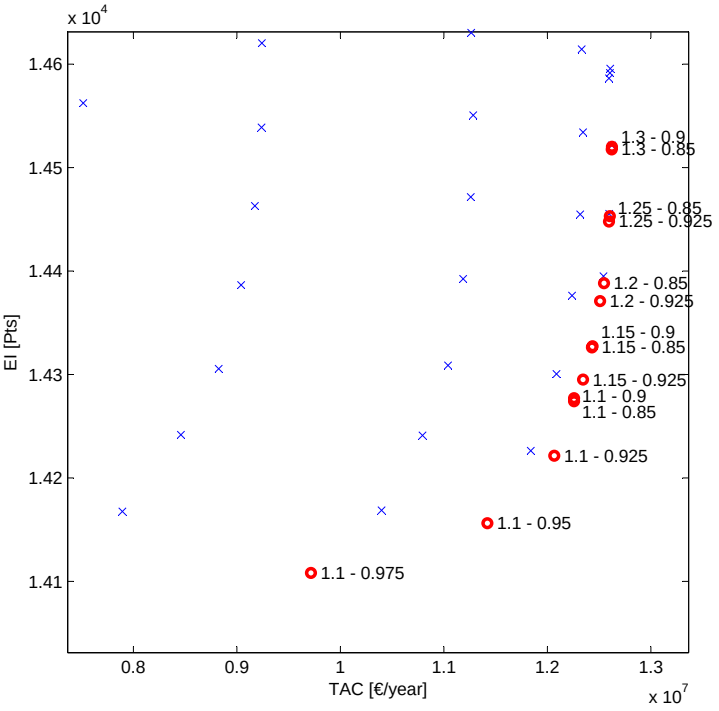


Figure 5.43: Pareto plot of TAC and EI for $N_{st} = 50$ and $p_{Cond} = 5000$ mmHg while varying the conversion and IPA/MA inlet ratio. Red circles indicate non-dominated solutions, while crosses dominated ones. Numbers in the graph show the IPA/MA ratio and the overall IMA conversion.

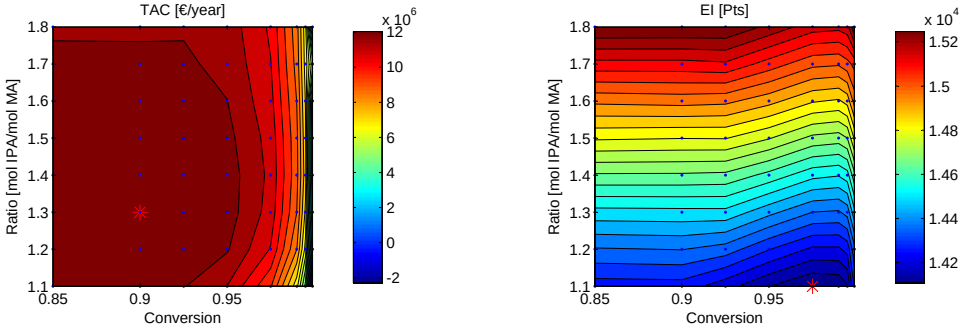
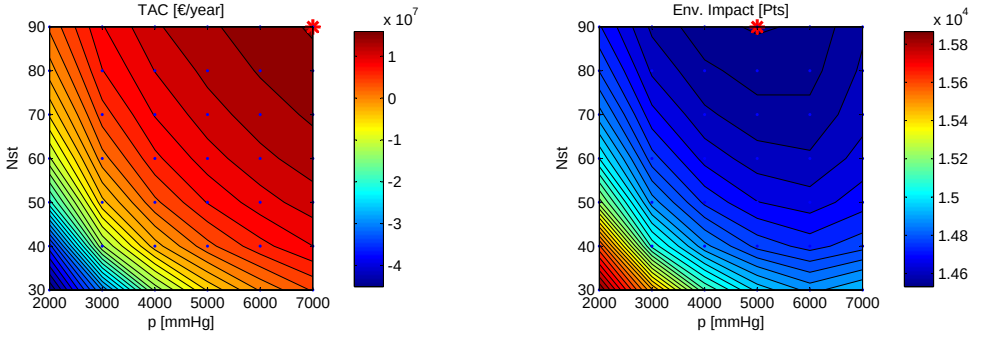
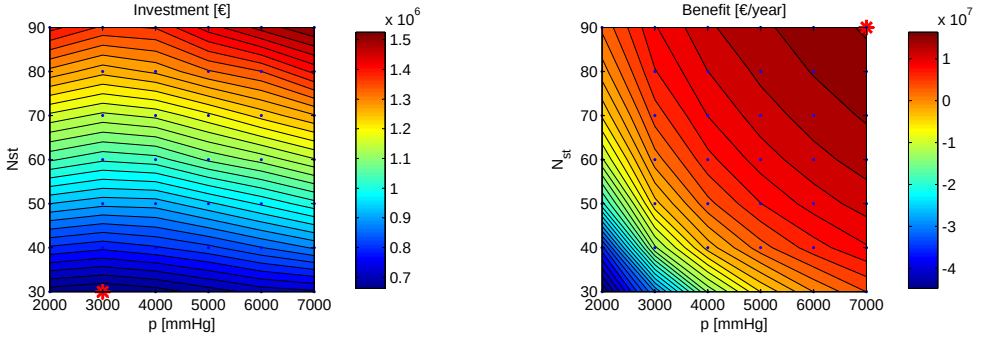


Figure 5.44: Conversion and raw material inlet ratios effects on TAC and EI values. Blue dots show simulated solutions, red cross indicate highest TAC and lowest EI.

plotting data in two dimensions, the analysis was split in two, one where conversion and feed ratios were studied for a fixed number of stages and pressure (see the Pareto front in Fig. 5.43 while the contour plot in Fig. 5.44), and other where changes of number of stages and pressure were also analysed for fixed values of feed ratio and conversion (see the contour Figures 5.45 and the Pareto fronts in Fig. 5.46). Figures 5.44 and 5.45 were generated using the `contour` Matlab function which uses the simulation results as inputs, and provides with the appropriate isolines.



(a) TAC and EI results

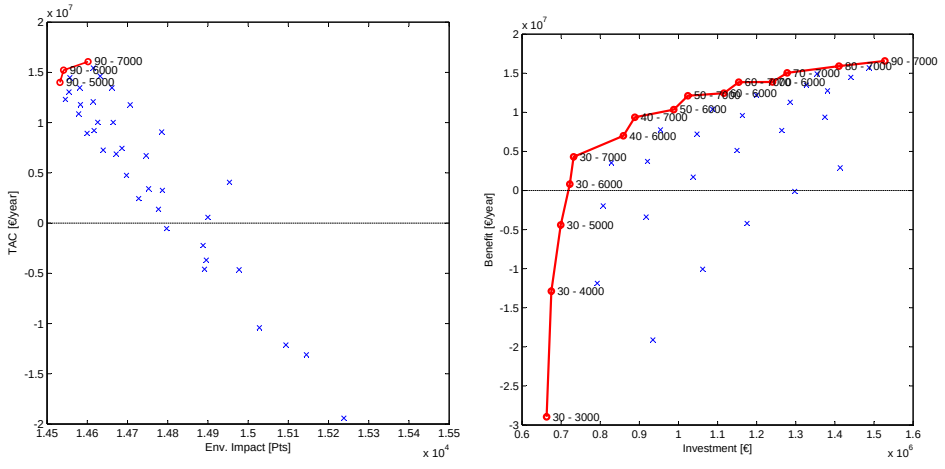


(b) Investment and Benefit results

Figure 5.45: Model output relationships for a fixed conversion and ratio of inlet raw materials while changing the N_{st} and p_{Cond} values. Blue dots show simulated solutions, red cross indicate optimal values.

Figure 5.44 shows the relationship between TAC and EI for the case of fixed column size and operating pressure, in both cases highly non linear behaviour is found. A high TAC value plateau is found for a wide range of conversion and IPA/MA ratios, and a very abrupt drop is found for conversions above 0.990 for all IPA/MA ratios. Increases of the ratio monotonically increase the EI value while for the conversion an optimal value is found around 0.975. The lowest EI solution is found for IPA/MA ratio=1.1 (lower bound) and $Conv$=0.975, while for TAC the best solution is for 1.3 and 0.9, and is not on the boundary. Figure 5.43 shows the other possible combinations of ratio and conversion that are non dominated, which could be also selected as possible operation points.

Figure 5.45, shows the contour plots for the case of fixed conversion and IPA/MA ratio at 0.995 and 1.5 respectively, which showed a close proximity to the optimal value in terms of environmental impact, while varying the N_{st} and the p^{Cond} values. In the case of TAC a monotonic behaviour is found for both N_{st} and p^{Cond}, increases in both variables show increases in TAC, being the optimal value at bound for both variables. In the case of EI, increments on the N_{st} generate less EI, while a non-monotonic behaviour is found for the case of pressure, where a minimal value is found for $p^{Cond} = 5000$ mmHg. The investment on equipment shows a minimal point at N_{st}=30 and $p^{Cond} = 3000$ mmHg (see Fig. 5.45(b)), which is due to the increase of the material factor (Fp, see Eq. 5.69) due to increments of pressure. In the case of benefits, the same relationship as in the TAC is found. It is clear that TAC is heavily influenced by the Benefits (sales and operation cost are in order of $1.0{\cdot}10^7$€) and it is not influenced by the investment (highest value in the order of $1.0{\cdot}10^6$€). Due to the monotonic behaviour of



(a) Pareto plot of TAC and EI

(b) Pareto plot of Investment and Benefits

Figure 5.46: Pareto plots for different combination of KPIs for the case of varying N_{st} and p_{Cond} values. Figure labels indicate number of stages - condenser pressure.

TAC with regards to N_{st} and p^{Cond} and of EI regarding N_{st}, the efficient solutions encompass values of constant $N_{st} = 90$, while p^{Cond} ranges from 5000 to 7000 mmHg (upper bound).

5.3.4 Step 4 Interpretation

The results regarding installation related effects in economic metric through the investment, and on the EI through the impact of construction material show that it can be disregarded given that it does not significantly affect the TAC and EI values appreciably, see Fig. 5.41. Moreover the distribution of TAC and EI into different contributions, shows that special attention has to be taken regarding raw materials consumption for both TAC and EI, while WWT impact is highly important in EI terms.

Column conversion was found to be the most influential parameter showing high values of the rank value for both objective functions. The Pareto Front considering variable Ratio and Conversion, does not contain higher ratios (above 1.3), but it contains all the range of possible conversion values.

By fixing conversion and fed ratios to the base case values, it was found that due to the non-influence of investment in the TAC nor in EI N_{st} optimisation will render its value to the upper bound (90 stages) for both OFs. In the case of pressure optimal values for EI and TAC are around 5000 and 7000mmHg, from this range the value of 6000mmHg was selected based on its closeness to the utopian point.

It was also found that Any optimisation strategy using the N_{st} as optimisation variable will render the variable value to its bound. This will require that other considerations are taken in order to set it appropriately. In the case of pressure it is seen that higher pressures will favour high TAC values while an optimal value is found in terms of EI. In the case of conversion and IPA/MA ratios it was shown that their value setting require of optimisation, and that they will affect greatly the results.

5.4 Remarks

In this chapter the proposed framework different capabilities have been tested using different case studies.

In section 5.1 the framework is applied by considering uncertainty in input variables to the selection of WWT options for a PA production plant. The PA production model was validated using regression and PCA related metrics. Both techniques provide with similar results regarding the model expected behaviour, which allowed for validating the model. The validated model allowed for the compilation of deterministic and stochastic LCIs.

A deterministic approach is used in section 5.1.3, these results helped in identifying the most important contributors to each EI category, as have been shown in section 5.1.3.1. These findings clearly show that process modifications which lead to reduced HF emissions and reduced consumption of raw materials score better, but that there exists trade offs between them. It was shown that efforts should be devoted to the reduction of raw materials use such as phosphate rock, sulphuric acid and neutralising agent, and that reduction of utilities consumption will be negligible compared to the former items. The former was possible due to the estimation of water and air fluoride emissions, which are both rigorously calculated by the use of the previously described AspenPlus simulation model.

Regarding uncertainty in model parameters it is found that the use of regression metrics and PCA helps in validating the overall model structure. Given that these tools helped in devising the model input-output variables relations, showing that in this case reactor operation temperatures and evaporator pressure have a high influence on the process air and water emissions, which are expected model results.

It was found that process model parameters uncertainty is almost negligible when compared to the uncertainty that is due to the parameters in LCIs. This clearly shows that despite the net gain put in modelling the complexities found in the process regarding emissions relation to operating parameters, the uncertainty present in LCI will hide any improvement.

Regarding the different decisions achieved by considering a deterministic or a stochastic approach, it has been found the options ordering based expected values of the stochastic results and the deterministic results coincide. However if the use of probabilities is considered there are some categories for which the decision maker has to introduce other considerations (in terms of accepted risk) in order to achieve to a decision.

In the case of endpoint metrics no agreement between them is achieved. In the case of cumCMLv2, EPS and EI99, these metrics select as best option 3, while IM02 selects option 1. If the nadir-utopian analysis is applied similar remarks as the one obtained for EPS are arrived. The discrepancy on the option selected by IM02 and EI99 or cumCMLv2, that share many mid point indicators, clearly points out the weighting and normalisation used to aggregate metrics defines the final decision.

In the case of the gasification plant operation (section 5.2) and reactive distillation column design (5.3), the framework was tested without considering uncertainty. For these cases simple local SAs shed light in the model input-output relations and were used, together with available industrial and literature data, for validating the proposed models.

In the case of the IGCC, modification of operating conditions were considered by using different raw material as feedstock. It can be concluded that for case study consideration, coal is a better fuel than petcoke in terms of raw material efficiency, due to its higher LHV value, but it is also the raw material that produces higher emissions. Regarding EI, measured using IM02, similar results to the use of CED and CExD are found due to the fact that this LCIA method assigns important weights to climate change and resource categories and that the calculated mid point LCIA shows that climate change and resource categories are the most important categories. The comparison between CC operation using NG or coal-petcoke gasi-

fication shows that the highest EI is related to the operation without biomass co-gasification, being the operation with NG the most environmentally friendly. In this sense, it is shown that co-gasification with biomass is a better choice in terms of CO_2 emissions and net power, as it results in lower emissions.

The last case presented a RD based novel production scheme for the production of IMA from IPA and MA, that is assessed in economic and environmental terms. Several operation (pressure, reactant ratio and conversion) and design (number of stages) factors were varied in a systematic way and the economic impact (expressed as TAC) and the EI (calculated using mid and end points of the IM02 methodology) were evaluated. The variables studied clearly show trade offs, as in the case of pressure, conversion and feeds ratio, and an optimal value could be found not bounded, while others variables value have to be decided using other different criteria. This last case is found for the number of stages, given that its influence on TAC and EI is small and no optimal value can be assigned.

The simulation model has proven to be useful for gathering information necessary for calculating several KPI. It allowed for the estimation of emission values for which no information was available, and it allowed for properly assess the emission uncertainty in terms of process variables. The case studies emphasised the systematic use of the proposed framework, by following the application procedure shown in section 4.2.3. The framework's step 2 which requires model validation has been performed using a different set of tools. In this sense the use of regression based metrics and PCA in the case of uncertainty treatment for the PA case showed the underlying input-output model relationships, while considering the possible ranges of process operation. The use of local SAs allowed for checking the other models when uncertainty was not considered. These validated models allowed for the exploration of a wide range of potential plant operating conditions taking into account different KPIs. In this sense, the use of process models allows for improving the verifiability, traceability and overall quality of data.

Chapter nomenclature

Table 5.37: List of indices and variables used in this chapter.

Name	Meaning	Units
Indices		
er	reactor number	
es	scrubber number	
i	trace species, chemical components	
j, j'	WWT options, and column stage numbering	
k, s	utility, raw material or waste treatment streams	
l	chemical reactions	
Variables		
α_i	trace specie i partition coefficient between liquid and solid streams	[dimensionless]
β_j	trace species allocation coefficient for option j between PA product and WW	[dimensionless]
γ_j	trace species allocation coefficient for option j between HF recovered product and waste water	[dimensionless]
Δp_{stage}	pressure drop for each stage	[mmHg]
η^i	i-th component column conversion	[dimensionless]
ρ_k	k-th utility, raw material or waste treatment price	[€/kg]
$CO_{2\,\text{air}}^{\text{OUT}}$	total outlet mass flow of CO_2 into air compartment	[kg/s]
CD	column diameter	[m]
D	column distillate rate	[mol/s]
DC_{area}	column down comer area	[m^2]
DI	discernibility index	[dimensionless]
EI_k	k-th utility, raw material or waste treatment environmental impact	[Pts/kg]
EI_{infr}	environmental impact due to infrastructure	[Pts]
Eff	plant-wide efficiency	[dimensionless]

Continued on next page

Table 5.37 – continued from previous page

Name	Meaning	Units
F_j^s	stream s feed stage j	[dimensionless]
Fu_k	mass flow of k-th stream, utility, raw material or waste treatment	[kg/s]
$gypsum\ Trace_{ij}^{out}$	phosphogypsum trace specie i flow for option j	[kg/s]
h	stage weir height	[m]
$H_2SO_4{}^{IN}$	total inlet mass flow of H_2SO_4	[kg/s]
$H_2SO_4{}_{water}^{OUT}$	total outlet mass flow of H_2SO_4 into water compartment	[kg/s]
$H_3PO_4{}_{water}^{OUT}$	total outlet mass flow of H_3PO_4 into water compartment	[kg/s]
HF_{air}^{OUT}	total outlet mass flow of HF into air compartment	[kg/s]
HF_{water}^{OUT}	total outlet mass flow of HF into water compartment	[kg/s]
$HF\ Traces_{ij}^{out}$	trace specie i amount recovered in HF recovered product for WWT option j	[kg/s]
k_{GE}	emission constant for PG	[dimensionless]
k_{WE}	emission constant for WW	[dimensionless]
k_l	l-th chemical reaction pre-exponential constant	[mol/lt/s]
Keq_l	reaction l molar fraction equilibrium constant	[dimensionless]
LHV_{RawMat}	Fuel raw material's Lower Heating Value	[MJ]
M_i^j	molar concentration of component i in j-th stage	[mol/lt]
m_{total}^j	j-th tray total mole flow	[mol/s]
N_{rst}	column number of reactive stages	[dimensionless]
N_{st}	column number of stages	[dimensionless]
$NetObtainedPower$	plant-wide obtained power	[MJ]
$p(j'^*\|j)$	option's j' prob. of being better than j	[dimensionless]
$p(j^*)$	option's j prob. of being the best option	[dimensionless]
$p(j^0)$	option's j prob. of being the worst option	[dimensionless]
p^{Cond}	column condenser pressure	[mmHg]
$PA\ Traces_{ij}^{out}$	amount of trace specie i that flows with PA product for WWT option j	[kg/s]
$PressEvaPA$	PA evaporator pressure	[mmHg]
$PressRC_{er}$	reactor er operating pressure	[mmHg]
$PressScrub_{es}$	scrubber es top stage pressure	[mmHg]
$rockFlow_j^{in}$, $Rock^{IN}$	inlet mass rock flow of waste treatment option j	[kg/s]
RR	column reflux ratio	[dimensionless]
$soil\ Emision_{ij}$	amount of trace specie i that is emitted from phosphogypsum for option j	[kg/s]
STM^{IN}	total inlet mass flow of steam	[kg/s]
$TempAir^{IN}$	inlet air temperature	[C]
$TempRC_{er}$	reactor er operating temperature	[C]
$TempWater^{IN}$	inlet water temperature	[C]
$total\ Trace_{ij}^{in}$	total inlet mass flow of trace specie i for option j	[kg/s]
$total\ WW\ Trace_{ij}^{out}$	total amount of i trace specie remaining in WW for option j	[kg/s]
$TrayVol$	stage volume holdup	[m^3]
v_{total}^j	j-th tray volumetric mole flow	[m^3/s]
w_i	mass fraction of trace specie i in rock inlet	[dimensionless]
$water\ Emision_{ij}$	amount of trace specie i that is emitted from waste waters for option j	[kg/s]
$WW\ Trace_{ij}^{out}$	amount of trace specie i that flows with waste waters for WWT option j	[kg/s]
x_j^i	j-th tray component i liquid molar fraction	[dimensionless]

Chapter 6

Batch processes and operating level decisions

In batch process scheduling, production trade-offs arise from the simultaneous consideration of different objectives. Economic goals are expressed in terms of plant profitability and productivity, whereas the environmental objectives are evaluated by means of metrics originated from the use of life cycle assessment (LCA) methodology. This chapter illustrates a novel approach for decision making by using multiobjective optimisation. In addition, different metrics are proposed to select a possible compromise based on the distance to an nonexistent utopian solution, whose objective function values are all optimal. Thus, this chapter provides a deeper insight into the influence of the metrics selection for both environmental and economic issues while considering the trade-offs of adopting a particular schedule. The use of this approach is illustrated through its application to a case study related to a multiproduct acrylic fibre production plant, special attention is put to the influence of product changeovers.

6.1 Introduction

Process industry faces increasing environmental, social and economic requirements which entail complex decision making. Specifically, batch process scheduling, which is important for the maximisation of the production facility utilisation while meeting market demands (Korovessi & Linninger, 2006), should cope with a wide variety of criteria to obtain good schedules according to the decision maker's preferences. In this respect, the consideration of multiple criteria decision making (MCDM) provides the path to deal with complex problems involving multiple and conflicting objectives. As a result, a set of compromise solutions, known as Pareto solutions (Wiecek *et al.*, 2008), is usually obtained; from them, the decision maker should choose the most suitable.

Regarding the increasing environmental concerns in chemical industry, more accurate approaches to assess process sustainability are required. Several authors highlight the importance of considering life-cycle assessment of production processes at process synthesis, product design and its integration with processing (Barbosa-Povoa, 2007; Grossmann, 2004). Therefore, waste minimization, material recovery and utilities rationalisation have been mainly dealt as integral parts at the design stage of batch plants (Barbosa-Povoa, 2007; Melnyk *et al.*, 2001; Stefanis *et al.*, 1997; Yao & Yuan, 2000).

In the literature, different methodologies are proposed that account for environmental considerations in process design, planning and scheduling applied to the case of batch industries. Stefanis *et al.*(1997) propose a methodology that embeds principles from life cycle assessment (LCA) in order to incorporate environmental considerations in the optimal design and scheduling of batch and semi-continuous processes. Process economics and pollution metrics are adopted as the design objectives in a multiobjetive formulation. Such methodology is illustrated through some examples from the dairy industry. A combinatorial process synthesis, using multiobjective goal programming under economic and environmental criteria is proposed by Chakraborty *et al.* (2002, 2003). The decision variables are operational variables, which depend on the design superstructure being optimised, and the presented case study consists of the design of plant-wide waste treatment facilities related to the batch industry. The economic function beholds operating cost and the environmental function uses the waste reduction algorithm (WAR) (Cabezas *et al.*, 1999; Young & Cabezas, 1999). Dietz *et al.* (2006) define a multicriteria design framework for multi-product batch plants, which aims at minimizing both investment costs and environmental impact. The problem is solved through a multi objective genetic algorithm (moGA), and a discrete event simulation environment is used to solve the scheduling and planning problem level in the design process.

Once plant design is fixed, process operation decisions, i.e. scheduling related, are the only subject to modifications and undoubtedly have a strong influence on the economics and environmental impact. Song *et al.* (2002) consider the scheduling problem, modelled by a MILP formulation, of a refinery process taking into account the environmental impact. The ϵ-constraint method is used to obtain a set of Pareto solutions for the multiobjective optimisation which considers global environmental impacts by means of the critical surface-time 95 (CST95) assessment methodology. Berlin *et al.* (2007) consider a case study of the dairy industry, where the production sequencing affects the environmental impact from a life-cycle perspective. They developed a heuristic method to minimise production waste based on production rules. Their methodology is further applied by Berlin & Sonesson (2008) to a case study with two dairy products. The authors conclude that the environmental impact of processing cultured milk products can be greatly reduced by adopting sequences with fewer changes of product. Park *et al.* (2007) present a goal constrained programming (GCP) algorithm for the multiobjective optimisation with priority for the scheduling of cutting papers, and various optimal schedule sets are provided.

As reported by the former authors, different scheduling of products provides trade-offs between economic and environmental aspects. This work aims at gaining insight into those trade-offs of batch process scheduling when alternative methods for product changeover are available. Batch changeovers are time consuming, affecting process schedule. One significant aspect to be considered for these changeovers are cleaning operations, that may be regularly performed between two consecutive batches for the sake of product quality or process safety. In addition, their environmental impact and economic cost may vary largely depending on the cleaning technique. Thus the consideration of multiple changeover possibilities increases the number of production schedules to be considered and the appearance of eventual trade-offs.

Several mathematical formulations have been recently proposed to solve the scheduling problem of multistage batch plants under sequence dependent changeovers. Erdirik-Dogan & Grossmann (2008) present a time slot based formulation which incorporates mass balances and propose a bilevel decomposition algorithm for dealing with medium sized problems. Maravelias & Grossmann (2003) propose a continuous time MILP model, based on the state task network (STN) representation and apply it to the case of multiproduct batch plants. The resource task network (RTN) representation is adopted by Castro *et al.* (2006) for two new

continuous-time formulations to optimise multistage batch plants, and compare them with alternative approaches to the problem, such as constraint programming and global sequencing variables. Alternative formulations, which can deal specifically with sequential processes, are based on the general and immediate precedence concepts. The former is firstly introduced by Mendez *et al.* (2001), whereas Gupta & Karimi (2003) present an immediate precedence model for multiproduct batch plants including sequence dependent changeover time.

Compared to the general precedence formulation, the immediate precedence model eases the mathematical formulation required for the consideration of sequence dependent schedules and the product batching problem. Consequently this work represents the scheduling problem, using the immediate precedence model (Gupta & Karimi, 2003). The model has been extended to consider possible use of different product changeover cleaning methods and to measure the results by using different sets of metrics.

When considering the scheduling problem, the objective function nature depends on the decision maker criteria, which are based both on his/her experience and the nature of the problem. Hence, a unique objective function is not suitable for all scheduling problems. Therefore, several possible objective functions and their scope are discussed along this work. As for economic objective functions, both plant productivity and profit are considered, whereas metrics derived from the life cycle assessment (LCA) methodology are adopted to assess the environmental impact from "cradle to gate" of the production process. Makespan is also considered as a process wide resource use efficiency metric.

The analysis of the decision maker's alternatives under conflicting objectives is performed by means of multi-objective optimisation. Specifically, the normalised normal constraint method, presented by Messac *et al.* (2003), is applied to obtain a set of Pareto solutions, which are compromise solutions of the multiobjective problem. Furthermore, different metrics are proposed to select a compromise among the Pareto solutions.

Finally, the methodology is illustrated through a case study based on a multiproduct batch facility producing acrylic fibres.

6.2 Goal and scope definition

This work represents a comprehensive step over the approaches presented in the former section by systematically assisting in the product scheduling under economic and environmental impacts considerations. The resulting model is solved by using moMILP/MINLP algorithm, which allows observing possible trade-offs between selected indicators. The problem can be stated as follows, given:

Process operations planning data

- a given time horizon;
- a set of materials: final products, intermediates and raw materials;
- a set of expected final products minimum and maximum demands;
- a fixed batch topology consisting of a set of equipment technologies for processing stages;
- a set of fixed product recipes for processing, concerning mass balance coefficients, resources utilisation and processing times;
- a set of different product changeover methods;

Economic data

- direct cost parameters such as production and raw material costs;
- changeover cost parameters associated to every possible product sequence combination;
- selling price for every final product;

Environmental data

- raw material production environmental interventions
- product manufacturing environmental interventions
- equipment change over environmental interventions

The goal is to determine:

- the number of batches required to meet the demand (batching);
- the assignment and sequencing of the batches (scheduling);
- the appropriate changeover methods required between batches;
- the amount of final products to be sold;
- the environmental impact associated to each process schedule;

such that different sets of metrics, discussed in the following sections, are optimised. Within this model, and in order to avoid emission double counting, raw material emissions are not aggregated to product manufacturing, similarly cleaning environmental interventions are considered separately.

This work models the scheduling problem through a mathematical formulation based on an immediate precedence model (Gupta & Karimi, 2003) which is able to consider the product batching and extends existing formulations to consider different product changeover cleaning methods. However, the multiobjective approach proposed and further discussion are still valid regardless the mathematical model selected.

When considering the scheduling problem, the objective function nature depends on the decision maker criteria, which are based both on his experience and the nature of the industry. Hence, a unique objective function is not suitable for all scheduling problems. Therefore, several possible objective functions and their scope are discussed along this work. As for economic objective functions, both plant productivity and profitability are considered, whereas metrics derived from the LCA methodology are adopted to assess the environmental impact from "cradle to gate" of the production process.

Regarding the FU, it can be argued that is should be fixed to a certain amount of produced products. However one of the possible scheduling objectives might be to diminish the total environmental impact irrespective of which products are being produced.

The system boundaries are drawn from cradle to the plant gate, product use, distribution and disposal are not considered. In the case of cradle concerns, raw materials production is taken into account, while in the case of the manufacturing step emissions due to cleaning and production are explicitly taken into account.

6.3 Model building and data gathering

In order to model the scheduling problem, a mathematical formulation based on the immediate precedence concept (Gupta & Karimi, 2003) has been adopted. The model has been extended to consider different interbatch cleaning methods, additional objective functions (e.g. makespan, productivity and environmental impact) and product batching. The scheduling model is decomposed in two parts. First, the product batching problem is considered based on demand and acceptable product batch sizes. This allows for the subsequent scheduling problem to opt for the number of batches to be produced instead of fixing them beforehand. In this sense, given a demand that could be fulfilled and a fixed batch size, the maximum number of batches has to be set accordingly.

Next, the allocation, sequencing and timing of the batches resulting from the first problem and associated tasks (i.e. cleaning) are modelled and optimised along a production time

horizon according to different objective functions. Scheduling decisions, such as product sequencing, affect environmental considerations. In this work, the environmental impact associated with the products and the different cleaning methods for changeovers among products are assessed. As a result, the mathematical programming model considers product flows, raw materials and utilities consumption, and changeover operations to simultaneously deal with environmental and productivity features.

In order to model the scheduling problem under different alternative cleaning methods, a mathematical formulation based on the immediate precedence concept has been adopted and adequately extended. The model is described in section 6.3.1. Environmental and economic metrics are discussed in section 6.3.2.

6.3.1 Scheduling model description

The scheduling model is decomposed in two parts. First, a feasibility problem for product batching based on demand and product batch sizes is posed. Next, the allocation, sequencing and timing of previous batches are modelled and optimised along a production time horizon according to different objective functions.

First stage: batch assignment. The problem consists of the assignment of production to batches, so that the maximum demand of each product can be fulfilled. The number of batches considered must be enough to allow the complete assignment of production. Each batch i can be assigned to at most one product p (Eq. 6.1), and the total demand of each product has to be assigned, considering a fixed product batch size (Eqs. 6.2 and 6.3). Given that the problem being addressed considers a fixed batch topology, product batch sizes BS_p are fixed. Please note that a fixed amount of produced product is not required, but only minimum (D_p^{min}) and maximum demands (D_p^{max}) are enforced on each p product.

$$\sum_p Y_{ip} \leq 1 \qquad \forall i \tag{6.1}$$

$$\sum_i BS_p Y_{ip} \leq D_p^{max} \qquad \forall p \tag{6.2}$$

$$\sum_i BS_p Y_{ip} \geq D_p^{min} \qquad \forall p \tag{6.3}$$

An additional aim of this stage consists of the definition of process features for each batch, that is, the assignment to each batch of the processing time through the different processing stages, selling price, and the environmental impact. Therefore, Eqs. 6.4 and 6.5 establish the time required to fulfil stage k of batch i, and the related o operations: loading ($load$), preparation (pre), processing (pro) and unloading (unl) which all depend on the product p assigned to that batch. In the case of operation cleaning time, it has been assumed that it only depends on the products sequence, and different cleaning methods can not be used within the same batch. Eqs. 6.6, 6.7 and 6.8 are posed for batch selling price and product environmental impact.

$$T_{ik} = \sum_p time_{pk} Y_{ip} \qquad \forall (i,k) \tag{6.4}$$

$$T_{ik}^o = \sum_p time_{pk}^o Y_{ip} \qquad \forall (i,k) \tag{6.5}$$

$$BP_i = \sum_p BP_p Y_{ip} \qquad \forall i \tag{6.6}$$

$$BS_i = \sum_p BS_p Y_{ip} \qquad \forall i \tag{6.7}$$

$$EnvIm_i = \sum_p EnvIm_p Y_{ip} \qquad \forall i \tag{6.8}$$

Moreover, Eqs. 6.9 and 6.10 define the changeover time between any pair of batches for a given cleaning method c, depending on the products assigned to the batches. Similar equations are considered for changeover cost and environmental impact associated to every k stage and each pair i, i' of batches.

$$ChT_{ii'kc} \geq chanT_{pp'kc} - BigM \cdot \left(2 - Y_{ip} - Y_{i'p'}\right) \qquad \forall i, i', p, p', k, c \mid i \neq i' \tag{6.9}$$

$$ChT_{ii'kc} \leq chanT_{pp'kc} + BigM \cdot \left(2 - Y_{ip} - Y_{i'p'}\right) \qquad \forall i, i', p, p', k, c \mid i \neq i' \tag{6.10}$$

Finally, Eq. 6.11 enforces that each batch can only be assigned if all previous ones have already been, in order to avoid degenerated solutions.

$$\sum_p Y_{ip} \leq \sum_p Y_{i+1p} \qquad \forall i \mid i < max(i) \tag{6.11}$$

Regarding the objective function to optimise the first part, it has been decided to use the total profit; this way, the maximum number of batches is pre-assigned, and this provides with a starting point that does not restricts artificially the following stage optimisation.

Second stage: batch scheduling. Once the batching problem is solved, the production and sequencing of the previously assigned batches, which are gathered in a set ($dynI$), is decided at this stage. A special feature of the formulation proposed is the production of a starting and finishing batch, required to address the cleaning for the first and last batches, which produce no product, but represent the initial and final still state of the plant. For nomenclature reasons, an unreal product, whose processing time, cost and environmental impact are zero, is assigned to the aforementioned two batches.

