Study of solid particle materials as high temperature Thermal Energy Storage and Heat Transfer Fluid for Concentrating Solar Power

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"Sustainability is not an implicit natural phenomenon, but instead a behavioral quality to be nurtured as a species. Planet Earth will continue to endure inevitable change through its existence. Sustainability is a solid and versatile proficiency, which allows a thriving interrelation with that change."

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SUMMARY

Renewable energies have a major role in today's energy systems development, energy security and climate change fight. Thermal Concentrating Solar Power (CSP) has the potential to get up to 11.3% of world's electricity production with the adequate support. This type of renewable energy has proved to be price competitive and to have the advantage of integrating Thermal Energy Storage (TES). This adds the generation flexibility that other renewable energies, like wind or photovoltaics, does not have integrated.

In order to continue developing this technology, solid particle CSP has been proposed. This design uses granular solid materials as Heat Transfer Fluid (HTF) and TES material in solar towers in order to be able to achieve higher operation temperatures, than current commercial CSP. Higher temperature means more efficiency in heat-to-electricity conversion, due to the use of better power generation cycles.

The main objective of this thesis is to enhance relevance and provide theoretical and experimental background for solid particles to be used as TES material and HTF for CSP tower power plants, from the materials perspective, by using existent or new methodologies.

During this dissertation, current scientific output and relevance were studied in two separate contributions, one for CSP and the other for TES, both by using bibliometric methods. For the CSP study, additional analyses were carried out according to the harvesting technologies (parabolic trough, solar tower, Stirling dish and linear Fresnel). For the TES study, the additional analyses were performed according to the different ways to store thermal energy (sensible, latent and thermochemical). For both analyses, most productive countries, regions, authors, journals and research communities were identified. Moreover, funding impact and cooperation between countries and authors were analyzed. For developing these bibliometric analyses, a specific methodology was implemented following Bibliometrics principles. For these purposes, two existing software programs were used for

a part of the analysis, while for performing the rest of the analysis a special software was developed ad-hoc for this study.

For providing background, two state-of-the-art analyses were performed in order to get current development status of solid particle CSP. The first one was oriented to the plant design itself. Several solar receivers were analyzed, as well as TES, Heat Exchanger (HEX) and conveyance systems. During the second state-of-the-art, a material driven study was carried out in order to understand the behavior expected by the particle media and to identify some of the materials proposed by the most relevant researchers in this field.

Next step of this dissertation was focused on establishing the design criteria for solid particle CSP technology, from the materials science perspective. This was achieved by finding the most relevant objectives that a power plant of this kind must comply, as well as the influence of the particle media properties and parameters.

Last part of this dissertation is related with two studies regarding the durability of some of the most promising solid particle materials from high temperature exposure effect perspective. The first study was focused on analyzing the effect of long term high temperature (900 °C) in the optical, mechanical, thermal and chemical properties and parameters of the solid particle material. The second study was focused in the effect of long term thermal cycling, in which is considered that the materials should resist several thousand charge-discharge cycles remaining with acceptable operational conditions. For achieving an accelerated thermal cycling test with realistic thermal conditions, a novel device was developed to perform the thousands of thermal cycles required. Electronic, software and hardware design was developed and implemented. Current device has performed more than 20 thousand cycles for different kind of materials, analyzing the same properties and parameters as the first study.

RESUMEN

Las energías renovables tienen un papel importante en el desarrollo de los sistemas energéticos, la seguridad energética y la lucha contra el cambio climático. Con el soporte adecuado, el uso de la energía solar de concentración (CSP) podría alcanzar hasta un 11.3% de la producción mundial de electricidad. Esta tecnología ha demostrado tener un precio competitivo y tener la ventaja de poder integrar almacenamiento de energía térmica (TES). Esto da flexibilidad en la generación a esta tecnología renovable que otras no tienen integrada, tal como sucede con la energía eólica o la fotovoltaica.

Para continuar desarrollando esta tecnología, se ha propuesto el uso de solido particulados en plantas CSP. En este nuevo tipo de planta CSP de torre, se utilizan materiales sólidos granulados como Fluido de Transferencia de Calor (HTF) y material TES, de manera que se puedan alcanzar temperaturas de operación superiores a las plantas comerciales actuales. Una temperatura más alta se traduce en una mayor eficiencia en la conversión de calor a electricidad, debido al uso de mejores ciclos de generación eléctrica.

El objetivo principal de esta tesis es establecer la relevancia y proporcionar antecedentes, tanto teóricos como experimentales, sobre el uso de sólidos particulados como material de almacenamiento térmico y como fluido de transferencia calor para plantas de energía CSP de torre desde la perspectiva de los materiales, utilizando nuevas metodologías o existentes.

Durante este trabajo, la producción científica actual y la relevancia científica fueron estudiados mediante dos contribuciones, una para la energía solar de concentración y otra para el almacenamiento de energía térmica, ambas utilizando métodos bibliométricos. Para el estudio de CSP, se llevaron a cabo análisis adicionales de acuerdo con las tecnologías de aprovechamiento del recurso solar (cilindro parabólico, torre solar, disco Stirling y Fresnel lineal). Para el estudio TES, los análisis adicionales se realizaron de acuerdo con las diferentes formas de almacenar energía térmica (sensible, latente y termoquímica). Para ambos análisis, se identificaron los países, regiones, autores, revistas y comunidades de investigación más productivos. Además, se analizó el impacto del financiamiento y la cooperación entre países y entre

autores. Para desarrollar estos análisis bibliométricos, se implementó una metodología específica siguiendo los principios de la Bibliometría. Para estos fines, se utilizaron dos programas de software existentes con los que se desarrolló una parte del análisis, mientras que para realizar el resto del análisis se desarrolló un software hecho a la medida del estudio.

Para establecer los antecedentes de esta nueva tecnología, se realizaron dos análisis de estado del arte para obtener el estado actual de desarrollo de las plantas CSP con uso de sólidos particulados. El primero se encuentra orientado al diseño de la planta. Se analizaron varios receptores solares, así como sistemas de almacenamiento TES, intercambiadores de calor (HEX) y sistemas de transporte del material granulado. En el segundo estado del arte, se llevó a cabo un estudio basado en los sólidos particulados, con el objetivo de comprender el comportamiento de estos sólidos, así como identificar los materiales propuestos por los investigadores más relevantes en este campo.

El siguiente paso de esta tesis se centró en establecer los criterios de diseño de esta nueva tecnología, desde la perspectiva de los materiales. Esto se logró al encontrar los objetivos más relevantes con los que debe cumplir una central eléctrica de este tipo, así como la influencia de las propiedades y parámetros de estos materiales.

La última parte de esta tesis está relacionada con dos estudios sobre la durabilidad de algunos de los materiales más prometedores desde la perspectiva del efecto de exposición a altas temperaturas. El primer estudio se centró en analizar el efecto de la alta temperatura a largo plazo (900 ° C) en las propiedades y parámetros ópticos, mecánicos, térmicos y químicos del material. El segundo estudio se centró en el efecto de los ciclos térmicos, en el que se considera que los materiales deberían resistir varios miles de ciclos de carga-descarga de calor en condiciones operativas aceptables. Para lograr realizar pruebas de ciclos térmico acelerado con condiciones térmicas realistas, se desarrolló un nuevo dispositivo capaz de realizar los miles de ciclos térmicos requeridos. Se desarrolló e implementó el diseño electrónico, de software y de hardware. El dispositivo ha realizado más de 20 mil ciclos para diferentes tipos de materiales, caracterizando las mismas propiedades y parámetros analizados que en el primer estudio.

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List of Acronyms and Abbreviations

AA-CAES – Adiabatic Compressed Air Energy Storage

CAES – Compressed Air Energy Storage

CLAB – Complexity Lab Barcelona

CSP – Concentrating Solar Power

DSC – Differential Scanning Calorimetry

EDS – Energy Dispersive Spectroscopy

FB-HEX – Fluidized Bed Heat Exchanger

HEX – Heat exchanger

HTF – Heat Transfer Fluid

IEA – International Energy Agency

LHTES – Latent Heat Thermal Energy Storage

MBD – Materials Based Design

PCM – Phase Change Material

PSD – Particle Size Distribution

PSH – Pumped-Storage Hydropower

PV – Photovoltaic

SEM – Scanning Electron Microscope

SHTES – Sensible Heat Thermal Energy Storage

TCS – Thermochemical Storage

TES – Thermal Energy Storage

TGA – Thermogravimetrical Analysis

UTES – Underground Thermal Energy Storage

XRD – X-ray Diffraction

Part I

Introduction 1

Chapter contents

1. INTRODUCTION

It has been well established that renewable energy has a major role in energy systems development, energy security and climate change fight [1]. Electricity capacity additions have grown for renewable technologies such as photovoltaic and wind, reaching greater as shown in *Figure 1.1*. This can be understood by the current drop of renewable prices, which is expected to continue with the new IEA expected policies scenario (*Figure 1.2*) [2].

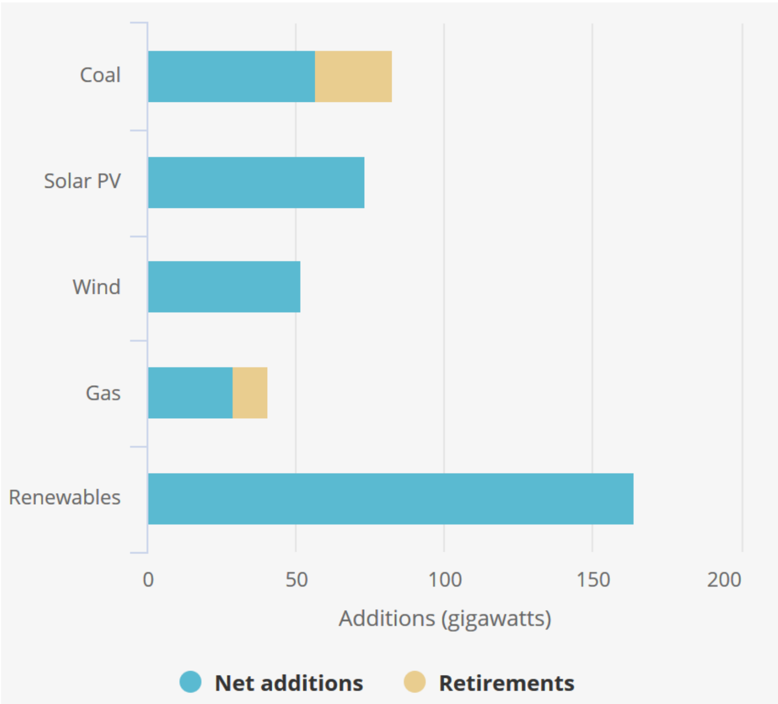

Figure 1.1. Worldwide electricity capacity additions by fuel, 2016 [3].

Today, solar photovoltaics (PV) and wind energy implementation lead new power plants construction over fossil fuel sources as shown in *Figure 1.3*. By 2020, new solar PV and wind power plants will add almost 400 GW. These new plants are expected to produce more than 1,150 TWh annually [4].

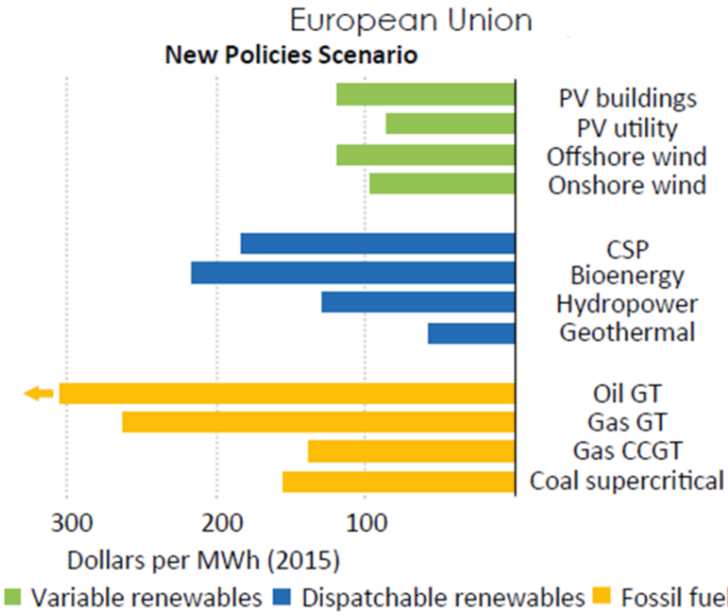

Figure 1.2. Levelized cost of energy (LCOE) in European Union in new IEA policies scenario [2].

Nevertheless, the variable renewable energies growth has some limitations due to flexibility problems. Solar and wind production (which are the ones that are being more implemented) does not match the electricity demand during the day. Other dispatchable renewables such as geothermal, hydropower or bioenergy have resource limitations either because lack of geographical resource availability or because there is conflict with other human activities (such as agriculture) [5–7].

Several strategies have been considered for solving this lack of flexibility. The first is to keep conventional power plants that can start electricity production when the variable renewables production falls. This reflects in CO_2 emissions and incrementing cost of electricity [8].

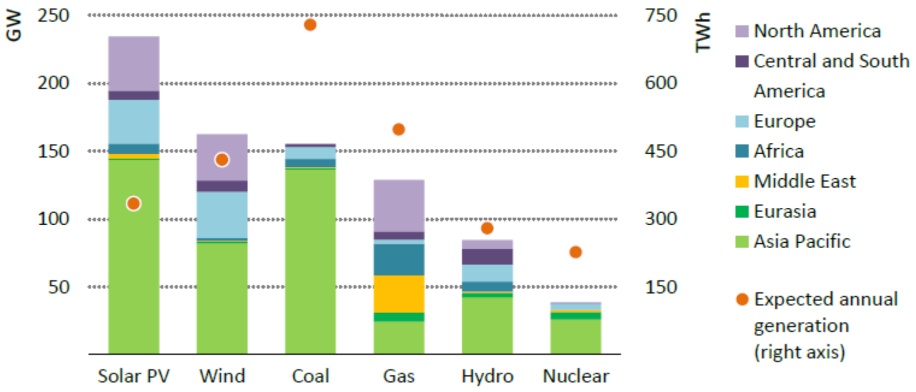

Figure 1.3. Power plants under construction or expected by 2020 in terms of power capacity (left axis) and the expected annual generation by source and region (right axis) [4].

The second strategy is based on interconnection between energy systems, which gives grid flexibility to renewables, energy security and tariff leveling between the interconnected systems [9]. Nevertheless, there are geological barriers that limit the energy exchange, as well as it only reduces the need of backup power plants but does not eliminate them completely, since renewables intermittence can affect more than one energy system at a time. Also, interconnection can potentially increment losses in the electricity transportation. The final strategy is energy storage, which can potentially eliminate the backup plants shifting production to supply demand and providing supply security. Nevertheless, the main drawbacks are the power losses in energy conversion, the elevated costs of some of the storage technologies, the lack of critical materials for some of the storage technologies and the geographical needs of several storage solutions [10].

Current electricity storage is dominated by reversible hydropower plants or Pumped-Storage Hydropower (PSH) (*Figure 1.4*), with a high efficiency energy conversion and commercially viable. Hydro storage has some limitations related to agriculture and large extension of land requirements. Nevertheless, pumped hydro implementation capabilities are important to countries under development in which hydro potential has not been fully deployed [11]. Other technologies like compressed air storage (CAES), flywheels, electrical batteries, vanadium redox flow cells, super capacitors, magnetic storage and thermal energy storage (TES) are currently under development for large commercial implementation or pre-commercial stage [12]. Thermal storage is not accounted in *Figure 1.4*, since TES has not yet been implemented for storing energy from the power grid. By now, the most commercially viable energy storage solution at high capacity with high efficiency (which is affected only by heat losses during the storage time) is the thermal energy storage (TES) system integrated with concentrated solar power (CSP) thermal plants, since there is no need for an additional energy conversion [13,14]. Even that there are some electrochemical storage plants, the lack of materials needed (such as lithium) limits big scale implementation.