As for timing constraints, Eq. 6.12 establishes the end time of stage k of batch i, as a function of the starting time (Ts_{ik}) and operation o time ($\overline{T^o_{ik}}$), in case that such batch is eventually produced, that is, the binary variable (W_i) is 1.

$$Tf_{ik} = Ts_{ik} + \overline{T_{ik}} W_i \qquad \forall (i,k) \mid i \in dynI \tag{6.12}$$

In addition, the timing constraints among the different stages are necessary. Eq. 6.13 defines the fact that for two consecutive stages, the unloading start time of the first one must be equal to the load starting time of the following one.

$$\begin{gathered} Ts_{ik+1} + \overline{T^{prep}_{ik+1}} = Tf_{ik} - \overline{T^{unlo}_{ik}} \\ \forall (i,k) \mid i \in dynI,\, k \in kcon \end{gathered} \tag{6.13}$$

In case two stages are simultaneous, that is, their loading, operation and unloading occur at the same time, Eq. 6.14 enforces the load starting time of both stages to be equal. This constraint allows for modeling of fed-batch stages, e.g. a filter that requires a feed and outlet pump to work simultaneously for its operation.

$$Ts_{ik+1} + \overline{T^{prep}_{ik+1}} = Ts_{ik} + \overline{T^{prep}_{ik}} \qquad \forall (i,k) \mid i \in dynI,\, k \in kpar \tag{6.14}$$

Eq. 6.15 imposes that the loading start time of a given $k+1$ stage is equal to the time at which the operation of the previous stage k starts. This condition is useful for semicontinuous operations.

$$Ts_{ik+1} + \overline{T_{ik+1}^{prep}} = Tf_{ik} - \overline{T_{ik}^{unlo}} - \overline{T_{ik}^{proc}} \quad \forall (i,k) \mid i \in dynI,\ k \in kpum \tag{6.15}$$

An additional timing constraint is defined by batch changeover time. Not only does production sequence affect the changeover time, but the changeover method c as well. Hence, Eq. 6.16 defines the changeover time for two consecutive batches in a given stage k, depending on the cleaning method used. Therefore, the binary variable $X_{ii'c}$ is 1 in case batch i is immediately processed before batch i' using cleaning method c.

$$Ts_{i'k} \geq Tf_{ik} + \overline{ChT_{ii'kc}} X_{ii'c} - BigM2(1 - X_{ii'c}) \quad \forall (i,i',k) \mid (i,i') \in dynI,\ i \neq i' \tag{6.16}$$

The production horizon H defines the maximum time at which the last stage of any batch is allowed to finish. Eq. 6.17 is valid due to the fact that all product batch sizes are fixed, that is, they do not vary between batches; (they were previously predefined at the first stage).

$$W_i H \geq Tf_{ik} \qquad \forall (i,k) \mid i \in dynI \tag{6.17}$$

As for production constraints, Eq. 6.18 imposes that a minimum demand for each product p must be fulfilled.

$$\sum_{i \in dynI} W_i \overline{BS_i} \geq D_p^{min} \qquad \forall p \tag{6.18}$$

It is necessary to define the sequence in which the batches are produced. Therefore, any batch i, with the exception of the first and the last, must have an immediate predecessor and an immediate successor. This condition is enforced by Eq. 6.19 and 6.20, respectively.

$$\sum_{i',c \mid i' \in dynI, i \neq i'} X_{ii'c} = W_i \qquad \forall i \mid i \in dynI,\ i < max\left(dynI\right),\ i > 1 \tag{6.19}$$

$$\sum_{i',c \mid i' \in dynI, i \neq i'} X_{i'ic} = W_i \qquad \forall i \mid i \in dynI,\ i < max\left(dynI\right),\ i > 1 \tag{6.20}$$

The sequencing conditions for the first and last batches, which are fixed and assigned to the still state, are imposed by Eqs. 6.21 to 6.24.

$$\sum_{i',c \mid i' \in dynI, i \neq i'} X_{ii'c} = 1 \qquad \forall i,p \mid i = 1,\ p = 0,\ \overline{Y_{ip}} = 1 \tag{6.21}$$

$$\sum_{i',c \mid i' \in dynI, i \neq i'} X_{i'ic} = 0 \qquad \forall i,p \mid i = 1,\ p = 0,\ \overline{Y_{ip}} = 1 \tag{6.22}$$

$$\sum_{i',c \mid i' \in dynI, i \neq i'} X_{ii'c} = 0 \qquad \forall i,p \mid i = max\left(dynI\right),\ p = 0,\ \overline{Y_{ip}} = 1 \tag{6.23}$$

$$\sum_{i',c \mid i' \in dynI, i \neq i'} X_{i'ic} = 1 \qquad \forall i,p \mid i = max\left(dynI\right),\ p = 0,\ \overline{Y_{ip}} = 1 \tag{6.24}$$

6.3.2 Scheduling environmental and economic assessment

The main objective of batch production planning and scheduling is to optimise capacity utilisation of batch manufacturing facilities and fulfill customer orders within a specific time horizon (Barker & Rawtani, 2005). In any case, as a main building block of enterprise-wide optimisation, the scheduling level pursues the overall company objectives which arise from economic, environmental and social aspects.

Economic criteria are of utmost importance in process industry. Hence, multiple economic objectives can be adopted in process scheduling, depending on the decision maker preferences, which stem from industrial demands. Thus, either an absolute economic measure, such as total profit, or a time relative measure, such as productivity could be adopted to assess the optimal decisions. The former criteria could be more suitable for those industrial environments where prices and demand have low uncertainty, and working hours are fixed; whereas process productivity is more interesting in those environments where late orders may arrive and variable costs are more important than fixed costs, and consequently the main objective is to produce the most profitable products using the least time. In academic studies related to scheduling, the economic objective function is usually regarded with time metrics, such as makespan, lateness or earliness (Korovessi & Linninger, 2006; Mendez *et al.*, 2006). However, makespan is only equivalent to productivity under certain conditions. Specifically, productivity and makespan are equivalent, if (i) the produced quantity is fixed, or (ii) under time constraints and variable production quantities if all products are equivalent from a profitability point of view, that is, they have the same profit and production time along the different stages. Only in such cases, productivity maximization can be reduced to makespan minimization.

Otherwise, companies must face nowadays tighter environmental regulations. Hence, environmental objectives have to be considered as part of the optimisation process (Cano-Ruiz & McRae, 1998). The objectives could be again expressed in absolute measures, for example, the minimization of the total environmental impact, which could lead to do not produce at all unless a minimal demand should be satisfied; or a relative measure, such as the minimization of the total environmental impact per mass of product produced. In this case, the lack of production would lead to higher penalties.

For the presented formulation, the total profit objective function, which considers product benefits ($\overline{BP_i}$) and changeover costs ($\overline{ChCost_{ii'kc}}$), is defined by Eq. 6.25. The productivity (Eq. 6.26) results from dividing the total profit by the production schedule makespan (Eq. 6.27).

$$z^{profit} = \sum_{i} \overline{BP_i} W_i - \sum_{i,i',c|i\neq i'} X_{ii'c} \sum_{k} \overline{ChCost_{ii'kc}} \tag{6.25}$$

$$z^{prod} = \frac{z^{profit}}{Mk} \tag{6.26}$$

$$Mk = Tf_{ik} \qquad \forall i,k \mid k = max(k),\ i = max(i) \tag{6.27}$$

On the other hand, total environmental impact (EI), which includes both the batch production process ($\overline{EnvIm_i}$) and batch changeover EI ($\overline{EnvIm_{ii'kc}}$), is expressed by means of Eq. 6.28, whereas relative environmental impact can be obtained dividing the total EI by the produced quantity (Eq. 6.29).

$$z^{ei} = \sum_{i,i',c|i\neq i',i'\in dynI} X_{ii'c} \sum_{k} \overline{EnvIm_{ii'kc}} + \sum_{i|i\in dynI} W_i \overline{EnvIm_i} \tag{6.28}$$

$$z^{rei} = \frac{z^{ei}}{\sum\limits_{i|i\in dynI} W_i \overline{BS_i}} \tag{6.29}$$

In the case of using any combination of objective functions defined in Eq. 6.25, Eq. 6.27 or Eq. 6.28, the resulting formulation entails an MILP; whereas the consideration of either Eq. 6.26 or Eq. 6.29 in combination with the former results in an MINLP. Please note that the non-linearity is only associated to the objective functions and not the scheduling model (Eq. 6.1 to Eq. 6.24).

Different objective functions may be used in the scheduling problem according to the decision maker's criteria. Multiple objective programming methods aim at finding suitable solutions of mathematical problems with multiple conflicting objective functions, and different alternative strategies can be applied to solve a multiobjective problem (Gandibleux *et al.*, 2004; Wiecek *et al.*, 2008).

One typical approach consists of aggregating the different objectives in a single objective function with varying numerical weights. Unfortunately, these coefficients usually lack of physical meaning, and entail an arbitrary assignment of values. Thus, there is not a unique optimal solution for multiobjective problems, but rather a set of feasible solutions which may be suitable. The preferred approach consists of providing a set of Pareto optimal solutions: a Pareto solution is one for which any improvement in one objective can only take place if at least another objective worsens. Pareto optimal solutions are also termed dominating solutions, while the remaining possible optimisation solutions are dominated.

The techniques for generating a set of Pareto optimal solutions should have some desirable properties. Namely, they should be able to find all available Pareto points, generate them evenly along the possible solutions in the feasible region, and they should not generate and explore dominated solutions (Messac *et al.*, 2003). However, all the available techniques present deficiencies in some of the former aspects. For example, the weighted sum must be carefully applied since it does not generate all available Pareto points, and the Pareto frontier does not represent an evenly set of solutions of the feasible region Steuer (1986). Finally, normal boundary intersection (NBI) (Das & Dennis, 1998) and normal constraint method (NC) (Messac *et al.*, 2003) generate points that are not in the Pareto frontier, but NBI is more prone to generate dominated solutions. In general, all previous procedures require of a filtering step to distinguish and classify dominated from non-dominated solutions. This work implements the NC method described in Messac *et al.* (2003) modified to obtain a reliable set of possible Pareto solutions, and applies a Pareto filter algorithm developed by Cao (2009).

The Pareto frontier (PF) associated to the problem at hand is discrete and results from a set of integer variables being defined (e.g. sequence, cleaning method), consequently evenly separated solutions can not be expected. A key point in the NC method is the number of solutions that should be generated to obtain evenly separated Pareto solutions over the PF. Thus, the application of the NC method requires special attention. The selection of the number of solutions to be explored is performed by dividing the utopian line (hyperplane, in case of more than two objectives being considered), and exploring each constrained segment. To explore a high number of points will lead to an excessive computational effort, whereas an inadequate number of solutions would result in a fictitious PF that contains dominated solutions due to unexplored Pareto optimal solutions. Additionally, when the solution space is discrete, any increase in the number of divisions asked for a constrained based strategy does not guarantee the generation of more Pareto solutions. Hence, an iterative approach is proposed to be applied in order to generate a reliable estimation of the PF. The number of divisions of the utopian hyperplane is incremented on each iteration and the points explored are added as new solutions. Different termination criteria are possible, (i) PF similarity and (ii) PF similarity percentage. The first termination criterion consists of checking the PF at the end of each iteration, if no changes are found in two consecutive iterations the PF is accepted as solution to the multiobjective problem. The latter termination criterion imposes the end of the

Table 6.1: Product batch sizes and prices

Product	Batch size [ton/batch]	Batch price [m.u./ton]
A	2.5	30
B	1.8	20
C	1.5	15

Table 6.2: Cleaning methods description.

Cleaning method	Time	Cost	Env. Impact	Method based on the use of
1	Very low	Medium	Medium	Steam
2	Very high	Very low	Low	Water
3	Medium	High	Medium	Organic solvent

iteration procedure, when the number of new Pareto solutions divided by the total number of explored solutions is lower than a specific tolerance (tol) percentage. Specifically in this case, a minimum of fifty points (nd_0) are initially generated and in the next iteration at least fifty new different points are further studied (nd_1). These parameters values (nd_j and tol) can be changed according to the problem characteristics. The algorithm has been previously described in Alg. 4.1.

Once the PF is generated, the decision maker should choose the solution to be adopted (Wiecek *et al.*, 2008). Metrics that may assist the decision-maker to choose a final solution can be derived from the values of the different objectives expressed in terms of the normalised distance from their individual (single objective) optimal solution. The point which considers the best possible single objective outcomes is known as utopian point, while the one which considers worst solutions is the nadir point. The best compromise solution could be thought as the one that minimises the overall distance to the utopian point (Eq. 6.30), as proposed by Hwang & Yoon (1981) in the Technique for Order by Similarity to Ideal Solution (TOPSIS). An alternative strategy consists on measuring the distances from the PF solutions to the nadir point. Therefore another compromise solution could be chosen as the one whose geometric distance to the nadir is maximum (Eq. 6.31).

$$\mu^{best} \rightarrow \min \left\{ \sum_g \left(\frac{\mu_g^* - \mu_g}{\mu_g^* - \mu_g^0} \right)^2 \right\} \tag{6.30}$$

$$\mu^{best} \rightarrow \max \left\{ \sum_g \left(\frac{\mu_g - \mu_g^0}{\mu_g^* - \mu_g^0} \right)^2 \right\} \tag{6.31}$$

6.3.3 Case study description

The methodology proposed is illustrated in a case study which was originally posed by Grau *et al.* (1996). It consists of a multi-product batch process plant that produces three acrylic fibre formulations by a suspension polymerization process (Fig. 6.1) requiring 14 processing stages. Due to minimisation of inventory costs, the possible storage of polymer (considered as intermediate product) after stages deaeration (stages 11,12) has been disregarded and polymer extrusion (stage 13) is performed right after polymer deareation is done. Production recipes contain a detailed description of the product batch sizes and prices (Table 6.1), as well as operational times (Table 6.3) and energy demands of each of the production stages (Table 6.4).

Table 6.3: Operation times and equipment associated to each stage for all possible produced products [h].

	Product	Fibre A					Fibre B					Fibre C				
Stage	Equipment	P	L	O	U	TOT	P	L	O	U	TOT	P	L	O	U	TOT
1	R1	0.2	0	2	0.3	2.75	0.2	0	3	0.75	4.2	0.2	0	1	0.3	1.75
2	P1	0.2	0	0.3	0	0.75	0	0	0	0	0	0.2	0	0.3	0	0.75
3	C1	0.5	0.3	2.5	0.75	4.8	0	0	0	0	0	0.5	0.3	2	0.75	4.3
4	P2	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2
5	F1	0.5	0	0.75	0	1.75	0.5	0	0.75	0	1.75	0.5	0	0.75	0	1.75
6	P3	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2
7	R2	0.3	0.75	1	0.75	3.05	0.3	0.75	0.75	0.75	2.8	0.3	0.75	0.5	0.75	2.55
8	P4	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2
9	F2	0.5	0	0.75	0	1.75	0.5	0	0.75	0	1.75	0.5	0	0.75	0	1.75
10	P5	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2
11	D1	0.2	0	0.75	0	1.15	0.2	0	0.75	0	1.15	0.2	0	0.75	0	1.15
12	P6	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2
13	E1	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2	0.2	0	0.75	0	1.2
14	V1	0.3	0.75	3.5	0	5.3	0.3	0.75	3	0	4.8	0.3	0.75	1.5	0	3.3

Table 6.4: Heating and cooling demands for each process and all products [kW].

	Heating needs			Cooling needs		
Stage-Operation	A	B	C	A	B	C
1-O	0.0	0.0	0.0	288.0	125.0	495.0
3-O	100.0	0.0	265.0	89.9	0.0	238.0
7-U	0.0	0.0	0.0	12.9	0.0	155.0
11-O	65.8	47.4	0.0	0.0	0.0	0.0
13-O	730.3	525.8	886.5	1347.4	970.2	1279.7
14-L	1197.0	861.8	897.0	0.0	0.0	0.0
14-O	699.4	503.6	497.0	0.0	0.0	0.0

Between any two batches, a changeover operation must be carried out. Three different changeover cleaning methods, which differ in time use, cost and environmental impact, are defined as summarised in Table 6.2.

To ease the computation of the environmental impacts, instead of adding up all the LCI results associated to the consumption/use of raw materials, utilities and cleaning agents, the Life Cycle Impact Assessment (LCIA) results from each of the activities (e.g. water use, steam generation or raw material production) have directly been used. These LCIA results hold the combined environmental impact of each activity from a cradle to gate point of view. The LCIA methodology applied is Impact 2002 (Humbert *et al.*, 2005). Simapro (de Schryver *et al.*, 2006) has been selected to calculate these LCIAs from the corresponding LCIs (Ecoinvent, 2008) and the LCIA information is used in the model. It is found that the environmental impact of raw materials is quite large compared to the remaining quantities. This fact was expected given that this impact is significantly larger than either the environmental impact associated to the use of utilities or changeover operations. Hence, this analysis distinguishes between them accordingly. As for environmental impact of the production itself, the LCI entailing residues, non-controlled emissions, raw materials, steam, water, and electricity consumption is calculated using good engineering practises, and it is based on the available literature data.

Raw materials consumption estimation. Raw materials (solvent, mono-mers and initiators) addition for fibre production is considered at stage 1 (polymerization). An overall reaction yield of 95% is assumed. In addition, a 40% of the total initial amount introduced in the reactor is solvent, and the remaining 60% is monomer mixture, which is composed by 85% acrylonitrile, 10% methyl metacrylate and 5% vynil chloride. The solvent is considered to be pure acetone, while vynil chloride, styrene, acrylonitrile and methyl metacrylate are the possible co-monomers. Each one of the former raw materials LCI data has been retrieved from their corresponding Ecoinvent LCI (Ecoinvent, 2008).

Residues generation. The remaining quantity of each batch (5% in mass) is released in the last stage (evaporation), and treated as production waste. A certain percentage of consumed water (30%) is also considered as residue to be treated. The LCI associated to its treatment

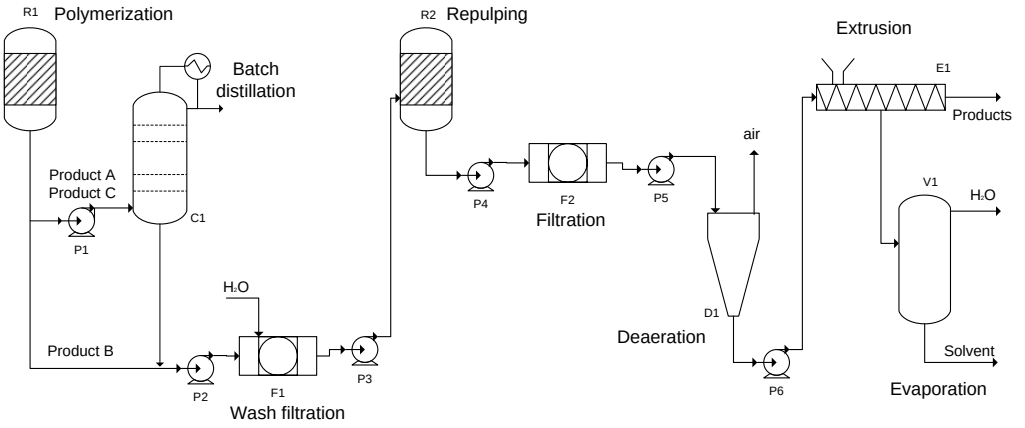


Figure 6.1: Flowsheet of the production process of acrylic fibers manufacturing.

as waste has been related to treatment of "heat carrier liquid, 40% $C_3H_8O_2$, to waste water treatment, class 2/CH S" in Ecoinvent.

Non-controlled emissions. According to USEPA (1984, pg. 33), acrylonitrile emissions in this production process occur at the pelletizer (repulping) and polymer dryer (deaeration) (stages 7 and 11 of the recipe) and estimates an air emission of 41.4 lb/ton product released in acrylic wet spun homopolymer manufacturing. In this case, these emissions are considered as air emissions of pure acetone, disregarding any monomer emission.

Electricity consumption. Electricity consumption includes pumping required for product movement between stages that are not gravity driven and also for pumping cooling water and steam compression. In the case of pumping cooling water, a pumping ΔP=1 bar and a flow of 20 m^3/h, which requires and approximate power of 1.5kW, is considered. On the other hand, for compressing heating steam, a yield which represents 0.6kWh useful heat of steam/kWh electricity is used. In all cases, the LCI information for electricity consumption is considered as "Electricity, medium voltage, at grid/ES U".

Heating and cooling needs. In the case of heating, it is considered to be supplied using steam, the LCI has been gathered using the "Steam, for chemical processes, at plant/RER U" Ecoinvent unit. It is a medium-low pressure saturated steam, at 9 bar (2029,45 kJ/kg steam). Steam is used to heat streams according to the recipe provided in Grau *et al.*(1996). For the estimation of cooling needs, water is used to cool down the streams. All cooling requirements are computed as water cooling and assuming no electrical refrigeration required. Cooling water consumption is computed by taking into account its specific heat (liquid water is 1kcal/kg), and an average ΔT for water of about 20^{o}C.

Water consumption. Process water is considered to require softening, consequently the Ecoinvent LCI "Water, completely softened, at plant/RER U" is used. Process water is required in some recipe stages besides cooling. The filtering stages require a water flow of 40 m^3/h, and for the cleaning of these units a water flow of 10 m^3/h is needed.

Changeover characterisation. According to Allen *et al.*(2002), the nature of the cleaning process should be considered taking into account several aspects: (i) nature of the vessels to be cleaned (capacities, materials of construction and shape), (ii) the cleaning schedule, (iii)

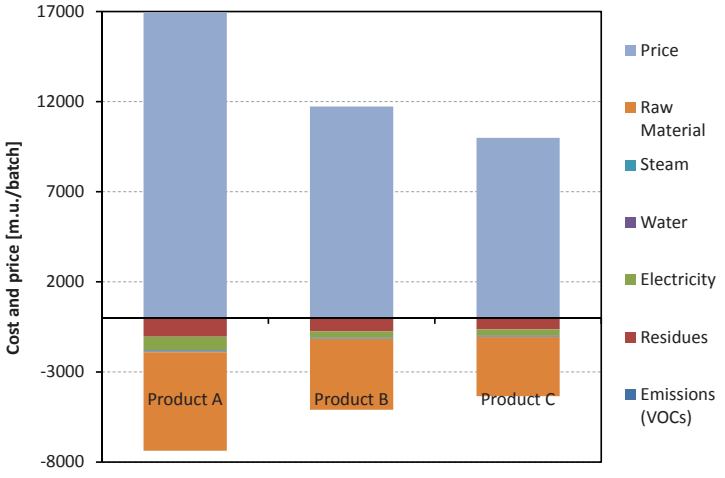
the residual quantity of chemical left to be cleaned in the vessel, (iv) the cleaning agent (aqueous/organic, chemical solubility/miscibility), and (v) the requirements of waste treatment for the used cleaning agent. Mainly in the batch industries where individual unit operations are utilized for multiple products, many pieces of equipment are subject to long clean-out periods using large solvent volumes and/or aqueous detergents. It is current practice to try to use clean-in-place (CIP) procedures instead of break down and rebuild approaches where unit operation allows it (Constable *et al.*, 2009) Although in some cases the unit operation requires its break down and rebuild (e.g. plate filtration) most vessel cleaning is performed using CIP.

Regarding clean up scheduling (ii), it depends on the process or product and cleaning between batches could be due to product requirements (colour changes in paint manufacturing), or process requirements (solidification of product in a filter requires its clean up). Estimation of point (iii) requires knowing vessel characteristics and some rough estimate of the viscosity and surface tension of the liquid to be cleaned however as a rule of thumb the amount in weight percent left in vessels ranges from 3 to 0.03% (Allen *et al.*, 2002). With regard to (iv) in the case of aqueous cleaning agents, these are sent to waste water treatment (WWT) plants, while organic solvents are recycled or incinerated. In general, the actual amount of clean up agent will depend on the amount of this agent that can be recycled/reused in other cleaning operations.

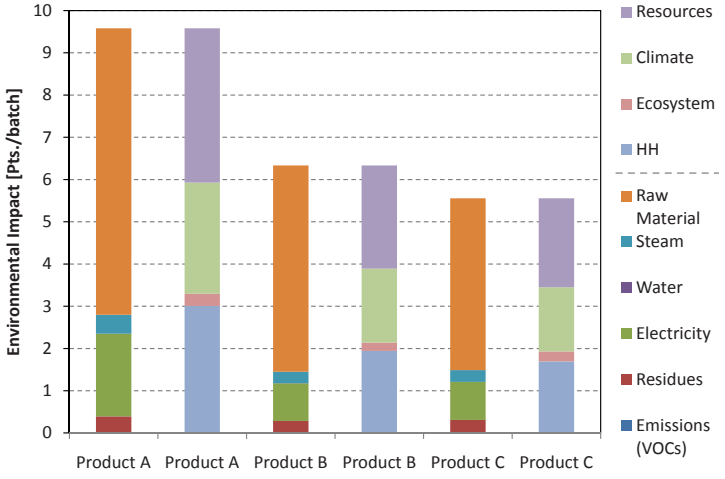
In the case study, three different product changeovers are possible. Each of them has associated different costs, inventory/impact and duration (Table 6.2). Since cleaning options are very different, a comparison based on used volume or energy would be too simplistic, consequently it has been decided to use the environmental impact and cost of those stages to select among them by including such aspects in the objective function calculations. A few assumptions have been made regarding the LCI for each of the three available changeover policies.

- Regarding costs, they have been assigned according to the cleaning requirements and general engineering principles used for the estimation of former production costs.
- Electricity consumption [kWh] has been considered to be a function of changeover time ($ChanT$), it is calculated considering the $ChanT$ [h] multiplied by the power of a pump with a flow of 20 m^3/h and a ΔP of 2 bar, which is nearly 1.5kW. Electricity consumption also includes electricity requirements for steam compression.
- As for water consumption, a pump of 20 m^3/h is considered in the water cleaning method; so the changeover time multiplied by the pump capacity is approximately the water consumption in that stage.
- Similarly to the estimation of water consumption, solvent is estimated considering a pump capacity and the required changeover time. Solvent recycle has been disregarded.

Figure 6.2 presents the batch cost and environmental impact for the production a batch of each product. Raw materials represent the most important operating cost for all products, followed by residues treatment and electricity. However, there are no great differences in production costs among products because their recipe is similar in terms of raw materials and processing stages. In the case of Figure 6.2(b), environmental impacts for each product are shown in two different columns distributed in different items. One of them in terms of raw materials, utilities consumption, residues treatment and emissions and the other column using the different end point environmental impact categories that Impact 2002 implements (resource use, global climate change, damage to ecosystem and human health impacts). In the first case, the highest contribution to environmental impact is due to raw materials production, followed by electricity and thirdly water consumption and residues which have approximately the same impact. The distribution along end point categories shows similar im-



(a) Costs and price.



(b) Environmental impact distributed along different items, left column operation related, while right column in different end point categories.

Figure 6.2: Batch cost and price, and environmental impact for the three acrylic fibers.

pacts to resource use, climate change and human health, while smaller effects to ecosystem quality.

Figures 6.3,6.4 and 6.5 show the changeover costs, environmental impacts and time for each pair of products using the three available cleaning methods. The differences briefly outlined in Table 6.2 can be appreciated, and the contribution of each operating resource to the total cost is unveiled. Therefore, the high operating cost of method 3 is basically due to fresh acetone consumption. In the case of changeover 1, cost is basically due to electricity consumption, whereas steam represents a smaller fraction of total cost, and electricity and water are the main costs of cleaning method 2.

6.4 Metrics calculation

The previous case study is solved considering a demand of 2 batches of each product, and that a minimum of the 50% of the demand (i.e. 1 batch) of each product must be satisfied.

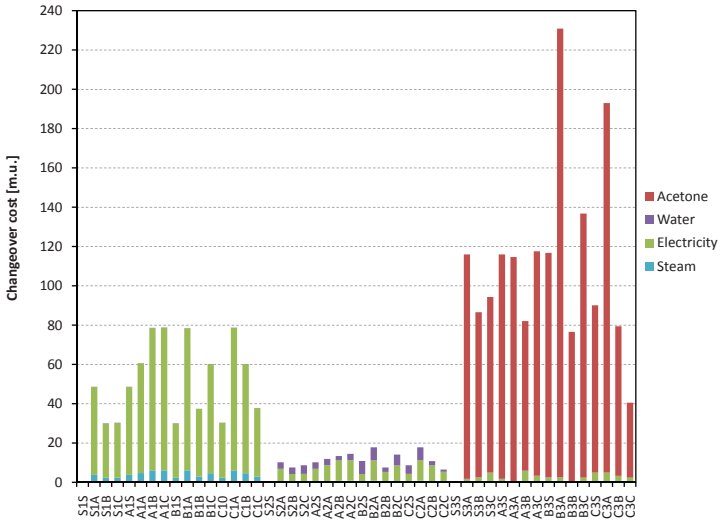


Figure 6.3: Changeover costs between pairs of products (S-still state, A, B, C) for the three methods (1, 2, 3).

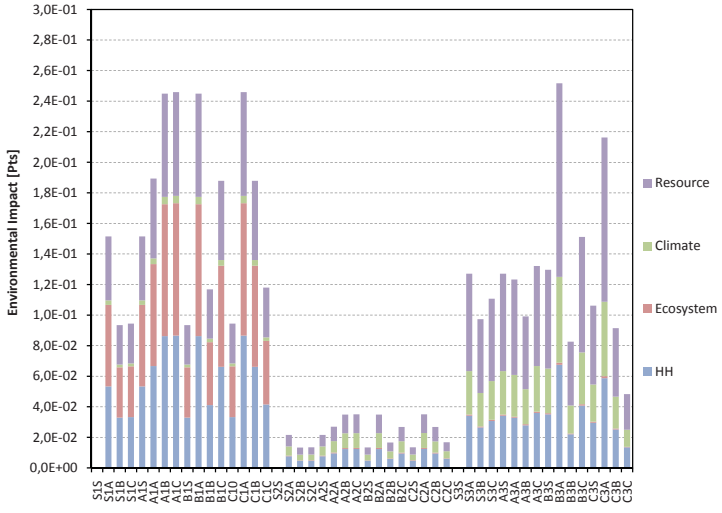


Figure 6.4: Changeover environmental impacts between pairs of products (S-still state, A, B, C) for the three methods (1, 2, 3).

Three different combinations of objective functions are studied which result in different multiobjective problems, namely (i) a three-objective optimisation considering makespan, profit and environmental impact, and two biobjective optimisation problems which consider: (ii) productivity and environmental impact, and (iii) productivity and relative environmental impact. The selection of the former problems was done based on the consideration of "extensive" and "intensified" system characteristics. The extensive characteristics are mainly driven on the amount of product produced, while the later are centred on efficiency, by relating the metric directly linked to production to others such as time or amount produced. In this sense, the first case considers only extensive metrics, the second considers a mixture of them, while the third case analyses only intensified metrics. The mathematical formulation and the NC method have been implemented in GAMS, and solved using CPLEX 11.2 in the MILP case (problem i), and BARON 8.1 in the MINLP (problems ii and iii). Pareto filtering of the solutions

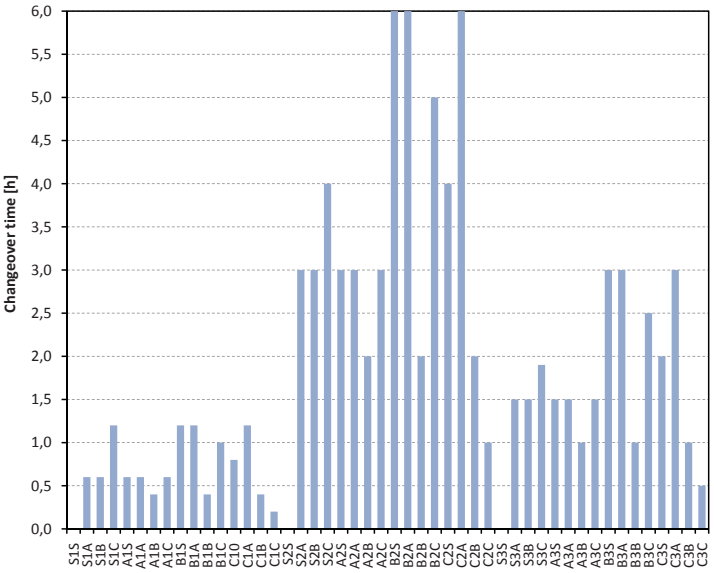


Figure 6.5: Changeover time between pairs of products (S-still state, A, B, C) for the three methods (1, 2, 3).

Table 6.5: Case (i), iterations in the number of Pareto points generation, for the multiobjective optimisation considering total profit, total environmental impact and makespan.

Iteration	0	1	2	3	4	5	6
Number of utopian line divisions (nd_j)	11	21	31	41	46	51	56
Number of explored points	58	256	701	1479	2468	3679	5143
Total Pareto solutions (np_j^{PF})	26	42	59	71	76	85	89
Changing Pareto frontier solutions	26	16	20	12	6	10	4
Pareto solutions z^{profit} - z^{ei}	10	11	13	15	15	16	16
Pareto solutions z^{profit} - Mk	10	18	31	34	36	40	42
Pareto solutions z^{ei} - Mk	4	4	5	7	7	9	9

has been done in Matlab (Cao, 2009; Mathworks, 2009), and the algorithmic strategy (Alg. 4.1) was implemented in Matlab and the whole solving process automated using Matgams Ferris (2005).

Case i considers the multiobjective optimization of profit, environmental impact and makespan. Figure 6.6 contains the Pareto solutions in the three dimensional space. Given the fact that fixed batch sizes are considered, the Pareto frontier is a collection of points that represent different production sequences. The evolution of the algorithm proposed in terms of the resulting Pareto solutions are presented in Table 6.5. A total of 5143 MILP have been solved to optimality, which result in 89 non-dominated solutions. The iterative procedure has been stopped when the percentage of new Pareto solutions divided by the total number of explored points is below 0.1%, (tol=1·10^{-5}).

PFs of the two dimension projections do not contain all the Pareto points of the three dimensional problem, but show existing trade-offs between any two objectives. Therefore, the projections of the solutions on two dimensional planes and their respective Pareto points are further discussed.

Figure 6.7 presents the PF for the two-objective optimisation of total profit and total environmental impact, which was considered separately (as Case ia) from the 3 objective Case (i). The utopian line has been iteratively divided in multiples of 500, from 500 up to 2000 (Ta-

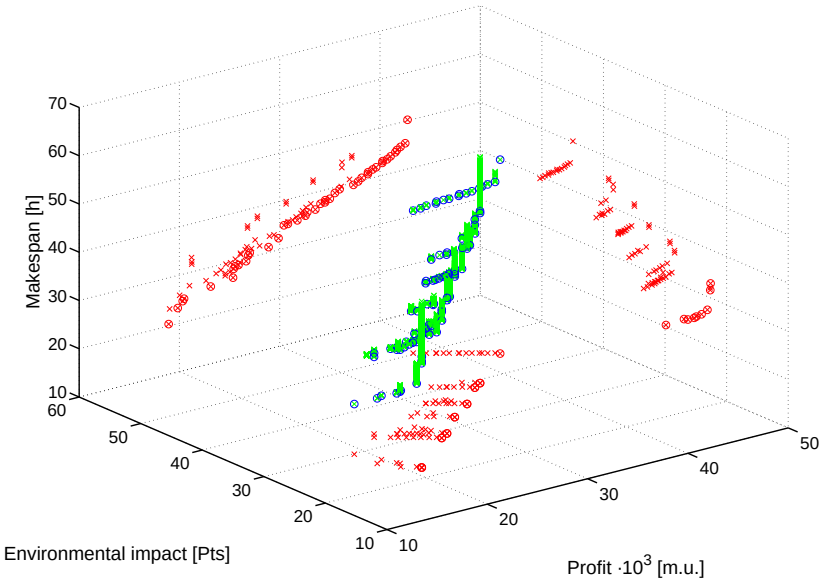


Figure 6.6: Case (i), Pareto frontier for three objective optimisation considering total profit, environmental impact and makespan (green crosses are all explored solutions, non-dominated solutions are encircled in blue; red crosses are all explored solutions in two dimensional planes, red encircled solutions are non-dominated in such planes).

Table 6.6: Case (ia). iterations in the number of Pareto points generation, for the multiobjective optimisation considering profit and environmental impact.

Iteration	0	1	2	3
Number of utopian line divisions (nd_j)	501	1001	1501	2001
Number of explored points	501	1001	2001	3001
Total Pareto solutions (np_j^{PF})	19	22	24	24
Changing Pareto frontier solutions	19	3	2	0

ble 6.6). As a result, a total number of 3000 points along the utopian line have been solved to optimality (green crosses), from which 24 non-dominated Pareto solutions (blue circles) are obtained after applying the Pareto filter.

The solution with highest profit satisfies the total demand (i.e. 2 batches of each product), whereas the most environmentally friendly option only processes the minimum amount of each product (1 batch for each product). In any case, the same changeover cleaning method 2 is selected in all solutions, because it is the most economic and environmental advantageous (see Figures 6.3 and 6.4), in spite of the time required, which is not considered in this sub problem. Pareto points are found to be grouped between the two extreme optimal solutions in six clusters, whose difference consists of the number of batches of each product. Regarding the most environmentally friendly solution cluster, product C offers more increment in profit and less environmental impact. The following less environmentally advantageous sequence with higher gain in profit includes an additional batch of product B instead of C; and then, a batch of A instead B or C. Next, an additional batch is considered in the production sequence, and finally, the complete fulfilment of demand entails the highest economic profit. In every cluster, solutions differ in the production sequences. To start producing with fibre C is slightly more environmentally friendly and less economically profitable than with fibre A.

Table 6.7 shows that the compromise solution according to the minimum distance to the utopian point consists of sequence 2A2A2C2B2, which is located approximately in the mid-

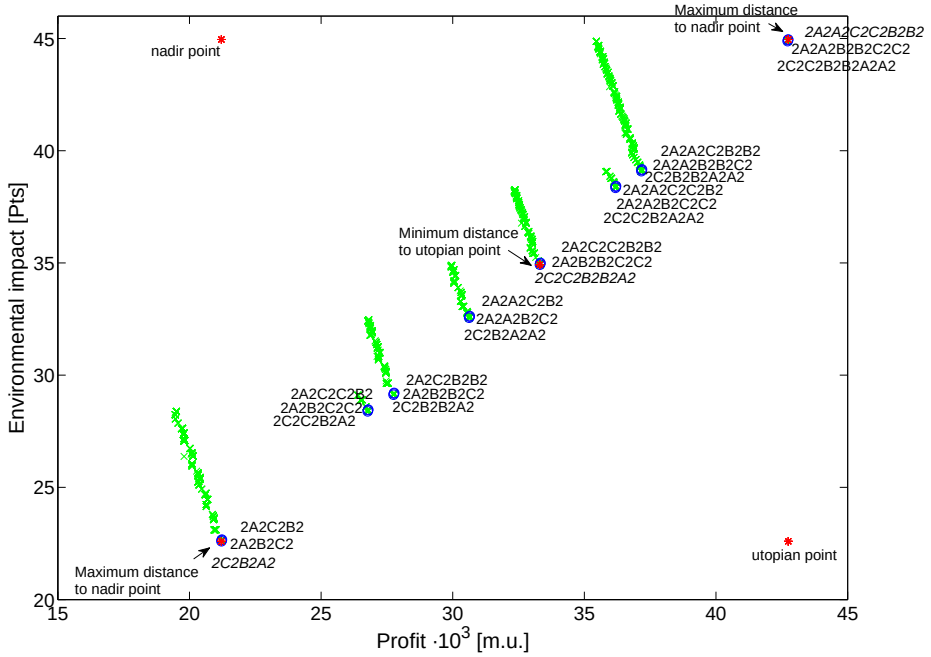


Figure 6.7: Case (ia). Pareto frontier for two-objective optimisation considering profit and environmental impact (green crosses are all explored solutions; non-dominated solutions are encircled in blue; red stars are nadir, utopian points; and sequences in italics represent compromise solutions shown in Table 6.7).

Table 6.7: Case (ia). Utopian, nadir and solutions of compromise according to the different metrics considering total profit and environmental impact (* defines utopia and $^-$ nadir). Distances are reported normalised.

$z^{profit} \cdot 10^3$ [m.u.]	z^{ei} [Pts]	Sequence	Distance utopian	Distance nadir
21.213$^-$	22.595*	2C2B2A2	1.000	**1.000**
33.310	34.921	2A2A2C2B2	**0.704**	0.719
42.7455*	44.956$^-$	2A2A2C2C2B2B2	1.000	**1.000**

dle of the whole range of both objective functions. If the maximum distance to the nadir point was selected as decision criterion, there would be two possibilities: either the solution of maximum profit or the solution of minimum environmental impact, since both of them have the same maximum normalised distance to the nadir solution.

On the other hand, the biobjetive projections for environmental impact vs makespan (case ib), and profit vs makespan (case ic), are given in Figures 6.8 and 6.9. The solution with lowest makespan contains one batch of each product, and includes changeover 1, whose time is the shortest, as it could be expected (see Figure 6.5). Sequences starting with fiber A have higher environmental impact but lower makespan than those with C. In addition, those sequences starting with product A dominate other sequences in the profit and makespan biobjective problem, even though starting with product A has the highest cost regarding the other two products.

For the overall three objective optimisation, the utopia, nadir and solutions of compromise selected according to the criteria proposed are shown in Table 6.8. Sequence 2A2A2C2B1 is the one whose distance to the utopian is minimum; whereas solution 2A2B1C1 has the highest distance to the nadir point.

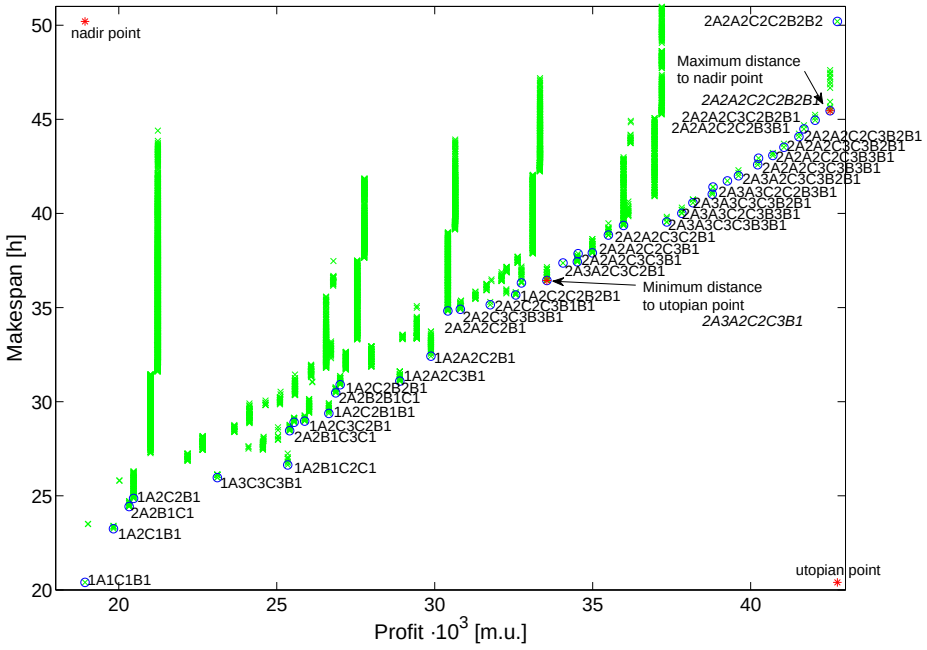


Figure 6.8: Case (ib), Pareto frontier for two-objective optimisation considering profit and makespan (green crosses are all explored solutions; blue circles the non-dominated solutions; red stars are nadir, utopian points; and sequences in italics represent compromise solutions).

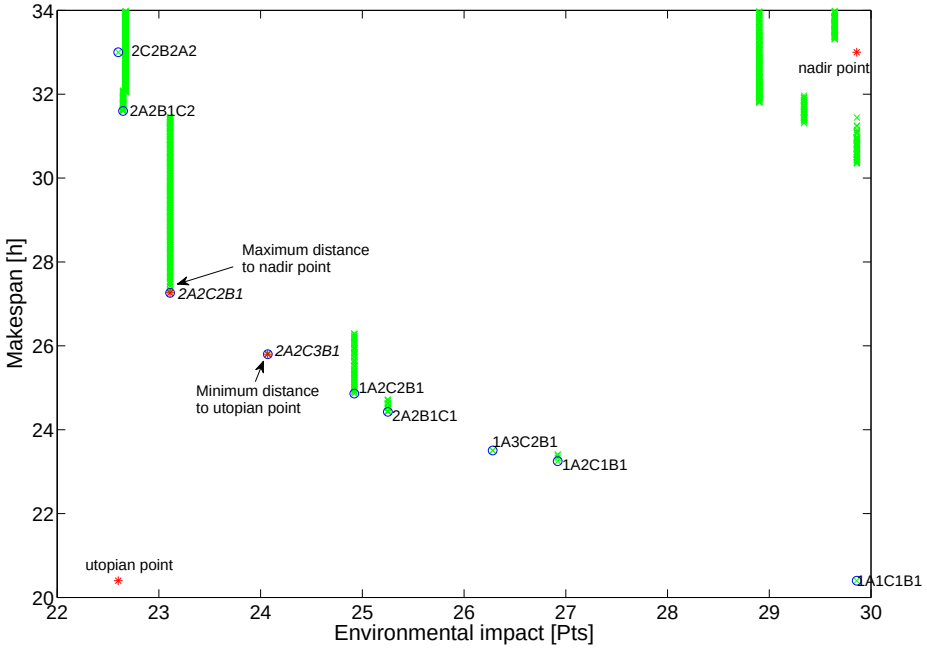


Figure 6.9: Case (ic), Pareto frontier for two-objective optimisation considering total environmental impact and makespan (green crosses are all explored solutions; blue circles the non-dominated solutions; red stars are nadir, utopian points; and sequences in italics represent compromise solutions).

Table 6.8: Case (i) utopian, nadir and solutions of compromise according to the different metrics considering total profit, environmental impact and makespan (* defines utopia and $^-$ nadir). Distances are reported normalised.

$z^{profit} \cdot 10^3$ [m.u.]	z^{ei} [Pts]	Mk [h]	Sequence	Distance utopian	Distance nadir
21.213	22.595*	33.000	2C2B2A2	0.998	1.159
42.745*	44.956$^-$	50.200$^-$	2A2A2C2C2B2B2	1.285	1.018
18.931$^-$	29.861	20.400*	1A1C1B1	1.034	1.243
30.417	33.069	34.820	2A2A2C2B1	**0.803**	0.941
20.327	25.251	24.427	2A2B1C1	0.956	**1.253**

Table 6.9: Case (ii), iterations in the number of Pareto points generation, for the multiobjective optimisation considering productivity and environmental impact.

Iteration	0	1	2
Number of utopian line divisions (nd_j)	51	101	151
Number of explored points	51	101	201
Total Pareto solutions (np_j^{PF})	31	38	37
Changing Pareto frontier solutions	31	7	7

It is important to note that in this case, single objective optimal solutions are bounded by the minimum and maximum demand requirements. Regarding minimum requirements, in the case of environmental impact and makespan, their ultimate minimum will be zero which is associated to not producing any product, while in the case of profit, it fulfills all required demand. If these bounds are changed the behaviour would be the same, consequently special attention has to be put in the modelling of demand requirements given that for these metrics, its selection will be of paramount importance.

Case ii considers the analysis of the scheduling results when productivity and environmental impact are compared. Figure 6.10 presents the PF with 38 non-dominated Pareto solutions (blue circles) for the biobjective optimisation of productivity and environmental impact. In this case, the utopian line is divided iteratively in multiples of 50, from 50 up to 150 (see Table 6.9). As a result, a total number of 200 points along the utopian line have been solved. In about 13% of all problems, the MINLP solver (BARON) was not able to guarantee global optimality, after a reasonable computational effort (65000 CPU seconds). The iterative procedure has been stopped when the percentage of new solutions is below 5% ($tol = 5 \cdot 10^{-2}$).

The most productive sequence consists of producing full demand of the three products with changeover method 1, which is the one that takes the least time. It is worth noting that the former sequence consists of AACBBC, which entails three inter-product changes and with higher overall changeover time than sequences such as AACCBB (with two inter-product changes). The reason for this issue is not evident and it can be understood from the Gantt charts in Figure 6.11. In sequence AACCBB, there are two pieces of equipment that are bottlenecks (C1 and V1); which results in a total makespan of 33.75h (Fig. 6.11(b)). However, sequence AACBBC avoids the bottleneck in equipment C1 and has a total makespan of 33.15h (Fig. 6.11(a)); consequently, its profitability increases in spite of the higher costs incurred by sequence changes.

Table 6.10 contains the solutions of compromise according to the different metrics. Note that in this case, the solution whose distance to the utopian point is minimum includes one batch of each product using cleaning method 1. In addition, Figure 6.10 highlights the relative position of the compromise solutions regarding the other Pareto solutions.

Case iii encompasses the analysis of scheduling results considering productivity and relative environmental impact metrics. In Figure 6.12, Pareto solutions differ in the number of

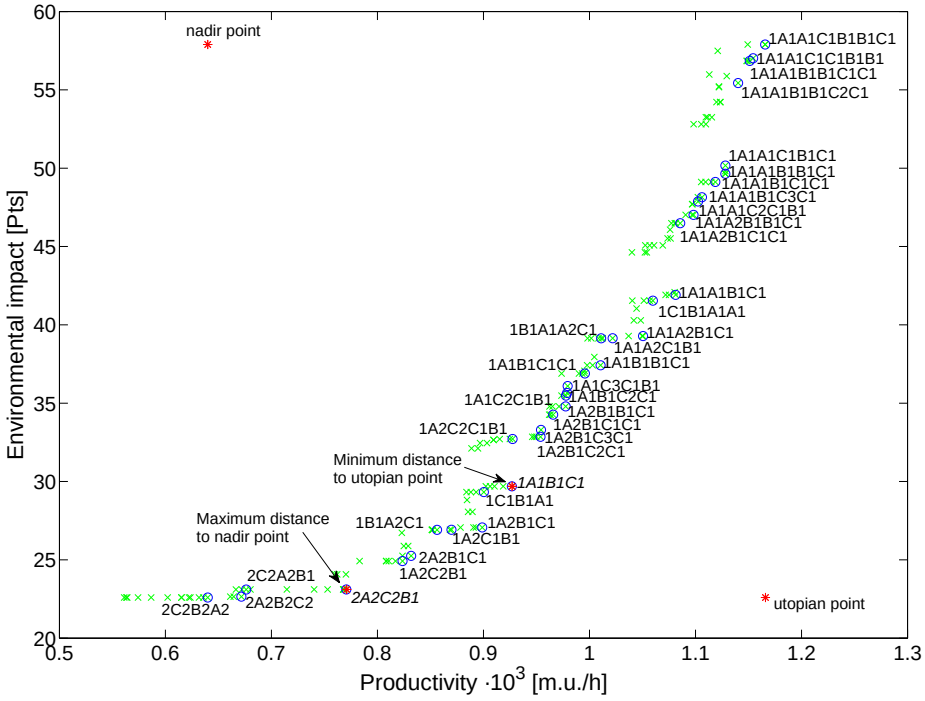
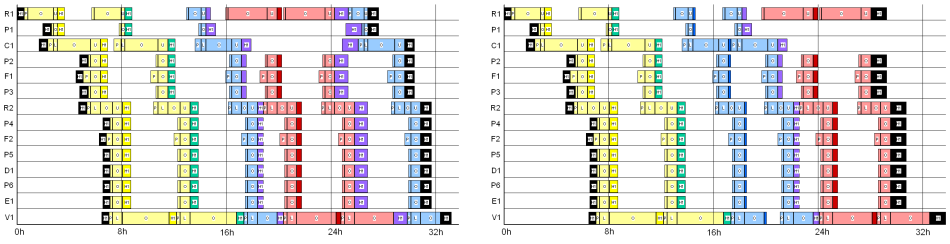


Figure 6.10: Case (ii), Pareto frontier for two-objective optimisation considering productivity and environmental impact (green crosses are all explored solutions; non-dominated solutions are encircled in blue; red stars are nadir, utopian points; and italic sequences represent compromise solutions shown in Table 6.10).



(a) Sequence 1A1A1C1B1B1C1.

(b) Sequence 1A1A1C1C1B1B1.

Figure 6.11: Gantt charts for sequences AACBBC and AACCBB, (black: starting and finishing cleaning tasks; yellow, red and blue: fibers A, B and C, respectively; darker coloured areas represent changeover methods).

Table 6.10: Case (ii), solutions of compromise according to the different metrics considering productivity and environmental impact (* defines utopia and $^-$ nadir). Distances are reported normalised.

$z^{prod} \cdot 10^3$ [m.u./h]	z^{ei} [Pts]	Sequence	Distance utopian	Distance nadir
0.640$^-$	22.595*	2C2B2A2	1.000	1.000
0.927	29.691	1A1B1C1	**0.497**	0.968
0.771	23.110	2A2C2B1	0.752	**1.016**
1.166*	57.898$^-$	1A1A1C1B1B1C1	1.000	1.000

Table 6.11: Case (iii), iterations in the number of Pareto points generation, for the multiobjective optimisation considering productivity and relative environmental impact.

Iteration	0	1
Number of utopian line divisions (nd_j)	51	101
Number of explored points	51	101
Total Pareto solutions (np_j^{PF})	31	34
Changing Pareto frontier solutions	31	10

Table 6.12: Case (iii), utopian, nadir and solutions of compromise considering productivity and relative environmental impact (* defines utopia and $^-$ nadir). Distances are reported normalised.

$z^{prod} \cdot 10^3$ [m.u./h]	z^{rel} [Pts/ton]	Sequence	Distance utopian	Distance nadir
0.711^-	3.833^*	2C2B2B2A2	1.000	1.000
0.936	3.913	2A2A2C2C2B2B1	0.510	**1.054**
1.005	4.173	1A2A2C2C2B1B1	**0.459**	0.958
1.166^*	4.991^-	1A1A1C1B1B1C1	1.000	1.000

batches of each product, the sequence in which they are produced, and cleaning method used. Some of these solutions have already appeared when optimisation of total profit was considered, although they are still valid, most of them are not part of the PF for this case. In the Pareto frontier solutions are not grouped as in the two-objective case of total profit and environmental impact.

The Pareto frontier for the two-objective optimisation of productivity and relative environmental impact contains 34 non-dominated solutions (Fig. 6.12). In this case, the utopian line is divided iteratively in multiples of 50, from 50 up to 100 (see Table 6.11), when the percentage of new Pareto solutions is below 10%. When minimising the environmental impact per unit of product, both the sequence and cleaning method is the same as when minimising the total environmental impact, but an additional batch of fibre B is produced. The main reason stems from the fact that by dividing the produced quantity, producing the smallest quantity of the products is not advantageous from the environmental point of view. Therefore, this relative objective function measures the most environmentally efficient way of producing.

Table 6.12 contains the solutions of compromise according to the different metrics. In this case, both solutions are different to the extreme points. Figure 6.12 highlights the relative position of the solutions of compromise according to Eqs. 6.30 and 6.31, which are both different to the single objective optimal solutions. Both selected sequences produce the same amount of products and in the same order, but they differ in the cleaning methods used for the changeover between pairs of batches.

To sum up, the relative environmental impact and productivity metrics have been considered for comparison. In Figure 6.13 it can be seen that the solutions obtained for the other metrics optimisation (case i and ii), are not contained in the PF found for the relative environmental impact and productivity (case iii). It can be seen that the solution with optimal profit is dominated by other solution whose cleaning methods are the same, but its production sequence is different. With regards to the Mk solution it is found be far way from the PF, while the environmental impact optimization solution is closer.

6.5 Interpretation

The consideration of environmental impact as an additional objective in the optimisation of the scheduling problems, rises a trade-off which can be rigorously studied using multiobjective optimisation. In this context, the normal constrained (NC) method is a technique that allows for a good description of the Pareto frontier; however, a high number of solutions has

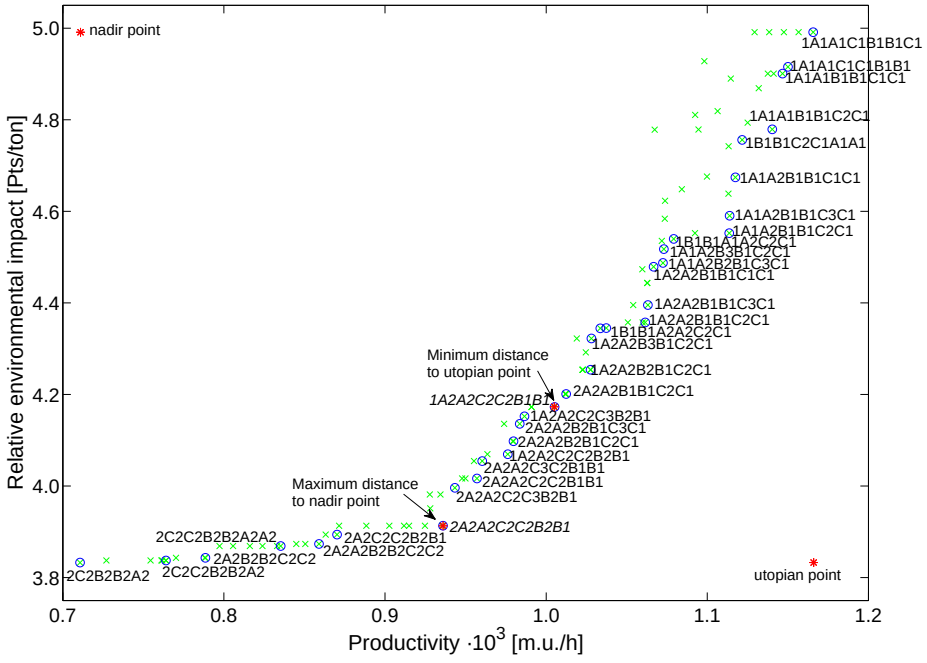


Figure 6.12: Case (iii), Pareto frontier for two-objective optimisation considering productivity and relative environmental impact (green crosses are all explored solutions; non-dominated solutions are encircled in blue; red stars are nadir, utopian points; and sequences in italics represent compromise solutions shown in Table 6.12).

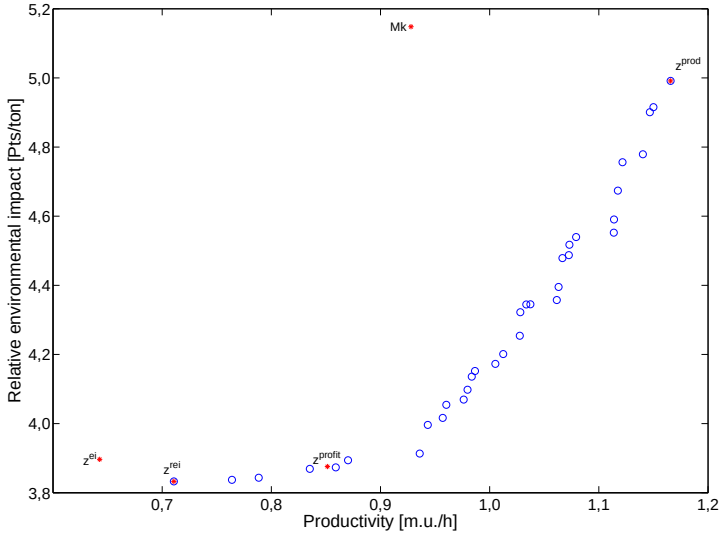


Figure 6.13: Pareto frontier for two-objective optimisation considering productivity and relative environmental impact, and optimal single objective solutions (non-dominated solutions are encircled in blue; red stars are single objective optimal solutions).

to be explored and generated in order to avoid missing Pareto optimal solutions. Hence, the strategy proposed of increasing the number of utopian hyperplane divisions to explore the Pareto frontier has demonstrated its capacity to produce reliable Pareto frontiers with limited computational effort.

Pareto frontiers provide the decision maker with highly valuable information about production schedule trade-offs. This information sheds light into production and sequencing relationships that may not be obvious. In addition, it is highly important to thoroughly consider which is the objective of the decision maker (e.g. plant manager) which could be economic, such as to maximise the profit or the productivity of the plant, or environmental, for instance to minimise the total environmental impact or the environmental impact per unit of product. In this context and depending on the selected objective functions, the solutions obtained are found to be completely different in spite of the same economic or environmental concerns. The decision maker will reach completely different Pareto frontiers, in terms of number and sequence of product batches, as well as in selected cleaning methods by considering different objective functions .

The approach proposed for obtaining a compromise solution, which uses the concept of utopian and nadir points, allows to choose a single solution among the Pareto efficient ones. These solutions are balanced in terms of relative distance to reference points, namely the utopian and nadir of each Pareto frontier.

From a LCA point of view, ratios seem to provide more sense, at least in terms of rational use of resources, and consequently have to be considered. However the best ratios to be considered depend on the circumstances (e.g. demand characteristics), and its use greatly affects the mathematical characteristics of the problem to be solved.

It has been found that in this case study environmental impact rises mainly from upstream echelon impacts, namely raw materials production. Figure 6.7, clearly shows this situation, almost no difference is found between sequence dependant environmental impact, and solutions which provide with the same amount of products are clustered all together. The use of profit and Mk also shows that the trade-offs between these objectives are also mostly due to the amount of products manufactured rather to the sequence in which they are produced. Regarding Mk and EI, a different behaviour is found, one single batch of each product is found in each of the sequences that are present in the Pareto frontier. Here the trade off between Mk and EI is the sequence in which products are produced and not the amount produced as when considering profit.

In the case of the analysis productivity, which represents a certain trade off existent between profit and makespan, and EI; the Pareto front shows a similar behaviour to the one obtained for profit and EI, however greater separation between sequences is along the abscissas is found due to the normalising effect of using Mk. Furthermore, sequences which use shorter cleaning times (1) instead of (2) are found in the PF.

Interestingly in the case of normalised EI and profitability, most Pareto sequences contain four or more batches of products produced and three product sequences are not considered. All solutions are more evenly distributed along the PF than in the former cases.

The consideration of environmental impact as an additional objective in the optimisation of the scheduling problems, rises a trade-off which can be rigorously studied using multi-objective optimisation. In this context, the normal constrained (NC) method is a technique that allows for a good description of the Pareto frontier; however, the number of solutions to be explored have to be generated to avoid dominated solutions in the Pareto frontier and to avoid missing Pareto optimal solutions. Hence, the strategy proposed of increasing number of divisions to explore the Pareto frontier, is highly valuable.

Pareto frontiers provide the decision maker with highly valuable information about the

production schedule trade-offs; this information allows to shed light into production and sequencing relationships that are not be obvious. In addition, it is highly important to thoroughly consider which is the objective of the decision maker (e.g. plant manager) which could be either to maximise the profit, or the productivity of the plant; and to minimise the total environmental impact, or the environmental impact per unit of product produced. In this context and depending on the selected objective functions, the obtained solutions may be completely different in spite of the fact that the general economical or environmental objectives are the same. The decision maker may reach completely different Pareto solutions, in terms of number and sequence of product batches, as well as in selected cleaning method.

The decision metrics proposed allow to choose a single solution among the Pareto efficient. These solutions are balanced in terms of distance to the optima, either in terms to the total distance to utopia and nadir points relative to the solution interval. In the former case, solutions that are near the extreme optimal are more prone to be obtained; whereas the latter measures favour solutions that are equally distanced to all the objectives.

Chapter nomenclature

Table 6.13: List of indices and variables used in chapter.

Name	Meaning
Sets and subsets	
i	Batches.
p	Products (product 0 simulates plant 'still' state).
k	Stages.
c	Cleaning modes between products.
g	Objective functions.
$dynI$	Batches i that have been assigned to a product.
$kpar$	Stages k which are parallel in operation to the following one.
$kcon$	Stages k whose following stage operation is parallel to their unload.
$kpum$	Stages k whose following stage is being loaded while they are operating.
Parameters	
$demand_p$	Demand of product p.
$mindemand$	Minimum percentage of the demand that is obliged to be accomplished in the time horizon.
$maxdemand$	Maximum percentage of the demand that can be exceeded.
$bsize_p$	Batch size of product p (which is fixed) .
$ptime_{pk}$	Total processing time before stage k of product p.
$chanT_{pp'kc}$	Changeover time between products p and p' in stage k with cleaning mode c.
$prodI(p)$	Production impact resulting of producing a batch of product p. It includes: raw materials, electricity, residues, steam, water and emissions. .
py_{ip}	States if product p is being carried out in batch i (it is defined after the first stage, which assigns products to batches).
$batchprice_i$	Price resulting from the production of batch i.
$batchsize_i$	Batch size of batch i.
$pChT_{ii'kc}$	Changeover time between batches i and i' for stage k using changeover type c.
$pChCost_{ii'kc}$	Changeover cost between batches i and i' for stage k using changeover type c.
$pEnvCost_{ii'kc}$	Environmental impact associated to changeover type c between batches i and i' for stage k.
$ptotT_{ik}$	Total processing time of stage k of product i.
$pprepT_{ik}$	Preparation time parameter of stage k in batch i.
$ploadT_{ik}$	Loading time of stage k of batch i.
$pcleaT_{ik}$	Cleaning time of stage k of batch i.
$poperT_{ik}$	Operation time of stage k of batch i.
$punloT_{ik}$	Unloading time of stage k of batch i.
$BigM$	Parameter with a big value, in this case its minimum value is 3 times the maximum cost, environmental impact or time between any pair of products.
$BigM2$	Parameter with a big value, in this case its minimum value is the time horizon.
H	time horizon.
Continuous variables	
pT_{ik}	Time of stage k in order i.
$ChT_{ii'kc}$	Changeover time of doing i and then i' in stage k through cleaning method c.

Continued on next page

Table 6.13 – continued from previous page

Name	Meaning
s_{ik}	Starting time of stage k of batch i.
Tf_{ik}	Finishing time of stage k of batch i.
z^{profit}	Objective function that aims at maximising profit.
z^{prod}	Objective function that aims at maximising productivity.
Mk	Objective function that aims at minimising the makespan.
z^{ei}	Objective function that aims at minimising the environmental impact.
z^{rei}	Objective function that aims at minimising the relative environmental impact.
μ^{best}	Vector of objectives for the best compromise solution.
μ^{*}	Vector of objectives that contains the optimal μ_g^* objectives (utopia point).
μ^{0}	Vector of objectives that contains the worst μ_g^0 objectives (nadir point).
μ	Vector that contains the μ_g objectives for a Pareto solution.
Binary variables	
Y_{ip}	Assignment of product p to batch i.
$X_{ii'c}$	Assignment of cleaning method c to changeover, if batch i is produced immediately before batch i'.
W_i	Production of batch i.

Chapter 7

Strategic level decisions: corporate and Supply Chain Management

Corporate approaches aiming at reducing its environmental footprint cannot be undertaken in isolation. Nowadays, it is recognised that a concerted effort is required, embracing the different supply chain entities, in order to correctly estimate environmental burdens and to propose effective environmental strategies. Such an effort poses an important and complex challenge to managers. On the one hand, the economical and environmental trade-offs existing within a supply chain network must be pondered so as to take proper decisions. This is not a straightforward task, thus analytical tools are desirable to support environmental decision-making. On the other hand, environmental performance is seldom quantified appropriately. Traditional current accountant practises which do not clearly consider environmental issues and the availability of diverse environmental metrics make it arduous to assess firms' environmental performance.

This chapter proposes the use of the framework presented in chapter 4 to tackle environmental planning. The intended approach addresses the optimisation of the supply chain (SC) planning and design incorporating economic and environmental issues. The strategic decisions contemplated in the mathematical model proposed are facility location, processing technology selection and production-distribution planning issues. The Impact 2002+ methodology (Humbert *et al.*, 2005) is selected to perform the environmental impact assessment within the SC, since it provides a feasible implementation of a combined midpoint-endpoint evaluation. Moreover, traditional accountancy practises have been extended to include different costs associated to environmental issues. The environmental costs estimation has been carried out using a Total Cost Assessment (TCA) approach and taking into consideration a CO_2 trading scheme as well.

Additionally, the model performs an impact/cost mapping along the nodes and activities that comprises the supply chain. Such mapping allows focusing financial efforts to reduce environmental burdens to the SC echelons that impact the most. Criteria selected for the objective functions (OF) are environmental end point impacts, overall impact factor and net present value (NPV) considering different environmental costs. The mathematical formulation of this problem becomes a multi-objective MILP (moMILP). The advantages of this model, regarding the ability to cope with multiple objectives, and the general treatment of

production/distribution sites are highlighted through a realistic case study of a maleic anhydride (MA) SC production and distribution network in Europe.

7.1 Introduction

Because an LCA ideally covers a cradle-to-grave approach, LCA fits as a suitable tool for quantitatively assessing the environmental burdens associated with designing and operating a SC. Two possible LCA approaches can be carried out, namely, comparison/selection and improvement (Klassen & Greis, 1993). The former approach focuses on identifying environmentally preferable products or processes alternatives as an attempt to leverage market-place/financial forces to displace environmentally harmful activities (Klopffer & Rippen, 1992). The latter one uses LCA as a tool to identify the SC stages that have a particularly strong negative impact on the environment, and thus, where improvements would be most beneficial. This last alternative allows to improve the allocation of limited management time and financial resources within the SC (Freeman *et al.*, 1992).