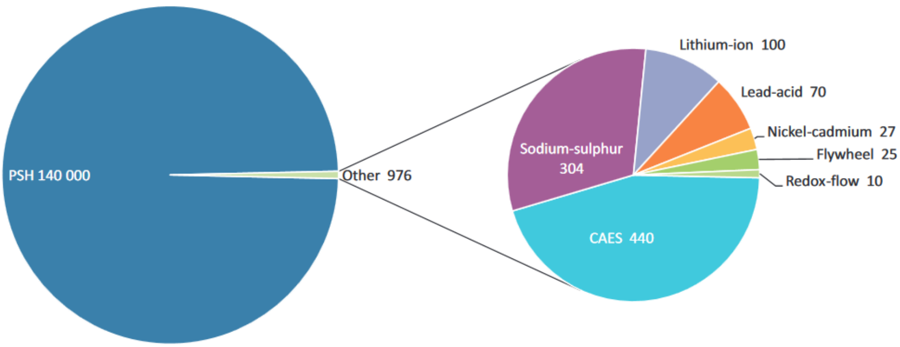

Figure 1.4. Current global installed grid-connected electricity storage capacity (MW) by technologies [11].

1.1. Concentrating Solar Power (CSP)

It is projected that CSP power can reach up to 11.3% of world's electricity production if a good policy support is endorsed [13,15]. Nevertheless, the regions more capable for developing CSP are clearly located in highly irradiated areas with a technical potential of almost 3 million TWh per year. In these regions, installed capacity has reached over 4,500 MW in 2015, in contrast with the almost 1,300 MW of 2010 [14,16,17]. CSP development is more viable for North Africa, the Middle East, northwestern India, the southwestern United States, Mexico, Peru, Chile, the western part of China and Australia. Also, it has a more moderate development potential for southern Europe, Turkey, central Asian countries, Brazil, Argentina, central USA and China [13]. The first commercial plants were built in Spain and the USA, but recently other countries are developing their CSP potential (such as the 160 MW plant in Ouarzazete, Morocco) [18]. Either for population increase, economic development or both, regions with more thermal CSP potential are also the ones that are expected and desirable to grow renewable energy development [3].

Solar energy can be harnessed by different technologies as shown in *Figure 1.5.* Parabolic trough concentrator, also called linear concentrator, uses one dimension curved mirrors, which allow concentrating sunlight in a tube which transports the heat transfer fluid (HTF) to the heat storage or directly to the power block for electricity generation [19]. Parabolic trough collectors usually use water, synthetic oil, molten salts or steam. On one hand, steam can be used directly in the power generation cycle, making it expensive to incorporate heat storage using the same HTF as TES medium [20]. On the other hand, water, synthetic oil and molten salts can be easily used [21]. Magnitude of parabolic trough power plants can be noted in *Figure 1.6*. Linear Fresnel reflectors are similar to parabolic trough, but instead of one single curved mirror they use several smaller curved mirrors in a flat disposition. Fresnel reflectors have better land usage efficiency and lower construction costs compared with parabolic trough [13]. A parabolic dish concentrates solar heat in one single point. The parabolic dish concentrator allows achieving higher temperatures compared with parabolic trough; nevertheless, the power output is limited and therefore it is most suitable for small capacities (up to 50 kW) [22].

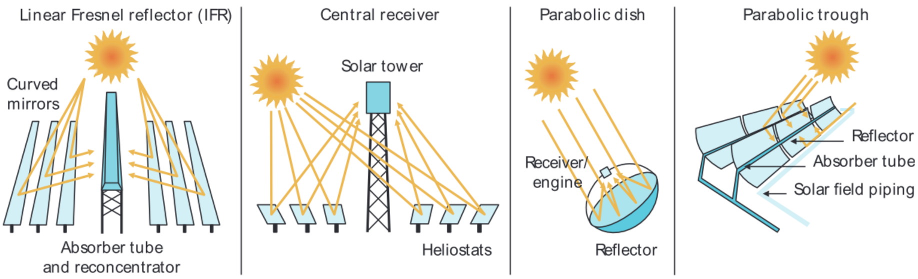

Figure 1.5. Most commonly used CSP technologies for achieving high temperatures [15].

Figure 1.6. Parabolic trough power plant in Mojave Desert [23].

For the central receiver concentrator both high temperatures and high power output are possible (up to hundreds of MW) [24]. CSP central tower is one of the most favorable technologies, since it can achieve high power, and high efficiency in the electric generation cycle due to the high operation temperatures, and high land efficiency and enough heat storage to overcome solar energy resource variability [13,14]. In a central receiver concentrator, there is a field of curved tracking mirrors called heliostats that concentrate solar flux in a single point in a receiver on the top of a tall tower. This can be appreciated in *Figure 1.7*.

Using a HTF material, solar heat from the concentrated solar flux is absorbed at the receiver getting the energy input in the power plant [25]. Thermal energy is then transported by moving the HTF either to a heat exchanger for providing thermal energy to the power generation block or to a thermal storage. The thermal energy moves using HTF as a carrier thru the system pipe network that connects the storage (charged or exhausted storage) and heat exchanger just to go back to the receiver when the solar resource is available for recharging. There are some cases where the same HTF goes directly to the generation cycle, so there is no heat exchanger and the HTF heat energy is transformed directly to electricity [26].

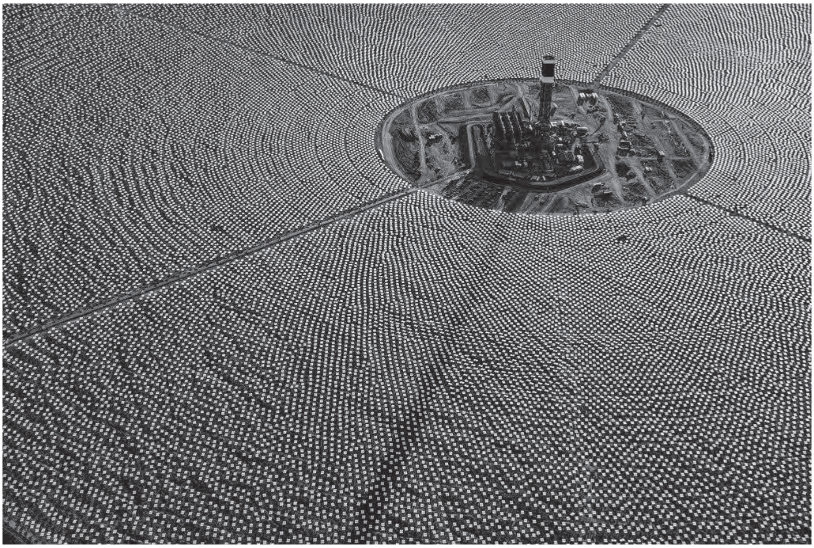

Figure 1.7. 392 MW Ivanpah solar power facility in California [27].

Power output in CSP thermal plants is important, but so is the temperature; achieving high temperature reflects in an increase of heat to electricity conversion efficiency; therefore, increasing the operation temperature is desirable. Central receiver tower concentrator using molten salts reaches temperatures up to 565 °C. This is determined by molten salt material itself. At higher temperatures molten nitrates salt is chemically unstable, becoming highly corrosive and decomposing [28].

CSP tower plants offer the best configuration of the four solar harvesting technologies with an acceptable power output. Theoretically, CSP tower can reach over 2000 °C, while only Stirling dish (parabolic dish) can get over 4000 °C but with a low power output [29]. For this reason, CSP tower can be furtherly developed for reaching higher temperatures.

1.2. Thermal Energy Storage (TES)

As mentioned before, thermal energy storage in CSP is already implemented in current commercial power plants. The main advantage is to shift the solar energy harvesting availability into the demand curve. In free electricity markets this has more advantages since this shift can be implemented to the moment the electricity is more expensive, making the CSP plant more economically feasible. *Figure 1.8* illustrates this shift in which sunlight heat flow at the first hours is stored for later use at hours when there is no sunlight. Thus, CSP plants with thermal energy storage have only few hours of storage capacity, only enough for a daily shift [13].

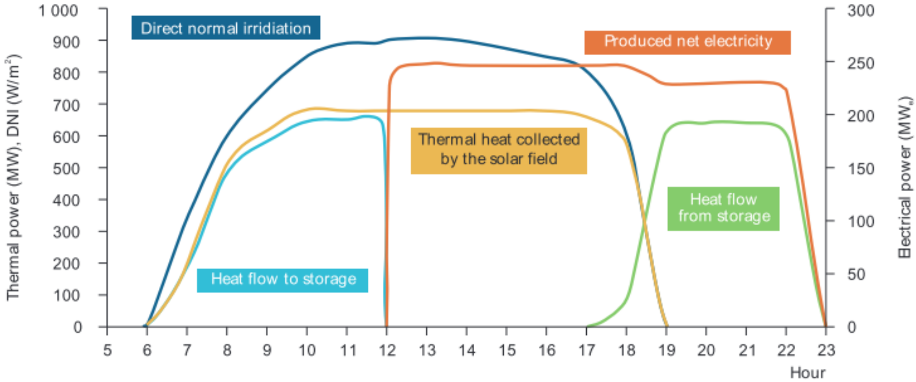

Figure 1.8. Use of thermal storage for shifting production to cover evening peaks [15].

From the TES materials perspective, there are three different ways for storing heat or cold for later use. They are classified according to the way of storing the heat in sensible, latent and thermochemical storage as shown in *Table 1.1*. These systems can be implemented in passive or active systems. An active system has forced convection heat transfer in or out the TES media, while a passive system does not. Active systems can be direct (use the same TES and HTF media) or indirect (use different HTF and TES media). Passive storage usually has different media for TES and HTF, since HTF passes through TES material for charging/discharging processes [30].

Table 1.1. Typical parameters of TES systems [31].

Type of storage	**Capacity (kWh/t)**	**Efficiency (%)**	**Cost (€/kWh)**
Sensible	10 - 50	50 - 90	0.1 - 10
Latent	50 - 150	75 - 90	10 - 50
Thermochemical	120 - 250	75 - 100	8 - 100

Sensible heat storage

In sensible heat TES materials, the heat energy is stored according to their specific heat capacity (C_p), and the stored energy can be expressed as:

$$Q = m \cdot C_p \cdot \Delta\mathrm{T} \qquad \text{(Eq 1.1.)}$$

where m is the mass (kg), C_p is the specific heat capacity ($kJ \cdot kg^{-1} \cdot K^{-1}$) and ΔT is the temperature increment during the heat absorption process. During this process, there is no phase change expected (not even solid-solid allotropic changes) and TES materials experience a raise in their temperature. The amount of energy absorbed is proportional to the density, volume, specific heat capacity as well as to the change of temperature of the material itself. Typical materials and media used for sensible storage include water, thermal oils, molten salts, minerals (rocks, sand, gravel, etc.) and concrete [32,33]. Current commercial CSP power plants use sensible heat storage for storing energy by using molten salts and thermal oils. There are new approaches under research for storing sensible heat in CSP, such as solid particle materials. Sensible TES has enough technological maturity to be developed in state-of-the-art commercial CSP plants (*Figure 1.9)*, mainly parabolic trough, linear Fresnel and solar towers. Sensible heat storage is also used in other applications like district heating, waste heat harvesting, high temperature industrial processes and adiabatic compressed air energy storage (AA-CAES) [34].

Figure 1.9. Two-tank thermal storage system of Andasol CSP plant [35].

As shown in Table 1.1, sensible heat storage has the lowest energy density and the lowest cost with an acceptable charging/discharging efficiency that can reach up to 90%. Storage period depends on thermal loses on the barriers of the storage system, and on the amount of stored energy. Therefore, the greater energy density the lower thermal losses, and a greater efficiency. Storage period is determined by the application and the way it affects thermal losses. Thus, applications like CSP have a daily typical storage period, while in other technologies such as underground thermal energy storage (UTES) monthly storage periods can be reached [31].

According to the application, sensible TES have different barriers and research and development goals. *Table 1.*2 shows development status, barriers and R&D topics for different sensible TES applications. Use of solids at high temperature outstands as a technology under development in which main R&D concerns are focused on the materials that can be used at these temperatures [34].

Table 1.2. State of development, barriers and main R&D topics for sensible TES [31].

Sensible TES application	**Status (%) Market/R&D**	**Barriers**	**R&D topics**
Hot tower tanks	95/5	-	Super insulation
Large water tanks	25/75	System integration	Material tank, stratification
UTES	25/75	Regulation, high cost, low capacity	System integration
High temperature - Solids	10/90	Cost, low capacity	High temperature materials
High temperature - Liquids	50/50	Cost, temperature above 400 ^oC	Materials

Latent heat storage

Latent heat storage works storing the energy during a phase change (usually solid-solid or solid-liquid). The temperature is stable during the phase change and the energy storage density is higher compared to the sensible storage [30]. The thermal energy stored can be expressed as:

$$Q = m \cdot \Delta \mathrm{T} \qquad \text{(Eq 1.2.)}$$

where m is the mass (in kg), ΔH (in $J \cdot kg^{-1}$) is the heat absorbed during phase change also known as phase change enthalpy or latent heat. Latent heat storage materials, or phase change materials (PCMs), include paraffin, fatty acids, esters, alcohols, glycols, salts, salt eutectics, salt hydrates, and metals and alloys [36].

PCM implementation and development depends largely on the application temperature range. Low temperature applications in building, food industry, cooling for medications or cooling for medical transplants are almost fully developed but their introduction to the market is slow. Nevertheless, use of PCM in high power systems are yet under research and development [34].

Thermochemical heat storage

Thermochemical storage is achieved by reversible chemical reactions that can absorb or release heat associated to the reaction enthalpy. The reaction depends mostly on the pressure and temperature, as most of the reactions studied are solid-gas reactions. Energy density is higher compared with latent and sensible heat storage [30,36]. Nevertheless, thermochemical storage is under early development and there is almost no commercial application. High costs and complexity as well as materials in the reactor design are the main concerns to this technology [31].

As shown in *Table 1.1*, energy density is very attractive for thermochemical storage. In chemical reactions, reagents can be stored separated from each other for long periods of time without thermal losses. Other way of storage is by sorption processes, which include adsorption or physical bonding, and absorption. Sorption heat pumps are the only fully developed thermochemical application, while other applications are still under development. Chemical reactions are still under research and will require more time to develop [34,36].

1.3 Power generation cycles

As mentioned before, in CSP the temperature has a main role since it is directly related to the heat to electricity conversion efficiency. One same power generation block can consist on more than one different thermodynamic cycles, especially when the heat input has high temperature (since exhausted gas from one thermodynamic cycle can be used for a different lower temperature thermodynamic cycle). Common single cycles include Rankine and Brayton cycles, whose efficiency depends on the operating temperature and the pressure as shown in *Figure 1.10*. The main Rankine cycle has four stages:

a) Compression of the working fluid to high pressure.
b) Heating and vaporization of the working fluid by the input heat energy source.
c) Expansion to get to a lower pressure over a turbine, generating the mechanical work needed for electricity generation.
d) Cooling the working fluid to the initial state.

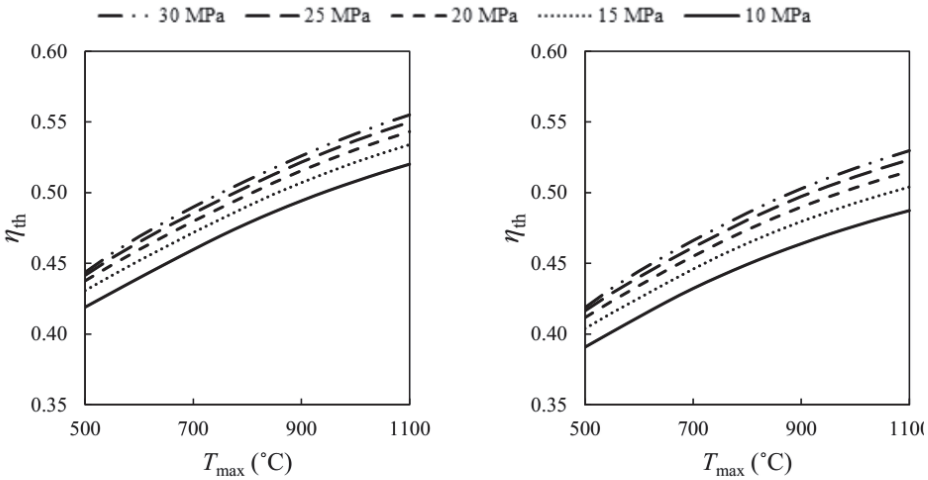

Figure 1.10. Rankine generation cycle efficiency under (a) wet-cooling and (b) dry-cooling conditions [37].