Recently, Mele *et al.* (2008) have shown a quantitative tool for decision making support in the design of sugar cane to ethanol SCs. Also Hugo and Pistikopoulos (2005) have shown how a set of SC network designs can form an environmentally conscious basis for the investment decisions associated with strategic SC level. Chakraborty *et al.* (2003, 2004), propose a methodology for long term operation and planning. In their approach the estimation of wastes is of key importance; design decisions to be made include choosing the plant-wide waste treatment facility, while planning decisions incorporate a forecast on environmental regulation and a CO_2 emission cap is enforced as a constraint into the model.

One topic that deserves further attention is the accounting of environmental costs. It has been recognised within accounting practises that words such as "full", "total" and "life-cycle" are used to indicate that not all costs are captured in traditional accounting and capital budgeting practises. Since these costs fall outside the conventional accounting framework of the polluter, they are called external costs or externalities. Several techniques, that fall within the environmental cost assessment umbrella (ECA, see section 2.2.3.1), have been developed to assess such costs and to further include them into traditional accounting practises.

It is pointed out that tools, specifically LCA models, should be useful in pursuing more effective climate change policies and international trade should be included within this analysis. Finally, it is noteworthy that climate change policies are applied based on the temporal distribution of emissions. Usually SC environmental impacts are evaluated at the end of the planning horizon, and in the case of an LCA the temporal distribution is disregarded at all. Consequently, the incorporation of constraints associated to the temporal emission distributions is necessary when studying climate change policies in a SC planning model.

The analysis of partial environmental impacts for every echelon is performed with the aim of discovering improvement opportunities; this analysis also provides information about where to focus emission control activity and hints on possible strategies for emission reduction at source. The temporal emissions distribution and trading schemes considerations contributes to understand how regulatory schemes may induce environmental impact reductions.

Recalling all the aspects that have been mentioned before, this chapter presents a novel approach for SC design and planning focusing on environmental impact and its sources. SC Comparison/selection and improvement analysis are performed in this work by means of a SC design-planning optimisation model. An optimisation step is included allowing for selecting the appropriate technology and the appropriate raw material/service supplier. It encompasses direct emissions, purchased energy emissions, raw materials production emis-

sions and transport distribution emissions[1]. Furthermore, the impact and costs associated to every SC echelon are mapped aiming at discovering possible opportunities to focus management efforts and resources for environmental impact reduction. Moreover, the temporal emission distribution is considered for the calculation of environmental and financial metrics, accounting for possible emissions trading. In this way the current LCA scheme is further extended by including emissions temporal distribution.

7.2 Goal definition and problem statement

This work represents a comprehensive step over the approaches presented by Mele *et al.* (2005) and Hugo and Pistikopoulos (2005) by assisting in the planning and design of a SC under economical and environmental impacts considerations. The resulting model is solved using a moMILP algorithm, which allows observing possible environmental trade-offs between damage categories and the economic indicator. This approach reduces the value-subjectivity inherent to the assignment of weights in the calculation of an overall SC environmental impact, which is also calculated.

The problem can be stated as follows. Given:

Process operations planning data

- a fixed time horizon;
- a set of materials: products, raw materials and possible intermediates;
- a set of markets in which products should be available to customers and their expected demand;
- a set of potential geographical sites for facilities location;
- a set of potential equipment technologies for different processing stages;
- lower and upper bounds for feasible equipment and storage capacity increments;
- product recipes, manufacturing and transport requirements (such as, mass balance coefficients and resources utilisation);
- minimum/maximum utilisation rate installed capacity bounds;
- suppliers capacity bounds;

Economic data

- direct cost parameters such as production, handling, transport and raw material costs;
- price for every product in each market during the time horizon;
- relationship between capital investment and facilities capacity;
- relationship between indirect expenses and facilities capacity.
- GHG emission prices.

Environmental data

- product manufacturing environmental interventions (including GHG emissions).
- maximum GHG free emission allowance
- raw material production environmental interventions
- distribution environmental interventions
- environmental setting for characterisation and aggregation of environmental interventions

The goal is to determine:

- the active SC nodes and links;

[1] In this respect the approach proposed calculates tier 3 and partially tier 4 related emissions.

- the facilities capacity in each time period;
- the best assignment of the manufacturing and distribution tasks to the network nodes;
- the amount of final products to be sold;
- the environmental impact associated to each SC node;

thus, the economic and environmental metrics are optimised at the end of the planning horizon.

The model assumes that processing technologies are available for eventual installation at potential locations and assists in their selection. Within this model, and in order to avoid emission double counting, raw material emissions are not aggregated to product manufacturing. Similarly transport and energy consumption are considered separately.

Regarding the environmental concerns, the Impact 2002+ has been considered for the calculation of the environmental impacts of the SC considering a cradle-distribution system boundary. Regarding the economic dimension of sustainability, some authors (Laínez *et al.*, 2007, 2008), proposed the use of corporate value (CV) instead of NPV (see section 2.2.3), due to consideration of debt and net working capital, in this case they are disregarded and NPV is used. The consideration of sustainability social concerns is disregarded.

7.3 Models required-mathematical formulation

The mathematical formulation of the LCA-SC problem is briefly described next. The variables and constraints of the model can be roughly classified into three groups. The first group concerns process operating constraints given by the SC topology. The second group deals with the environmental model used. Finally, the third refers to the economic metric applied.

7.3.1 Supply Chain - Design-planning model

The design-planning approach presented in this work is an extension of the state task network (STN) formulation (Kondili *et al.*, 1993) to SC modeling, which was developed by Laínez *et al.* (2008). This extension is suitable to collect all SC node information through a single variable, which eases environmental formulation. This way SC node characteristics are modelled with a single equation set, since manufacturing nodes and distribution centres are treated in the same way as well as production and distribution activities. Subsequently, it turns out that the model most important variable is $P_{ijff't}$; which represents the activity magnitude of task i performed using technology j receiving input materials from site f and "delivering" output materials to site f' during period t. Indeed, to model a production activity it must receive and deliver material within the same site (P_{ijfft}). In case of a distribution activity, facilities f and f' must be different.

Materials mass balance must be satisfied in each of the nodes; Eq. 7.1 represents the mass balance for each material (state in the STN formulation) s consumed at each potential facility f in every time period t. Parameter α_{sij} is defined as the mass fraction of material s that is produced by task i performed using technology j; T_s is the set that refers to those tasks that have material s as output, while $\bar{\alpha}_{sij}$ and $\bar{T}_s$, refer to tasks that consume material s.

$$S_{sft} - S_{sft-1} = \sum_{f'} \sum_{i \in T_s} \sum_{j \in (J_i \cap \bar{J}_{f'})} \alpha_{sij} P_{ijf'ft} - \sum_{f'} \sum_{i \in \bar{T}_s} \sum_{j \in (J_i \cap \bar{J}_f)} \bar{\alpha}_{sij} P_{ijff't} \qquad \forall s, f, t \tag{7.1}$$

The model assumes that process parameters are fixed (such as reaction conversion, separation factors, temperatures, etc.), this is one of the reasons for the model to be linear. In this

sense α_{sij} and $\bar{\alpha}_{sij}$ are fixed and constant due to the replacement of all the potentially non-linear terms by specified parameters. This assumption is acceptable since the model deals with strategic and tactical decisions. Such decision levels require the use of aggregated figures in which some details (e.g. process parameters, scheduling decisions) are disregarded, allowing the decision making process to be manageable.

Equation 7.2 models the temporal changes in facility capacities. Equation 7.3 serves for total capacity (F_{jft}) bookkeeping taking into account the amount increased during planning period t (FE_{jft}).

$$V_{jft} FE^{L}_{jft} \leq FE_{jft} \leq V_{jft} FE^{U}_{jft} \qquad \forall f, j \in \tilde{J}_f, t \tag{7.2}$$

$$F_{jft} = F_{jft-1} + FE_{jft} \qquad \forall f, j \in \tilde{J}_f, t \tag{7.3}$$

Equation (7.4) ensures the total production rate in each plant to be greater than a minimum desired production rate and lower than the available capacity. Furthermore, parameter β_{jf} defines a minimum utilisation rate of technology j in site f, while $\theta_{ijff'}$ determines the resource utilisation factor.

$$\beta_{jf} F_{jft-1} \leq \sum_{f'} \sum_{i \in I_j} \theta_{ijff'} P_{ijff't} \leq F_{jft-1} \qquad \forall f, j \in \tilde{J}_f, t \tag{7.4}$$

$\theta_{ijff'}$, is the capacity utilisation rate of technology j by task i whose origin node is location f and its destination location f'. This parameter is one of the key factors to be determined when addressing aggregated planning problems, considering strategic and tactical decisions. The presented operational model may be applied in continuous as well as in semi-continuous processes. Firstly let us consider the continuous processes, for these cases, the capacity utilisation factor is a conversion factor, which allows taking into account the equipment j capacity in site f in terms of task i production time per kg of produced material. In this way the factor is the maximum throughput per planning period. On the other hand, this parameter is closely related to tasks operation time in the case of semi-continuous (batch) processes. Notice that in this kind of production processes, the time period scale utilised in aggregated planning is usually larger than the time a task (production/distribution activity) requires to be performed. Therefore, the sequencing-timing problem of short term scheduling is transformed into a rough capacity problem where aggregated figures are used. It is important to have in mind that capacity is expressed as equipment j available time during one planning period, then $\theta_{ijff'}$ represents the time required to perform task i in equipment j per unit of produced material. Thus, once operation times are determined this parameter can be easily estimated.

Eq. 7.5 forces the amount of raw material s purchased from site f at each time period t to be lower than an upper bound given by physical limitations (A_{sft}). Also, the model assumes that part of the demand can actually be left unsatisfied because of limited production or supplier capacity. Thus, Eq. 7.6 forces the sales of product s carried out in market f during time period t to be less than or equal to demand.

$$\sum_{f'} \sum_{i \in \tilde{T}_s} \sum_{j \in J_i} P_{ijff't} \leq A_{sft} \qquad \forall s \in RM, f \in Sup, t \tag{7.5}$$

$$\sum_{f'} \sum_{i \in T_s} \sum_{j \in J_i} P_{ijf'ft} \leq Dem_{sft} \qquad \forall s \in FP, f \in Mkt, t \tag{7.6}$$

For further model details the reader should refer to Laínez *et al.* (2008). Please note that the current SC formulation is discussed considering the "forward" SC, i.e. a cradle to market boundary. However this formulation is general enough to consider "backward" flows from the reuse and recycle flows, given that they can be generally modelled using the $P_{ijff't}$ variable, irrespective of what they represent.

7.3.2 Supply Chain - Environmental model

The results of the LCI, which gathers all SC environmental interventions (emissions or natural raw material consumption), can be interpreted by means of different environmental metrics. These metrics differ in their position along the environmental damage chain (environmental mechanism). Environmental interventions are translated into metrics related to environmental impact (EI) as endpoints or midpoints metrics by the use of Characterisation Factors (CF). The environmental metrics used are the ones devised by Humbert *et al.* (2005), in the Impact 2002+ methodology, which present an implementation working at both midpoint and damage levels. This approach contains the advantages of being able to calculate both mid and endpoint indicators. In this work, end-point metrics are used as objective functions since these metrics are easier to comprehend compared to mid-point values.

The environmental model equations are briefly described next. Equation 7.7 models IC_{aft}, which represents the mid-point a environmental impact associated to site f which rises from activities in period t; $\psi_{ijff'a}$ is the a environmental category impact CF for task i performed using technology j, receiving materials from node f and delivering it at node f'.

$$IC_{aft} = \sum_{j \in \tilde{J}_f} \sum_{i \in I_j} \sum_{f'} \psi_{ijff'a} P_{ijff't} \qquad \forall a, f, t \tag{7.7}$$

Similarly to the case of α_{sij} and $\tilde{\alpha}_{sij}$, the value of $\psi_{ijff'a}$ is fixed and constant, provided that all environmental impacts are directly proportional to the activity performed in that node (P_{ijfft}). This issue is common practise in LCA, where all direct environmental impacts are considered linear with respect to the functional unit (Heijungs & Suh, 2002).

Environmental impacts associated to materials transport are assigned to their origin node, raw material transport is charged to suppliers nodes and product transport to the productions site. The study of environmental impacts associated to transport or production can be performed by setting the indices summation over the corresponding tasks (i.e $i \in Tr$ or $i \in NTr$). Furthermore the value of $\psi_{ijff'a}$ can be calculated by Eq. 7.8 in the case of transport. Here ψ^T_{ija} represents the a environmental category impact CF for the transport of a mass unit of material over a length unit.

$$\psi_{ijff'a} = \psi^T_{ija} distance_{ff'} \qquad \forall i \in Tr, j \in J_i, a, f, f' \tag{7.8}$$

Equation 7.9 introduces $DamC_{gft}$ which are a weighted sum of all mid-point environmental interventions combined using g endpoint damage factor ζ_{ag} and then further normalised with $NormF_g$ factors. Equation 7.10 is used to compute the g normalised endpoint damage along the whole SC ($DamC^{SC}_g$).

$$DamC_{gft} = \sum_{a \in A_g} NormF_g \zeta_{ag} IC_{aft} \qquad \forall g, f, t \tag{7.9}$$

$$DamC^{SC}_g = \sum_f \sum_t DamC_{gft} \qquad \forall g \tag{7.10}$$

CO_2 emissions trading is modelled by introducing Eq. 7.11. The climate change damage category accounts for all the equivalent CO_2 kg. Eq. 7.11 states that the total equivalent CO_2 emission occurring in the SC (Tier 4 minus product use and end of life emissions) in period t to be equal to the free allowance emissions cap ($MaxCO_{2t}$) plus the extra rights bought to emit ($Buy^{CO_2}_t$) minus the sold rights ($Sales^{CO_2}_t$) in period t. T_L is the subset of those periods when the emission trading is executed, usually every year. In this model it is assumed that

any amount of rights can be sold or obtained at the emissions market. L is the number of periods that accounts for the emission trading interval (e.g. in case that emissions trading occurs yearly and each period t represents one month, L is equal to 12).

$$\sum_{f}\sum_{a\in A_g}\sum_{t'=t-L+1}^{t}\zeta_{ag}IC_{aft'} = MaxCO_{2t} + Buy_t^{CO_2} - Sales_t^{CO_2} \qquad \forall g = ClimateChange, t \in T_L \tag{7.11}$$

Equations 7.12 and 7.13 sum up the environmental damage category results for each site f and for the whole SC, respectively.

$$Impact_f^{2002} = \sum_g\sum_t DamC_{gft} \qquad \forall f \tag{7.12}$$

$$Impact_{overall}^{2002} = \sum_f\sum_g\sum_t DamC_{gft} \tag{7.13}$$

$DamC_g^{SC}$ or $Impact_{overall}^{2002}$ are both used as objective functions in the moMILP formulation.

7.3.3 Supply Chain - Economic model

Many economic performance indicators have been proposed to assess the economic performance of a SC network design. The most traditional indicators are profit, net present value (NPV), and total cost. However, other more holistic measures have been recently proposed which take into account the dynamic change of net working capital. In this sense, Laínez *et al.* (2007) proposed a model that pursues the maximisation of a financial key performance indicator, the corporate value of the firm at the end of the time horizon. The corporate value is computed by a discounted-free-cash-flow (DFCF) method which can be introduced as part of the mathematical formulation. Most SC modeling approaches usually ignore net working capital (NWC), which represents the variable assets associated with the daily SC operations (e.g., material inventories, accounts receivable, accounts payable). By using the DFCF method to compute the corporate value, the actual capital cost, the changes in NWC, the liabilities and other financing funds required to support SC operations and thus liquidity are explicitly considered when appraising SC performance. Next expressions to calculate (i) operating revenue, (ii) operating cost, and (iii) capital investment are presented which would allow for the integration with financial models. For the sake of simplicity and comprehensiveness, NPV will be used as economic objective function in this work, mostly due to the fact that NWC do not change importantly in this SC case.

Operating revenue is calculated by means of net sales which are the income source related to the normal SC activities. Thus, the total revenue incurred in any period t can be easily computed from products sales executed in period t as stated in Eq. 7.14.

$$ESales_t = \sum_{s\in FP}\sum_{f\in Mkt}\sum_{f'\notin(Mkt\cup Sup)} Sales_{sf'ft}Price_{sft} \qquad \forall t \tag{7.14}$$

In order to calculate overall operating cost an estimation of indirect costs and direct costs are required. The total fixed cost of operating a given SC structure can be computed using equation 7.15. Where $FCFJ_{jft}$ is the fixed unitary capacity cost of using technology j at site f.

$$FCost_t = \sum_{f\notin(Mkt\cup Sup)}\sum_{j\in\bar{J}_f} FCFJ_{jft}F_{jft} \qquad \forall t \tag{7.15}$$

The cost of purchases from supplier e, which is computed through Eq. 7.16, includes raw materials purchases, transport and production resources.

$$EPurch_{et} = Purch^{rm}_{et} + Purch^{tr}_{et} + Purch^{prod}_{et} \qquad \forall e,t \tag{7.16}$$

The purchases ($Purch^{rm}_{et}$) associated to raw materials made to supplier e can be computed through Eq. 7.17. It should be noted that in this formulation and for the case of raw material suppliers and transport providers each one of them uses a different technology. χ_{est} is the cost associated to raw material s purchased from supplier e.

$$Purch^{rm}_{et} = \sum_{s\in RM}\sum_{f\in F_e}\sum_{i\in\tilde{T}_s}\sum_{j\in J_i} P_{ijfft}\chi_{est} \qquad \forall e\in E_{rm},t \tag{7.17}$$

Production and transport costs are determined by Eqs. 7.18 and 7.19, respectively. Here, $\rho^{tr}_{eff't}$ denotes the e provider unitary transport cost associated to material movement from location f to location f' during period t. τ^{ut1}_{ijfet} represents the unitary production cost associated to perform task i using technology j, whereas τ^{ut2}_{sfet} represents the unitary inventory costs of material s storage at site f, both of them using provider e during period t.

$$Purch^{tr}_{et} = \sum_{i\in Tr}\sum_{j\in J_i\cap\tilde{J}_e}\sum_{f}\sum_{f'} P_{ijff't}\rho^{tr}_{eff't} \qquad \forall e\in\tilde{E}_{tr},t \tag{7.18}$$

$$Purch^{prod}_{et} = \sum_{f}\sum_{i\notin Tr}\sum_{j\in(J_i\cap\hat{J}_f)} P_{ijfft}\tau^{ut1}_{ijfet} + \sum_{s}\sum_{f\notin(Sup\cup Mkt)} S_{sft}\tau^{ut2}_{sfet} \qquad \forall e\in\tilde{E}_{prod},t \tag{7.19}$$

In the case of τ^{ut1}_{ijfet}, this parameter entails restrictions associated with α_{sij} and $\bar{\alpha}_{sij}$, which forces the plant to operate at the same fixed conditions, meaning that the amount of utilities and labour spent is proportional to the amount of raw material processed. Despite the fact that utilities and labour unitary cost may change along time, they were considered constant and proportional to the raw material processed. Moreover, possible cost decrease associated to economies of scale are disregarded by using the former assumption, higher production rates are associated linearly to higher production costs.

Finally, the total investment on fixed assets is computed through Eq. 7.20. This equation includes the investment made to expand the technology's capacity j in facility site f in period t ($Price^{FJ}_{jft}FE_{jft}$), plus the investment required to open a manufacturing plant in location f, in case it is opened at period t ($I^{J}_{ft}JB_{ft}$).

$$FAsset_t = \sum_{f}\sum_{j} Price^{J}_{jft}FE_{jft} + I^{J}_{ft}JB_{ft} \qquad \forall t \tag{7.20}$$

With regards to Eq. 7.20, the model assumes that $Price^{FJ}_{jft}$, is constant and independent of the FE_{jft} production facility expansion size; assuming that eventual effects of scale are not significant. The following expressions 7.21 and 7.22 define binary variables JB_{ft}. Here, JB_{ft} is a binary variable which takes a value of 1 in case the facility being represented by node f is opened in period t.

$$\sum_{j\in\tilde{J}_f}\left(\sum_{t'\le t} JB_{ft'} - V_{jft}\right) \ge 0 \qquad \forall f\notin(Sup\cup Mkt),t \tag{7.21}$$

$$\sum_{t} JB_{ft} \le 1 \qquad \forall f\notin(Sup\cup Mkt) \tag{7.22}$$

In order to take into consideration the compliance with environmental regulations the environmental cost (Net_t^{env}) is considered as in the TCA methodology. These costs include type 2 costs related to waste treatment costs, and environmental reporting, and type 3 costs related to environmental liabilities, see Eq. 7.23.

$$Net_t^{env} = Cost_t^{WT} + Cost_t^{compliance} + Cost_t^{EnvLiab} \qquad \forall t \tag{7.23}$$

Waste treatment (WT) costs ($Cost_t^{WT}$) are usually pooled for the whole site, and consequently are very hard to quantify, however there exists order of magnitude prices ($Price_w^{WT}$) that can be used for the calculation of these costs depending on the WT facility and the different w waste sinks (e.g. air, water, landfill or incineration, see Sinclair-Rosselot and Allen (2002a)), and the waste flow ($Flow_{wt}^{WT}$), as in Eq. 7.24.

$$Cost_t^{WT} = \sum_w Flow_{wt}^{WT} Price_w^{WT} \qquad \forall t \tag{7.24}$$

In the case of regulatory costs, these are also "hidden" when a project is evaluated; given that these costs are usually personnel costs associated to staff that might divide their time between many different tasks. In the case of the US, the Resource Conservation and Recovery Act (RCRA) requires to maintain records, to notify, and to report for relevant legislation while in the case of the EU similar legislation is found (e.g., REACH, EMAS). These activities entail several costs, which can be roughly estimated considering: a frequency of occurrence ($FreqOcc_{rt}$), and an associated cost for the generation of the required documents ($CostDoc_r$)[2], see Eq. 7.25.

$$Cost_t^{compliance} = \sum_r FreqOcc_{rt} CostDoc_r \qquad \forall t \in T_L \tag{7.25}$$

Similarly to compliance costs, environmental liabilities can be estimated by assuming a frequency of environmental ($FreqLiability_{lt}$) events that might end in: administrative or civil fines ($CostFine_l$).

$$Cost_t^{EnvLiab} = \sum_l FreqLiability_{lt} CostFine_l \qquad \forall t \tag{7.26}$$

The Net income ($Net_t^{co_2}$) due to emissions trading is calculated by Eq. 7.27. Here, $Cost^{co_2}$ and $Price^{co_2}$ represent the emission right cost and price respectively.

$$Net_t^{co_2} = Price_t^{co_2} Sales_t^{co_2} - Cost_t^{co_2} Buy_t^{co_2} \qquad \forall t \in T_L \tag{7.27}$$

Accordingly, the profit calculation in period t is represented in Eq. 7.28 incorporates such issue. To conclude, NPV is computed by means of Eq. 7.29.

$$Profit_t = ESales_t + Net_t^{co_2} - Net_t^{env} - (FCost_t + \sum_e EPurch_{et}) \qquad \forall t \tag{7.28}$$

$$NPV = \sum_t \left(\frac{Profit_t - FAsset_t}{(1+rate)^t} \right) \tag{7.29}$$

The selection of the discount rate ($rate$) for any time discounted metric is subject to controversy, given that it represents the trade-off between the enjoyment of present and future benefits and affects directly the intergenerational aspects of sustainability. Higher values of

[2] In the case of the RCRA, some guidelines are available, Allen & Shonnard (2002a, appendix E).

discount rate, devaluate future impacts and consequently they influence little on long time horizon projects, which could be perceived as contrary to the interest of future generations. Identically to the case of a weighting set for a composite environmental index, the selection of a given discount rate is highly subjective and should represent the decision maker beliefs in terms of intergenerational aspects.

Thus, the SC network design-planning problem whose objective is to optimise a given set of objective functions can be mathematically posed as follows:

$$\begin{gathered} \underset{\mathscr{X},\mathscr{Y}}{Min}\left\{-NPV, DamC_g^{SC}, Impact_{overall}^{2002}\right\} \\ \text{subject to} \\ \text{Eqs. 7.1 to 7.29} \\ \mathscr{X} \in \{0,1\}; \mathscr{Y} \in \mathbb{R}^+ \end{gathered}$$

Here $\mathscr{X}$ denotes the model's binary variables set, while $\mathscr{Y}$ corresponds to the model's continuous variable set.

7.3.4 Case Study: maleic anhydride production

The case study used to illustrate the concepts behind the presented strategy addresses a SC design problem in which different technologies for maleic anhydride (MA) production are compared. MA is an important raw material used in the manufacture of phthalic-type and unsaturated polyester resins, co-polymers, surface coatings, plasticisers and lubricant additives (USEPA, October 1980). Two main technologies are available for its manufacture by catalytic oxidation of different hydrocarbons, benzene or butane (Chen & Shonnard, 2004). Main process reactions are as follows:

$$Butane\ Route: C_4H_8 + 3O_2 \rightarrow C_4H_2O_3 + 3H_2O \tag{7.30}$$

$$Benzene\ Route: C_6H_6 + 4.5O_2 \rightarrow C_4H_2O_3 + 2CO_2 + 2H_2O \tag{7.31}$$

From an atom economy point of view (Domenech *et al.*, 2002), the procedure considering the conversion of butane/butene is more environmentally friendly (see Eq. 7.30), as all butene C atoms end up as MA. In the benzene reaction (see Eq. 7.31), only 67% of C atoms are converted into MA. In addition, in the butene reaction, the oxygen efficiency is greater than in the benzene reaction (50% vs. 33%); just in terms of hydrogen consumption benzene reaction renders a higher atom efficiency than butene reaction (33% vs. 25%). Several factors such as advances in catalyst technology, increased regulatory pressures, and continuing cost advantages of butane over benzene have led to a rapid conversion of benzene- to butane-based plants, consequently to the conversion of the whole MA SC (Felthouse *et al.*, 2001). Its use in the plastics industry changes MA irreversibly and it is not technically feasible to recover it nor some of its raw materials for reuse. The former fact coupled to the wide variety of products where MA is used makes unfeasible the consideration of reuse and recycle possibilities. Consequently the SC is focussed on the forward flows.

The studied SC comprises raw material extraction facilities, processing sites, distribution centres and marketplaces, fitting a cradle to distribution centre boundary setting. Different raw material suppliers are modelled with the assumption that each of them provides the same commodity quality. However, the production process uses different technologies. Two technologies can be implemented: (i) benzene-based (MA Technology 1) and (ii) butane-based (MA Technology 2) feedstock. Table 7.1 shows raw materials requirements for each of these technologies.

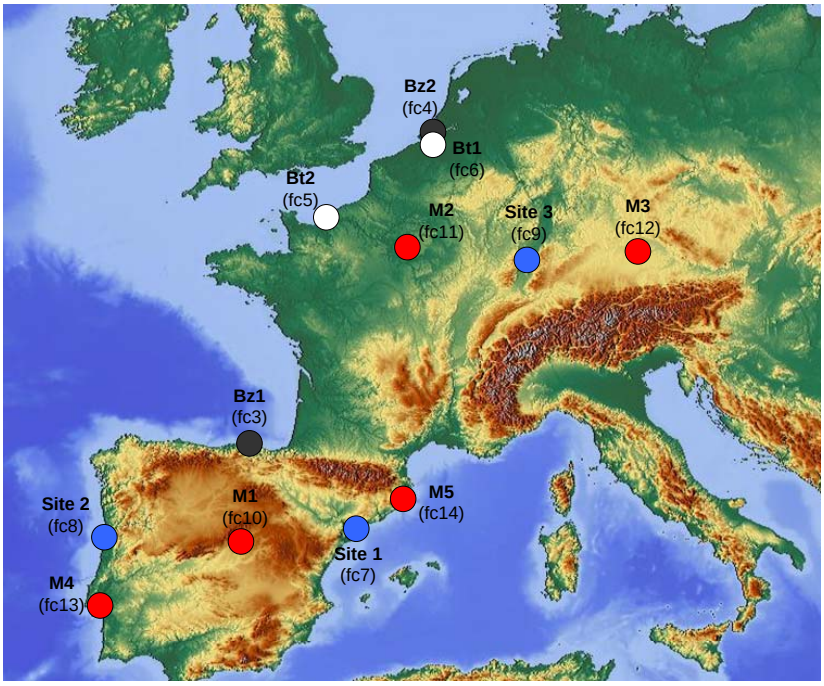


Figure 7.1: SC supplier, production, distribution and market nodes location.

A simplified potential network is proposed and restricted to Europe (see Figure 7.1). Tarragona ($Site_1$, fc_7), Estarreja ($Site_2$, fc_8) and Drusenheim ($Site_3$, fc_9) are considered as possible facilities location nodes. Benzene is supposed to be available at Bilbao ($Bz1$, fc_3) and Rotterdam ($Bz2$, fc_4), while n-butane can be supplied from Rotterdam ($Bt1$, fc_6) and Le havre ($Bt2$, fc_5). MA is assumed to be sold at five markets Madrid (M_1, fc_{10}), Paris (M_2, fc_{11}), Munich (M_3, fc_{12}), Lisbon (M_4, fc_{13}) and Barcelona ($M5$, fc_{14}).

The environmental impacts associated to MA production without consideration of raw material production, transport use and electricity consumption are found in Table 7.5. Two potential benzene suppliers are considered, benzene can be obtained from a coke plant (Benzene Supplier-Tech 1-$Bz1$), or from a 50% mixture of ethylene reforming and pyrolysis gasoline (Benzene Supplier-Tech 2-$Bz2$). For the case of butane production, two suppliers are considered, one that considers a European typical refinery (Butane Supplier-Tech 1-$Bt1$), while the other is a refinery, but which considers the production impact of a mixture of the top 20 most important organic chemicals (Butane Supplier-Tech 2-$Bt2$). The values were retrieved from Ecoinvent v1.3 database (Ecoinvent, 2006) using SimaPro 7.1.6 (de Schryver *et al.*, 2006). The environmental impact, calculated using Impact 2002+ impact assessment method[3], for

Table 7.1: Maleic Anhydride raw material and utilities consumption (α_{sij}) and CO_2 direct production emissions per MA kg (Ecoinvent, 2006).

Technology	MA Tech. 1[a]	MA Tech. 2[b]
Electricity consumption [kWh]	0.540	1.08
Propane-butane [kg]	0.000	0.99
Benzene [kg]	1.026	0.00
CO_2 direct emissions [kg]	1.800	3.87

[a] MA Benzene based production
[b] MA Butane based production

[3]Human toxicity (HHC, HHNC), respiratory effects (inorganics HHRI, organics HHRO), ionising radiation

Table 7.2: Raw material and product prices (χ_{est}, $Price_{sft}$).

Commodities		Price/cost [$]
Electricity [kWh]	Supp. 1	0.057
	Supp. 2	0.038
Benzene [kg]	Supp. 1 (Coke plant - Bilbao)	0.171
	Supp. 2 (Gasoline pyrolysis - Rotterdam)	0.214
Butane [kg]	Supp. 1 (Refinery - Rotterdam)	0.224
	Supp. 2 (Proxy - Le Havre)	0.280
	Maleic anhydride [kg]	1.672

Table 7.3: Materials transportation costs (m.u $1 \cdot 10^{-4}$/(kg·km), $\rho^{tr}_{eff't}$)

Material	Cost (32 ton)	Cost (16 ton)
Benzene	2.99	2.69
MA	2.75	2.48
Butane	4.25	3.83

raw material production can be also found in Table 7.5 which does not consider impacts associated to transportation, nor facilities installation.

Two different types of transportation services are assumed to be available, 16-ton lorries and 32-ton lorries. Benzene is liquid at standard conditions and therefore it is stored and transported as a liquid. Butane, on the other hand, is a gas at standard conditions and thus needs to be liquefied in order to be transported and stored. In this case, butane liquefaction takes place during its production. Consequently both products are transported in liquid state, with similar environmental impacts by the same kg·km. Medium voltage electricity production from different countries grids is considered[4]. The environmental impacts associated to transport services and electricity production are found in Table 7.6. Raw material, electricity, product and transportation prices were estimated from current economical trends, see Table 7.2 and 7.3.The return rate is assumed to be 25%.

The capital investment associated to equipment and its operating costs are based on previously published results which were obtained using process simulation (Chen & Shonnard, 2004). These figures are from a design basis of $2.27 \cdot 10^4$tn/year of MA, see Table 7.4.

7.4 Metrics calculation

Thirty-seven monthly planning periods are considered. The implementation in GAMS (Brooke *et al.*, 1998) of the SC-LCA formulation leads to a MILP model with 15440 equations, 137652 continuous variables, and 1093 discrete variables. It takes 13.2 CPU s to reach a solution with a 0% integrality gap on an 2.0 GHz Intel Core 2 Duo computer using the MIP solver of CPLEX (ILOG-Optimization, 2008).

To evaluate comparable alternatives, the first step has consists in determining an SC which maximises NPV, which is then used to fix a total production rate. From the available data, it is

Table 7.4: Facilities capital investment and operating costs ($Price^{FJ}_{jft}$, τ^{utl}_{ijfe}), m.u.$1 \cdot 10^7$.

	MA Tech. 1 (Benzene-based)	MA Tech. 2 (Butane-based)
Capital investment	1.61	1.95
Operating cost	1.42	1.30

(HHIR), ozone layer depletion (ODP), aquatic ecotoxicity (AqE), terrestrial ecotoxicity (TeE), terrestrial acidification/nutrification (TeAN), aquatic acidification (AqA), aquatic eutrophication (AqEu), land occupation, global warming (GWP), non-renewable energy (ADener) and mineral extraction (ADmin)

[4]This SC model considers that electricity consumption can be from different countries grid and consequently is not fixed to the production node that is selected.