For Brayton cycles the workflow is similar, although in this case the working fluid remains in the gas phase throughout the cycle (also known as supercritical). This change allows Brayton cycles to get to much higher temperatures and, in consequence, increase the conversion efficiencies [37] (determined by the maximum efficiency for a Carnot engine).

Combined generation cycles include two or more thermodynamic cycles, a topping cycle (high temperature) and one or several bottom cycles (low temperature). Combined generation that use a Brayton thermodynamic cycle as a top cycle offers the best use of concentrated solar energy when the ideal service temperature is far beyond to the one used in sub-critical Rankine thermodynamic cycles. Thermodynamic cycles that can be used in CSP include Organic Rankine cycle, steam Rankine cycle, He-Brayton cycle, CO_2 recompression cycle, CO_2 Brayton cycle, regenerative Brayton cycles, etc. A comparison of some of these cycles is presented in *Figure 1.11*.

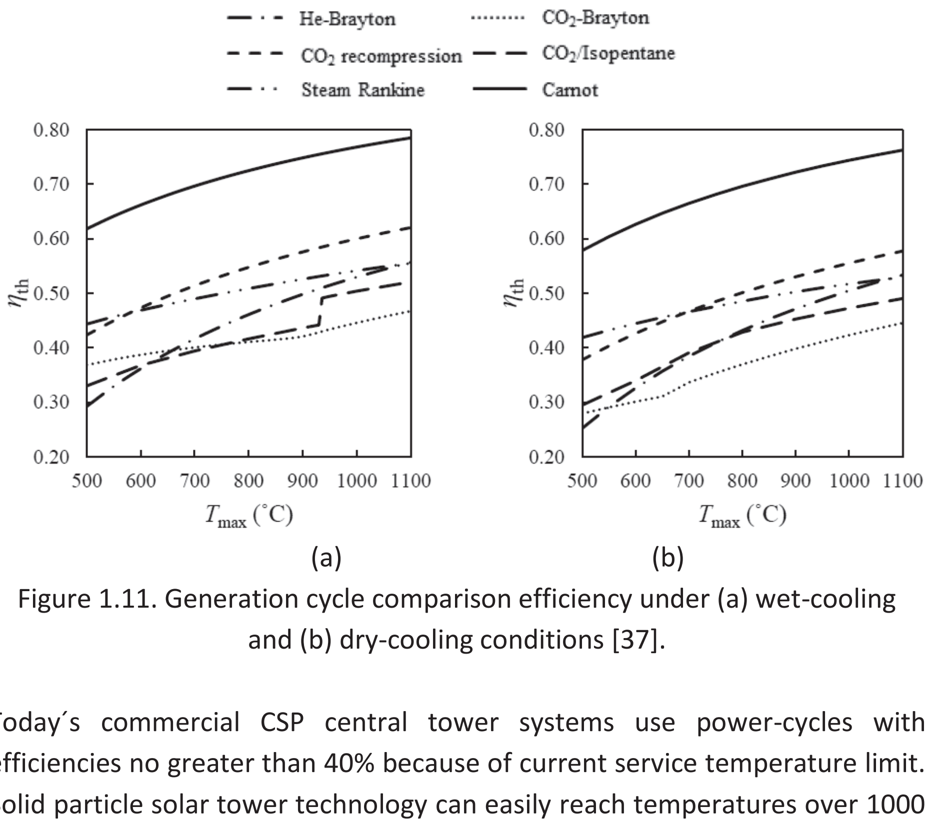

Figure 1.11. Generation cycle comparison efficiency under (a) wet-cooling and (b) dry-cooling conditions [37].

Today´s commercial CSP central tower systems use power-cycles with efficiencies no greater than 40% because of current service temperature limit. Solid particle solar tower technology can easily reach temperatures over 1000 °C, and, therefore, power-cycle efficiency can increase up to 50-60% by using high temperature thermodynamic cycles (like Brayton cycle and supercritical CO_2 or steam cycles) and even combined generation cycles [38,39]. Further to this, particle media for sensible heat storage is expected to have low price and a lowering effect in the levelized cost of electricity [38].

Solid particle CSP overcome the temperature and stability drawbacks, since solid particles are used as both TES and HTF material [25]. The solid particle TES system has high performance due to the high temperature operation, and low cost from the materials perspective [40]. By using direct solar absorption, receivers in which particles fall through a beam of concentrated radiation have the potential to increase temperature of HTF/TES media over 1000 °C [38]. Therefore, a complete CSP solar tower system that operates over 600 °C and up to 1000 °C is possible, since stable materials can be used and thermal self-insulation can be used to minimize thermal losses in the heat storage medium [41]. Finally, media storage system are projected to have lower price maintenance and materials costs [28].

Thus, we can recap on three main advantages relative to the storage media itself compared with current commercial molten salts solution:

a) Proposed solid particles materials are chemically inert and stable beyond 1100 ˚C.
b) Particles are capable of storing energy over a greater temperature span compared with other media currently in use, thus increasing the energy storage density.
c) Materials costs are expected to be relatively low.

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Objectives 2

Chapter contents

2. OBJECTIVES AND THESIS STRUCTURE

2.1. OBJECTIVES

The main objective of this thesis is to enhance relevance and provide theoretical and experimental background for solid particles to be used as high temperature TES and HTF for CSP tower plants from the materials perspective by using existent or new methodologies. The study must allow an evaluation of the material performance during the system lifetime due to high temperature effect. In addition, relevance of TES and CSP has been developed as well as a state-of-the-art analysis of solid particles for CSP. To achieve this goal several specific objectives were established:

- Provide TES and CSP background in order to display the solid particle materials main research area. This includes a CSP and TES classification as well as to show the main capabilities of these research topics.

- Perform analyses that recognize, in a quantitative way, the importance of CSP and TES research fields by using bibliometric methods.

- Use available tools or develop new software to perform the bibliometric analyses. This program code must be easy to reuse for other research analyses.

- Perform a state-of-the-art analysis of the solid particle system development research, identifying the different ways proposed by different research groups to achieve a viable plant.

- Recognize the main solid particle materials concerns acknowledged by the most relevant researchers in solid particle materials for CSP research field. Find the properties and parameters that have more influence in this technology viability.

- Introduce the design criteria for solid particles CSP from the materials perspective. Find the most relevant key objectives that the power plant must comply and the influence of the different material properties and parameters.

- Find the materials index for the different system functional parts in order to perform a material selection to find the best available materials.

- Characterize the main properties and parameters of the solid particle materials according to the design criteria.

- Study the effect of long term high temperature treatment (thermal aging) in the materials parameters and properties. This study considers the effect of the constant heat itself.

- Examine the effect of high temperature thermal cycles in the materials parameters and properties for complementing the thermal aging study.

- Develop a thermal cycling device, since existing commercial devices do not comply with the conditions of control, cycling speed and temperature range needed for simulating thermal aging under service conditions.

2.2. THESIS STRUCTURE

This dissertation is based on scientific articles that have been or are being published in different high quality scientific journals in the energy storage, solar energy and materials science research field. The thesis is divided in six main chapters. *Figure 2.1* shows the content framework by chapter as well as seven scientific articles. Each chapter is summarized as well as the distribution of the papers.

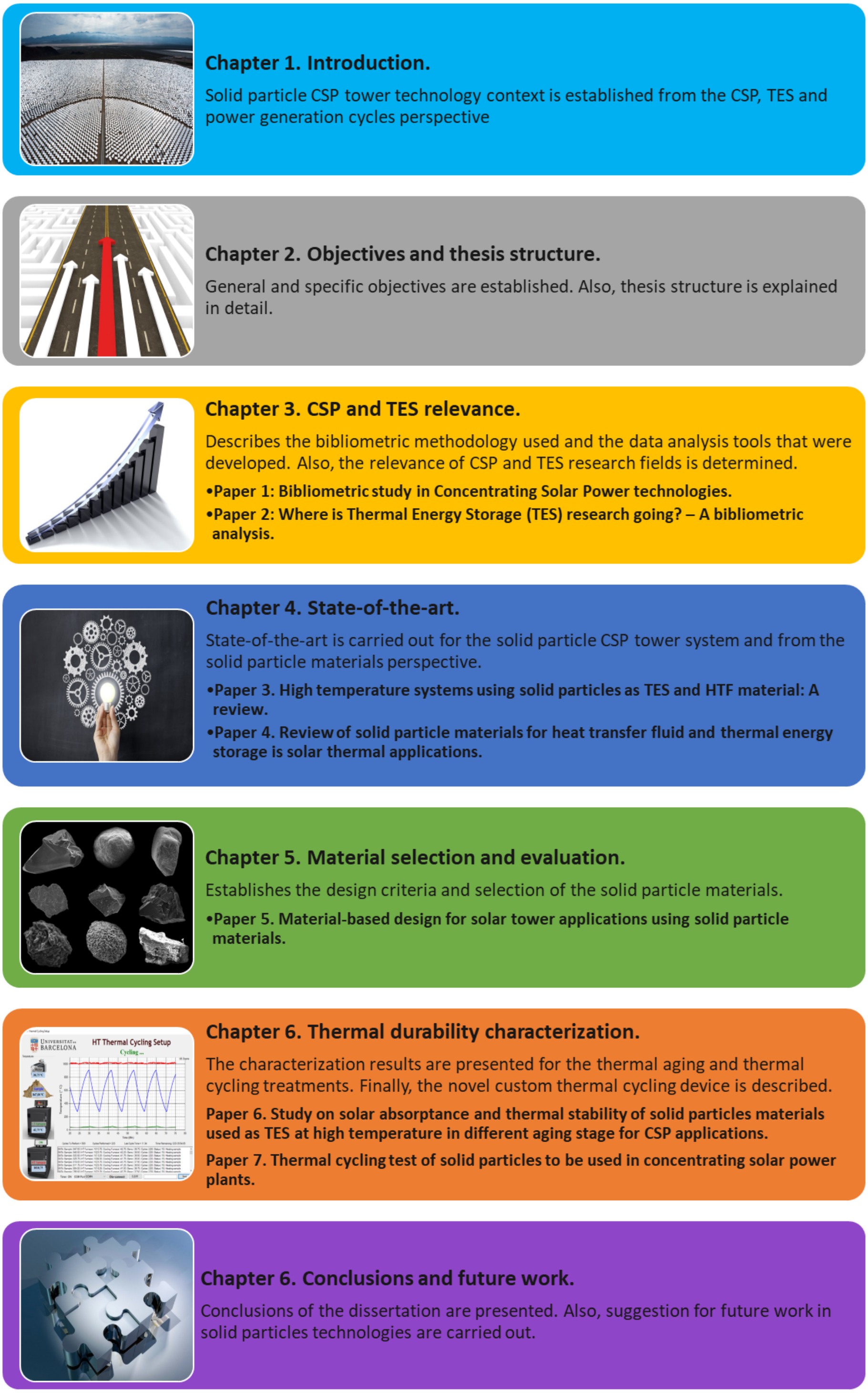


Figure 2.1. Thesis content framework by chapter with the scientific articles.

CSP and TES relevance

3

Chapter contents

3. CSP AND TES RELEVANCE

Renewable energies have gained attention during the last decades for several reasons, such as increasing energy security, reduce fossil fuel dependence or reduce environmental damage [1]. Since solar energy resource is abundant enough to meet human needs, renewable energies related to harvesting sunlight are very promising. Also, energy storage has gained attention due to the possibility to be used as an energy carrier (like batteries) and to the effect in energy networks by increasing the share of renewable energies that use variable primary energy resources (such as wind and solar power) [2,3]. The research relevance of these topics is obvious when considering them in a qualitative manner, but not necessarily in a quantitative one.

3.1. BIBLIOMETRICS

Evaluating impact of scientific output, as an abstract concept, is inherently immeasurable. Nevertheless, several techniques have been developed to quantify scientific impact and, therefore, scientific relevance [4]. Scientific literature has a long history, especially during the last century. Before Internet and electronic information were invented, documented scientific research was limited. Web of Science general database reports that about 5400 scientific articles were produced during 1920, and it was not until 1960s that annual production reached 100 thousand articles. It was during that decade that Bibliometrics appeared replacing its predecessor, the statistical bibliography [4]. The first time that the term *bibliometrics* appeared in print was during 1969 by Alan Pritchard, year in which annual production reached 155 thousand of scientific articles [5]. At that time, Bibliometrics was defined as the "applications of mathematical and statistical methods to books and other media of communication". In the same year, the term *scientometrics* was coined by Nalimov and Mulchenko for the use of quantitative methods for analyzing science information. This two terms are actually used as synonyms [6].

As science literature grew, definition of bibliometric analysis grew as well. In order to include the use of information technologies, the term *informetrics*, *webometrics* or *cybermetrics* began to be used. During 2018 over 2.6 million of scientific articles were published, meaning that for the last decades every 15 years scientific published output has been doubled [6]. Several thousands of papers on specific research fields require the use of different methodologies and tools to analyze this large amount of information.

Nowadays, Bibliometrics is being used for measuring relevant scientific output in fields such as management, econometrics, data envelopment, gray systems, innovation, health economics, marketing, statistics, ecology, production management and renewable energies, among others [7]. Bibliometrics is now considered useful for getting an overview of a particular research field, the cooperation between authors, countries and other entities and for research management and evaluation [8].

Energy related fields are suitable for bibliometric analysis [9]. In order to quantify TES and CSP relevance, two bibliometric studies have been carried out with a specific methodology and tools for this purpose. This methodology will be described in the following section and then the bibliometric studies will be presented.

3.2. TOOLS AND METHODOLOGY

In order to perform the two bibliometric analyses several stages were followed. These stages can be appreciated in *Figure 3.1*. Each step has different complexity to be completed. For example, selecting the data source is much easier compared to programming a specific code to perform a particular analysis.

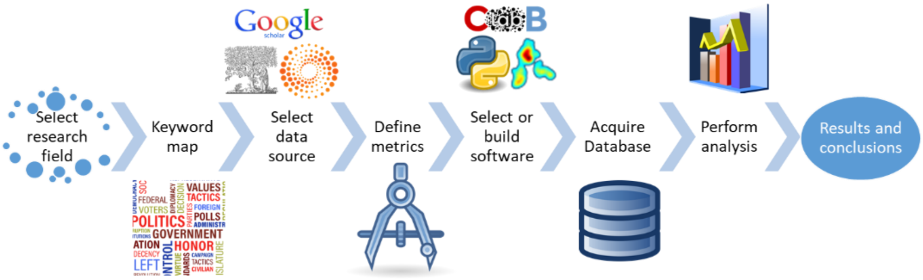


Figure 3.1. Methodology stages for performing a bibliometric analysis.

Selecting the research field

Although it seems obvious that selecting a research field of study is done before deciding to perform the bibliometric analysis, it is important to define the boundaries on the analysis. Selecting a vast research field will lead into enormous efforts to build the keyword map, acquire the database, perform the analysis and get to conclusions. On the other hand, a narrow particular research field could result in small number of papers and wrong generalizations in the conclusions. For example, if a bibliometric analysis is required for all the energy research field, it would lead into a huge database with subjects too different from each other, like oil refining combined with solar photovoltaics, led lights or even energy consumption studies. Even if the analysis could be performed with large human and computational resources, getting to conclusions could be very challenging.

Research field can also include sub-research fields that could be compared between each other. For example, CSP bibliometric analysis could be furtherly analyzed by harvesting technology (parabolic trough, Stirling dish, Fresnel and solar tower). Each of this sub-research fields can be analyzed with the same metrics used for the main research field analysis.

Finally, to define the subject areas is also important for refining the boundaries. Current data sources group papers into subject areas in order that the main aim of each article could be aligned with one or several research areas. Using the CSP research field example, papers which are focused in Medicine or Social Sciences subject areas could not be on the objective of a CSP bibliometric analysis centered in the mentioned technologies, even that they are related to CSP research field.

Building a keyword map

In order to browse the different data sources, a *search string* must be defined. Usually there is an easy (but not too effective) way to search by using the words or phrases that are related to the selected research area. Nevertheless, more effective *search strings* can be defined by using quotation marks for searching an exact phrase, Boolean operators (AND, OR, NOT) for excluding or include multiple criteria, as well as parenthesis for correct grouping of these operators.

For the elaboration of this *complex string*, a spreadsheet was build-up with several formulas to automatically generate the string based on several phrases grouped by rows. *Search string* is divided by rows; each one represents a *complex condition* to be complied. An article needs to comply with one or more of these *complex conditions* in order to be included in the search results (since all the *complex conditions* are linked by AND Boolean operator).

The *complex conditions* are elaborated by a *main phrase*, *complement phrases* and *exclusion phrases*. In order to include a paper in the search results, a *main phrase* must be present in one of the search fields (title, abstract, author keywords or journal keywords) as well in at least one of the *complement phrases*. If there are no *complement phrases* in the row only the main phrase is required. Finally, if at least one of the *exclusion phrases* of the row is present in anywhere of the search fields the paper is discarded. *Figure 3.2* shows an example of the main structure of the keyword map for mechanical energy storage, each row representing one *complex condition* and the last row showing the *search string*.

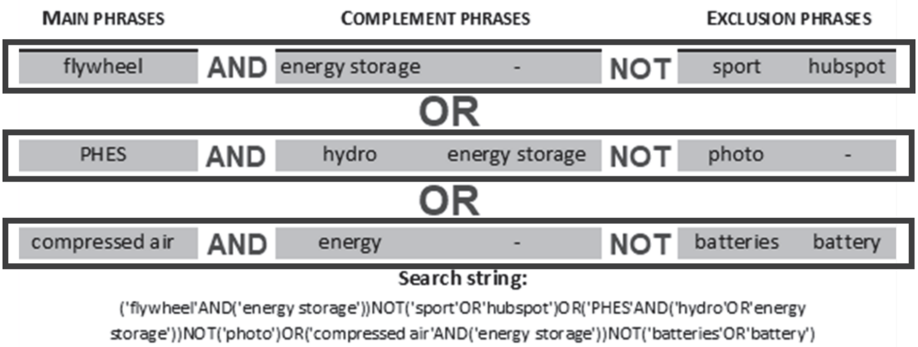


Figure 3.2. Keyword map example with the resulting *search string*.

Building a good keyword map is essential for getting valid results. Therefore, it must be built by experts in the research field who have knowledge of the terms used by the area of study. Also, verifying the results of all the search string as well as of each row is recommended to ensure the future database integrity, since it must be guaranteed that the selected articles fall into the research field boundaries.

Selecting the data source

For performing a bibliometric analysis, a data source is needed. A data source groups scientific journals, conference proceedings, books, etc. Data sources are commonly used for looking for scientific content rather than for bibliometrics. Nevertheless, sometimes information is facilitated in order to perform an analysis. The most common data sources are Web of Science (produced by Clarivate Analytics), Scopus (produced by Elsevier) and Google Scholar (produced by Google). For bibliometric analysis, Web of Science and Scopus are the most commonly used, since Google Scholar doesn´t facilitate bulk data sharing thus making database extraction too complicated. Also, there is little information of what is covered by Google Scholar [8].

Web of Science databases contain over 104 million of scientific articles. Within Web of Science, there is a special database called Web of Science Core Collection. This special database has more citation information available for a bibliometric analysis. Core collection includes more than 64 million of papers in different citation indices such as Science Citation Index Expanded, Social Sciences Citation Index, Arts & Humanities Citation Index, Emerging Sources Citation Index, Conference Proceedings Citation Index and Book Citation Index. Other specialized collections are also included such as MEDLINE, BIOSIS Citation Index, CAB Abstracts, among others [10].

Scopus covers over 62 million articles included in scientific journals, conference proceedings and books. Nevertheless, Scopus is limited in their coverage in social sciences and humanities, as well as in conference proceedings and books [8,11].

Google Scholar is not friendly for bibliometrics. It is a free on-line search engine for scientific and scholar literature. The collection has more coverage compared to Web of Science or Scopus, but some of it is of lower quality. Other problems that Google Scholar presents are duplicate records and fake publications [8].

There are other regional databases such as Chinese Science Citation Database, Russian Science Citation Index, SciELO Citation Index, etc. Nevertheless, these options are not considered since part of the metrics used are based in country and regional research efforts.

For the bibliometric studies in this dissertation, Web of Science Core Collection database was used, since it has the most complete registry of the considered databases with high quality publications and it complies with the metrics considered for the analyses.

Defining the metrics

Bibliometric metrics are used for studying different facets of a research field, such as research evaluation, research management, measuring impact, among others. In addition, metrics can be oriented to evaluate specific regions or countries, institutions, individuals, communities, etc.

For current analysis different metrics have been defined according to these criteria and are listed in *Table 3.1*. Different metrics have been defined to analyze the research field in general, country/regions, authors and journals performance. Each metric can be presented using a chart, table or both, depending on the best appreciation of the metric.

Table 3.1 Metrics used for bibliometric analyses.

METRIC	DOMAIN OF ANALYSIS	PROGRAM/TOOL
Total publications	Main research field and sub-research fields	Python code
Total Citations	Main research field	Python code
Keyword evolution	Main research field	VOS Viewer®
Most cited publications	Main research field	Python code
Publications evolution per country	Main research field and sub-research fields	Python code
Country performance ratio	Main research field	Python code
Tech comparison evolution	Sub-research fields	Python code
Most productive authors (h-index)	Main research field and sub-research fields	Python code
Country co-authorship	Main research field	VOS Viewer®
Scientific communities	Main research field	CLab tool
Relevant Journals/publications	Main research field and sub-research fields	Python code
Journal co-citation relevance	Main research field	VOS Viewer®
Funding analysis	Main research field	Python code

Total publications and total citations metrics show the evolution during the last decades of each research field. Keyword evolution illustrates the changes of the most used keyword thru time. Country evolution and country performance ratio allow to identify the most productive and relevant country efforts, while country co-authorship shows the cooperation between different countries.

The tech comparison evolution shows the number of publications for each sub-research field for the last decades. Scientific communities are identified according to the co-authorships without any institution or country relation. This can be useful to connect relevant research communities for the research field whom does not cooperate with each other. Finally, funding analysis can be relevant for evaluating funding efforts and their relation to scientific output.

Acquiring the database

Downloading the database is more a mechanical task than a complex one. Web of Science Core Collection only allows to export the records in groups of 500 publications. Each 500 set exportation must be performed twice since parameters differ for two of the three software tools, since one of them should include all the references used in the publication. Thus, for each thousand articles in database, four export procedures are required. These records are divided by columns, and each element of each column can contain a single record or a list of records. For example, it could contain the date of the publication or the list of authors.

Selecting/building the software

The bibliometric analyses require a set of software tools for obtaining the different metrics. In this case three different tools were used. The metrics in which each software was used can be observed in *Table 3.2*.

First, a program commonly used for bibliometric analysis called VOS Viewer® made by the Centre for Science and Technology Studies of Leiden University in The Netherlands [12]. This software tool was used to construct and visualize several bibliometric networks, for the keyword evolution, country co-authorships and journal co-citation relevance metrics.

The second program was made by Complexity Lab Barcelona (CLAB) of the Department of Fundamental Physics in University of Barcelona. This tool allows to group and identify communities that usually cooperate through publications co-authorships only by using Python and JavaScript coding. CLAB tool was used for identifying the scientific communities in the research field [13].

The third program was fully developed using Python coding. Most of the metrics were carried out using this set of tools. Between two and three thousand Python line codes were required for developing this tool. *Figure 3.3* shows the process to analyze the database. First, the data structure was formed in a Data Frame Python structure, which is a database that can have objects inside its registries. This was particularly useful for storing lists of authors, citations or countries inside a single registry. Also, Data identification was carried out in this stage, since exported data from Web of Science Core Collection was basically a text file. This identification step requires a lot of processing power, and was divided by groups in order to use multiple processor cores for registry identification. Once the main Data Frame was formed, different keywords were used to make a classification of the sub-research fields (mentioned as technologies in the bibliometric studies). This second stage formed new particular databases for each sub-research field so that the same code used for main research field database metrics could be used for the other databases.

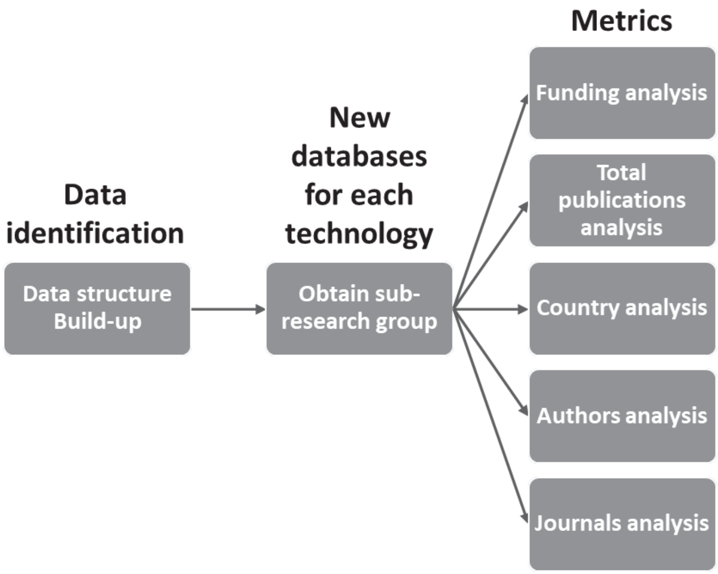


Figure 3.3. Database analyze process.

Different codes were developed for each metric. The authors and journal analyses outstands, since new data structures were formed to obtain author citing and number of publications per year, getting a particular h-index for the research or sub-research field only. Country analysis allows to group several countries by region for comparison with other countries or regions or within the region itself. For example, this was used in TES bibliometric analysis for grouping EU countries for comparison to other power countries in the field as well as within the EU.

Finally, funding analysis was accounted when there was some mentioned funding in the registry. No further analysis was performed since not all the funding agencies reported the same. For example, Chinese Academy of Sciences are mentioned for almost all funded Chinese research, while EU research funding efforts can be identified in several European programs or even in regional ones. In order to perform a more detailed funding analysis, a funding agencies directory must me formed and identified.

Performing the analysis

Once the program tools have been established and database has been properly acquired, the analysis is performed. In concordance with the research field selection, only the selected metrics are taken into the account, since not all available metrics are relevant to all bibliometric analysis. Furthermore, the manner of presenting the analysis results should be selected between a table or a graphic. Finally, additional processing can be made in order to enhance or denote specific results.

Results and conclusions

Final stage is interpreting the results and getting to conclusions. It is important to try to explain the bibliometric results with connection to well documented research field aspects, like funding efforts, technology maturity, economic aspects, as well as market driven forces.

3.3. P1: BIBLIOMETRIC STUDY IN CONCENTRATING SOLAR POWER TECHNOLOGIES

3.3.1. INTRODUCTION

Concentrating Solar Power has become a main role technology for the last decades. CSP had a first commercial wave between 1984 and 1995. Between 1995 and 2005 there was a period of commercial inactivity. Nevertheless, since 2005 CSP commercial implementation has been accelerating [14]. During 2017, CSP power generation accounted 11 TWh, and it is expected to get to 54 TWh in 2025 and 8550 TWh in 2040 with a sustainable development scenario. Even with current policies, it is expected to grow 270% in 2025 and 1,080% in 2040 [1].

Before 2015, CSP expansion was limited to Spain and the United States, and by 2017 there are installations constructed or under construction in Australia, Chile, China, India, Israel, Mexico, Morocco, Saudi Arabia and South Africa [15].

Research and development in CSP is mainly driven by partnerships between private and public sectors. Research is focused in reducing current system costs, developing high temperature processes, improving efficiency and implementing TES into CSP projects [15,16].

In order to measure the research activity in CSP research field, a bibliometric analysis was performed applying the mentioned bibliometric methodology. Results and analysis were incorporated in the scientific article named "Bibliometric study in Concentrating Solar Power technologies".

Research field

The field of study was CSP thermal technologies without accounting for applications in areas not related to the technology, such as photovoltaics, electricity storage in batteries, medicine, law, among others. Four sub-research fields were analyzed within main research field database according to the way the solar energy is harvested: parabolic trough, solar tower, Stirling dish and linear Fresnel. The period of analysis includes all the publications from 1969 to early-2019. In several metrics only the complete last 20 years of this period were analyzed (1999-2018).

Keywords

The keyword map defined for CSP research field can be observed in *Table 3.2*.

Table 3.2. Keyword map for CSP research field.

MAIN PHRASES	COMPLEMENT PHRASES			EXCLUSION PHRASES				
solar tower								
solar field	concentrated			pv	pvhotovoltaic			
parabolic through								
concentrated solar	power	thermal						
fresnel reflector								
stirling dish								
molten salts	power plant	storage	solar	pv	photovoltaic	polymer	barrier	lithium
heat transfer fluid								
heliostats								

These keywords were defined to include all the papers relevant for CSP as well as to establish the boundaries that cannot be cribbed from the data source. Also, additional keywords were defined to extract each of the sub-research fields for each technology analysis (*Table 3.3*).

Table 3.3. Sub-research field keywords.

PARABOLIC TROUGH	SOLAR TOWER	STIRLING DISH	LINEAR FRESNEL
parabolic trough	solar tower	stirling	fresnel
trough	tower	dish	linear fresnel
linear collector	heliostat		

Data source

The data source selected was Web of Science Core Collection due to the high quality publication selection and to the quality of bibliographic information available. Also, some of the research field boundaries were considered within the data source. Scientific articles, books, book chapters and conference proceedings were included.

Conference proceedings are very relevant for CSP research field and, therefore, were included even considering that some of this papers have also a scientific article associated for the same study. Finally, research areas that were not related, as defined during research field delimitation, were omitted from the selection.

Metrics

For performing the current study, several metrics were selected for CSP research field as well as of the sub-research fields. *Table 3.1* shows the metrics used for the CSP bibliometric analysis.

3.3.2. CONTRIBUTION

The tendencies of CSP research field were determined by the scientific article "Bibliometric study in Concentrating Solar Power technologies". Country and regional efforts, and country co-authorship collaborations were analyzed. CSP scientific communities and the most relevant journals and conferences were identified. Also, tech maturity was analyzed from the author keywords point of view. Funding efforts were pondered with number of publications evolution. Finally, each sub-research field was analyzed from the country, authorship and journal point of view.

The first and most relevant indicator is the current publication evolution (*Figure 3.4*), which includes also the citations. Even that there are some years in which the number of papers decreases, the final tendency is a growth in the number of citations and publications.

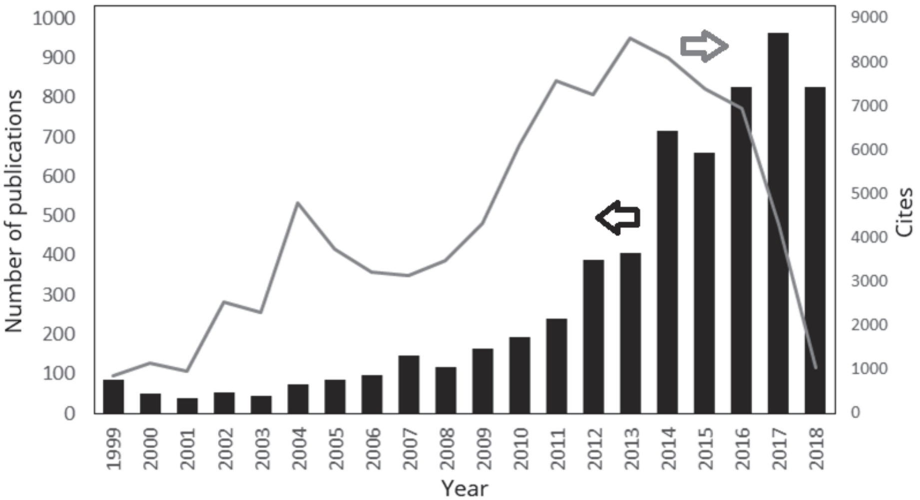


Figure 3.4. CSP publications and cites during the last two decades.