Table 7.5: Environmental impact for 1 kg of product and raw materials production ($\psi_{ijff'a}$) (Ecoinvent, 2006)

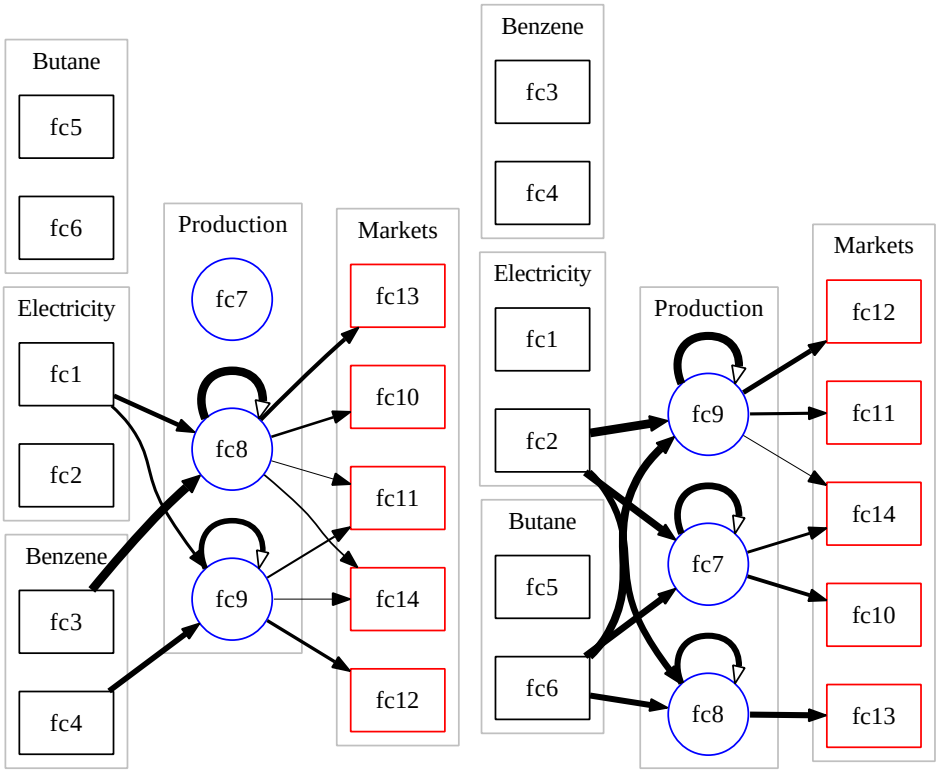
Impact category	Unit	MA Tech. 1[a]	MA Tech. 2[b]	Benzene Sup. 1[c]	Benzene Sup. 2[d]	Butane Sup. 1[e]	Butane Sup. 2[f]
HHC	kg C_2H_3Cl	1.4E-09	0.0E+00	3.9E-01	2.0E-01	6.3E-03	9.1E-02
HHNC	kg C_2H_3Cl	2.7E-04	0.0E+00	1.4E-02	8.9E-04	7.6E-03	7.5E-03
HHRI	kg PM2.5	0.0E+00	0.0E+00	4.3E-03	1.3E-03	8.1E-04	1.5E-03
IR	Bq C-14	0.0E+00	0.0E+00	1.3E+01	5.9E-03	9.3E+00	2.2E+01
ODP	kg CFC-11	0.0E+00	0.0E+00	2.4E-07	2.9E-11	4.7E-07	1.4E-07
HHRO	kg C_2H_2	7.9E-06	1.3E-05	9.2E-03	9.2E-04	8.5E-04	1.4E-03
AqE	kg TEG water	8.8E-07	2.3E-07	1.5E+02	6.0E+01	1.5E+02	1.0E+02
TeE	kg TEG soil	1.7E-07	3.2E-07	3.4E+01	2.4E-02	3.1E+01	1.7E+01
TeAN	kg SO_2	0.0E+00	0.0E+00	2.5E-02	3.8E-02	1.5E-02	3.9E-02
Land	m^2 org-arable	0.0E+00	0.0E+00	2.0E-02	1.4E-05	3.4E-03	4.8E-03
AqA	kg SO_2	0.0E+00	0.0E+00	6.6E-03	8.3E-03	6.3E-03	9.4E-03
AqEu	kg P-lim	5.4E-04	5.4E-04	1.6E-05	4.4E-06	3.5E-04	4.4E-04
GWP	kg CO_2	1.8E+00	3.9E+00	6.4E-01	1.4E+00	5.6E-01	1.6E+00
ADener	MJ primary	0.0E+00	0.0E+00	5.4E+01	7.1E+01	5.6E+01	6.7E+01
ADmin	MJ surplus	0.0E+00	0.0E+00	3.4E-03	2.5E-04	2.6E-03	1.5E-02

[a] MA Benzene based production
[b] MA Butane based production
[c] Benzene from coke plant, Bilbao fc_3
[d] Benzene from gasoline pyrolysis, Rotterdam fc_4
[e] Butane from refinery, Rotterdam fc_6
[f] Butane proxy organics production, Le Havre fc_5

Table 7.6: Environmental impact associated to transport services (ψ^T_{ija}) and electricity production ($\psi_{ijff'a}$) (Ecoinvent, 2006).

Impact category	Unit	Transport lorry 32ton [tn·km]	Transport lorry 16ton [tn·km]	Electricity supplier 1 [kWh]	Electricity supplier 2 [kWh]
HHC	kg C_2H_3Cl	1.2E-03	2.0E-03	1.6E-04	1.4E-04
HHNC	kg C_2H_3Cl	2.4E-03	3.9E-03	1.4E-04	1.4E-04
HHRI	kg PM2.5	2.8E-04	6.5E-04	3.7E-05	2.8E-05
IR	Bq C-14	1.4E+00	3.8E+00	1.1E-01	3.8E+00
ODP	kg CFC-11	2.3E-08	4.9E-08	5.1E-09	1.7E-09
HHRO	kg C_2H_2	1.7E-04	6.7E-04	1.1E-05	4.1E-06
AqE	kg TEG water	1.8E+01	3.2E+01	1.9E+00	1.9E+00
TeE	kg TEG soil	1.1E+01	1.8E+01	5.2E-01	3.4E-01
TeAN	kg SO_2	7.6E-03	1.5E-02	8.7E-04	5.0E-04
Land	m^2 org-arable	1.3E-03	4.7E-03	5.8E-05	7.3E-05
AqA	kg SO_2	1.2E-03	2.4E-03	3.0E-04	1.9E-04
AqEu	kg P-lim	1.6E-05	3.4E-05	2.0E-06	5.3E-07
GWP	kg CO_2	1.6E-01	3.6E-01	5.2E-02	3.6E-02
ADener	MJ primary	2.8E+00	6.0E+00	7.4E-01	8.2E-01
ADmin	MJ surplus	1.3E-03	1.9E-03	6.8E-05	9.0E-05

found that the production rate should be $8.13{\cdot}10^5$ ton of MA for a 3 years planning horizon. Then, since two objective functions are to be optimised, namely NPV and IMPACT 2002+, the multi-objective optimisation procedure known as the weighted sum is followed (Statnikov & Matusov, 1995). To be able to make comparisons not only the production rate is the same for both solutions, but the amount of sales has been set to the same figure. In this sense the SC functional unit is the total amount of sales. Figure 7.2 shows the resulting SCs from single objective optimisation, while Tables 7.7 and 7.8, summarise the objective function values. Following the former procedure, Figure 7.2(a) shows the dominant SC that maximises NPV. Production in this SC is based on benzene feed-stock, which is bought from both available suppliers. Production of MA is located in Estarreja (fc_8) and Drussenheim (fc_9) and sold in all markets. Alternatively, when the environmental impact indicator is minimised the resulting SC (see Figure 7.2(b)) uses butane as feedstock and buys raw materials from a single supplier. N-butane is selectively bought from one single supplier (fc_6, refinery in Rotterdam) and is processed at all three possible manufacturing sites (fc_7-fc_9). Arrows width in figure 7.2 shows activity level. Tables 7.7 and 7.8 summarise the most significant values that correspond to both solutions regarding environmental and economic aspects. Figure 7.3 shows the distribution of the environmental impacts along SC echelons for these two cases. According to Baumann & Tillman (2004, Ch. 11), most LCA studies show that the production of materials often causes a major proportion of a product's environmental impact, whereas assembly frequently causes a very minor proportion. If the product requires energy during its use phase,



(a) SC configuration for the most profitable SC option (NPV optimisation). It shows a benzene based SC with production of MA located in Estarreja (fc_8) and Drussenheim (fc_9).

(b) SC configuration for the most environmental friendly option (Overall impact 2002+ optimisation). It shows that n-butane is selectively bought from one single supplier (fc_6, refinery in Rotterdam) and is processed in all three possible manufacturing sites (fc_7-fc_9).

Figure 7.2: SC configurations for single objective optimisation. Arrows width shows activity level.

Table 7.7: Environmental impacts arising from single economic and overall environmental objective function optimisation results [Impact 2002+ Pts].

End-point	NPV Optimisation		Impact 2002+ Optimisation	
impact category	Direct value	Normalised value	Direct value	Normalised value
Human Health	3.03E+03	4.27E+05	7.87E+02	1.11E+05
Ecosystem Quality	3.35E+08	2.45E+04	3.55E+08	2.59E+04
Climate Change	2.62E+09	2.65E+05	3.85E+09	3.89E+05
Resources	5.69E+10	3.76E+05	4.94E+10	3.26E+05
Impact 2002+	1.09E+06		**8.52E+05**	
SC-structure	Figure 7.2(a)		Figure 7.2(b)	

Table 7.8: Economic aspects arising from single objective optimisation (NPV and Impact 2002+). [m.u.]

Economic aspect	NPV Optimisation		Impact2002+ Optimisation	
	Non discounted	Discounted	Non discounted	Discounted
Investment	1.09E+08	1.09E+08	1.61E+08	1.61E+08
RM Cost	2.31E+08	1.61E+08	2.28E+08	1.59E+08
RM Transport Cost	1.37E+08	9.36E+07	4.52E+08	3.15E+08
Product Transport Cost	1.08E+08	7.52E+07	7.92E+07	5.53E+07
Production cost	5.10E+08	3.56E+08	4.69E+08	3.27E+08
Fixed cost	2.91E+07	2.03E+07	3.62E+07	2.53E+07
Sales	1.36E+09	9.50E+08	1.36E+09	9.50E+08
Profit	**2.37E+08**		-6.56E+07	
NPV		**1.32E+08**		-9.44E+07
IRR		**99.10%**		-31.06%

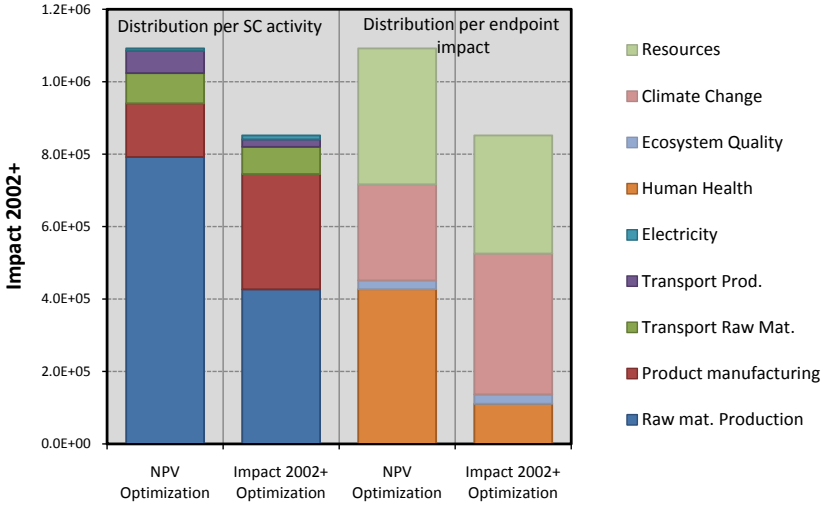


Figure 7.3: Distribution of environmental impacts for single objective optimisation solutions, according to different SC activities and end-points.

this phase often dominates the environmental profile, whereas if the product is used in a more passive way, the production phase dominates and notably the production of materials. Although transport being a major source of pollution in society, transportation and distribution often contribute less than expected to the environmental impact. In this case study, raw material production is the most important factor that contributes to the overall environmental impact in both single objective optimisation cases. In contrast, electricity consumption and transportation are the aspects that have least impact (see tables 7.7 and 7.8). This clearly shows that activities to reduce environmental impact should be focused on the raw material production echelon. Moreover, from Fig. 7.3, it can also be concluded that if raw material production would be disregarded then different solutions would be obtained, thus showing the influence of "purchase" decisions on the environmental impact of a SC. In the case of minimisation of environmental impact, a negative NPV and Internal Rate of Return (IRR) are found, (see Table 7.8). If the costs are analysed it can be seen, that raw material transportation cost associated to environmental impact minimisation is significantly higher and it constitutes the most significant difference between economic and environmental optimisation. Figure 7.4 clarifies this situation. This difference is due to the following reasons: the location of butane suppliers are far from the production facility locations and butane transport is 42% more expensive than benzene transport. In addition, the environmental impact optimisation selects lorries of 32 tons which are less polluting, but more expensive (see Table 7.3). The second and

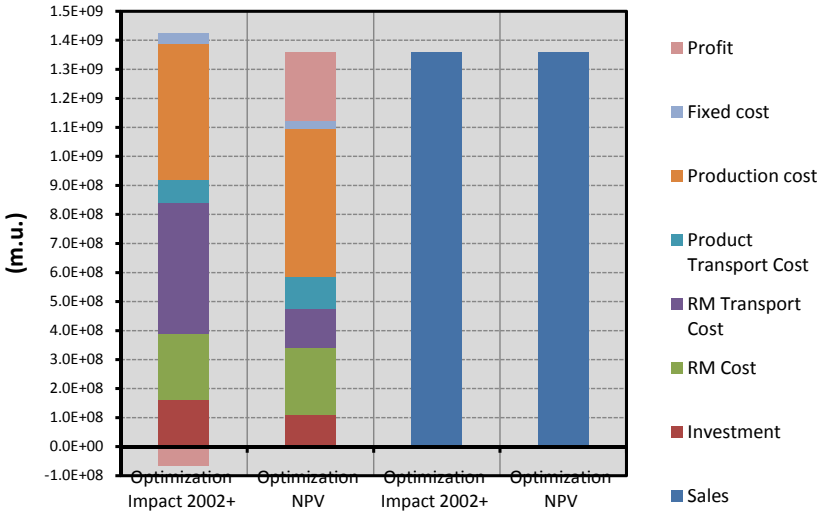


Figure 7.4: Distribution of costs for single objective optimisation solutions, distributed in different SC activities.

Table 7.9: Single end-point optimisation results distributed along different environmental end-point metrics. Last row presents the resulting overall Impact 2002+ [Impact 2002+ pts]. Bold values indicate lowest environmental impact in that category.

End-point indicator	Human Health Optimisation	Ecosystem Quality Optimisation	Climate Change Optimisation	Resources Optimisation
Human Health	**110953**	210863	520133	353555
Ecosystem Quality	25946	**12633**	27337	24271
Climate Change	388736	293764	**219817**	279434
Resources	326140	418723	320895	**315826**
Impact 2002+	851776	935983	1088183	973085
SC configuration	Fig. 7.5(a)	Fig. 7.5(b)	Fig. 7.5(c)	Fig. 7.5(d)
SC raw materials	n-Butane	Benzene	Benzene	n-But+Ben

third biggest differences between the solutions obtained are those regarding investment and fixed operating costs which also penalise butane-based production.

Instead of optimising the overall environmental impact this model allows for the optimisation of each of the four possible end point categories. Each optimisation renders a different SC solution as can be seen in Figure 7.5. Tables 7.9 and 7.10, summarise the objective values.

Table 7.9 rows show, as expected, that the minimum value for each of the partial environmental impacts is obtained by the optimisation of the corresponding objective function (see bold values). The solution obtained by optimisation of the human health end-point is the same as the one obtained when optimising the overall Impact 2002+: a SC based on butane

Table 7.10: Environmental impact associated to different SC activities for single end-point optimisation [Impact 2002+ pts]. Bold values indicate lowest environmental impact in that activity.

SC activity	Human Health Optimisation	Ecosystem Quality Optimisation	Climate Change Optimisation	Resources Optimisation
Raw mat. Production	**427169**	684044	862463	695986
Product manufacturing	318002	**147994**	**147994**	213013
Transport Raw Mat.	75313	73128	46546	**34968**
Transport Prod.	20470	25406	25770	**20401**
Electricity	10822	**5411**	**5411**	8717

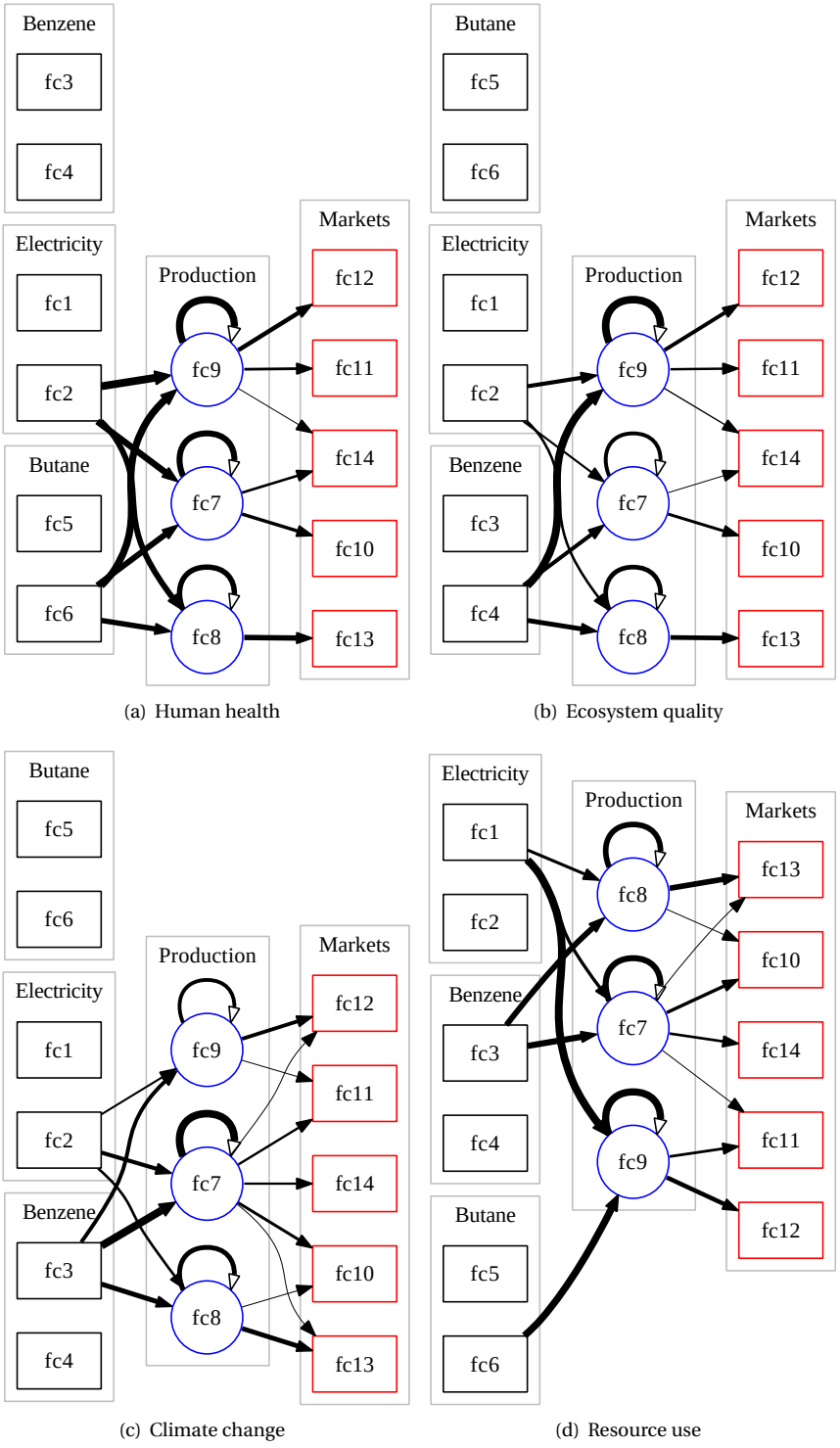


Figure 7.5: SC configurations for single objective optimisation, considering different end-point environmental metric. Arrows width shows activity level.

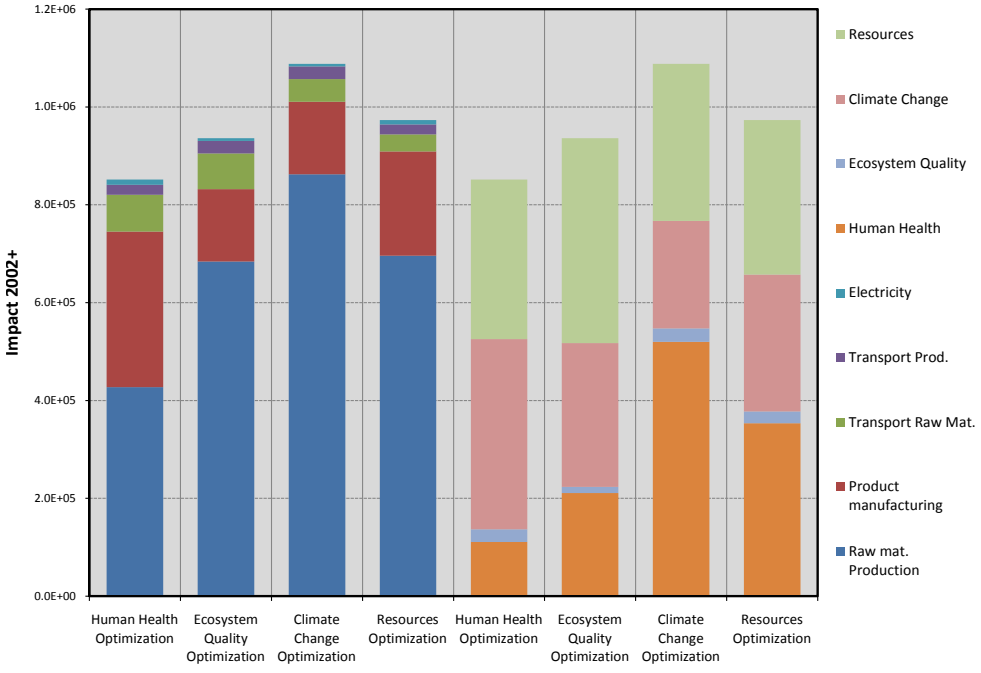


Figure 7.6: Distribution of environmental impacts along SC activities and end-point categories for single end-point environmental optimisation's.

as in Fig. 7.2(b) and Fig. 7.5(a). This is partly due to the fact that the weighting and normalisation coefficients for that end-point value are the largest in the methodology[5]. Interestingly, each one of the other end-point's optimisation results in a different SC structure, (see Figs. 7.5(b), 7.5(c), 7.5(d)). In the case of ecosystem quality and climate change optimisation (Figs. 7.5(b) and 7.5(c)), the production is based on benzene and the SC structures are similar to the one depicted in Fig. 7.2(a). The difference between solutions is the MA production load on each different site and the benzene supplier used, which in the case of ecosystem quality is the provider that uses pyrolysis gasoline (fc_4 located in Rotterdam) and the case of minimisation of climate change is a coke plant (fc_3 located in Bilbao). Please note that arrows widths are wider in the case of nodes closer to the supplier to minimise environmental impact from transportation. In the case of resources impact optimisation a combined use of benzene and butane technologies is suggested (see Fig. 7.5(d)). Regarding the optimisation of ecosystem quality and climate change, they both show minimum amount environmental impact due to electricity consumption. Figure 7.6 summarises the information in tables 7.9 and 7.10.

One way to reduce SC environmental impacts may be to look for new feedstock providers whose production processes are more environmental friendly. Human health impacts are also considerable high in both solutions. In the case of NPV optimisation this is due to the toxic properties of benzene. It is expected that CO_2 emissions trading considerations will make butane-based production more economically attractive. This aspect is analysed in section 7.4.1.

Furthermore, there is an SC-structure dependence against its total production. Other studies on SC design and environmental issues consider that demand must be completely met. This assumption leads to an invariable total production rate and sub optimal solutions. In

[5]The normalisation constants for human health, ecosystem quality, climate change and resources use are as follows: $1.41{\cdot}10^{2}$, $7.30{\cdot}10^{-5}$, $1.01{\cdot}10^{-4}$ and $6.58{\cdot}10^{-6}$.

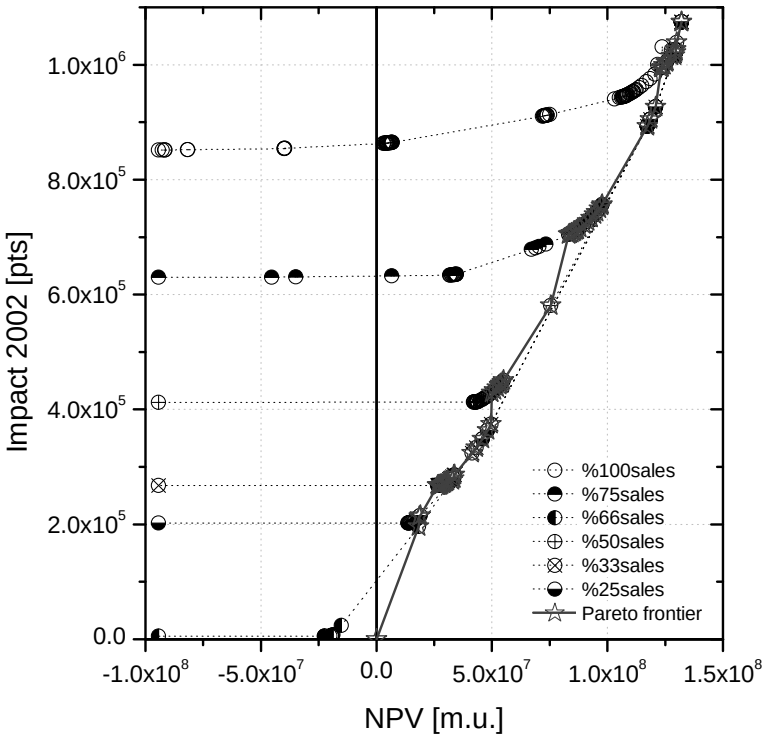


Figure 7.7: Iso production-sales curves for different production amounts based on a percentage of best NPV sales value ($8.13 \cdot 10^5$ ton of MA). Continuous line shows Pareto frontier for overall environmental impact vs. NPV.

Fig. 7.7 iso-production/sales curves correspond to solutions following this assumption. For these cases minimum overall impact always leads to negative NPVs. These solutions are obviously dominated by the zero-production/sale solution (origin). The actual Pareto curve is shown in Fig. 7.7 as a continuous black line which is obtained by allowing unmet demand (i.e. a fixed produced amount is not considered). It can be seen that positive NPVs can be achieved by reducing the MA production. This trade-off is absolutely necessary. Regardless of emissions, every productive sector has a "break-even" point below which "profit" becomes negative. It establishes the minimum production capacity required to make a profitable business. Results obtained in this way draw a clear picture of the problem, which is of paramount importance for objective selection among the different SC alternatives. As it can be observed (see Fig. 7.7), the multi-objective optimisation results in a set of Pareto solutions. Connecting lines do not represent solutions, and only the vertices of the curve are feasible SC alternatives. The decision maker must select one of the solutions from this non-dominated set. The stakeholder's selected solution will depend on the weights that he/she subjectively assigns to each of the objectives (i.e., NPV and Impact2002+). Several multi-attribute decision analysis (MADA) techniques are available for this purpose, for a review of these techniques the reader is referred to the work of Seppala *et al.* (2002).

With regards to the effect of interest rate on the optimal SC configuration, an analysis was performed by increasing gradually the annual interest rate from 0% to 40%, while optimising the NPV. The results obtained are shown in Figure 7.7. Figure 7.8 shows that for interest rates lower than 7.5% one SC structure is found. This SC is based on the installation of benzene and butane based production technologies and is similar to the one shown in Figure 7.5(d). For

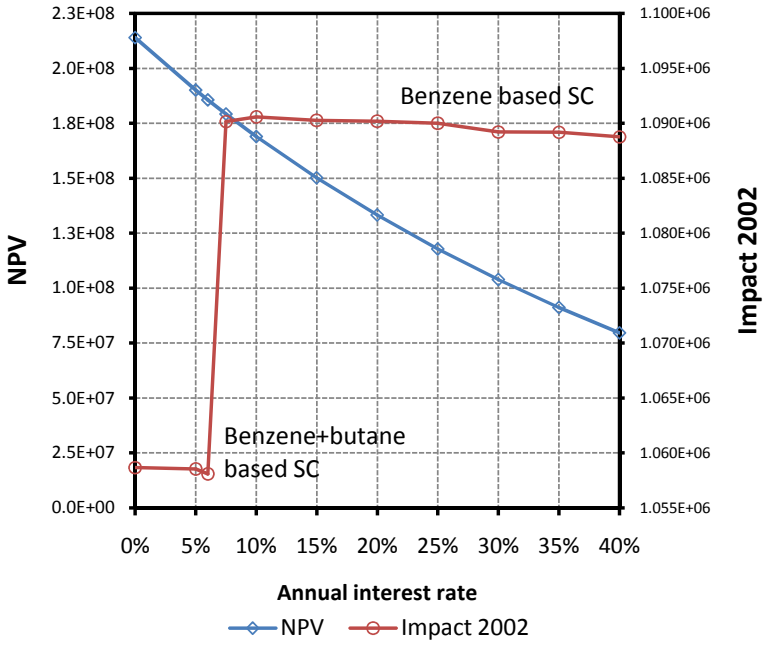


Figure 7.8: NPV optimisation results for different values of interest rate.

Table 7.11: CO_2 emissions associated to 1 MA kg of production (Ecoinvent, 2006), and BAT data ($MaxCO2_t$, adapted from Chen and Shonnard (2004))

Tiers	MA Tech. 1[a]	MA Tech. 2[b]
BAT Tier 2 CO_2 emissions [kg]	3.41	3.02
Tier 1 CO_2 emissions [kg]	1.80	3.87
Tier 2 CO_2 emissions [kg]	2.05	4.38
Tier 3 CO_2 emissions [kg]	3.53	4.93

[a] MA Benzene based production
[b] MA Butane based production

values of interest rate greater than 7.5% the optimal NPV SC is based on the production of MA from benzene only and has the same structure as the one shown in Figure 7.2(a).

7.4.1 CO_2 emission trading considerations

Recent estimates indicate that the level of CO_2 in the atmosphere has increased by a third since the beginning of the industrial age (1800s), and that it currently contributes about 73% to the potential for global warming (Grossmann, 2004). Values for maximum free emissions caps are required to take into account CO_2 emissions. One way of assessing such values is to take the best available technology (BAT) in terms of CO_2 emissions. Chen and Shonnard (2004) have studied both MA production schemes finding through simulation optimum flow sheets (see Table 7.11). Given that the data provided by Chen and Shonnard (2004) does not consider steam co-production, the BAT value has been increased accordingly (32%), so that it is comparable to the one reported by Ecoinvent (2006). According to this data the production of MA from butane has the lowest CO_2 emissions and will be used to set the free emission quota. Tier 1, Tier 2 and Tier 3 CO_2 emissions were retrieved from Ecoinvent (2006), by analysing each technology.

In the economic formulation it is considered that CO_2 emissions credits are bought at the

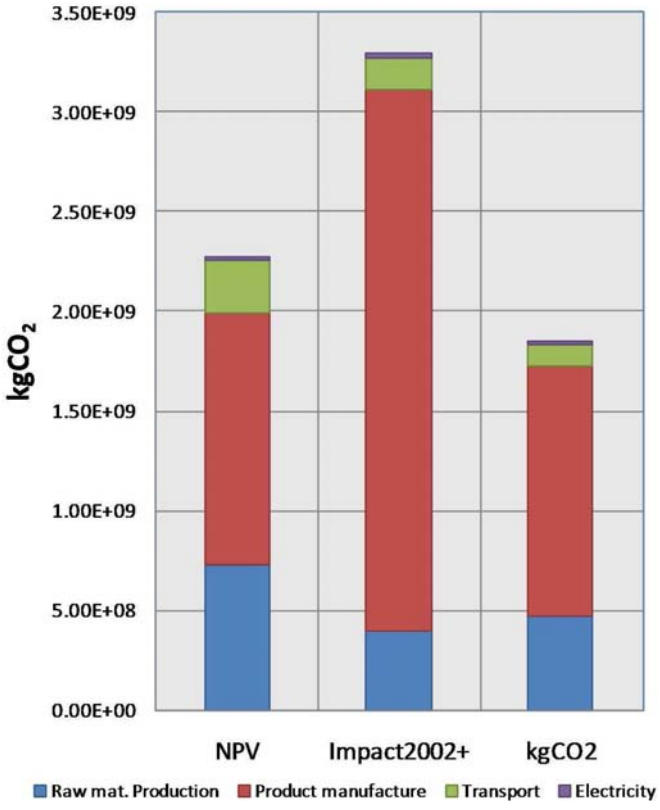


Figure 7.9: CO_2 emissions allocation along the maximum NPV configuration, minimum overall impact configuration, and minimum CO_2 emissions configuration

end of each year to cope with CO_2 emissions that exceed the maximum allowed using the BAT. The trading cost and price of emission rights is considered as US$23 which is a proxy of the values currently found in the trading market.

The optimal SC configuration when the emissions trading scheme is considered remains equal to that obtained when the NPV is optimised without this consideration (Fig. 7.2(a)) regardless of the free emissions cap and the emission right price. As stated above the minimum overall environmental impact is achieved by installing butane-based technologies, while the most profitable solution is based on benzene as feedstock. The CO_2 emission allocation throughout the SC is depicted in Figure 7.9 for the maximum NPV, minimum overall impact, and minimum CO_2 emissions network configurations, which are optimised by taking into account the CO_2 trading scheme. The least CO_2 pollutant configuration is based on benzene technology. This figure shows that the optimal overall impact configuration (butane-based) is the one that emits more CO_2, most of which comes from the MA production. Under the trading scheme this configuration would be strongly penalised.

As mentioned above, regulatory pressures were expected to lead to a conversion of benzene- to butane-based plants since benzene is considered to be more environmental harmful.