The most common keywords used by authors are presented in *Figure 3.5*. The evolution of these keywords can be used as an indicator of technology maturity. In recent years, terms like “optimization”, “plants” or “simulation” have been used with coincidence with large CSP plants deployment over the world [15].

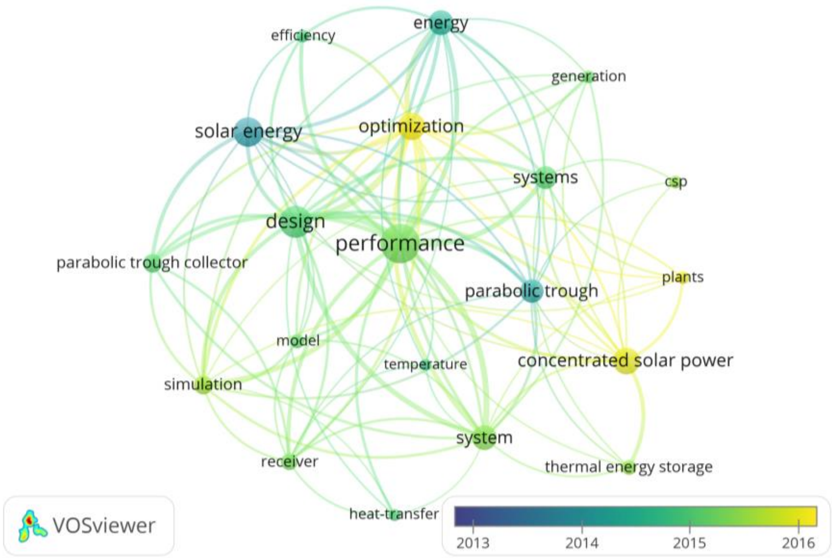


Figure 3.5. Evolution of trend keywords on CSP publications.

Country and regional analysis

During the early years of CSP, USA and Spain were the main leaders in development and implementation of this technology respectively. Nevertheless, in recent years other countries have made important research and implementation efforts [1,17]. Research efforts can be observed in the country evolution metric analysis shown in *Figure 3.6*. Today’s CSP research is leaded by European Union, with Spain, Germany, Italy and France as the main supporters in this region. Nevertheless, USA, China and, more recently, India started to have a main role in CSP technology development.

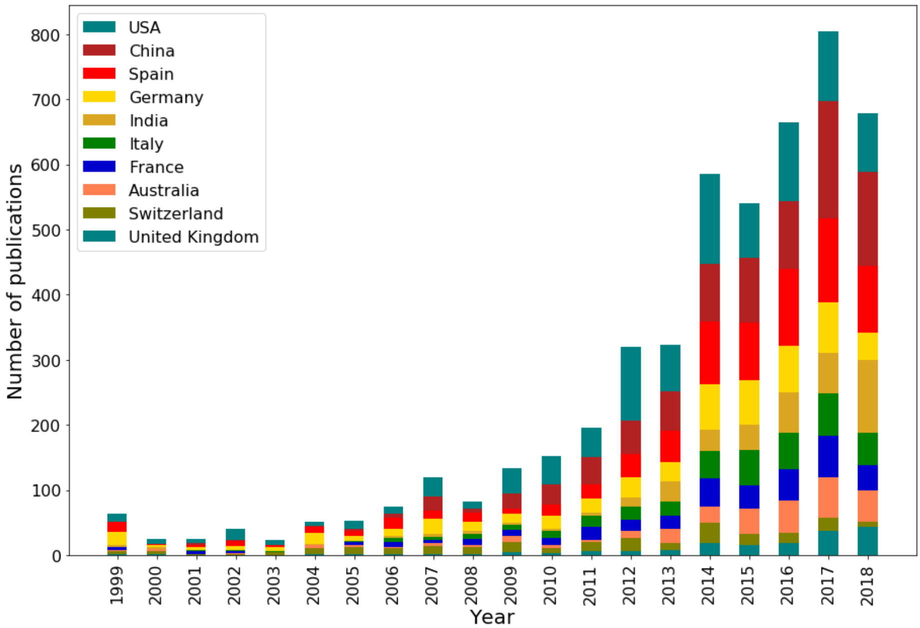


Figure 3.6. Publication evolution regarding CSP field in the last 2 decades by countries.

Another highlight of CSP analysis is the cooperation between different countries. This can be observed in *Figure 3.7*, in which co-authorship between European Union countries is clearly visible. Also, China, India, Australia and some Middle East countries had become more active during 2015 and 2016. This is related with recently announced and under construction projects planned in these countries [18]. A strong co-authorship cooperation between Germany and Spain is also visible. It is remarkable the key role of Germany as a CSP promoter even that there are no plans to develop CSP facilities there.

Authorship analysis

Main authors have been identified by the number of publications or by the h-index, which is used to measure the productivity and impact of the authors. One of the most important analysis was the author research communities (*Figure 3.8*). These research communities are defined by the co-authorship level, no matter the country or institution. There are two main research communities leaded by Dr. Aldo Steinfeld and Dr. Robert Pitz-Paal. Also, a cooperation opportunity was found between these two communities and the one leaded by Dr. Covault.

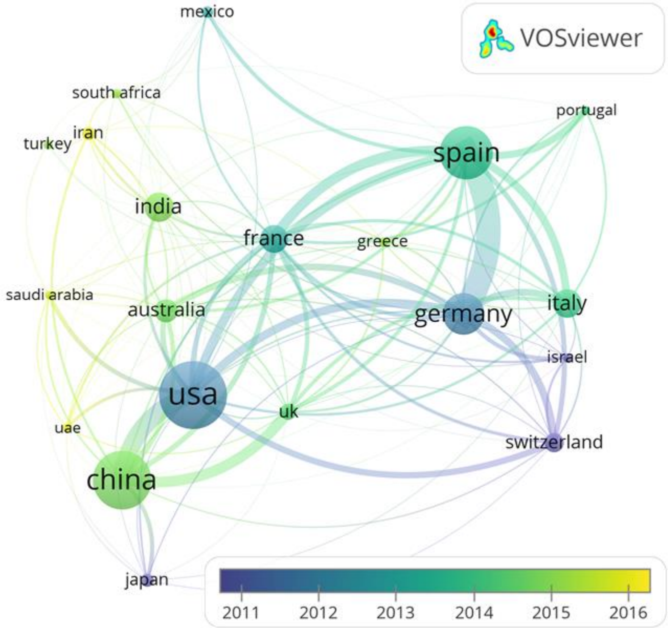


Figure 3.7. Country co-authorship interaction collaboration of the top 20 countries by number of publications.

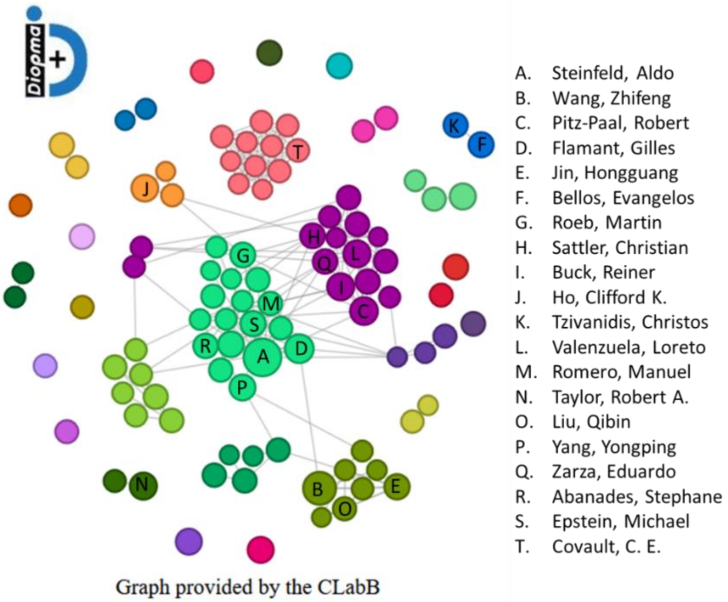


Figure 3.8. Authorship communities based on the interaction of published papers in CSP field [19].

Journals and conference proceedings

The main publishing houses in CSP research were identified as shown in *Figure 3.9* and *Table 3.4*. The most outstanding journal is Solar Energy, followed by Applied Energy; both with the higher CSP journal h-index. However, when considering the performance ratio (total CSP cites divided by total CSP publications) Energy Policy and Renewable & Sustainable Energy Reviews journals show to be the ones with higher impact with 49 and 43 ratios respectively.

Table 3.4. Top 20 journals in CSP field.

JOURNAL	PAPERS	CITES	PERFORMANCE RATIO	IMPACT FACTOR	QUARTILE SCORES
ENERGY POLICY	32	1579	49	4.039	Q1
RENEWABLE & SUSTAINABLE ENERGY REVIEWS	175	7553	43	9.184	Q1
APPLIED ENERGY	259	7171	28	7.9	Q1
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY	104	2689	26	4.229	Q1-Q2
SOLAR ENERGY	609	13956	23	4.374	Q1
ENERGY	208	4696	23	4.968	Q1
JOURNAL OF SOLAR ENERGY ENGINEERING	240	5143	21	1.367	Q2
DESALINATION	42	898	21	6.603	Q1
SOLAR ENERGY MATERIALS AND SOLAR CELLS	127	2488	20	5.018	Q1
INTERNATIONAL JOURNAL OF HEAT AND MASS TRANSFER	44	820	19	3.891	Q1

Conference proceedings in CSP field is of big relevance, especially the Solar Paces Conference. Other relevant conferences that were identified are the Energy Sustainability Conference and the Solar World Congress. Just the three mentioned conferences account more than 13% of the CSP total publications. Still, conference proceedings characterize by a low CSP h-index and a low CSP performance ratio.

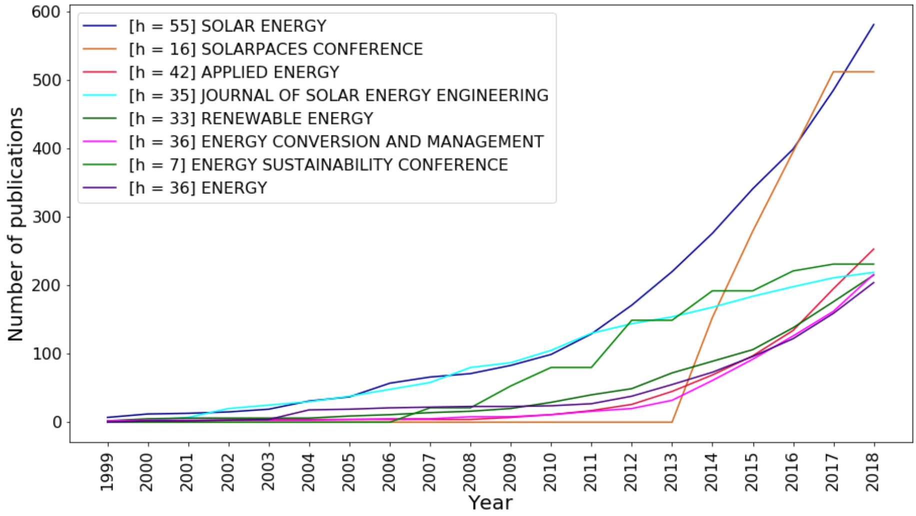


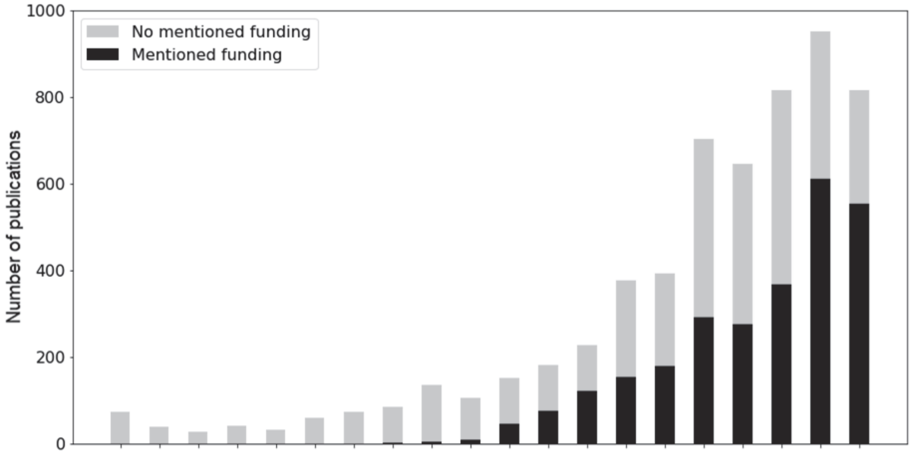
Figure 3.9. Cumulative journal evolution, by number of publications.

Funding

As mentioned before, CSP research and development is mainly driven by government programmes in cooperation with public and private sectors [15]. Therefore, it is expected that funded publications grow with the total number of publications.

This can be appreciated in Figure 3.10, in which publications that mention at least one funding agency are represented in dark blue, while publications without any mentioned funding in cyan.

It is noticeable that around two thirds of the total publications recognize some kind of funding, even that there is the possibility that publications without any mentioned funding have indeed some kind of public or private financial resources.



Year	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018
Not funded	73	39	27	42	32	61	74	84	131	95	106	107	106	221	215	411	369	448	341	261
Funded	0	0	0	0	0	0	0	2	4	10	46	75	122	155	179	293	277	367	611	554
% funded	0%	0%	0%	0%	0%	0%	0%	2%	3%	10%	30%	41%	54%	41%	45%	42%	43%	45%	64%	68%

Figure 3.10. Funding evolution for CSP publications.

Sub-Research fields

Four different technologies were analyzed within CSP database. Each of these technologies were defined as sub-research fields of study. Parabolic trough, solar tower, Stirling dish and linear Fresnel are the technologies under individual study. A comparison in the number of publications is presented in *Figure 3.11*.

Parabolic trough is displayed by far as the most active in research of the four technologies. However, all technologies present a constant publications increase for the last years. It is notable that solar tower technologies account as the second technology under research. Nevertheless, solar tower publications decrease during 2018 match with the market expectance about the viability of several projects currently under construction [18,20].

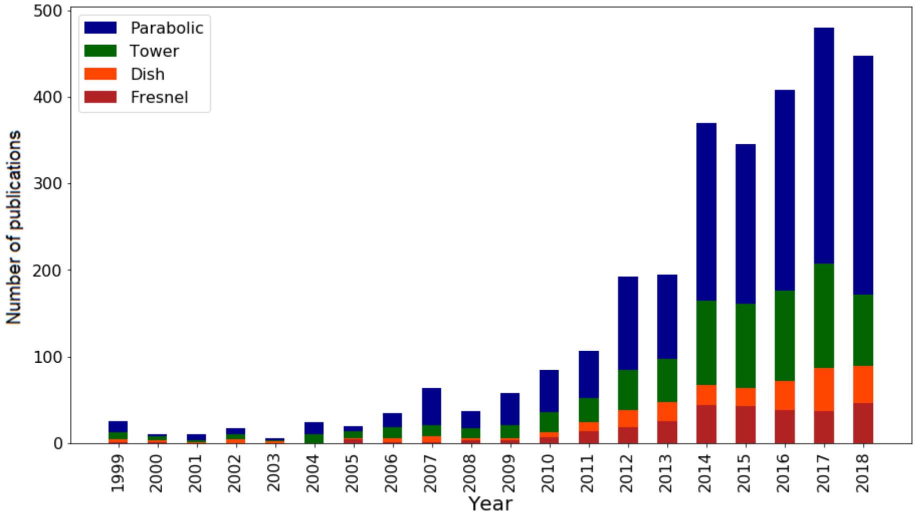


Figure 3.11. Number of publications per year for each CSP technology.

Of the four technologies analyzed it is solar tower technology which is more directly related with this dissertation. *Figure 3.12* shows the leading countries in solar tower technology research over the last two decades. During last lustrum China has become the country with more research output which is in line with their increase on CSP investment [21]. However, when accounting for regional initiatives, it turns out that European Union has the biggest research output for solar tower power.

When compared to other technologies, solar tower technology was expected to be the main CSP technology driver. However, recent price falls in parabolic trough and low energy production (than expected) in commercial solar tower power plants has slowed down this technology growth. This is reflected also in the research output, leaving solid particle solar tower and thermochemical solar tower as the main drivers for solar tower research.

Most relevant authors in solar tower technology are in line with the main countries that develop it. Authors from China, USA, Germany and Spain are the most productive ones.

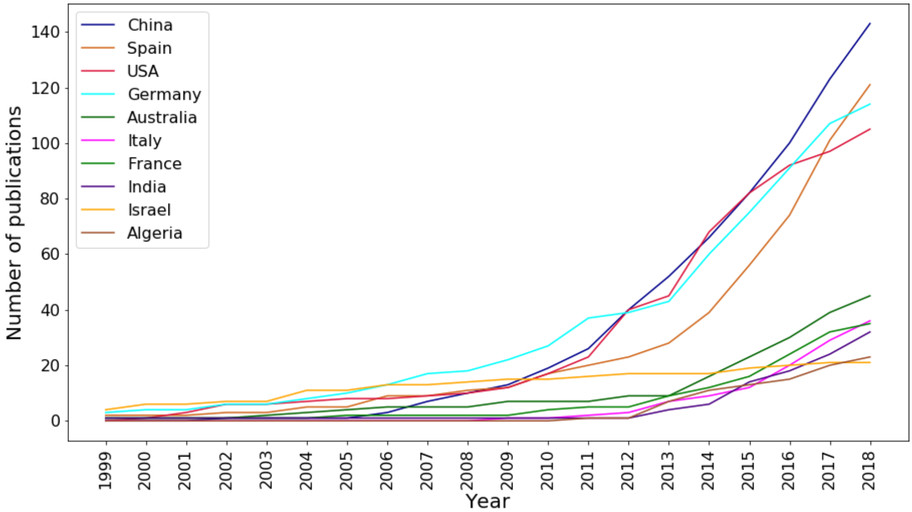


Figure 3.12. Total publications in solar tower per country.

Solid particle solar tower technology is the most specific research line that involves the following chapters. It has shown to be of great interest and is expected to continue to develop in the following years. The goal to achieve higher operational temperatures than current commercial molten salts solar tower can help to relaunch solar tower technology as a low cost, utility scale, and renewable energy source.

3.3.3. JOURNAL PAPER

The journal paper named “Bibliometric study in Concentrating Solar Power technologies” has been submitted to Applied Energy journal with reference number: APEN-D-19-09076.

Highlights

- This work use bibliometric techniques to study CSP publications.
- Countries, authors, journals and communities have been identified for CSP field.
- CSP technologies were analyzed by parabolic trough, tower, dish and Fresnel.
- CSP scientific research has grew exponentially over last decade.
- US, China and Spain led CSP research with China increasing rapidly.

Elsevier Editorial System(tm) for Applied Energy

Manuscript Draft

Manuscript Number: APEN-D-19-09076

Title: Bibliometric study in Concentrating Solar Power technologies

Article Type: Research Paper

Keywords: Bibliometric; Solar Energy; Concentrating Solar Power; solar tower; parabolic trough; Stirling dish

Corresponding Author: Dr. Ana Inés I Fernandez, Ph.D

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Abstract: Bibliometric analysis is a key study in order to elucidate the relevance of a research field. This study will point out the main evolution of a research performed in a topic considering the significance of each sub-topic. This study aims to perform a bibliometric analysis in concentrating solar power (CSP) technology. CSP had a first commercial wave between 1984 and 1995. Between 1995 and 2005 there was a period of commercial inactivity. Nevertheless, since 2005 CSP commercial implementation has been accelerating. This topic accounts almost 6,300 publications on relevant journals and conference proceedings. Regional analysis showed that China is becoming the most relevant country for CSP research. European Union still leads the development and will continue that way at least in the short term. Authors' keyword evolution analysis has been useful as an indirect measure of technological maturity. It was found that conference proceedings have an important effect in the overall CSP publications and need to be consider when working within this field. However, the journal publications use to have more impact since they are more frequently cited. Funding analysis had shown a direct relationship between funding and research output. Finally, it was concluded that inside CSP field, parabolic trough has shown to have great relevance in the research output.

3.4. P2: Where is Thermal Energy Storage (TES) research going? A bibliometric analysis

3.4.1. Introduction

Energy Storage has become a key facilitator for energy transition into clean energies. Most implemented renewables have problems with the mismatch between production and demand. Wind and photovoltaics depend on the primary energy availability [2]. Even for offshore wind farms that have constant wind resource, they do not match with the market electricity demand. Hydro energy has the problem of matching the human activities water demand with the grid demand. The possibility to store energy allows to match demand and production so that backup fossil power plants could become unnecessary or can help to increment these clean energies participation into the energy mix. However, storing electricity is limited with current technology. More research and large-scaling development must be done before implementing it in large scale [1].

Thermal storage has some advantages compared to electricity storage, especially for heating or cooling applications. Solar thermal electricity offers the opportunity to store thermal energy before converting it to electricity. This storage offers high efficiency energy storage, which is related to the thermal losses of the system thru time [22]. In addition, different ways of storing thermal energy have different discharge times. Sensible and latent heat efficiency are related to energy density and geometry of the storage, while thermochemical efficiency is related to the charge-discharge cycles and the reversibility of the reaction [23].

There are different ways to classify TES according to the technology, storage material, application and the end-use (*Figure 3.13*). Classification by technology offers a better technology maturity view, since each technology has typical storage materials. In order to measure the research activity in TES research field a bibliometric analysis was performed applying the previously described bibliometric methodology. Results and analysis were incorporated in the scientific article named “Where is Thermal Energy Storage (TES) research going? - A bibliometric analysis”.

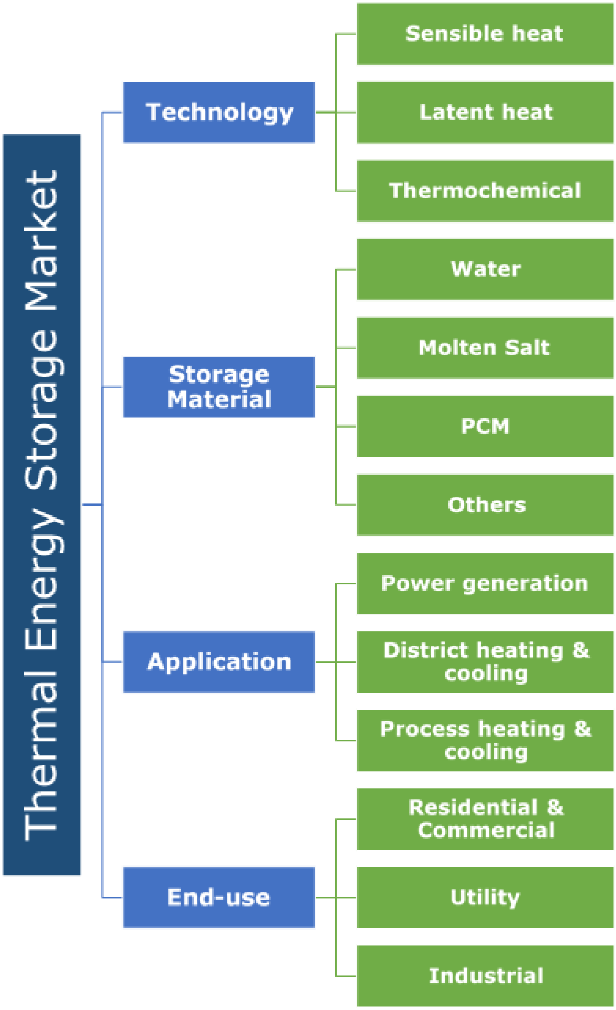

Figure 3.13. TES market classification [24].

Research field

The field of study was Thermal Energy Storage technologies without accounting for applications in areas not related to the technology, such as photovoltaics, informatics, communications, law, among others. Four sub-research fields were analyzed within main research field database according to the way the thermal energy is kept: sensible heat, latent heat and thermochemical storage. The period of analysis includes all the publications from 1910 to mid-2018. In several metrics only the complete last 20 years of this period were analyzed (1998-2017).

Keywords

The keyword map defined for TES research field can be observed in *Table 3.5*.

Table 3.5. Keyword map for TES research field.

MAIN PHRASES	COMPLEMENT PHRASES					EXCLUSION PHRASES		
thermal storage								
thermal energy	storage							
cool storage	thermal							
concentrated solar power								
phase change material								
thermochemical storage								
molten salts	solar	energy	power plant		storage	pv	photovoltaic	
csp	solar	energy	renewable	power	storage	cloud	internet	software
heat storage								
latent heat	storage							
sensible heat	storage							
thermochemical	energy storage							
pcm	energy storage							

These keywords were selected to include all the papers relevant for TES field as well as to establish the boundaries that cannot be removed directly from the data source. Additional keywords were defined to extract each of the sub-research fields for each technology analysis (*Table 3.6*).

Table 3.6. TES sub-research field keywords.

SENSIBLE	LATENT	THERMOCHEMICAL
sensible heat	pcm	thermochemical
molten salt	phase change	thermo-chemical
nitrate salt	phase-change	Tcm
water	latent heat	Chemical reaction
heat transfer fluid	phase transition	Sorption
htf	encapsulated	Reaction
	ice	

Data source

The data source selected was Web of Science Core Collection due to the high quality publication selection and to the quality of bibliographic information available. In addition, some of the research field boundaries were considered within the data source: scientific articles, books and book chapters. Conference proceedings were not included, since several conference papers were found to be very similar to journal papers with the same authors.

Metrics

For performing the current study several metrics were. *Table 3.7* shows the metrics used for the TES bibliometric analysis.

Table 3.7. Metrics used for TES bibliometric analysis.

METRIC	DOMAIN OF ANALYSIS
Total publications	Main research field and sub-research fields
Publications evolution per country and EU	Main research field and sub-research fields
Tech comparison evolution	Sub-research fields
Most productive authors (h-index)	Main research field and sub-research fields
Country co-authorship	Main research field
Scientific communities	Main research field
Relevant Journals/publications	Main research field and sub-research fields
Journal co-citation relevance	Main research field
Funding analysis	Main research field

3.4.2. CONTRIBUTION

TES research tendencies were studied in the article "Where is Thermal Energy Storage (TES) research going? A bibliometric analysis". Publications evolution, regional and national efforts, as well as co-authorship between different countries were studied. In addition, researcher communities were recognized based on their co-authorships. Most relevant authors and journals were identified based on their publications outcome and their citations. Effect of funding in TES research outcome was identified thru last year analysis.

Finally, sensible heat, latent heat and thermochemical technologies were studied. Most relevant authors, journals and country efforts were brought out in this paper for each of these technologies.

World's publication evolution for TES can be appreciated in *Figure 3.14*. for the last years of analysis there is a constant exponential growth in TES research. Energy storage and energetic efficiency world goals make TES a fertile land for new applications research and new commercial applications.

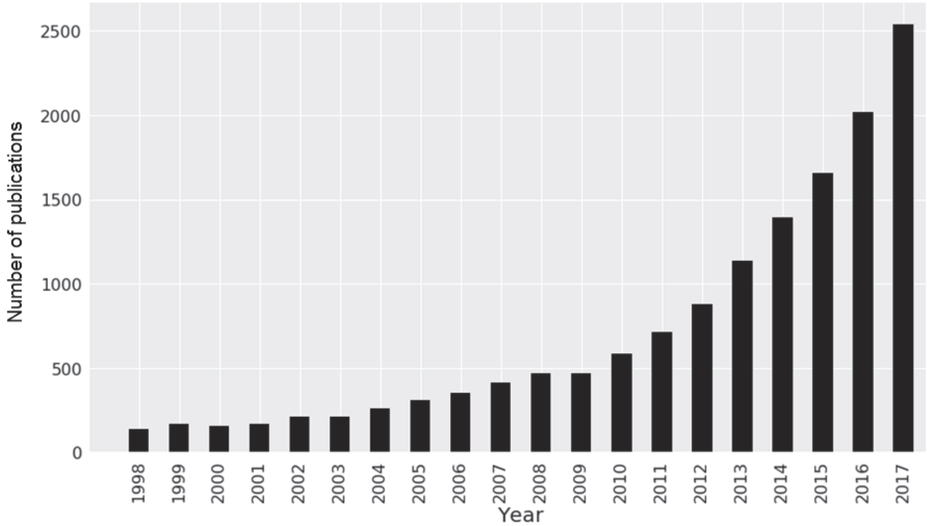

Figure 3.14. TES publications between 1998-2017.

Regional TES research output evolution exponential increment is accentuated in European Union and China (*Figure 3.15*). USA research output seems stagnated during the last 3-4 years. Based on current tendencies, China is expected to be leading TES research over the next years, followed not too far by European Union.

Within EU, TES research is leaded by Germany, Spain, France, United Kingdom and Italy. *Figure 3.16* shows that all EU leading countries have the same growing tendency. H2020 and other EU energy policies are a big influence to these results.

By now, there is no sign of slowing down TES research in EU. Denmark, Italy and Germany have a constant growing rate during last years, while in Spain the research rate output has been slowing down.

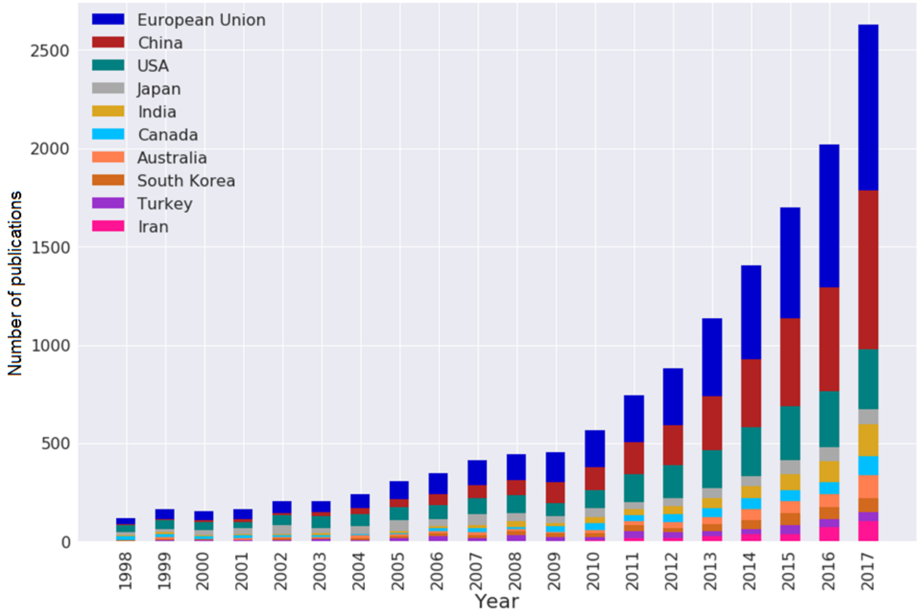

Figure 3.15. Publications evolution regarding TES field in the last 2 decades by country.