Actually, benzene based SCs show greater overall impact (see Tables 7.7 and 7.9). Their damage category that has the more impact is that which affects human health due to benzene's carcinogenicity. However, a CO_2 trading emission scheme, such as the one modelled in the case study, will not cause benzene-based production to move towards butane; on the contrary, this could be a factor that leads to change of butane-based into benzene-based MA

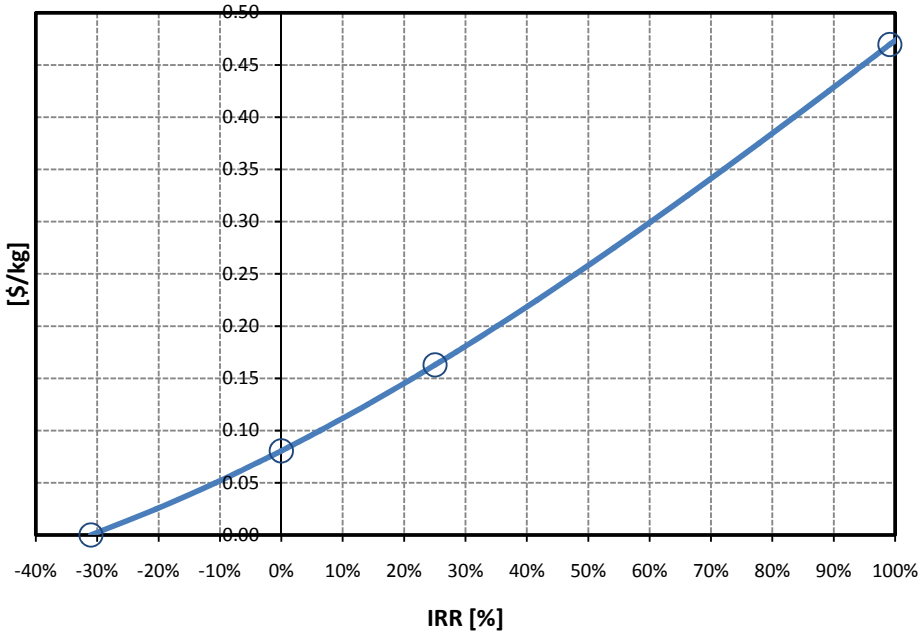


Figure 7.10: IRR values for different amount of government subsidy based on MA production. Circles shows values of Table 7.12.

production.

7.4.2 Monetary subsidies considerations

From the results observed from single objective optimisation of NPV and Impact 2002+, it was found that an IRR of nearly 100% is associated to a MA production SC benzene-based. In contrast production based on butane is the most environmentally friendly but is not profitable (see Table 7.7). Instead of imposing taxes on CO_2, another possible way of solving this issue, is that the government subsidises on the production of MA based on butane. This subsidy could be of different forms which can be grasped from the distribution of cost in Fig. 7.4. In this sense, the possible options are: (i) to increase the MA selling price, (ii) to decrease in the production cost of MA, and (iii) to decrease the butane and MA related transportation costs. Options (i) and (ii) are similar, in the sense that both are based on the MA amount produced, that and can be measured in m.u/kg of MA. Figure 7.10 shows the change in the IRR value for the SC based on butane when in-creasing the subsidy per kg of MA produced. Table 7.12 shows the MA government subsidies results for different IRR values.

In the case of transportation costs associated to MA and n-butane, Table 7.13 and Figure 7.11 show the results obtained. The analysis was performed considering one single transport being subsidised. It is found that a subsidy on n-butane transportation is more efficient than that on MA transport. However, in both cases in order to make the butane based SC equally

Table 7.12: Current and possible MA prices and production government subsidies.

IRR [%]	MA subsidized price [$/kg]	Operating cost subsidy [$/kg]
-31.10%	1.672	0
0.00%	1.753	0.081
25.00%	1.835	0.163
99.10%	2.142	0.47

Table 7.13: MA and n-butane transportation cost with and with out government subsidies.

IRR [%]	Butane subsidy [$/kg·km]	Butane Transport Cost [$/kg·km]	MA subsidy [$/kg·km]	MA Transport Cost [$/kg·km]
-31.10%	0	4.25E-04	0	2.75E-04
0.00%	6.17E-05	3.63E-04	2.28E-04	4.73E-05
25.00%	1.27E-04	2.98E-04	4.69E-04	-1.94E-04
99.10%	3.89E-04	3.56E-05	1.43E-03	-1.16E-03

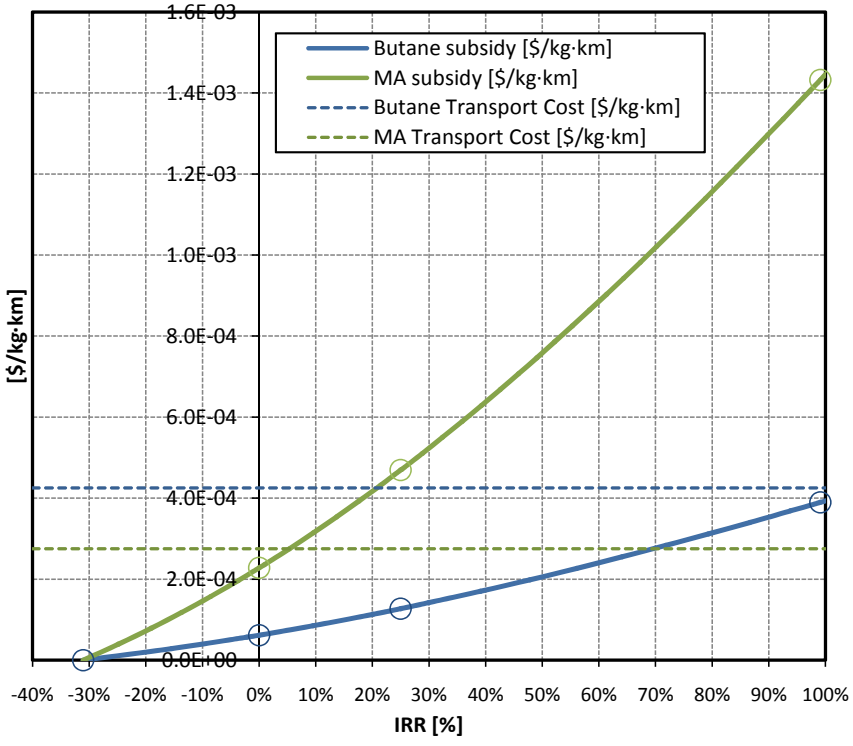


Figure 7.11: IRR values for different amount of government subsidy based on transports of MA and butane. Circles shows values of Table 7.13.

profitable than the benzene one, government subsidies must be higher than the actual transportation cost (negative values in Table 7.13 indicate a higher subsidy than the actual cost). On the contrary in the case of a subsidy on MA production or sale price, a subsidy of 0.538 $/kg of butane (being it as sales price or as operating cost reduction), will make the butane based SC as profitable as the one based on benzene.

7.4.3 Uncertainty considerations

The analysis of uncertainty in model parameters is studied in this section. The objective is to analyse how model results are modified by the effect of model input parameters. Despite the fact that many parameters can be described using scenarios, due to the lack of knowledge of possible scenario trees, it has been decided to use probability distribution functions (pdfs) for all input variables. Moreover all model input variables are modelled considering uniform probability distributions, this way no emphasis is given to any variable. This assumption can be modified if appropriate variable input information is available, that allows for better sce-

nario tree or pdf estimation. In Table 7.14, P1 is the lower bound for the uniform pdf while P2 the upper value; the typical value reported is the half interval between P1 and P2.

The problem has been further simplified considering the following assumptions: (i) only six time periods are considered, (ii) demands in four possible markets are different but constant along time (Barcelona market has been disregarded), no relationship among markets is considered and (iii) raw materials prices and operation costs are constant along time. The model outputs selected for sensitivity analysis are the following: supply chain's net present value (NPV), supply chain's overall impact (ImpactSC), installed capacities for the different available technologies ($\text{installedCapTech}_{\text{Ben}}$ and $\text{installedCapTech}_{\text{But}}$), the amount of total raw material purchases ($totalPurch_{But}$, $\text{totalPurch}_{\text{Ben}}$ and $\text{totalPurch}_{\text{Elec}}$), and the total amount of MA produced ($\text{totProduced}_{\text{MA}}$) and satisfied demand ($\text{totSatisfiedDemand}_{\text{MA}}$).

The overall objective of the analysis is to quantitatively know which input variables affect the most to model output variables. Moreover the analysis of how input model variables affect the selection of one SC structure against others is desired. In this sense the analysis aims at prioritise and map input variables effect on different model output.

The model output results were obtained by applying each of the sampled scenarios to the SC model coded in GAMS via the Ferris (2005) software interface. The model was studied using regression and variance decomposition metrics. In all cases a single model run requires for 2-5 seconds of processing time. All model runs were done optimising the economical metric,and no attempt at analysing the environmental metric was performed given that such analysis will imply to force a given demand to be met, and in this case the markets demand was considered to be uncertain, the model allows for not coping with the full market demand.

Table 7.14: SCM model variables and parameters uncertainty location and nature

Variable Name	Typical Value	P1	P2
$\text{FIXCF}_{\text{Tech}_{\text{Ben}}}$	4.26E-01	8.51E-02	7.66E-01
$\text{FIXCF}_{\text{Tech}_{\text{But}}}$	5.15E-01	1.03E-01	9.27E-01
INVS_0	1.00E+07	2.00E+06	1.80E+07
$\text{PriceFE}_{\text{Tech}_{\text{Ben}}}$	1.24E-02	2.47E-03	2.23E-02
$\text{PriceFE}_{\text{Tech}_{\text{But}}}$	1.50E-02	3.00E-03	2.70E-02
$\text{PRC}_{\text{Tech}_{\text{Ben}}}$	6.27E-01	1.25E-01	1.13E+00
$\text{PRC}_{\text{Tech}_{\text{But}}}$	5.75E-01	1.15E-01	1.04E+00
$\text{IHC}_{\text{Mat}_{\text{Elec}}}$	1.87E-03	3.74E-04	3.36E-03
$\text{IHC}_{\text{Mat}_{\text{But}}}$	5.93E-03	1.19E-03	1.07E-02
$\text{IHC}_{\text{Mat}_{\text{Ben}}}$	7.76E-03	1.55E-03	1.40E-02
$\text{IHC}_{\text{Mat}_{\text{MA}}}$	3.35E-01	6.70E-02	6.02E-01
$\text{As}_{\text{Mat}_{\text{Elec}}}$	9.33E+08	2.40E+08	1.20E+09
$\text{As}_{\text{Mat}_{\text{Elec}}}$	9.34E+08	2.40E+08	1.20E+09
$\text{As}_{\text{Mat}_{\text{But}}}$	9.34E+08	2.40E+08	1.20E+09
$\text{As}_{\text{Mat}_{\text{But}}}$	9.33E+08	2.40E+08	1.20E+09
$\text{As}_{\text{Mat}_{\text{Ben}}}$	9.34E+08	2.40E+08	1.20E+09
$\text{As}_{\text{Mat}_{\text{Ben}}}$	9.34E+08	2.40E+08	1.20E+09
$\text{dem}_{\text{Mark}_1}$	4.89E+07	9.78E+06	8.80E+07
$\text{dem}_{\text{Mark}_2}$	3.98E+07	7.96E+06	7.16E+07
$\text{dem}_{\text{Mark}_3}$	6.41E+07	1.28E+07	1.15E+08
$\text{dem}_{\text{Mark}_4}$	8.09E+07	1.62E+07	1.45E+08
CostEmission_0	3.24E-02	6.49E-03	5.84E-02
$\text{Price}_{\text{Mark}_1}$	1.67E+00	3.35E-01	3.01E+00
$\text{Price}_{\text{Mark}_2}$	1.67E+00	3.35E-01	3.01E+00
$\text{Price}_{\text{Mark}_3}$	1.67E+00	3.35E-01	3.01E+00
$\text{Price}_{\text{Mark}_4}$	1.67E+00	3.35E-01	3.01E+00
PriceEmission_0	3.24E-02	6.49E-03	5.84E-02
$\text{TTRC}_{\text{Mat}_{\text{But}}}$	4.25E-05	8.51E-06	7.65E-05
$\text{TTRC}_{\text{Mat}_{\text{Ben}}}$	2.99E-05	5.98E-06	5.38E-05
$\text{TTRC}_{\text{Mat}_{\text{MA}}}$	2.75E-05	5.51E-06	4.95E-05
RR_0	2.50E-01	5.01E-02	4.50E-01
$\text{g1}_{\text{Mat}_{\text{Elec}}}$	5.74E-02	1.15E-02	1.03E-01
$\text{g1}_{\text{Mat}_{\text{Elec}}}$	6.39E-02	1.28E-02	1.15E-01
$\text{g1}_{\text{Mat}_{\text{But}}}$	1.71E-01	3.43E-02	3.08E-01
$\text{g1}_{\text{Mat}_{\text{But}}}$	2.14E-01	4.29E-02	3.85E-01
$\text{g1}_{\text{Mat}_{\text{Ben}}}$	2.24E-01	4.48E-02	4.03E-01
$\text{g1}_{\text{Mat}_{\text{Ben}}}$	2.80E-01	5.60E-02	5.04E-01

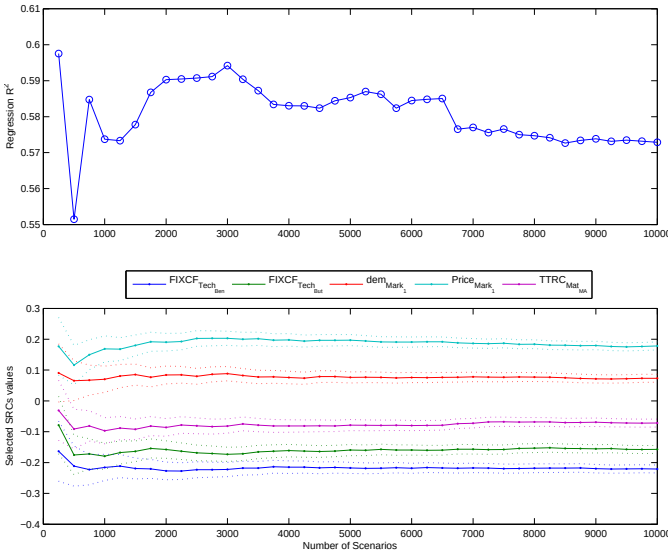


Figure 7.12: R^2_{NPV} regression values and selected NPV SRCs change with number of scenarios; dotted lines show the 95% confidence interval for the SRCs.

Regression based metrics analysis In order to determine the number of scenarios, the algorithm proposed by in section 3.2.2, was used. In this case 10000 scenarios have been generated and run to check for the minimum number of possible scenarios. The results are shown in Fig. 7.12. Regression based metrics (SRCs), and the regression coefficient of multiple determination $R^2_{y_l}$ value (which provides a measure of the extent to which the regression model can match the observed data), were used to analyse the results. As output variable y_l, the NPV was selected, it can be seen that after 4000 scenarios the R^2_{NPV} value, (see Eq. 3.26), remains around 0.58. In the case of the NPV's SRCs and their confidence interval values calculated for some significant input variables ($FIXCF_{Tech_{Ben}}$, $FIXCF_{Tech_{But}}$, $Price_{Mark_1}$, dem_{Mark_1} and $TTRC_{Mat_{MA}}$) remain almost unchanged after 2000 scenarios. Model input-output regressions were calculated using MATLAB's statistical package function regress.

Model results are summarised in Table 7.15. It can be seen that from the 10000 scenarios run, 790 of them result in null SC solutions, meaning that the best solution is not to install any technology nor to produce MA. In this sense the technology that gets installed more times is the benzene based tech (5079 scenarios), consequently it shows higher mean value for the NPV compared to the mean value for the butane based SC (3191 scenarios).

This trend was an expected result given that the benzene based SC was found to be more economically attractive compared to the one based on butane (see section 7.3.4 and Table 7.7), and given that in this case NPV is being optimised, more scenario runs with a benzene based SC as a result are expected to be found. With regards to the SCs that use both technologies, these were the SC structures that were found least times (940 scenarios), their NPV mean value is higher than the butane or benzene based technology a similar trend is found while looking at the total MA produced and total MA satisfied demand, this issue could be due to the combination of scenarios where MA demands and sale prices are higher, making profitable to install more than one technology (see bottom plots of Fig. 7.13). Moreover in the case of the top left plot in Fig. 7.13, it can be clearly seen that the inequality allowing the model not to cope with the full demand is satisfied in some cases, while in some others it is not active.

Table 7.15: Model output results mean and standard deviation values for different SC structures found in the problem

Model results	All		Non zero		Benzene tech only		Butane tech only		Both techs	
No. scenarios	*10000*		*9210*		*5079*		*3191*		*940*	
Output variable	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
NPV	3.5E+08	3.5E+08	3.8E+08	3.5E+08	3.8E+08	3.6E+08	3.4E+08	3.1E+08	5.1E+08	4.2E+08
$ImpactSC$	1.7E+06	2.0E+06	1.8E+06	2.0E+06	1.8E+06	2.0E+06	1.5E+06	1.6E+06	2.9E+06	3.0E+06
$installedCapTech_{Ben}$	2.7E+08	5.0E+08	2.9E+08	5.2E+08	4.5E+08	5.9E+08	—	—	4.0E+08	5.5E+08
$installedCapTech_{But}$	1.5E+08	3.1E+08	1.6E+08	3.2E+08	—	—	3.6E+08	4.1E+08	3.2E+08	3.7E+08
$totProduced_{MA}$	1.3E+09	1.5E+09	1.4E+09	1.6E+09	1.3E+09	1.5E+09	1.2E+09	1.2E+09	2.3E+09	2.4E+09
$totSatifiedDemand_{MA}$	6.6E+08	3.8E+08	7.2E+08	3.5E+08	7.1E+08	3.4E+08	6.8E+08	3.4E+08	9.1E+08	3.2E+08
$totalPurch_{Elec}$	9.5E+08	1.2E+09	1.0E+09	1.2E+09	7.2E+08	8.1E+08	1.3E+09	1.3E+09	1.8E+09	1.8E+09
$totalPurch_{But}$	4.7E+08	9.5E+08	5.1E+08	9.8E+08	—	—	1.2E+09	1.2E+09	1.0E+09	1.2E+09
$totalPurch_{Ben}$	8.2E+08	1.4E+09	8.9E+08	1.4E+09	1.4E+09	1.5E+09	—	—	1.3E+09	1.7E+09

Table 7.16: Variation of $R^2_{y_l}$ coefficients of regression depending on the selected scenarios.

Output variable	All		Non zero		Benzene tech only		Butane tech only		Both techs	
Rank Transformation	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes
NPV	0.573	0.701	0.558	0.666	0.639	0.746	0.680	0.735	0.620	0.756
$ImpactSC$	0.440	0.599	0.435	0.566	0.508	0.663	0.552	0.675	0.575	0.704
$installedCapTech_{Ben}$	0.480	0.682	0.491	0.698	0.553	0.618	—	—	0.605	0.566
$installedCapTech_{But}$	0.459	0.642	0.472	0.674	—	—	0.600	0.628	0.605	0.597
$installedCapTech_{Tr_1}$	0.012	0.011	0.012	0.012	0.019	0.019	0.017	0.016	0.049	0.049
$installedCapTech_{Tr_2}$	0.354	0.512	0.333	0.451	0.384	0.540	0.397	0.544	0.462	0.612
$totProduced_{MA}$	0.441	0.576	0.432	0.521	0.504	0.625	0.547	0.634	0.589	0.649
$totSatifiedDemand_{MA}$	0.677	0.660	0.635	0.608	0.654	0.626	0.659	0.628	0.667	0.578
$totalPurch_{Elec}$	0.434	0.543	0.427	0.491	0.504	0.625	0.547	0.634	0.581	0.645
$totalPurch_{But}$	0.459	0.644	0.471	0.675	—	—	0.547	0.634	0.530	0.508
$totalPurch_{Ben}$	0.477	0.682	0.483	0.696	0.504	0.625	—	—	0.561	0.529

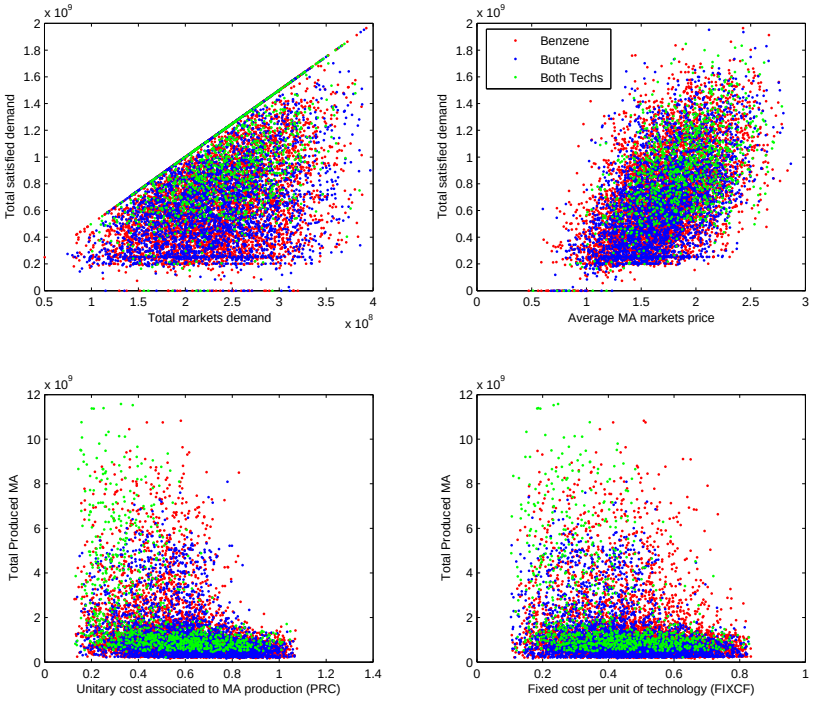


Figure 7.13: Scatter plot of scenario results coloured by SC installed technology.

Given that several SC parameters depend on the technology/ies that has/have been installed, an analysis on the filtered results was done. The regression results are summarised in Table 7.16, which also contains the $R^2_{y_l}$ metric calculated for the ranked transform. It is found that the $R^2_{y_l}$ coefficient of regression is higher for the case of SC structure dependent output parameters, such is the case of: $installedCapTech_{Ben}$, $installedCapTech_{But}$, $totalPurch_{But}$ and $totalPurch_{Ben}$. Although for the other output variables different trends are found. In the case of the ranked transform metrics, the $R^2_{y_l}$ value increases in most cases, showing that a monotonic behaviour is the prevalent one if a single technology is selected, as this monotonic behaviour disappears when both technologies are installed.

In order to find out which input variables affect the most to the output variables the regression metrics proposed in Eqs. (3.27) and (3.28) were calculated. The SRCs for all input variables for the selected model output variables are shown in Table 7.17. It can be seen that the model outputs are dependant on some of the model inputs and that many model inputs changes do not have a significant impact on the model output response, this issue can also be seen from the PCCs results which are summarised in Table 7.18. Please note that this results are based on the 10000 scenarios sample with no SC structure classification.

From Tables 7.17 and 7.18 it can be seen that variables that represent the:

- investment required to establish a processing facility in location f in period t, $INVS$
- investment required per unit of technology j capacity increased at facility f in period t: $Price^J_{jft}$
- maximum availability of raw material s in period t in location f: A_{sft},
- emissions right cost in period t: $Cost^{co_2}_t$
- emissions right price in period t: $Price^{co_2}_t$

do not affect significantly the values of the model outputs, given that SRCs are all near zero and their 95% confidence interval (CI) contains the zero value. Similarly their PCC value is

also close to zero. However, in the case of the following variables certain information can be withdrawn.

- fixed cost per unit of technology j capacity increase at location f in period t, ($FCFJ_{jft}$, $FIXCF(j,fc)$) it is found that an increase in these variables render lower NPVs, and lower overall SC environmental impacts. Moreover it can also be seen that increases on the price of one technology render an increase in the installed capacity of the other, and in the consumption of the other raw material. Increases of this variable also render a lower total production of MA.
- unitary cost associated with task i performed in equipment j from location f and payable to external supplier e (τ^{utl}_{ijfe}, $PRC(i,j,fc)$), it is found that increases of these variables render lower NPV and overall environmental impacts. The rising of the cost of one technology renders an increase of the installed capacity of the other, and consequently an increase of the other's technologies raw materials consumption.
- unitary cost associated with handling the inventory of material s in location f and payable to external supplier e, (τ^{ut2}_{sfe}, $IHC(s,t1p)$), surprisingly in the case of these variables associated to raw materials (butane or benzene), no effect is shown on NPV or overall environmental impact, however increases of these variables render lower total installed capacities and purchases of the associated raw materials.
- demand of product s at market f in period t, (Dem_{sft}, $dem(s,fc,t)$), no differences are found between markets, and all four markets produce similar results. Any increases in the MA demand generates higher NPV and no appreciable effect is found in the overall environmental impact. Also, the total satisfied demand is found to be higher when the product demand is increased.
- sales price of product s at market f in period t, ($Price_{sft}$, $Price(s,m,t1p)$), in this case increases of these variables provide a higher NPV, higher overall environmental impact and positive variations in all output variables (i.e., all selected output variables increase), due to the requirement of higher production rates the consumption of raw materials increases.
- unitary transportation costs from of transporting material s ($\rho^{tr}_{eff'}$, $TRC_{ijfcfc'}$, $TTRC^{tr}_{s}$), surprisingly, an increase of these values do not affect NPV nor whole SC environmental impact, but they do affect negatively the installed production capacity of the technology that uses such raw material.
- discount rate ($rate$, RR), this variable affects the NPV value, if the return rate (RR) increases then NPV decreases; none of the other variables is changed by a change in its value.
- unitary cost of raw material s offered by external supplier e in period t (χ_{est}, $g1(s,fc,t1p)$), despite the low values obtained for the SRCs (the CI does not contains zero) and PCCs, these variables show a small impact on output variables such as installed capacities for the technologies associated to the supplied raw material, similarly the total amount of those raw materials change.

In order to assess quantitatively how much each of the model inputs affects to model outputs the step wise regression methodology proposed in Algorithm 3.2 is used. In this case different regressions are made combining different input variables for which most output variability is explained. However it should be noted that the former regression metrics explain only a certain part of each output model variability, i.e. they account only for the variability explained by the linear regression.

Table 7.19 shows the ranking of the most important model input variables in terms of each model output variable variability. Similar information can be seen in Fig. 7.14. Again, it can be seen that output variables are affected in different ways by input variables. $PRC(i,j,fc)$,

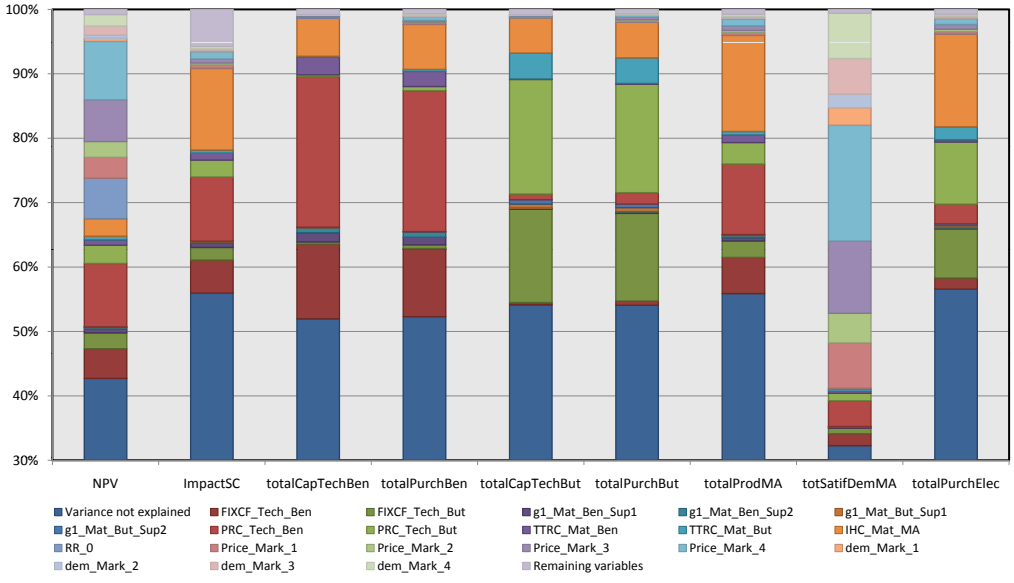


Figure 7.14: Amount of ouput variable variance explained by each input variable.

$FIXCF(j,fc)$, $IHC(s,t1p)$, $Price(s,m,t1p)$, $g1(s,fc,t1p)$ and $dem(s,fc,t)$, are found to significantly modify the value of most output model variables. Please note that all time dependence is not taken into account given that prices, costs and demands are considered to be constant along time.

Table 7.17: SRCs for most important model outputs considering all model input variables

Variable Name	NPV	ImpactSC	totProdMA	satifDemMA	totPurchBut	instTechBut	totPurchBen	instTechBen	totPurchElec
$FIXCF_{Tech_{Ben}}$	↘ -0.221	↘ -0.227	↘ -0.238	↘ -0.135	↗ 0.080	↗ 0.059	↓ -0.327	↓ -0.342	↘ -0.133
$FIXCF_{Tech_{But}}$	↘ -0.157	↘ -0.140	↘ -0.160	→ -0.093	↓ -0.365	↓ -0.377	↗ 0.077	↗ 0.059	↘ -0.274
$PRC_{Tech_{Ben}}$	↓ -0.306	↓ -0.317	↓ -0.331	↘ -0.201	↗ 0.132	↗ 0.092	↓ -0.469	↓ -0.484	↘ -0.176
$PRC_{Tech_{But}}$	↘ -0.165	↘ -0.161	↘ -0.181	→ -0.107	↓ -0.401	↓ -0.413	↗ 0.078	→ 0.050	↓ -0.305
$IHC_{Mat_{But}}$	→ -0.014	→ -0.011	→ -0.010	→ -0.009	→ -0.009	→ -0.008	→ -0.005	→ -0.003	→ -0.011
$IHC_{Mat_{Ben}}$	→ -0.006	→ 0.010	→ 0.011	→ -0.006	→ 0.004	→ 0.004	→ 0.010	→ 0.006	→ 0.010
$IHC_{Mat_{MA}}$	↘ -0.158	↓ -0.348	↓ -0.377	→ 0.035	↘ -0.231	↘ -0.230	↘ -0.264	↘ -0.243	↓ -0.368
dem_{Mark_1}	↗ 0.073	→ 0.037	→ 0.031	↗ 0.165	→ 0.019	→ 0.009	→ 0.022	→ 0.006	→ 0.030
dem_{Mark_2}	↗ 0.068	→ 0.030	→ 0.031	↗ 0.149	→ 0.029	→ 0.020	→ 0.015	→ 0.010	→ 0.035
dem_{Mark_3}	↗ 0.115	→ 0.041	→ 0.046	↗ 0.228	→ 0.026	→ 0.008	→ 0.034	→ 0.009	→ 0.044
dem_{Mark_4}	↗ 0.128	↗ 0.062	→ 0.058	↑ 0.263	→ 0.023	→ 0.009	→ 0.049	→ 0.023	→ 0.051
$Price_{Mark_1}$	↗ 0.178	↗ 0.073	↗ 0.069	↑ 0.261	→ 0.031	→ 0.016	→ 0.056	→ 0.034	↗ 0.062
$Price_{Mark_2}$	↗ 0.156	→ 0.053	→ 0.053	↗ 0.216	→ 0.049	→ 0.034	→ 0.025	→ 0.006	↗ 0.059
$Price_{Mark_3}$	↑ 0.252	↗ 0.079	↗ 0.083	↑ 0.337	↗ 0.063	→ 0.036	→ 0.049	→ 0.026	↗ 0.086
$Price_{Mark_4}$	↑ 0.295	↗ 0.107	↗ 0.103	↑ 0.419	→ 0.055	→ 0.037	↗ 0.078	→ 0.033	↗ 0.097
$TTRC_{Mat_{But}}$	→ -0.079	→ -0.069	→ -0.074	→ -0.060	↘ -0.202	↘ -0.204	↗ 0.059	→ 0.039	↘ -0.141
$TTRC_{Mat_{Ben}}$	→ -0.091	→ -0.105	→ -0.108	→ -0.056	→ 0.037	→ 0.029	↘ -0.149	↘ -0.161	→ -0.060
$TTRC_{Mat_{MA}}$	→ -0.072	→ -0.026	→ -0.016	→ -0.070	→ -0.030	→ -0.019	→ 0.003	→ 0.011	→ -0.024
RR_0	↘ -0.252	→ 0.005	→ 0.005	→ -0.005	→ 0.017	→ -0.002	→ -0.006	→ -0.047	→ 0.011
$g1_{Mat_{Elec}}$	→ -0.034	→ -0.028	→ -0.031	→ -0.016	→ -0.022	→ -0.023	→ -0.019	→ -0.025	→ -0.031
$g1_{Mat_{Elec}}$	→ -0.017	→ -0.025	→ -0.025	→ -0.018	→ -0.025	→ -0.025	→ -0.010	→ -0.008	→ -0.029
$g1_{Mat_{But}}$	→ -0.023	→ -0.038	→ -0.030	→ -0.016	→ -0.080	→ -0.081	→ 0.022	→ 0.020	→ -0.057
$g1_{Mat_{But}}$	→ -0.023	→ -0.006	→ -0.027	→ -0.018	→ -0.073	→ -0.080	→ 0.021	→ 0.026	→ -0.051
$g1_{Mat_{Ben}}$	→ -0.075	→ -0.083	→ -0.072	→ -0.040	→ 0.040	→ 0.030	→ -0.110	→ -0.120	→ -0.033
$g1_{Mat_{Ben}}$	→ -0.051	→ -0.041	→ -0.060	→ -0.022	→ 0.030	→ 0.026	→ -0.089	→ -0.088	→ -0.029

Table 7.18: PCCs for most important model outputs considering all model input variables

Variable Name	NPV	ImpactSC	totProdMA	satifDemMA	totPurchBut	instTechBut	totPurchBen	instTechBen	totPurchElec
$FIXCF_{Tech_{Ben}}$	**0.319**	0.290	**0.302**	0.231	0.108	0.080	**0.411**	**0.428**	0.173
$FIXCF_{Tech_{But}}$	0.234	0.184	0.209	0.162	**0.444**	**0.455**	0.106	0.081	**0.342**
$PRC_{Tech_{Ben}}$	**0.423**	**0.390**	**0.405**	**0.334**	0.176	0.125	**0.544**	**0.557**	0.227
$PRC_{Tech_{But}}$	0.244	0.210	0.235	0.185	**0.478**	**0.489**	0.107	0.069	**0.375**
$IHC_{Mat_{But}}$	0.021	0.014	0.013	0.016	0.012	0.011	0.006	0.004	0.015
$IHC_{Mat_{Ben}}$	0.009	0.014	0.015	0.011	0.006	0.006	0.014	0.009	0.013
$IHC_{Mat_{MA}}$	0.235	**0.421**	**0.449**	0.061	**0.299**	**0.298**	**0.343**	**0.319**	**0.439**
dem_{Mark_1}	0.111	0.050	0.042	0.278	0.025	0.012	0.031	0.008	0.040
dem_{Mark_2}	0.103	0.040	0.041	0.253	0.039	0.027	0.020	0.014	0.046
dem_{Mark_3}	0.173	0.055	0.062	**0.371**	0.036	0.011	0.047	0.013	0.059
dem_{Mark_4}	0.192	0.082	0.077	**0.419**	0.032	0.012	0.067	0.032	0.068
$Price_{Mark_1}$	0.263	0.098	0.091	**0.417**	0.041	0.021	0.078	0.047	0.082
$Price_{Mark_2}$	0.232	0.070	0.070	**0.354**	0.066	0.046	0.035	0.009	0.078
$Price_{Mark_3}$	**0.360**	0.105	0.110	**0.509**	0.085	0.049	0.067	0.036	0.114
$Price_{Mark_4}$	**0.411**	0.141	0.136	**0.593**	0.074	0.050	0.106	0.045	0.127
$TTRC_{Mat_{But}}$	0.120	0.092	0.098	0.105	0.264	0.267	0.081	0.054	0.184
$TTRC_{Mat_{Ben}}$	0.138	0.138	0.143	0.098	0.050	0.040	0.202	0.218	0.080
$TTRC_{Mat_{MA}}$	0.109	0.035	0.021	0.122	0.040	0.026	0.005	0.015	0.032
RR_0	**0.360**	0.007	0.007	0.009	0.023	0.002	0.009	0.064	0.015
$g1_{Mat_{Elec}}$	0.052	0.037	0.041	0.028	0.030	0.032	0.027	0.034	0.041
$g1_{Mat_{Elec}}$	0.026	0.033	0.033	0.031	0.035	0.035	0.014	0.012	0.038
$g1_{Mat_{But}}$	0.035	0.051	0.040	0.028	0.108	0.109	0.031	0.028	0.075
$g1_{Mat_{But}}$	0.035	0.009	0.036	0.032	0.098	0.108	0.029	0.036	0.068
$g1_{Mat_{Ben}}$	0.114	0.110	0.096	0.070	0.054	0.041	0.150	0.164	0.044
$g1_{Mat_{Ben}}$	0.077	0.054	0.080	0.039	0.041	0.036	0.122	0.121	0.038

Table 7.19: Most important input variables ranking based on SRCs values for different model output, columns show variable ranking of importance and variables variance explained

Variable	NPV		ImpactSC		$totProd_{MA}$		$totDem_{MA}$		$totPur_{But}$		$totPur_{Ben}$		$totTech_{But}$		$totTech_{Ben}$	
	Rank	Var	Rank	Var	Rank	Var	Rank	Var	Rank	Var	Rank	Var	Rank	Var	Rank	Var
Not Explained	—	0.47	—	0.62	—	0.57	—	0.50	—	0.55	—	0.53	—	0.54	—	0.52
$FIXCF_{Tech_{Ben}}$	**5**	0.05	**3**	0.05	**3**	0.06	**10**	0.02	**6**	0.01	**2**	0.11	**8**	0.00	**2**	0.12
$FIXCF_{Tech_{But}}$	**10**	0.02	**6**	0.02	**5**	0.03	12	0.01	**2**	0.14	**9**	0.01	**2**	0.14	**7**	0.00
$PRC_{Tech_{Ben}}$	**1**	0.10	**2**	0.10	**2**	0.11	**7**	0.04	**5**	0.02	**1**	0.22	**5**	0.01	**1**	0.23
$PRC_{Tech_{But}}$	**7**	0.03	**4**	0.03	**4**	0.03	11	0.01	**1**	0.17	**7**	0.01	**1**	0.18	**9**	0.00
$IHC_{Mat_{MA}}$	**8**	0.03	**1**	0.13	**1**	0.15	17	0.00	**3**	0.06	**3**	0.07	**3**	0.06	**3**	0.06
$As_{Mat_{Elec}}$	25	0.00	23	0.00	22	0.00	32	0.00	13	0.00	33	0.00	**10**	0.00	20	0.00
$As_{Mat_{Elec}}$	40	0.00	22	0.00	17	0.00	34	0.00	15	0.00	22	0.00	**9**	0.00	15	0.00
$As_{Mat_{Ben}}$	23	0.00	17	0.00	16	0.00	39	0.00	25	0.00	**10**	0.00	19	0.00	**8**	0.00
$Price_{Mark_1}$	**6**	0.03	13	0.01	11	0.00	**4**	0.07	16	0.00	12	0.00	23	0.00	13	0.00
$Price_{Mark_2}$	**9**	0.02	16	0.00	14	0.00	**6**	0.05	11	0.00	17	0.00	13	0.00	34	0.00
$Price_{Mark_3}$	**3**	0.06	12	0.01	**8**	0.01	**2**	0.11	**9**	0.00	14	0.00	12	0.00	16	0.00
$Price_{Mark_4}$	**2**	0.09	**9**	0.01	**7**	0.01	**1**	0.18	**10**	0.00	**8**	0.01	11	0.00	14	0.00
$TTRC_{Mat_{But}}$	15	0.01	14	0.00	**9**	0.01	14	0.00	**4**	0.04	11	0.00	**4**	0.04	12	0.00
$TTRC_{Mat_{Ben}}$	13	0.01	**10**	0.01	**6**	0.01	15	0.00	14	0.00	**4**	0.02	15	0.00	**4**	0.03
RR_0	**4**	0.06	37	0.00	38	0.00	30	0.00	28	0.00	31	0.00	40	0.00	**10**	0.00
$gl_{Mat_{But}}$	22	0.00	21	0.00	21	0.00	22	0.00	**7**	0.01	19	0.00	**7**	0.01	21	0.00
$gl_{Mat_{But}}$	21	0.00	34	0.00	23	0.00	20	0.00	**8**	0.01	20	0.00	**6**	0.01	18	0.00
$gl_{Mat_{Ben}}$	14	0.01	11	0.01	**10**	0.00	16	0.00	12	0.00	**5**	0.01	14	0.00	**5**	0.01
$gl_{Mat_{Ben}}$	19	0.00	19	0.00	12	0.00	18	0.00	17	0.00	**6**	0.01	16	0.00	**6**	0.01

7.5 Interpretation

This chapter presented an approach for designing and planning environmental friendly and profitable SC. The model consisted of a multi-period MILP that accounts for the multi-objective optimisation of economic and environmental metrics. The model considered the long-term strategic decisions (e.g. installation of plants, selection of suppliers, manufacturing sites, and distribution centres) with the mid-term planning for SCs. Each end-point damage categories was considered as objective function in order to avoid the subjectivity associated to their aggregation into an overall environmental impact indicator, showing the various SC possibilities obtained for each indicator. The Impact2002+ metric was adopted as a measure of overall environmental impact. Moreover, joint consideration of end point damages and trading schemes enables the approach proposed for supporting (i) the assessment of current regulatory policies and (ii) the definition of more adequate policy parameters (e.g. free emissions allowance cap for each industry, emissions trading price, subsidies).

A maleic anhydride SC case study is presented where two potential technologies are available. Two problems were solved, a first approach that did not consider a CO_2 trading scheme and a second one that took it into account. It has been shown the possibility of tackling such problem with ease. A SC for MA production based on butane was found to be more environmentally friendly than that one based on benzene. In this sense the current model allowed for possible selection between optimal solutions obtained. Most of works related to SC and environmental issues consider a fixed production/demand, it was demonstrated that such constraint leads to dominated solutions. By allowing unsatisfied demand, the actual Pareto curve is obtained.

Raw material production was found to be the most important contributor to overall environmental impact, while transportation and electricity consumption were the least important. This clearly shows that the current model allows for selection of improvement actions and the necessity of an approach with visibility of the whole SC. The environmental impact potential significant dependence on purchase decisions which cannot be assessed without a SC approach has been shown. Additionally, it was determined by using the optimisation model that the production process was the activity that emits most of the CO_2.

Optimisation using end-point metrics showed that the use of overall weighted environmental metrics hinder the trade offs that are inherent to the SC impacts. Each optimisation gave a different SC structure. Different subsidies were studied aiming at making the most environmental friendly SC more attractive in economic terms. It has been found that a subsidy based on the production amount is more convenient than that one based on transport considerations.

Additionally, the model helped in discovering that the CO_2 trading scheme will favour benzene based over butane based production. The results obtained for this specific case study question the suitability of a single CO_2 trading scheme applicability to every industry sector: different regulatory schemes may be required in different industrial scenarios. Current regulations merely consider climate change damage, which certainly is a very important factor, however other aspects such as human health, ecosystem quality and abiotic resources consumption should be also considered so that effective industrial changes regarding the environment are induced.

The utilisation of multiobjective optimisation for each damage category shows to be helpful at discovering in-sights regarding how different policies will affect SC strategic and tactical decisions.

It is important to point out that environmental metrics for the interpretation of LCIs involve determining aggregated measures. Normalising factors are used to determine the weight of each end point metric (climate change, human health, resources depletion, ecosystem

quality) in the overall measure which may favour different solutions. When this type of analysis is performed for the selection among different SC alternatives a careful sensitivity/uncertainty analysis related to the application of these normalising factors is required. Such analysis can be done by using a multi-criteria optimisation that accounts for end-point damage categories as presented in this chapter. In the case study presented each end point metric provides with a different SC design associated to different planning decisions.

Besides environmental impact metrics, this chapter considered the use of economic metrics (NPV), showing different SC structures depending on the economic model parameters (interest rate), while no apparent changes are shown in the case of the consideration of TCA/FCA considerations.

One of the main achievements of this case study is not building and solving a complex SC-environmental model, but emphasising the potential dangers associated to the deployment of CO_2 emission related policies in isolation from other pollution related issues. Also, it has been shown how this type of models can be used to determine subsidy policies in order to actually drive industry towards more environmental friendly practises.

Chapter nomenclature

Table 7.20: List of indices and variables used in this chapter.

Name	Meaning
Indices	
e	suppliers
f, f'	facility locations
i	tasks
j	equipment technology
s	materials (states)
t, t'	planning periods
a	mid point environmental impact categories
g	end point environmental impact categories
Sets	
A_g	set of midpoint environmental interventions that are combined into endpoint damage factors g
E_{rm}	set of suppliers e that provide raw materials
$\hat{E}_{prod}$	set of suppliers e that provide production services
$\hat{E}_{tr}$	set of suppliers e that provide transportation services
F_e	set of locations f where supplier e is placed
FP	set of materials s that are final products
I_j	set of tasks i that can be performed in technology j
$\hat{J}_e$	technology j that is available at supplier e
$\bar{J}_f$	technology j that can be installed at location f
J_i	technologies that can perform task i
Mkt	set of market locations
RM	set of materials s that are raw materials
Sup	set of supplier locations
T_L	set of periods when the emissions trading is executed
T_s	set of tasks producing material s
$\bar{T}_s$	set of tasks consuming material s
Tr	set of distribution tasks
Parameters	
A_{sft}	maximum availability of raw material s in period t in location f
Dem_{sft}	demand of product s at market f in period t
$Cost_t^{co_2}$	emissions right cost in period t
$distance_{ff'}$	distance from location f to location f'
$FCFJ_{jft}$	fixed cost per unit of technology j capacity at location f in period t
I_{ft}^J	investment required to establish a processing facility in location f in period t
$MaxCO_{2t}$	free allowance emissions cap at period t
$NormF_g$	normalising factor of damage category g
$Price_{sft}$	price of product s at market f in period t
$Price_t^{co_2}$	emissions right price in period t
$Price_{jft}^J$	investment required per unit of technology j capacity increased at facility f in period t

Continued on next page

Table 7.20 – continued from previous page

Name	Meaning
$rate$	discount rate
α_{sij}	mass fraction of task i for production of material s in equipment j
$\bar{\alpha}_{sij}$	mass fraction of task i for consumption of material s in equipment j
β_{jf}	minimum utilisation rate of technology j capacity that is allowed at location f
ζ_{ag}	g end-point damage characterisation factor for environmental intervention a
$\theta_{ijff'}$	capacity utilisation rate of technology j by task i whose origin is location f and destination location f'
$\rho^{tr}_{eff't}$	unitary transportation costs from location f to location f' during period t
τ^{ut1}_{ijfet}	unitary cost associated with task i performed in equipment j from location f and payable to external supplier e during period t
τ^{ut2}_{sfet}	unitary cost associated with handling the inventory of material s in location f and payable to external supplier e during period t
χ_{est}	unitary cost of raw material s offered by external supplier e in period t
$\psi_{ijff'a}$	a environmental category impact CF for task i performed using technology j receiving materials from node f and delivering it at node f'
ψ^{T}_{ija}	a environmental category impact CF for the transportation of a mass unit of material over a length unit

Binary Variables

JB^{l}_{ft}	1 if a processing site at location f is established in period t, 0 otherwise
V_{jft}	1 if technology j is installed at location f in period t, 0 otherwise

Continuous Variables

$Buy^{co_2}_{t}$	amount of emissions extra rights bought in period t
$DamC_{gft}$	normalised endpoint damage g for location f in period t
$DamC^{SC}_{g}$	normalised endpoint damage g along the whole SC
$EPurch_{et}$	economic value of purchases executed in period t to supplier e
$ESales_{t}$	economic value of sales executed in period t
$FAsset_{t}$	investment on fixed assets in period t
$FCost_{t}$	fixed cost in period t
$Fjft$	total capacity of technology j during period t at location f
FE_{jft}	capacity increment of technology j at location f during period t
IC_{aft}	midpoint a environmental impact associated to site f which rises from activities in period t
$Impact^{2002}_{f}$	total environmental impact for site f
$Impact^{2002}_{overall}$	total environmental impact for the whole SC
$Net^{co_2}_{t}$	Net income due to emissions trading in period t
NPV	net present value
$P_{ijff't}$	activity magnitude of task i in equipment j in period t whose origin is location f and destination location f'
$Profit_{t}$	profit achieved in period t
$Purch^{pr}_{et}$	amount of money payable to supplier e in period t associated with production activities
$Purch^{rm}_{et}$	amount of money payable to supplier e in period t associated with consumption of raw materials
$Purch^{tr}_{et}$	amount of money payable to supplier e in period t associated with consumption of transport services
$Sales^{co_2}_{t}$	amount of emissions rights sold in period t
$Sales_{sff't}$	amount of product s sold from location f in market f' in period t
S_{sft}	amount of stock of material s at location f in period t

Superscripts

L	lower bound
U	upper bound

Part IV

Conclusion

Chapter 8

Thesis conclusion

The main objective of this thesis is aimed at proposing a consistent framework for decision support of sustainable design. The approach presented is based on the combined use of different methods and accompanying tools encompassing: process simulation, general modelling, LCt principles and sampling techniques into a single framework that takes advantage of their complementary strengths. Besides, this model-based framework can be applied to decision making related to the design, operation and planning of chemical processes.

Within this strategy, models of different type are used to generate reliable data to carry out an accurate sustainability assessment of alternative process opportunities. Local and global sensitivity analysis techniques are employed to test these models and check their validity regarding the reality that they represent. LCt concepts, via the use of LCA, are applied to holistically evaluate different process alternatives that could be implemented to achieve sustainability improvements. This holistic approach is required because of the inherent multiobjective characteristics of sustainability considerations. With this purpose, different metrics are proposed to tackle with each one of the possible sustainability dimensions. In spite of the large effort required in building, testing and validating appropriate models and metrics, the use of the methodology proposed allows for improved reproducibility and traceability of results obtained.

This thesis contributions can be seen in three aspects related to (i) the structure: models and interfaces, (ii) the application procedure and (iii) the framework application.

8.1 Software and models

Software The whole framework is materialised in a set of software tools that allows for connecting and applying the different models as required. The following software components have been developed:

- a toolbox for the connection of Matlab and AspenPlus.
- a toolbox based on ANNs for the connection of AspenHysys and AspenPlus.
- a toolbox for calculating uncertainty metrics based on regression and variance decomposition.

- a set of auxiliary methods for tackling with Pareto frontier generation and MCDA using TOPSIS.
- a set of methods for calculating sustainability metrics.

The first two items represent different approaches developed in this thesis that allow for different software connection. While the last three are Matlab based toolboxes for analysing model results.

Models Each one of the case studies presented required model building and validation. In the case of continuous process simulation most of the unit operation modelled use already developed models from the AspenHysys or AspenPlus model library. However, its overall connectivity into a flowsheet, i.e. its behaviour as the process they represent is novel. Moreover, in the case of the IGCC case, a set of unit operations behaviour could not be addressed with currently available models and new models were developed.

Regarding emission and chemical environmental fate models, the phosphoric acid case study presents a model for emissions estimation based on simulation results and chemical fate. The other case studies assume a simpler approach by using the corresponding characterisation factor. In all cases the estimation of environmental metrics is done using the Ecoinvent database results via SimaPro. Economic metrics such as TAC or NPV are calculated using Matlab.

Regarding the scheduling and supply chain decision models developed in GAMS, they are built using state of the art techniques and considerations. Its novelty value lies in the use of sustainability considerations and its connectivity to other tools, which allows for its use as servers of a client application.

8.2 Procedure proposed

Chapter 4 presents the procedure proposed for the use of the developed tools as a whole framework. The procedure consists of four steps: (i) goal definition, (ii) model building and data gathering, (iii) metrics calculation and (iv) decision making aid, see section 4.2.3.

Due to the consideration of different metrics (in steps iii and iv), the decision maker has to elicit his/her preferences in order to select some alternative. These alternatives are in general a part of a set, that can be further pruned by analysing the dominance of some alternatives over the others, thus allowing to generate the Pareto front of alternatives. While many of the currently used methodologies stop at this point, the framework proposed encourages the use of different heuristics, like TOPSIS which uses the concept of utopian and nadir points, to generate compromise alternatives. These solutions are balanced in terms of relative distances to the utopian and nadir reference points, of the Pareto frontier. The approach proposed has to be thought as one complementary to any objective function weighting scheme and any other MCDA technique can be also applied.

While the former four steps can be traced back to a LCA, the use of: non linear models, optimisation and Pareto considerations goes above the requirements of a typical LCA. The procedure proposed is aimed at the design of novel processes, thus its capabilities for synthesis and sustainability assessment of alternatives are also novel.

8.3 Framework application

Different case studies are selected to test the different capabilities of the framework isolated and in general. For the case of process design, the focus is set on two different production

ranges commodities: bulk chemicals of the fertiliser industry using the phosphoric acid (PA) production as example and speciality chemicals in the cosmetics sector by analysing production routes for isopropyl myristate (IMA). Not only chemical products have been analysed but also electricity generation, by considering the operating decisions in a IGCC based power plant. In these case studies, the system boundary does not includes the product use and disposal phases, because of the wide variety of product uses and its commodity nature. However, the inclusion of those phases can be done, given the modular approach adopted. In this respect, the requisites are to generate models which represent those phases and use these models results together with the currently developed ones.

The framework is also applied to the case of operating decisions: a polymer fibre production plant is analysed. This case has been selected due to the products requirements in terms of production sequence, which allows for introducing sequence dependent considerations, under sustainability criteria.

Lastly the framework is applied to the case of strategic and planning decisions, where the case study used represents the possible implementation of a international maleic anhydride production SC. This case is selected due to the absence of analysis performed in the chemicals additives sector and focused on the analysis of possible economic instruments to drive environmental friendly production.

In the case of scheduling and strategic decisions, the inputs required by the high level modelling that is used comes from the literature. However, these inputs could have been provided by lower level models similar to the ones used in the case of process design.

Continuous process design In these cases, discussed in chapter 5, the framework applied considers the use of commercial process simulation in tandem with Matlab and Simapro for the calculation of environmental and/or economic metrics. The cases studied encompass:

1. design alternatives for a WWT phosphoric acid production facility (section 5.1),
2. alternative feedstock changes in an IGCC power plant (section 5.2), and
3. the optimisation of the production of isopropyl myristate using reactive distillation (section 5.3).

In each case, emission modeling is emphasised and the study of how process conditions affect them is performed. While in the PA case emission modelling required of an extra modelling layer, in the other case studies a more simple approach is used, and emission is considered into a single environmental compartment.

In all cases, the use of process simulation helps in generating reliable data regarding process environmental and economic interventions, (see sections 5.1.2, 5.2.2 and 5.3.2). Please note that these interventions would have not been available otherwise, because they were not measured previously or were based on un-reconciled information. Hence the use of a model is necessary for generating them with the accuracy required by the case study in question. Process simulation also allows for considering literature and industrial data on a common ground. However, it has to be emphasised that the effort put in model building becomes also large.

The methodology proposed is able to identify the main sources of impact on the sustainability dimensions considered. It also helps to check the performance of the different process alternatives in terms of the different indicators, which in all cases include environmental indicators, and economic or efficiency metrics in the last two, hence providing valuable insights for decision making. Namely, the framework allows for: (i) identifying most important sources of environmental impact, (ii) possible efficiency trade offs regarding raw materials and (iii) highest cost items, as shown in sections 5.1.3, 5.2.3 and 5.3.3.

Regarding case (1), it is found, by the use of contribution analysis applied to the considered processing options, that for some mid point categories, major impact comes from the production echelon while for others, most of the impact rises from upstream echelons in the production of raw materials. This result clearly separates possible new design effort in two possible routes: either production echelon retrofit, aiming at minimising consumption of most impacting raw materials or further improvement of abatement systems; or upstream issues by focusing attention on operational considerations of possible raw material substitutes with possible lower environmental impact.

In case (2), electricity production has been shown to be heavily influenced on the raw material being used. More importantly, a clear trade-off between efficiency and emissions generated during electricity production is found. Similarly to the previous case, the framework identifies the most important echelons related to environmental impact in the electricity production. Environmental impacts metrics are in clear favour of the use of natural gas instead of coal co-gasification, but also show that the co-gasification of biomass reduces the overall environmental impact. With regards to the use of coal or coke, it is found that the operation with coal is more environmentally friendly.

While the previous two case studies relied mostly on industrial data, the third case (3), is based solely on literature information. Consequently, the process and sustainability considerations models are of paramount importance, because they provide data regarding situations that have not been addressed before. Such data encompasses the bill of materials, utilities and emissions required for calculating economic and environmental metrics. Different unit operations considerations regarding their design and operation are analysed and the effect of decision upon them is measured. The former analysis renders different process designs that are feasible implementations. The Pareto curve shapes are found to be different when considering different pairs of KPIs. A compromise solution is provided, but it has been found that some variable's values have to be set based on other considerations, given that optimisation will render its value to bound.

Validation Given the paramount importance of the model's results, its validation is considered extensively along the case studies presented. Validation is performed at two steps during the framework's application, process model's input-output relations are studied during model building and data gathering step (ii). While process model outputs and metrics results are studied during metrics calculation in step (iii).

The last two case studies are validated, during steps (ii) and (iii), using local sensitivity analysis. In the IGCC case model outputs are compared to industrial available data, while in the last the model's overall behaviour is checked against expected behaviour, see sections 5.2.2.2 and 5.3.2.2.

In the PA case, model validation is done in higher detail by considering model's input uncertainty, and using a global sensitivity analysis (SA). The SA studies the model's input-output variable's relationship (see section 5.1.3.2) and they are carried out on the production-emission model and the environmental impact model separately.

- In the first case, key model variables are identified by the use of regression metrics, and the use of PCA and LDA helps in determining if model behaviour is dependant on process alternatives. For the case of the emissions estimations, they are found to be primarily related to the operating temperatures and pressures. This result, which could not have been obtained if no model is used, shows other of the framework benefits.
- The SA used for the environmental metrics results, shows that process-emissions uncertainty, modelled in the way proposed does not influence impact results in an appreciable manner, and that most of the uncertainty in results comes from background

information gathered from the LCI database. This is an expected result for impact categories determined by upstream echelons, however in the case of impacts mostly determined by the process operation itself, the uncertainty in the emission estimation is hindered by the uncertainty of inventories belonging to other echelons.

Results In all cases, none of the process alternatives under study or generated by optimisation scored best in all metrics applied. This situation is found related to environmental mid and end point, efficiency and economic metrics. This is a clear indication of the trade-offs presence between alternatives and metrics, and the necessity of using other insights based on the decision makers values to score and rank the process design alternatives. In the PA case the use of multivariate analysis helps in devising possible indicators correlation, thus reducing the number of metrics to be considered.

In the case of environmental endpoint metrics use, it is found that different alternatives are chosen depending on which end point metric is selected. This fact clearly points out the bias underlying anyone of them and consequently the need for the decision maker to fully understand which are the key aspects underlying each end point metric before blindly adhering to it. Moreover, it shows that a Pareto front approach is far more informative, given that the actual alternative trade-offs are exposed. Moreover, in this respect it is clearly shown the framework ease for dealing with different metrics calculation, based on the same underlying information (i.e. process sustainability interventions).

The former examples and points risen allows for clearly showing the framework capabilities regarding its application to the design of process plants.

Application to scheduling concerns The consideration of environmental impact as an additional objective in the optimisation of the scheduling problems, provokes a trade-off which can be studied rigorously using multiobjective optimisation. In the case of batch operation decisions, discussed in chapter 6, the framework considers the use of a scheduling model (coded using GAMS) coupled to Matlab and Simapro, for the calculation of LCIA metrics. Simapro allows for gathering the required LCI information, while GAMS solves the scheduling model considering the novel Pareto Front algorithm which is implemented in Matlab.

The generated Pareto frontiers provide the decision maker with highly valuable information about production schedule trade-offs. This information sheds light into production and sequencing relationships that may not be obvious. It is found in the case study proposed, that the impact related to batches production is higher than that between batches. This result guides new design considerations into the product recipe, for developing alternative production routes using other raw materials.

In addition, the different schedules for different possible decision maker's objectives are analysed. In the case of metrics proportionally linked to production amount, such as profit, environmental impact and makespan, it is found that production schedules show a trade-off related to the amounts of product produced. This is achieved by relaxing the demand requirement, where big changes in the objective function value are observed due to the inclusion of different amount of batches. When considering as objectives productivity or relative environmental impact (environmental impact per unit of product produced), the scheduling obtained in each case is found to be completely different in spite of the same economic or environmental concerns, see section 6.4. By considering different objective functions, the decision maker reaches completely different Pareto Frontiers in terms of the number and sequence of product batches, as well as in the selected cleaning methods. The former result points out the importance of using a multiobjective approach where different metrics are analysed and compared in a Pareto efficient fashion producing different possible solutions.

Moreover, it shows that the use of metrics that are proportional to production such as profit, environmental impact and makespan provide with solutions that mainly differ on the number of batches produced, while the use of relative metrics such as profitability or relative environmental impact allow for more efficient use of resources to be committed.

Application to SC Design The framework allows for the study of environmentally friendly and profitable SCs, by considering the multi-objective optimisation of economic and environmental metrics. The model considers the long-term strategic decisions (e.g. installation of plants, selection of suppliers, manufacturing sites, distribution centres) along with the mid-term planning for SCs. Similarly to the scheduling case, it is coded in GAMS, while environmental information is gathered from the Ecoinvent LCI database using Simapro.

A maleic anhydride SC case study is presented where two potential technologies are available. Two problems are solved, (i) a first approach that does not consider CO_2 trading scheme and (ii) a second one, that takes it into account (see section 7.4). It has been shown the possibility of tackling such problems with ease.

In the first problem, one important finding is that the consideration of fixed production/demand, leads to dominated solutions, while by allowing unsatisfied demand, the actual Pareto Front is obtained. This is due to the fact that the overall SC minimum environmental impact is encountered in a situation where no production is allowed. Similar remarks have been found in the scheduling case study.

Otherwise, it is important to point out that environmental metrics for the interpretation of LCI involve determining aggregated measures. Usually, normalising factors are used to determine the weight of each damage factor (climate change, human health, resources depletion, ecosystem quality) in the overall measure which may favour different solutions. It is found, by using single objective optimisation, that each environmental end-point optimisation ends up with completely different SC structures (see Figures 7.2 and 7.5), offering different features. These results provide information for carrying out careful analysis related to the application of normalising and weighting factors if a single metric is required.

With regards to model's validation, a global sensitivity analysis is performed adopting a stochastic programming approach. As a result of this analysis a group of model inputs parameters have been identified as most influential on some model results. The sensitivity analysis results are in clear agreement with the expected behaviour of the SC, thus validating the overall model.

In the second problem, the results obtained question the suitability of a single CO_2 trading scheme applicable to every industry sector: different regulatory schemes may be required in different industrial scenarios (see section 7.4.1). Current regulations merely consider climate change damage which certainly is a very important factor but other aspects such as human health, ecosystem quality and abiotic resources use should be also considered so that effective industrial changes regarding the environment are induced. Subsequently, the model has been also used for the study of possible government subsidies, which could improve economic aspects of good environmental options (see section 7.4.2).

Finally, it has to be emphasised that, a major achievement of this work is not only the building and solving a complex SC-environmental model, but also to emphasise the dangers related to deploying CO_2 emission related policies in isolation from other pollution related issues.

8.4 Future work

This thesis work presents guidelines, initiatives and perspectives for future work.

Regarding framework application, its usability has been shown in the case of design considerations for continuous plants. However, the case studies presented focused on the production of a given predefined product, this case is typical of the commodities production. The extension and assessment of applicability of the methodology proposed to cope with the production of a service instead of product is still lacking.

With regards to uncertainty, the use of highest probability density CI, instead of CI calculated using classical statistical tools is envisaged, for providing a better picture of pdfs that are not normal. Moreover other sensitivity analysis than the regression based proposed in the case studies can be used to compare the results, e.g. the use of variance decomposition metrics.

The framework has been also applied to the case of operational decisions, its extension to the consideration of monitoring systems was not undertaken and could prove to be an important source of social concerns because of health impacts and safety considerations.

While the Pareto frontier generating algorithm proposed showed its feasibility, other approaches based on stochastic sampling can be applied.

In the case of the SC design, the approach applied to the consideration of CO_2 market considerations and price subsidies has to be extended to study other complex economic instruments. Moreover many of the simplifying assumptions of the economic model proposed can be further extended for the consideration of general equilibrium models, where consequential LCAs can be tackled. Another potential extension is to analyse back-flows from recycle and reuse activities. A suitable case study should focus on the metals industry (e.g. Cu, Fe, Pb), where high reuse and recyclability are currently feasible.

Appendixes

Appendix A

Publications

A.1 Journals

This is a list of the works carried out so far within the scope of this thesis, in reversed chronological order. The list has been divided in manuscripts to international refereed journals and conference proceedings.

1. Manuscripts published
   (a) Bojarski, A.D.; Laínez, J.M.; Espuña, A.; Puigjaner, L. Incorporating Environmental Impacts and Regulations in a Holistic Supply Chains Modeling: An LCA Approach. *Computers & Chemical Engineering*, 33 (10): 1747 – 1759 (**2009**).
   (b) Perez-Fortes M.M.; Bojarski, A.D.; Velo, E.; Nougués, J.M.; Puigjaner, L. Conceptual model and evaluation of generated power and emissions in an IGCC plant. *Energy*, 34, 1721-1732, (**2009**).
   (c) Bojarski, A.D.; Guillén-Gosálbez, G.; Jiménez, L.; Espuña, A.; Puigjaner, L. Life Cycle Assessment Coupled with Process Simulation under Uncertainty for Reduced Environmental Impact: Application to Phosphoric Acid Production. *Industrial & Engineering Chemistry Research*, 47 (21), 8286-8300, (**2008**).
2. Manuscripts submitted
   (a) Capón-García, E.; Bojarski A.D.; Espuña, A.; Puigjaner, L. Multiobjective optimisation of multiproduct batch plants scheduling under environmental and economic concerns. Submitted to *AIChE Journal*.
   (b) Bojarski A.D.; Zondervan E.; de-Haan, A.B.; Espuña, A.; Puigjaner, L. Generation of Pareto-efficient sustainable options in a reactive distillation process. Submitted to *Environmental Science & Technology*.

Manuscripts [1.b] and [1.c], are two of the three case studies of the use of the framework proposed in the case of continuous process design, see chapter 5, sections 5.1 and 5.2. Manuscript [1.c] also provides the basis for the framework proposed and is the basis of chapter 4. Manuscript [1.a], is the result of the work shown in chapter 7. Manuscript [2.a] draws from chapter 6, while manuscript [2.b] has been discussed in section 5.3.

The following manuscripts are not directly linked to this thesis given that they are using only parts of the tools proposed in this thesis.

1. Rojas, J.; Zhelev, T.; Bojarski, A.D. Modelling and Sensitivity Analysis of ATAD. *Computers & Chemical Engineering* 34 , 802-811, (**2010**).
2. Yélamos, I.; Bojarski, A.D.; Joglekar, G.; Venkatasubramanian, V.; Puigjaner, L. Enhancing Abnormal Events Management by the Use of Quantitative Process Hazards Analysis Results. *Industrial & Engineering Chemistry Research*, 48 (8), 3921-3933, (**2009**).
3. Tona-Vasquez, R.V.; Jiménez-Esteller, L.; Bojarski A.D. Multiscale Modelling approach for production of Perfume Microcapsules. *Chemical Engineering Technology*, 31 (8), 1216-1222, (**2008**).

Manuscript [1], which performs a sensitivity analysis of a model, shows the application of the regression metrics reviewed in section 3.2.3. While manuscripts [2] and [3] are examples of the application of the AspenPlus-Matlab interface of appendix C application to other simulation problems.

A.2 Book chapters

The following book chapters have been also published based on results of this thesis.

- Laínez, J.M.; Bojarski, A.D.; Puigjaner, L. Chapter Title: "*Environmental Considerations into Strategic and Tactical Planning of Supply Chains*", in Environmental Planning, Editor: Newton, R.D. Series: Environmental Science, Engineering and Technology (**2010**). Nova Science Publishers, Hauppauge NY, USA. ISBN: 978-1-61728-654-4.
- Pérez-Fortes, M.; Bojarski, A.D.; Velo, E.; Puigjaner, L. Chapter Title: "*IGCC Power Plants: Conceptual Design And Techno-Economic Optimization*" in Clean Energy: Resources, Production and Developments, Editor: Harris, A.D. Series: Energy Science, Engineering and Technology (**2010**) Nova Science Publishers, Hauppauge NY, USA. ISBN: 978-1-61671-509-2.

A.3 Conference proceeding articles

The work in this thesis has been also submitted to different international specialised conferences.