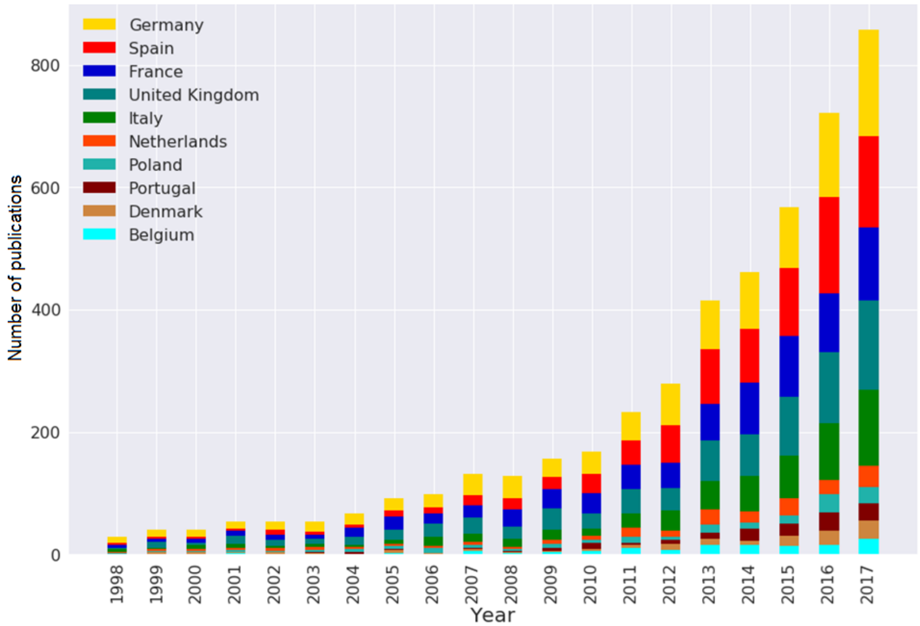

Figure 3.16. Publications evolution regarding TES field in the last 2 decades by top 10 European countries.

Country/region co-authorships were also studied. EU has the strongest co-authorship relation with China, followed by EU-USA relationship. Within EU, Germany and Spain have the strongest co-authorship bond.

From the top 20 author analysis it is notable that several of them are from research centers in Spain and China. However, when studying the authors without the country factor several communities were identified. These associations can be observed in *Figure 3.17*. Strong co-authorships make authors group no matter their affiliation. One of the most valuable results are the detection of cooperation opportunities between communities that actually have low or no co-authorship at all.

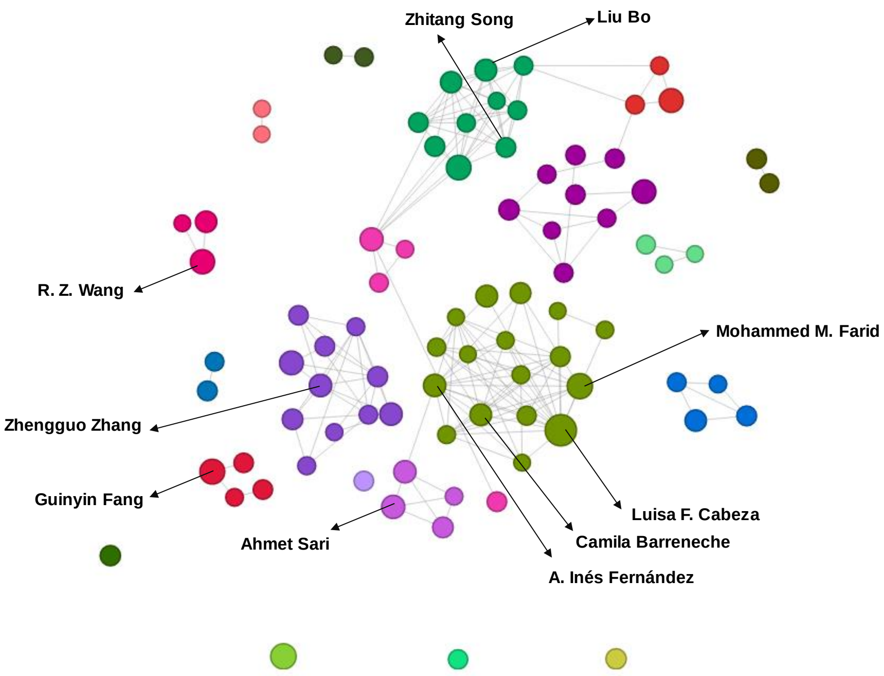

Figure 3.17. Authorship communities based on the affiliation interaction of published papers in TES field.

Main journals for TES research publication were found (*Table 3.8*). Applied Thermal Engineering is the one with most publications, followed closely by Applied Energy. However, Performance ratio was calculated based on their citation information. Renewable & Sustainable Energy Reviews have the highest performance ratio, which is expected since reviews usually have more cites. Energy Conversion and Management, and Solar Energy Materials and Solar Cells journals outcome with a high performance ratio for a non-reviews magazine.

Table 3.8. Top 10 journals in TES field.

JOURNAL	TES publications	TES Cites	Performance Ratio
APPLIED THERMAL ENGINEERING	876	16262	18.6
APPLIED ENERGY	829	19619	23.7
SOLAR ENERGY	703	16219	23.1
ENERGY CONVERSION AND MANAGEMENT	608	16824	27.7
ENERGY AND BUILDINGS	589	13522	23.0
ENERGY	513	9595	18.7
SOLAR ENERGY MATERIALS AND SOLAR CELLS	397	10577	26.6
RENEWABLE & SUSTAINABLE ENERGY REVIEWS	393	20194	51.4
RENEWABLE ENERGY	360	6601	18.3
INTERNATIONAL JOURNAL OF HEAT AND MASS TRANSFER	352	9031	25.7

Programs and policies to encourage research include funding. Thus, studying the relation between research outcome and funding is relevant. For TES research field, reported funding can be observed in *Figure 3.18*. A direct relation between funding and publication exponential growth was found.

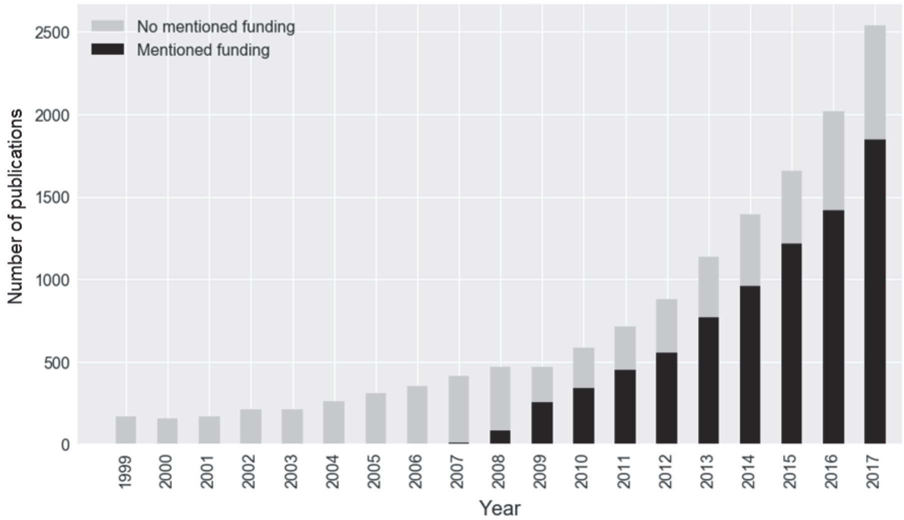

Figure 3.18. Funding evolution for TES publications.

It is noticeable that the main countries that make research in TES have strong funding agencies (EU commission, Chinese Academy of Sciences and Department of Energy).

Different technologies were studied by classifying them into Sensible Heat TES (SHTES), Latent Heat TES (LHTES) and Thermochemical Storage (TCS). In *Figure 3.19*, total number of publications per year and per TES technology are displayed. For the three technologies there is constant growth. LHTES is the technology with more research outcome. LHTES currently has several commercial applications, but there are several other uses that are under research. TCS is, by now, a technology with great promises but too far from commercial applications. SHTES is a mature technology with several commercial applications. Current SHTES research is focused in high temperature applications and improving systems performance [22].

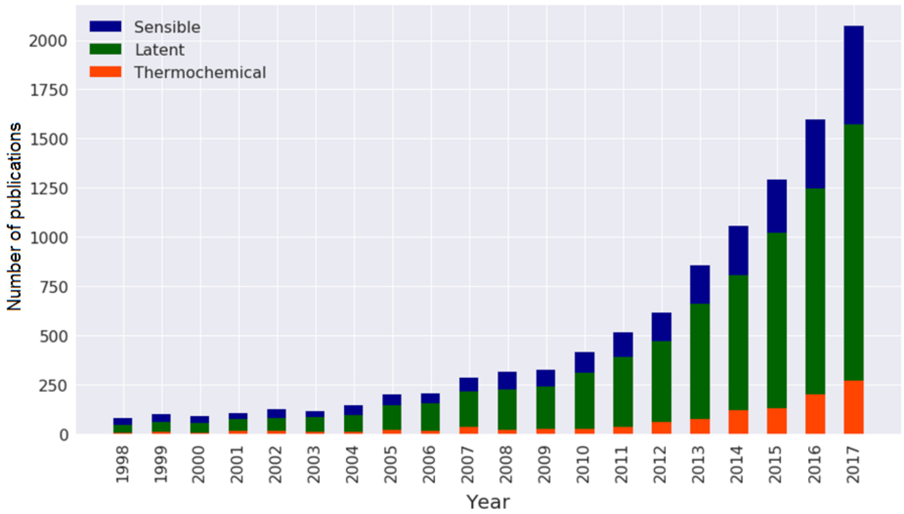

Figure 3.19. Number of publications per year for each TES technology and forecast technology calculation for 2017.

*Figure 3.*20 shows the SHTES publication evolution by region/country for the top 7 countries. EU is the region with more outcome followed by China and USA, all sharing a clear exponential growth during the last years. It is noticeable that Japan is the only country, from the top ones, that is not growing exponentially and seems stagnated.

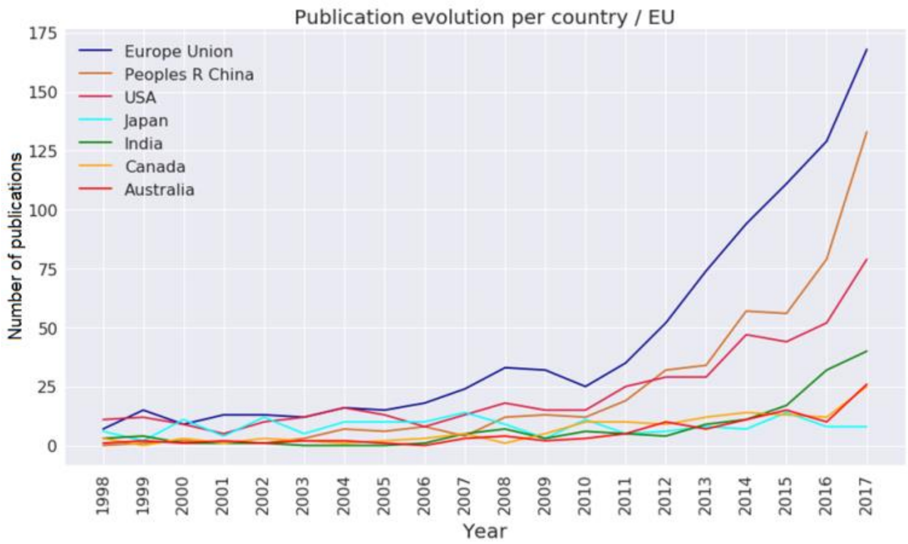

Figure 3.20. Publication evolution per country and EU for SHTES.

TES analysis included more than 14 thousand publications on the most relevant journals. As a result, 14 research communities were identified, as well as the most relevant authors and journals. In addition, regional analysis showed that research programs have strong influence in TES research output.

3.4.3. JOURNAL PAPER

The journal paper named "Where is Thermal Energy Storage (TES) research going? – A bibliometric analysis" has been sent to Solar Energy journal with the manuscript number: doi.org/10.1016/j.solener.2019.01.050.

Highlights

- This work use bibliometric techniques to study TES publications.
- Countries, authors, journals and communities have been identified for TES field.
- TES technologies were analyzed by sensible, latent and thermochemical TES.
- All TES scientific research has been growing exponentially over the last decade.
- EU led TES research followed by China which can start leading in the future.

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Where is Thermal Energy Storage (TES) research going? – A bibliometric analysis

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Sensible heat
Latent heat
Thermochemical

ABSTRACT

Energy storage technologies can provide energy security, fight climate change, and improve the value of current or future energy systems. Thermal Energy Storage (TES) is a key enable technology, it allows to stock thermal energy that can be further used for heating and cooling applications and power generation. The methods and tools used to analyse all the literature about the evolution of TES systems research are described in this paper. Bibliometrics is the science that studies, in a statistical way, the written publications of a certain field of research, and it is considered one of the few interdisciplinary research fields that can be extended to almost all scientific areas. The bibliometric analysis of the database Web-of-science (core collection) shows highlighted information in order to figure out the scientific outputs. The importance of the bibliometrics is to analyse a knowledge development from a strategic point of view in order to detect its evolution regarding the research in such a field and to detect which are the opportunities within this area. This study presents the publication evolution in TES field over the last two decades, per year, per country, per authors, per journal, and per TES technology, taking into account sensible heat TES (SHTES), latent heat TES (LHTES), and thermochemical energy storage (TCS), and considering the connection between authorship communities and country interactions. The communities are obtained from the co/authorships, regardless of the country or affiliation; this permits to view the size of the communities, as well as to identify collaboration opportunities between communities with low or no interaction. Furthermore, studies are included regarding detailed analysis on each TES technology, as well as other factors (such as funding) that can influence the current and future research.

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State-of-the-art 4

Chapter contents

4. STATE-OF-THE-ART

Using solid particles as sensible heat HTF and TES in solar towers concept was first studied during the early 1980s with the solar receiver concept only. At that time, molten salts concept prevailed as the most commercial viable solution [1,2]. However, due to molten salts temperature limitations, solid particles concept has been evolving for the last years. Improved models have been developed and validated during the last decade [3–8]. This interest in solid particle CSP research is reflected in the recent research output showed in *Figure 4.1*, in which free falling particle receiver publications over the years is presented.

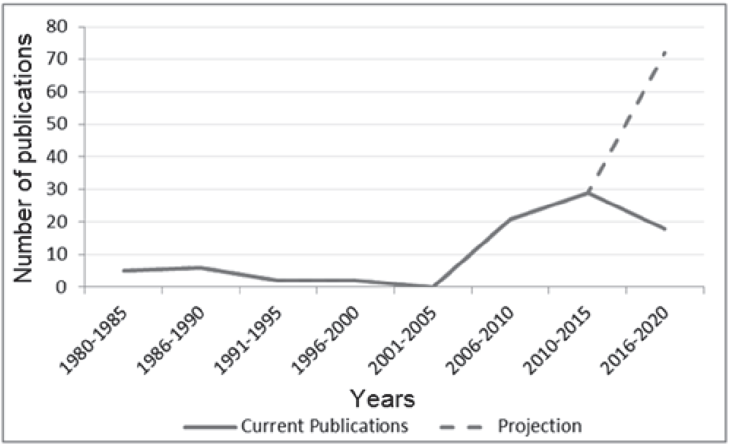

Figure 4.1. Research publications of free falling particle receiver by 2017 [9].

Main challenge for Solid Particle CSP is to achieve a commercial concept. For this, advances in the system concept and on the material selection must be carried out.

In this chapter, main progress is reported and divided in two sections. In the section 4.1, Solid Particle system concept and development are described. Then, in the section 4.2 the main reported concerns and tests of the solid particle material itself are reported. Also, different challenges and future work are reported for both parts. Two scientific articles are related to the state-of-the-art analysis, one for the system concept and the second for the solid particle materials properties and parameters, as well as the current suggested materials by the researchers in this area.

4.1. P3: HIGH TEMPERATURE SYSTEMS USING SOLID PARTICLES AS TES AND HTF MATERIAL: A REVIEW

4.1.1. INTRODUCTION

As mentioned before, Solid Particle CSP idea started with the receiver concept. The first challenges worked out were related to the receiver. Still, there are challenges for all the power plant concept, within the different functional sections and for the whole plant integration, as well as for the solid particle material itself.