1. Articles related to the phosphoric acid case study, discussed in section 5.1.
   (a) Bojarski, A.D.; Espuña, A.; Guillén-Gosálbez, G.; Jimenez-Esteller, L.; Puigjaner, L. Addressing uncertainty in the application of LCA and process simulation to the production of phosphoric acid. 18th International Congress of Chemical and Process Engineering (CHISA-PRES). (2008).
   (b) Bojarski, A.D.; Jiménez-Esteller, L.; Espuña, A.; Puigjaner, L. Life Cycle Assessment technique coupled with simulation for enhanced sustainability of phosphoric acid production. European Congress of Chemical Engineering (ECCE-6) Book of Abstracts. 327-328 (2007).
2. Articles related to the IGCC case study, discussed in section 5.2.
   (a) Bojarski, A.D.; Pérez-Fortes, M.; Velo, E.; Puigjaner, L. Life Cycle Assessment of Integrated Gasification Power Plants: Conceptual Design and Techno-Economic Evaluation. ECOS 2010 Meeting proceedings (2010).
   (b) Pérez-Fortes, M.; Bojarski, A.D.; Velo, E.; Puigjaner, L. Biomass and Waste Gasification: Feasible Contributions in Industrialised and Rural Areas. Proceedings of the 17th European Biomass Conference & Exhibition, from research to industry and markets. 732-739 (2009).
   (c) Pérez-Fortes, M.; Bojarski, A.D; Velo, E.; Nougués, J.M.; Puigjaner L. Integrated Tool for IGCC Power Plants Design. AIChE 2009 Annual Meeting proceedings. (2009).
   (d) Pérez-Fortes, M., Bojarski, A.D., Ferrer-Nadal, S., Kopanos, G.M., Nougués, J.M., Velo, E., Puigjaner, L. Enhanced modeling and integrated simulation of gasification and purification gas units targeted to clean power production. European Symposium on Computer Aided Process Engineering (ESCAPE - 18), CAPE vol 25, 793-798 (2008).

(e) Perez-Fortes, M.; Bojarski, A.D.; Ferrer-Nadal, S.; Kopanos, G.; Nougues, J.M.; Velo, E.; Puigjaner, L. Valorization of Waste in a Gasification Plant for Clean Power Production. Clean Technology 2008 book of abstracts. 558-561 (2008).

(f) Pérez-Fortes, M.; Bojarski, A.D.; Ferrer-Nadal, S.; Kopanos, G.; Nougués, J.M.; Velo, E.; Puigjaner, L. Conceptual model and evaluation of generated power and emissions from an integrated gasification combined cycle power plant. 18th International Congress of Chemical and Process Engineering (CHISA-PRES). (2008).

(g) Pérez-Fortes, M.; Ferrer-Nadal, S.; Bojarski, A.D.; Kopanos, G.; Nougués, J.M.; Velo, E.; Puigjaner, L. Conceptual Modeling and Simulation of an entrained bed gasifier reactor. AIChE 2007 Annual Meeting. (2007).

3. Articles related to the framework application to scheduling, as discussed in chapter 6.

   (a) Bojarski, A.D; Capón-García, E.; Espuña, A.; Puigjaner, L. Batch Process Scheduling Optimization of Multiproduct Plants Under Simultaneous Environmental and Economical Considerations. AIChE 2009 Annual Meeting proceedings. (2009).

   (b) Capón-García, E.; Bojarski, A.D.; Espuña, A.; Puigjaner, L. Environmentally friendly approach towards batch process scheduling for phosphite products. 18th International Congress of Chemical and Process Engineering (CHISA-PRES). (2008).

4. Articles related to the framework application in SC design retrofit and planning, as discussed in chapter 7.

   (a) Laínez, J. M., Bojarski, A.D., Espuña, A., Puigjaner, L. Mapping environmental issues within supply chains: an LCA based approach. European Symposium on Computer Aided Process Engineering (ESCAPE - 18), CAPE vol 25, 1131-1136 (2008).

5. Articles related to the use of sensitivity analysis metrics discussed in section 3.2.3.

   (a) Bojarski, A.D.; Alvarez, C.R.; Puigjaner L. Dealing with Uncertainty in Polymer Manufacturing by Using Linear Regression Metrics and Sensitivity Analysis. European Symposium on Computer Aided Process Engineering (ESCAPE - 19), CAPE vol 26, 725-730 (2009).

   (b) Passuello, A.; Bojarski, A.D.; Schuhmacher, M.; Jiménez, L.; Nadal M. Evaluating long-term contamination in soils amended with sewage sludge. The 4th International Symposium on Information Technologies in Environmental Engineering, (ITEE 2009). Information Technologies in Environmental Engineering, Environmental Science and Engineering, 465-477 (2009).

A.4 Participation in research projects

Throughout this thesis, most of the data used is based on industrial case studies which rose from the author's involvement in the following research projects.

ECOPHOS, *Waste utilisation in phosphoric acid industry through the development of ecologically sustainable and environmentally friendly processes for a wide class of phosphorus-containing products*, supported by the European Community 6th Framework Programme (INCO-CT-2005-013359), 2005-2009.

AGAPUTE, *Advanced GAs Purification TEchnologies for cogasification of coal, refinery by-products, biomass & waste,targeted to clean power produced from gas & steam turbine generator set fuel cells.*, supported by the European Community (RFC-CR-04006), 2004-2008.

Appendix B

Case Study Data

B.1 Case Study data for continuous process simulation

Eq. B.1 is used to model the solubility constant (H_{ij}) temperature dependency. Table B.1 contains the values for the coefficients.

$$\ln(H_{ij}) = A_{ij} + \frac{B_{ij}}{T} + C_{ij}\ln(T) + D_{ij}T + \frac{E_{ij}}{T^2} \tag{B.1}$$

Equilibrium constants temperature relationship is considered by Eq. B.2 using data from Table B.2. Some of the equilibrium constants, except the ones related to gypsum formation (K_{Dihy} and K_{Hemy}), are calculated from Gibbs free energies of formation which are retrieved from AspenProperties data bank.

$$\ln(Keq) = A + \frac{B}{T} + C\ln(T) + DT \tag{B.2}$$

Table B.1: Henry's law constant values retrieved from Aspen Properties used in Eq. B.1.

H_{ij} [a]	A_{ij}	B_{ij}, [K]	C_{ij}	D_{ij}	E_{ij}, [K^2]
CO_2	159.20	-8477.71	-21.96	5.78E-03	0
O_2	144.41	-7775.06	-18.40	-9.44E-03	0
N_2	164.99	-8432.77	-21.56	-8.44E-03	0
H_3PO_4	-31.51	0.00	0.000	0.00E-03	0
NH_3	-144.98	-157.55	28.10	-0.05	0
H_2S	346.63	-13236.80	-55.06	0.06	0
HCN	42.28	-8136.78	0.00	-0.04	0
HCl	46.94	-7762.83	0.00	0.00	0
HF	-150.00	-157.00	30.00	-0.05	0

[a] j-th component is H_2O

Table B.2: Equilibrium constant values retrieved from AspenProperties used in Eq. B.2

K	A	B [K]	C	D
K_{H_2O}, 5.46	132.90	-13445.90	-22.48	0.0000
$K1_{CO_2}$, 5.32, 5.44	231.46	-12092.10	-36.78	0.0000
$K2_{CO_2}$, 5.33, 5.45	216.05	-12431.70	-35.48	0.0000
$K1_{H_2S}$, 5.30, 5.47	214.58	-12995.40	-33.55	0.0000
$K2_{H_2S}$, 5.31, 5.48	-9.74	-8585.47	0.00	0.0000
K_{NH_3}, 5.34	-1.26	-3335.70	1.50	-0.0037
K_{NH_2COOH},5.35	-4.58	2900.00	0.00	0.0000
K_{HCN}, 5.40	22.90	-9945.53	0.00	-0.0496
K_{MDEA}, 5.43	-9.42	-4234.98	0.00	0.0000
K_{Dihy} [a]	421.78	-15510.10	-71.59	0.06695
K_{Hemy} [a]	-23.34	3651.92	-0.90	-0.00009

[a] These values represent the regression results obtained using literature data.

Appendix C

Matlab-AspenPlus interface

C.1 Methods developed

The following methods are the ones used for the connection of Matlab and AspenPlus[1].

- apconnect, it returns the activeX application server object, i.e. the pointer to the COM interface, (`model`), associated to opening a given AspenPlus Case. Use: `model = apconnect('file location',vis);`. `vis` is a boolean which makes the AspenPlus GUI visible if set to `1`, or not if set to `0`.
- aprun, it re-initialises the AspenPlus case and runs it from scratch. Use: `aprun(model);`.
- setAPValue, allows setting a value for a given AspenPlus variable. Use: `setAPValue(model, variablesValue, variableString);`, `variable-Value` holds the real / integer value to be set in AspenPlus, while `variable String` is the string (separated using \) that defines the variable in AspenPlus. Variable strings can be found using the AspenPlus Variable Explorer[2].
- getAPValue, allows getting values of a given AspenPlus variable. Use: `value = getAPValue(model,findNodeString);`, `findNodeString` is the string defining the AspenPlus variable name. Methods getAPVector and getAPMatrix can be used in the same way, but retrieving vectors and matrices data respectively.
- getAPStatus, is used after AspenPlus run, to retrieve the status of the simulation run. It is used to test if AspenPlus reached a converged solution or if errors were found.
- getAPCompNames, retrieves chemical component names used in the AspenPlus simulation case.
- getAPStreamNames, retrieves stream names used in AspenPlus simulation case.
- getAPStreamResults, retrieves stream information. Its use requires knowing the component names used (getAPCompNames) and the stream names (getAPStreamNames), that are to be retrieved from the AspenPlus simulation case. The generated streams structure, holds the most important information regarding the stream such as: total flow, component flows, temperature, pressure, V/L/S fractions, density and energy content. Flows can be retrieved in molar or mass basis.

[1] The basis for apconnect and aprun methods were previously outlined by Sergio Ferrer.
[2] Menu: Tools \ Variable Explorer..., the path to node string can be copy-pasted from there.

C.2 Possible algorithm implementation

The former setAPValue, aprun and getAPValue methods are the backbone of the developed interface and can be used for setting and retrieving the Monte Carlo scenarios values as shown in Algorithm C.1.

Algorithm C.1: Simple implementation of a Monte Carlo sampling using the developed methods.

Data: Input values for simulation (x_{ni}), AspenPlus input variable names `invarNameStr`$_i$, AspenPlus output variable names `outvarNameStr`$_j$, AspenPlus simulation case.
Result: AspenPlus output variable values y_{nj}.
begin
    call apconnect;
    for *all scenarios n* **do**
        for *all input variable i* **do**
            call setAPValue using x_{ni} and `invarNameStr`$_i$;
        run simulation: aprun;
        for *all output variable j* **do**
            call getAPValue using y_{nj} and `outvarNameStr`$_j$;

Appendix D

LCIA metrics

D.1 Typical LCIA indicators

Acidification The emission of acidifying substances can have a variety of impacts on aquatic and terrestrial ecosystems through multiple pathways. Impacts begin (after atmospheric reactions and transport) with either wet or dry deposition of sulphur or nitrogen ions on leaves[1], soil[2], or water[3]. AoPs affected by this impact category are natural environment, man made environment, human health and natural resources. The basis adopted for acidification metrics is the number of hydrogen ions (n_H^i) which can theoretically be deposited per unit mass of the released pollutant i (Guinee *et al.*, 2001a).

$$n_i i + \cdots \rightarrow n_H^i \cdot H^+ + \ldots \tag{D.1}$$

This metric is developed relative to one acidifying substance, in this case sulphur dioxide, using kg SO_2-equivalents, [kg SO_2eq.], which can be calculated given the stoichiometric coefficients n_i and n_H^i in Eq. D.1[4]. Since pollutant releases are specified in mass of emissions rather than moles, the coefficient n_H^i must be divided by the pollutant's molecular weight (MW_i) (Guinee *et al.*, 2001a; Pennington *et al.*, 2000).

$$AP_i = \frac{\frac{n_H^i}{n_i MW_i}}{\frac{(n_H)^{SO_2}}{n_{SO_2} MW_{SO_2}}} = \frac{MW_{SO_2}}{MW_i} \cdot \frac{n_H^i}{2n_i} \tag{D.2}$$

The acidification potential AP_i for chemical i defined in D.2 reflects the maximum acidification potential of a substance. The actual impact will be governed by local processes and

[1] Leaf exposure has been linked to tree stress and forest die-back.

[2] Sulphur ion deposition to soils is generally leached by rainwater, while deposited nitrogen may be retained in the soil (up to a point and depending upon a variety of factors). This leaching of acidifying substances may further contribute to lower the receiving water pH.

[3] Direct acid deposition to water may lower the pH, directly or indirectly (e.g. through mobilisation of metals that result in a toxic effect) impacting biota and fauna.

[4] It is assumed that one mole of SO_2, will produce two moles of H^+, $n_{SO_2} = 1$ and $n_H^{SO_2} = 2$; one mole nitrogen oxide compounds (NOx) will produce one mole of H^+; and one mole reduced nitrogen compound (NH_x) will produce one mole H^+.

circumstances, and will be reduced as mineralisation and denitrification rates increase[5]. This approach is considered to be too simple and further improvements of APs consider weighting emissions according to area sensitivity in which the emission occurs, assessing a maximum and minimum scenario and extending models to include regional sensitivity and fate (Guinee *et al.*, 2001a). Huijbregts *et al.* (2000a) used the RAINS (Regional Air Pollution INformation and Simulation) model to calculate region dependant CFs for Europe, other regions such as the US and Japan have also being studied in a similar way (Pennington *et al.*, 2004).

Eutrophication and Nutrification occur when mineral and organic nutrients (N or P sources) are added to soil or water, resulting in a nutrients equilibrium imbalance and consequently in increased biomass growth. In the case of water the increase of biomass growth leads to increases of water turbidity and decrease the level of dissolved oxygen which then increases fish mortality and the disappearance of bottom's fauna. While in the case of terrestrial environments the growth of plants is controlled by the limited availability of N[6]. The exposure of N-limited ecosystems to high loads of N will increase the competitive advantage of N-adapted species at the expense of others, this fact affects the overall ecosystem tolerance towards disease, drought, frost and herbivores (Pennington *et al.*, 2004)[7]. AoPs affected are natural environment, natural resources and man made environment.

A common mid-point in the EM for eutrophication in waters is oxygen depletion (OD) which is associated to the decomposition of dead algae, whose growth is promoted by mineral nutrient loading. Similarly to APs, eutrophication potentials (EPs) are determined by the contribution of each possible nutrient to biomass formation (considered as phytoplankton $C_{106}H_{263}O_{110}N_{16}P_1$, see Eq. D.3), assuming unlimited supply of other nutrients[8].

$$EP_i = \frac{\frac{\eta_i}{MW_i}}{\frac{\eta_{ref}}{MW_{ref}}} \tag{D.3}$$

η_i is the potential contribution to eutrophication of one mole of substance i while η_{ref} is the potential contribution to eutrophication of the reference substance, which in this case can be kg of PO_4^{3-}, NO_3^- or OD. Different EPs expressed in PO_4^{3-}, NO_3^- or OD-equivalent[9] can be calculated. However, it has to be emphasised that the former EPs are not strictly interchangeable, given that OD is a consequence of aquatic eutrophication (Seppala *et al.*, 2002), indicators for increases of COD or BOD[10] should be used with caution given that they reflect different cause-effect relationships to indicators of nutrient enrichment (Pennington *et al.*, 2004). Recently there has been improvements in the modelling of aquatic eutrophication taking into account source location, environmental transport and ecosystem sensitivity. Distinctions are also made between P-limiting (freshwater, rivers and lakes) and N-limiting (seawater) environments (Pennington *et al.*, 2001, 2004).

[5]The acidification caused by a particular substance may also be reduced if the anions accompanying the H^+ ions become bound to the impacted system (for a certain period, for it is not an infinite buffer) or absorbed and removed by biomass. This is particularly relevant for NOx and NH_3, where actual acidification may vary between 0% and 100% of the potential value (Guinee *et al.*, 2001a).

[6]Phosphorous seldom limits plant growth.

[7]Other potential negative impacts of excessive N addition on terrestrial ecosystems include increased susceptibility of some plants to disease and cold stress, changes in soil chemistry, nitrate leaching into ground water, changes in plant and microbial community structure, and changes in animal community structure (Pennington *et al.*, 2000).

[8]In this approach one mole of biomass requires 16 moles of N and 1 mole of P.

[9]The CF of substance i, in [g O_2eq./kg i], is the oxygen required for the mineralisation of the organic matter (average composition) produced from 1kg of i when i is the limiting nutrient, with one mole of N and P corresponding respectively to 8.6 and 138 moles of consumed O_2 (Guinee *et al.*, 2001a).

[10]BOD_5 is a measure of the amount of oxygen biologically consumed over a 5-day period is expected to be 0.5COD for a chemical with a 5-day half life (Pennington *et al.*, 2001).

Photochemical Oxidant Formation (POF) or photo-oxidant formation, is the formation of reactive chemical compounds such as ozone (O_3) and other intermediate reaction products (e.g. peroxyaceltyl nitrate, PAN), by the action of sunlight on certain air pollutants. These reactive compounds may be injurious to human health and ecosystems and may also damage crops. The relevant AoPs are human health, the man-made environment, the natural environment and natural resources (Guinee *et al.*, 2001a). According to Pennington *et al.* (2000) the focal point of equivalence metrics in the EM of POF (smog-respiratory) impacts to human health is the O_3 formation rate in the troposphere. O_3 formation rates in the troposphere are governed by complex chemical reactions, which are influenced by ambient concentrations of NO_x, the type and concentration of volatile organic compounds (VOCs), temperature, sunlight and advective flows. Guinee *et al.* (2001a) reviews three methods for comparing O_3 creation potential for different species of VOC based on:

- *Photochemical Ozone Creation Potentials* (POCPs) were originally developed to assess various emission scenarios for VOCs. A UN protocol defined the POCP of a VOC as the ratio between the change in O_3 concentration due to a change in the emission of that VOC and the change in the O_3 concentration due to a change in the emission of a reference compound (in this case ethene C_2H_4), as expressed in Eq. D.4.

$$POCP_i = \frac{\frac{a_i}{b_i}}{\frac{a_{C_2H_4}}{b_{C_2H_4}}} \tag{D.4}$$

  where a_i is the change in O_3 concentration due to a change in the emission of VOC i and b_i the integrated emission of VOC i up to that time, with the denominator containing these parameters for the reference substance.
- *Disability Adjusted Life Years* (DALYs), for respiratory diseases due to air pollution consider O_3-induced respiratory diseases for a number of VOCs and NOx, based on a fate factor and the DALY for O_3. The only difference between these characterisation values and the POCPs is located in two constants: the DALY for O_3 and FNMVOC (fate factor for non methane VOC). DALYs do not cover effects on ecosystems or crops, and these effects should be assessed separately, if desired.
- *Incremental Reactivity* (IR) of a VOC in a pollution scenario is defined as the change in O_3 caused by adding a small amount of the VOC to the emissions in the scenario, divided by the amount of VOC added. IRs are calculated using a so-called "base case scenario" that represents a specific O_3 exceedance episode in a given geographical area. The base case scenario is subsequently adjusted, resulting in three derived scenarios and three associated IRs: (i) Maximum Incremental Reactivity scenario (MIR)[11]; (ii) Maximum Ozone Reactivity scenario (MOR)[12]; and (iii) Equal Benefit Incremental Reactivity scenario (EBIR)[13].

Guinee *et al.* (2001a) points some differences between the approach based on IRs and that employing POCPs: (i) POCPs were developed on the basis of regional European scenarios, IRs are grounded in scenarios for urban areas in North America and (ii) POCPs are based on a trajectory model of VOC transport over Europe while IRs on a single-cell box model. Special attention has been paid to CFs for CH_4 and VOCs, both inventory results are suitable for indicators of possible POF in the troposphere, but CFs have to be assessed separately in order

[11] The NOx emissions in the base case scenario are adjusted to yield the highest incremental reactivity of the initially present VOC mixture (high-NOx).

[12] The NOx emissions in the base case scenario are adjusted to yield the highest peak O_3 concentration (high-NOx).

[13] The NOx emissions in the base case scenario are adjusted such that VOC and NOx reductions are equally effective in reducing O_3 (medium-NOx).

to avoid double counting, if inventory results are going to be used then VOCs should combined into a single category or, CH_4 and non methane VOCs should be used in combination (Seppala *et al.*, 2002).

Toxicological Impact to Humans and Ecosystems Toxicological impact can be assessed using different metrics, Pennington and Yue (2000) propose the following classification:

- *Direct data summation* of flow rate data for reference compounds such as: metals (Cd, Cr, Pb, Zn), non methane VOCs or radionuclides.
- *Effect normalisation*, by dividing each effluent flow rate by an effect criteria. Effect criteria are typically set using toxicity test results for human health or ecosystems, but can also based on legislative criteria or benchmarks (see critical volumes, Eq. 2.14).
- *Scoring and ranking* approaches, have been proposed for a range of applications in which key differences in fate, exposure and effect parameters are exploited to provide a basis for ranking chemicals and emissions (Davis *et al.*, 1994).
- *Model-based approaches*; consist of using dispersion models[14] that can predict exposure concentrations to provide a localised comparison basis or multimedia models[15] to account for regional, continental and global scale exposure scenarios.
- *Detailed impact assessment*; it includes site-specific considerations of toxicity, exposed populations, exposure pathways, background concentrations, contaminant intake and seasonal variation. Comparisons may be in terms of actual or future impacts.

For this category, ready to use LCIA techniques adopt a model based approach, and by using a given environmental model calculate the CFs corresponding to the emission of a given pollutant. Model based approaches are considered state of the art according to de Haes *et al.* (1999) and Finnveden *et al.* (2009). However in terms of representation of the EMs and for use in regional scale screening applications, multimedia model predictions have only been validated[16] in a limited number of case studies involving field data and demonstrated varying degrees of success (Pennington & Yue, 2000).

Recently the UNEP/SETAC analysed prominent toxicity related models and by consensus built a multimedia toxicity model: USEtox Hauschild *et al.* (2008) and Rosenbaum *et al.* (2008). It is a parsimonious multimedia chemical fate, exposure and effect model.

Stratospheric ozone depletion (SOD) refers to the thinning of the stratospheric O_3 layer as a result of anthropogenic emissions. These emissions contain O_3 depleting substances (ODSs). The thinning of the layer causes a greater fraction of solar UV-B radiation to reach the Earth's surface, with potentially harmful impacts on human health, animal health, terrestrial and aquatic ecosystems, biochemical cycles and materials (Guinee *et al.*, 2001a). Stratospheric O_3 depletion, thus affects all four AoPs: human health, natural environment, man-made environment and natural resources. There is international consensus on the use of Ozone Depletion Potentials (ODPs), a mid-point metric proposed by the World Meteorological Organisation (WMO), for considering the relative importance of chlorofluorocarbons (CFCs), hydro-

[14] They are typically mono-compartmental and help to estimate contributions to localised exposures for specific chemicals where dilution is the controlling factor.

[15] Multimedia models account for competing rates of degradation and transfer between environmental media, factors that become important in determining exposure concentrations at larger scales, see section 2.2.5.2.

[16] Validation efforts have tended to focus on specific aspects of the models to ensure conservatism but the implications may be limited in the context of the overall model predictions, which are commonly found to be non-conservative. The results should therefore be adopted with caution, particularly when using generic models for surface active, organo-metallic and inorganic compounds.

chlorofluorocarbons (HCFCs), and halons expected to contribute significantly to the breakdown of the O_3 layer.

$$SOD = \sum_{i}^{all\ species} m_i ODP_i \tag{D.5}$$

$$ODP_i = \frac{\delta[O_3]_i}{\delta[O_3]_{CFC-11}} \tag{D.6}$$

$\delta[O_3]_i$ represents the change in the stratospheric O_3 column from the equilibrium state due to annual emissions of substance i in [kg·yr^{-1}], and $\delta[O_3]_{CFC-11}$ the change in that column equilibrium state due to annual emissions of CFC-11[17]. The ODP_i provides a good indication of the relative changes in the O_3 column due to an instantaneous emission of i to the atmosphere based on eight time frames ranging from 5 year ODPs to 500 year ODPs. As the most significant deficiencies in the O_3 layer are expected to occur in a short time frame, many practitioners use the shorter time span calculations. Pennington *et al.* (2000) emphasises that a few ODSs, such as nitrous oxide (N_2O), are expected to exhibit significant effects but do not have calculated ODPs.

Global climate change (GCC) refers to the potential changes in the Earth's climate caused by the build-up of chemicals known as Green House Gases (GHGs), which trap heat from the reflected sunlight that would have otherwise passed out of the Earth's atmosphere. The AoPs that this impact category affects are human health, natural environment and man-made environment (Guinee *et al.*, 2001a; Pennington *et al.*, 2000). While sinks exist for GHGs (e.g. oceans absorb CO_2), the rate of emissions in the industrial age is exceeding the rate of absorption, and consequently the concentration of these gases increase.

To compare different GHGs emission impacts, each gas (i), has been assigned a Global Warming Potential index (GWP_i), expressing the ratio between the increased infrared absorption due to the instantaneous air emission of 1 kg of the substance i and that due to an equal emission of CO_2, both integrated over time, see Eq. D.7.

$$GWP_i^T = \frac{\int_0^T a_i c_i(t) dt}{\int_0^T a_{CO_2} c_{CO_2}(t) dt} \tag{D.7}$$

where a_i is the radiative force per unit of concentration of GHG i in [Wm^{-2}kg^{-1}], $c_i(t)$ is the concentration of GHG i at time t after the release in [kg m^{-3}], and T is the time over which integration is performed [yr][18]. The Intergovernmental Panel on Climate Change (IPCC)has compiled a list of "provisional best estimates" for GWPs with time horizons (T) of 20, 100 and 500 years, based on the expert judgement of scientists worldwide. The integration period to be applied in calculations must be decided and depends on the period over which the impacts are to be studied. A long horizon would appear to be preferable, if the aim of the assessment is to assess all rather than just short-term effects, however the longer the integration period, the more uncertainties are introduced into the model[19].

[17] Trichlorofluoromethane CCl_3F, also called freon-11, or R-11.

[18] A GWP_i^T value of 57 for substance i means that for a time horizon of T years the emission of 1 kg of such substance has the same potential GCC or GW effect than 57 kg of CO_2.

[19] Although the ODP concept resembles that of GWP, there is a major difference, ODPs are calculated for a given steady state while GWPs for several different time horizons with consequently different concentration profiles $c_i(t)$.

Resource Depletion Refers to the loss, diminishment or impairment of natural resources (water, minerals and biomass) such that the resource is no longer available as input into the system under consideration. Resources are classified as (Guinee *et al.*, 2001a; Pennington *et al.*, 2000):

- *Deposits or Stocks*: are not regenerated within human lifetimes, they are considered to be non-renewable such is the case of primary energy sources (e.g. natural gas, petroleum, coal), and minerals.
- *Funds*: can be regenerated within human lifetimes; such is the case of groundwater and soil.
- *Flow*: are renewable; although renewability depends on several factors such as rate of use and economic factors influencing consumption.

Other possible classification separates resources in two different groups: abiotic (non-living) and biotic (living, i.e forests, animals and plants) resources. It is debatable whether all three types of abiotic resources can or should be aggregated into one measure for abiotic depletion, even more difficult is to agree on a common yardstick to be used for its measurement. Given that resources are consumed over time and its scarcity increases along time, two approaches are available: (i) some authors propose that the analysis of depletion should be dealt in the inventory phase of a consequential LCA (Finnveden *et al.*, 2009), while others (ii) address the possibility of future resource extraction differently. citeGuinee01p3 consider size of reserves and extraction rates normalised to a yardstick specie (Sb), Goedkoop and Spriensma (2001) and Humbert *et al.* (2005) look at the possibility of future resource extraction measured in energy while Steen (1999a) assess it via estimation of environmental costs associated to the substitution of current extraction process. Another way to look upon deposits is to use thermodynamic insights, measuring useful reserves of energy or exergy (see section 2.2.6).

Despite the inventory issue, abiotic depletion characterisation depends on resource type, while coal depletion could be easily assessed, the same does not happen with topsoil or peat, given that they are partly biotic. There are more complex methods that distinguishes between depletion and impact on biotic resources such as Baumann & Tillman (2004, Ch. 5), but these have not yet received too much attention (Finnveden *et al.*, 2009), mainly in the area of water consumption. Moreover there are no characterisation methods for flow resources and very few for biotic resources.

Impacts on land use de Haes *et al.* (1999) distinguishes two aspects of land use[20]:

- *associated changes in quality of land*, this is due to transformation of land from natural state to other state. The net transformation impact represents the effects of the permanent or irreversible changes in the quality of an area of land. In this case the transformation impact is expressed in units of [quality·m^2], while the unit of this aspect is [m^2].
- *Occupation* refers to the time period during which the land is unavailable for other uses. The occupation impact represents the effects of the temporary changes in the quality of an area of land. The occupation impact can be expressed in units of [quality·m^2·year] and the unit is therefore [m^2·year].

There are ready available CFs that relate different industrial or agricultural activities to land occupation or transformation (Goedkoop & Spriensma, 2001; Guinee *et al.*, 2001a). Characterisation of land use is made difficult due to limited knowledge and data available scattered from different parts of the world, see Baumann & Tillman (2004, Ch. 5). It is not clear if land

[20]Land use and ecological footprint (EF), despite being measured in m^2 do not convey the same meaning, please refer to section 2.2.6, for clarification on EF.

use impacts should be accounted as mid-point impacts or end-point impacts. Land use impacts on biodiversity has been assessed in terms of loss of biodiversity in terms of reduction of number of species.

Appendix E

Glossary

Table E.1: List of acronyms used in this thesis. Many of the institution cited are provided with a hyperlink to their respective web pages.

Acronym	meaning
AD	abiotic depletion
ADP	abiotic depletion potential
AEP	annual equivalent profit
AHP	Analytic Hierarchy process
ANN	artificial neural networks
ANOVA	analysis of variance
AP	acidification potential
AoPs	Areas of Protection
BAT	Best available technique
BPEO	Best Practicable Environmental Option
CBA	Cost Benefit Analysis
CC	combined cycle
CED	cumulative energy demand
CExD	cumulative exergy demand
CEmD	cumulative emergy demand
CF	Characterisation Factor
CIP	clean-in-place
CT	Cleaner technology
CP	Cleaner Production
CV	Critical volumes, also used as Corporate Value
CFCs	chlorofluorocarbons
CRN	common random numbers
CSR	Corporate Social Responsibility
CSTR	continuous stirred tank reactor
DALY	Disability Adjusted Life Years
DfE	Design for the environment
EEA	European Environment Agency
EF	ecological footprint
EFRAT	Environmental fate and Risk Assessment Tool
EHS	Environmental, Health and Safety
EI	Environmental ImpactS
EI99	EcoIndicator 99 (Goedkoop & Spriensma, 2001)
EIA	Environmental Impact Assessment
ELF	Environmental load factor
ELU	Environmental Load Units
EM	Environmental mechanism

Continued on next page

Table E.1 – continued from previous page

Acronym	meaning
EMS	environmental management systems
ENRTL	Electrolytes-non random two liquid
ENVOP	Environmental optimisation
EOS	Equation Of State
EP	Eutrophication potential
EPE	Environmental Performance Evaluation
ERA	Environmental Risk Assessment
EU-ETS	European Union-Emissions Trading Scheme
FU	Functional Unit
FWAET	Fresh water Aquatic EcoToxicity
GA	Genetic algorithm
GCC	Global climate change
GDP	Gross Domestic product
GHG	Green House Gas
GT	gas turbine
GWP	Global Warming Potential
HAZOP	Hazard and Operability
HCFCs	hydro-chlorofluorocarbons
HT	Human toxicity
HTP	Human toxicity potential
HSS	Hammersley Sequence Sampling
ICCA	International Council of Chemical Associations
IE	Industrial ecology
IPCC	Intergovernmental Panel on Climate Change
IRR	Internal Rate of Return
ISO	International Organization for Standarization
LC	Life Cycle
LCA	Life Cycle Assessment
LCt	Life-cycle thinking
LCM	Life-Cycle Management
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LHS	Latin Hypercube Sampling
LLE	Liquid-Liquid equilibrium
MAET	Marine Aquatic EcoToxicity
MCDA	Multiple Criteria Decision Analysis
MCDM	Multiple Criteria Decision method
MCM	multimedia compartment models
MCS	Monte Carlo Sampling
MEIM	Methodology for Environmental Impact Minimisation
MFA	material flow analysis
MLI	Mass-loss indices
MOGA	multiobjective genetic algorithm
MOO	multiobjective optimisation
MSE	mean square error
MSMPR	mixed suspension mixed product removal
NEX	normalised extinction of species
NGO	non governmental organisations
NMVOC	Non Methane Volatile Organic Compound
NPV-NPW	net present value or worth
NRTL	non-random two liquid
ODP	Ozone (O_3) depleting substance
OECD	Organisation for Economic Cooperation and Development
OF	objective function
OLCAP	Optimum LCA Performance
PA	Phosphoric acid
PCA	Principal component analysis
pdf	probability distribution function
PDfS	Process Design for Sustainability
PEI	potential environmental impact
PFD	Process Flow diagrams
PFR	Plug Flow Reactor

Continued on next page

Table E.1 – continued from previous page

Acronym	meaning
POCP	Photochemical Ozone Creation Potential
POF	Photochemical Oxidant Formation or photo-oxidant formation
PP or P2	Pollution Prevention
PSD	Particle size distribution
RA	Risk assessment
RCG	Regular Crystal Growth
RD	reactive distillation
RMSE	Root Mean Squared error
RSM	response surface methods
SA	sensitivity analysis
SC	Supply Chain
SCM	Supply Chain Management
SD	Sustainable Development
SETAC	Society of Environmental Toxicology and Chemistry
SGA	scaled gradient analysis
SII	social impact indicator
SOD	Stratospheric ozone depletion
SPF	Spontaneous Nuclei Formation
SPI	sustainability process index
SPM	Suspended Particulate Matter
SRC	Standardised regression coefficients
SRK	Soave-Redlich-Kwong
SQP	sequential quadratic programming
SWS	Sour Water Steam stripper
TAC	Total Annual Cost
TAPPS	total annualised profit per service unit
TET	Terrestrial EcoToxicity
TRACI	Tool for the Reduction and Assessment of Chemical and other environmental Impacts
UN	United Nations
UNEP	United Nations Environmental Programme
UNIFAC	UNIversal Functional Activity Coefficient
UNIQUAC	UNIversal QUAsiChemical
USEPA	United States Environmental Protection Agency
VLE	vapour-liquid equilibrium
VOC	Volatile Organic Compound
VS	Venturi scrubber
WBCSD	World Business Council for Sustainable Development
WMO	World Meteorological Organisation
WTP	willingness to pay
WWT	waste water treatment
YLD	Years Lived Disabled
YOLL	Years of Life Lost

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