Main advantages for the solid particle CSP plant go around HTF and TES material stability at high temperature with a relatively low cost. Molten salts are today's commercial CSP technology that achieves a higher temperature (up to 565 ^{o}C). Solid particle materials can reach over 1100 ^{o}C due to its chemically stability in this range of temperatures. Additional advantages are that there is no solidification risk, the same material can be used as HTF and TES, and the low chemical corrosion at high temperature.

From the plant system view, the whole functional concept is the same as in molten salts. There is a solar field, which concentrates solar power in a receiver in the top of a tower. In this tower a HTF is heated up and then, either moved to a HEX or to a hot tank (part of the TES system). The TES system usually uses the same material as the HTF. For electricity production, thermal energy is transferred from the TES system into the HEX via the HTF. In the HEX the thermal energy is transferred to a power block, in which a power cycle generates electricity. The HTF that exits the HEX can be stored in a cold tank (also part of the TES system) or go directly to the receiver to harvest heat again.

The main differences between a molten salts and a solid particle power plant relies within each part of the plant, since dealing with a fluid is technically different to a granular material. *Figure 4.2* shows the solid particle main concept. For the solar field, there are no technical differences with the molten salts plants, only a dimension of the field size must be addressed according to the receiver operational parameters. The power block is likely to change, since higher temperature allows more efficient power cycles. However, these cycles are not the main objective of this work because they are already commercially developed for fossil and nuclear power plants.

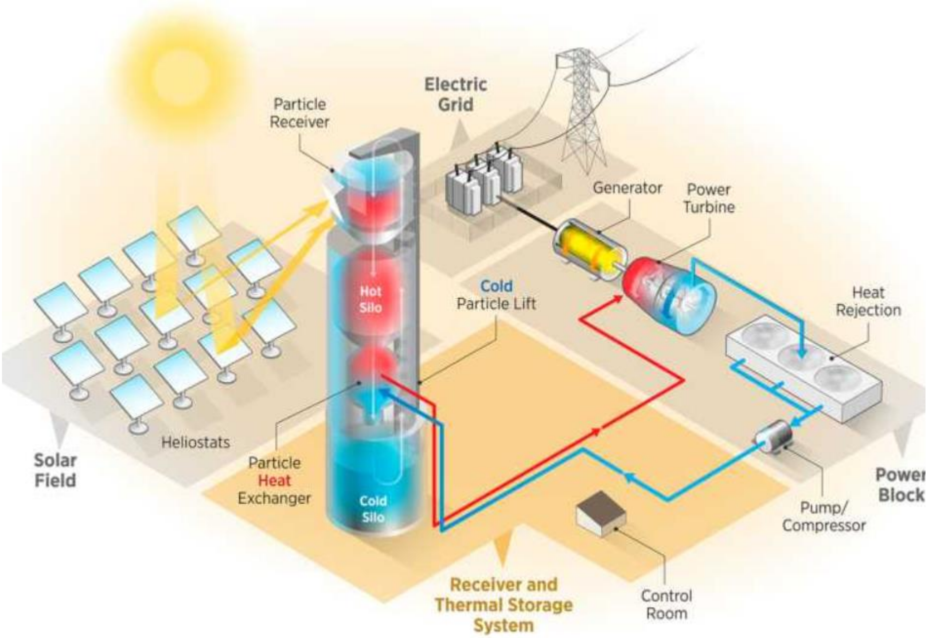

Figure 4.2. Solid Particle CSP plant layout [10].

The article named "High temperature systems using solid particles as TES and HTF material: A review" addresses the main components of a solid particles CSP plant and the main advances of each of these parts.

4.1.2. CONTRIBUTION

A complete and detailed analysis of solid particle CSP plant was carried out in this article. Different approaches for each part of the plant were documented, mentioning the main advances and challenges of each element proposed. No considerations of the solid particle materials were made at this point.

Solar receiver

From all the parts that form a solid particle CSP plant the receiver is the one that has been the most studied. Several designs have been proposed and they can be primarily classified according if the design allow particle material to be directly irradiated by concentrated sunlight. *Figure 4.3* shows the classification of the most developed solar particle receivers. From these possible receiver configurations, free falling receiver (also called solid particle curtain receiver) is the one more developed. Several years of research and pilot plant tests have been made for this receiver.

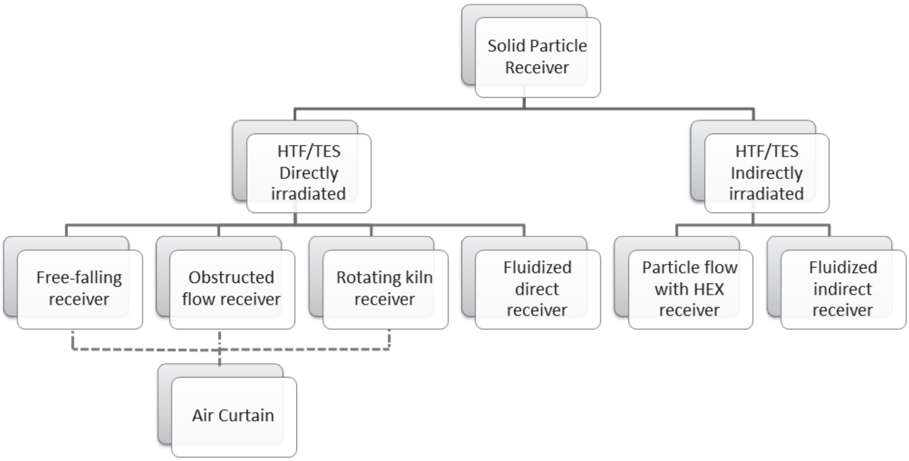

Figure 4.3. Solid Particle receiver classification.

The main goal for solid particle receivers is to hold enough time the particle media in order to achieve the desired temperature, either by slowing down the particle fall (obstructed flow, rotating kiln, fluidized bed) or by recirculating the particles (free falling receiver with recirculation). For directly irradiated receivers that are in contact with ambient air from the receiver aperture the thermal or particle media losses by the wind effect is a problem. To outcome this, an air curtain (aerowindow) has been proposed, which consists in producing an air flow that works as a cap for the receiver without interrupting concentrated sunlight. Each kind of receiver has been detailed in the article, including the main advantages and drawbacks of each one of them.

Conveyance system

The way to move the particles is of special concern for the plant overall efficiency due to the possible parasitic loads related to solid particles movement. This depends in great manner in the type of receiver, heat exchanger (fluidized, pack bed, etc.) and the location of each part of the plant (receiver, storage tanks, heat exchanger). However, the most challenging one is to lift the “cold” particle to the receiver on the top of the solar tower.

Lift up granular materials has been done for many years in the mining industry. Several designs used for mineral extraction have been considered for this new application, such as mine hoists, bucket elevators, pocket elevators, screw conveyors, Olds elevators, pneumatic conveyors, conveyor belts, cleated conveyor belts, metallic belted conveyors, En-masse's elevators, bucket wheels, linear induction motor powered elevators, and electromagnetic field conveyors. Some of these designs have been tested at high temperature for measuring energy efficiency and to test the durability due to the temperature.

Other conveyance elements used for particle transporting have been studied as well, especially based on the erosion effect of the particles in the conveyance system materials. Studies of material compatibility between the solid particle material and the material of the lift system or the other conveyance system elements have been slightly reported, and should be furtherly studied in the future.

Thermal energy storage system

The design of the TES system consists in two different tanks for storing the particle media, a "hot tank" for storing the material at the highest temperature before going to the heat exchanger, and a "cold tank" for storing the exhausted material after cooling down in the HEX several hundred degrees and before going up to the solar receiver again.

Since the particle media is used both as HTF and TES material, current studies consist on the shape design of the tanks and the durability of the materials in which the tanks are built up, especially the "hot tank".

For structural reasons a round shape is better for designing the tank. Additionally, this shape reduces the total surface of the tank in relation to its volume, which is desired to reduce thermal losses.

Beside from the shape design, thermal insulation is the main concern. Several material designs with different multi-layer insulation materials have been tested. Reducing the thermal conductivity of the wall, high durability at high temperature and an ideal price range of 35-50 €/kWh_{th} are the main drivers of current research.

Real density of the particle media should be studied from the storage tank design view. The way the particles are stored determine the effective density of the material and can influence in the durability of the granular material. Design and selection of the final materials is strongly influenced by the final service temperature and the thermal energy density of the particle media.

Heat exchanger

For moving the thermal energy from the CSP system into the power block a heat exchanger is needed. For particle media several designs have been studied. The most relevant are the fluidized-bed and packed-bed designs.

Fluidized-bed design (FB-HEX) has been reported in the article, since at that time was the most developed. However, recently a new moving packed-bed design CO_2 supercritical heat exchanger is under evaluation [11,12]. The parameters that must be controlled in the FB-HEX are focused on maximizing the heat transfer between the particles and the heating surface and guaranteeing a stable fluidization at the minimum possible fluidization conditions. In addition, exergy losses when transferring thermal energy from the HTF to the power cycle working fluid should be minimized.

Heat exchangers with particle media have been designed for other applications. However, many of these designs need to be evaluated and optimized for the desired high temperatures, the particle media candidates and the flow rate needed by the power block. Finally, properties and parameters of the solid particles must be considered in the HEX design, as well as the variation of the shape of the particles over time.

Current research and challenges

Three main challenges were identified for the solid particle CSP technology to be developed. The first consists on the integration of all the concepts and parts of the power plant looking for optimal optimization. The second challenge requires that each functional part of the system achieves commercial level viability. The third challenge relies in the finding of the particle media and unifying the selection criteria. It is fundamental to recognize the solid particle materials as the part of the system that connects the design criteria of all the plant concept. *Table 4.1* summarizes the specific challenges and current research efforts according to each part of the plant for the different design options.

Table 4.1. Particle CSP challenges and current research.

FUNCTIONAL PART	CHALLENGES	CURRENT RESEARCH
Open direct receivers	• Increase residence time. • Improve materials used for slowing flow structures. • Research for optimal solid particle materials for improving absorptance efficiency. • Study material compatibility of solid particles and material of the system itself. • Convective and radiant heat losses problems must be solved.	• Increase residence time and the effect on the receiver efficiency. • Prototype testing is under way looking for best geometries. • Energy balance and CFD for air curtain and particle recirculation are being enhanced.
Closed direct receivers	• Increase residence time. • Study possible thermal losses on the tube due to the optical properties. • Study parasitic energy requirements due to the fluidization. • Make pilot plant scale testing. • Work on enhancing the thermal isolation of the tube. • Poor heat transfer. Low conductivity in the particle side.	• Define desired properties of particles for fluidization on high temperature. • Optimize the design of the receiver according to the irradiated area. • Improve air intake according to particle size distribution.
Indirect receivers	• Increase residence time. • Define desired properties of particles for fluidization. • Study parasitic energy requirements due to the fluidization. • Work on enhancing the thermal isolation of the tube. • Maintain a uniform particle concentration and temperature. • Improve thermal isolation to decrease potential thermal loss.	• Exergy analysis on the heat exchange to the solid particles and according to the design used. • Define desired properties of particles for fluidization on high temperature. • Optimize the design of the receiver according to the irradiated area. • Improve air intake according to particle size distribution.
Conveyance system	• Material compatibility needed for assuring long term durability, especially on the particle lifting systems. • Research for using potential energy lost when particles go down from the receiver.	• Use technologies already developed for particle materials and adapt them. • Study of the parasitic charges related to the large masses of material that are expected to be moved.
Storage tanks	• Reach investment costs lower than 35 €/kWth. • Consider and evaluate changes on the solid particle material, such as variations on mean size and size distribution through the plant lifetime. • Study designs for avoiding particle agglomeration and sintering. • Evaluate the impact of density and/or temperature stratification inside de tanks.	• Tank built materials durability on the long term. • Adequate thermal isolation to minimize energy loses. • Interaction of the storage elements with the rest of the CSP plant. • Study of efficiency and durability of different tank geometries.
Heat exchanger	• Enhance heat transfer coefficients. • Evaluate particle changes during plant lifetime and due to temperature change over the exchanger (like possible allotropic changes). • Integrate parasitic loads on the energy balance.	• Improve fluidization stability. • Study of particle requirements.

Conclusions

Solid particle CSP technology has resurged as a promising evolving technology for CSP tower plants. However, several aspects such as particle conveyance, attrition resistance, heat losses and a unified plant design are needed for achieving a commercial viable plant. Several challenges and research efforts had been identified and reported. Current technology still needs development in several plant parts, such as conveyance system, heat exchanger and TES system, as well as in the particle media. Solid particle materials need to be furtherly studied, as well as their optimal parameters and properties.

4.1.3. JOURNAL PAPER

The journal paper named "High temperature systems using solid particles as TES and HTF material: A review" was published in Applied Energy journal in 2018 in volume 213, pages 100-111 and with the manuscript number: doi.org/10.1016/j.apenergy.2017.12.107.

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High temperature systems using solid particles as TES and HTF material: A review

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HIGHLIGHTS

- Several issues must be solved to transfer to the market solid particle CSP plants.
- Solid particles combine roles: as TES media and HTF within CSP plants configuration.
- Review of operating conditions and parameters that make solid particles attractive.
- Review about whole system: the storage, heat exchangers and material conveyance.
- Solid particle systems can increase heat conversion efficiency to electric power.

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ABSTRACT

Thermal energy constitutes up to 90% of global energy budget, centering on heat conversion, transmission, and storage; therefore, the technology for harvesting solar energy worth to be developed. One of them is the concentrated solar power (CSP) solar towers where sun-tracking heliostats reflect solar radiation to the top of a tower where the receiver is located. The great advantage of CSP over other renewable energy sources is that energy storage is feasible, particularly when the heat transfer fluid (HTF) is also used as thermal energy storage (TES) material which is the case of solid particles. A lot of development efforts are under way for achieving commercial direct solar solid-particle systems. Solid particle systems for transferring high temperature thermal energy are purposed for increasing the efficiency of these systems when converting heat into electric power. This review recapitulates the concept of these systems taking into account the main receiver designs, particle conveyance, particle storage systems and components, the heat exchanger, and the main challenges that must be overcome to split this technology as a commercial one, especially from the materials availability point of view. This review summarizes the actual status of the use of solid particles for TES and as HTF for CSP Tower, and condenses all the available information and classifies them considering the main functional parts and remarking the current research in each part as well as the future challenging issues.

4.2. P4: Review of solid particle materials for heat transfer fluid and thermal energy storage in solar thermal power plants.

4.2.1. Introduction

Solid particle CSP plant concept was explained in the previous section. It this part, this concept is considered from the particle media perspective. Information generated by different research groups was gathered and is presented in this chapter. In addition, relevant properties and parameters are furtherly explained from the solid particle CSP perspective.

The material science perspective has been studied from two main fronts. The first considers the different functional parts of the plant (receiver, conveyance, TES and HEX). The second front is more transversal, since considers the particle material stability and durability.

Several materials have been suggested by relevant researchers to be used as TES and HTF media for solid particle CSP plants. Experimental and theoretical information of these materials have been collected and summarized for evaluation and comparison. It is important to take into account that no formal material selection has been reported by any of the research groups, either a complete properties analysis for the whole system.

4.2.2. Contribution

Suitability of the particle media is one of the most important factors for making the power plant economically viable. For optimal performance, different properties and parameters must be congruent between them for each different functional part of the plant and with the desired particle media durability.

In order to perform a proper material selection, properties and parameters were identified in the literature, along with the explanation of their interaction in the system and the reported desired values. This information is presented in *Table 4.2*.

Table 4.2. Properties and functional parameters for solid particles for CSP.

Property/parameter	Range	Desired value	Unit
Receiver thermal efficiency			
Absorptivity	0.55-0.93	High	%
Emissivity	0.72-0.88	Low	%
Particle size	200-1000	ATD*	µm
Sphericity	0.9	High	parts per unit
Roundness	0.9	Low	parts per unit
HEX efficiency			
Particle size	160-504	Low	µm
Thermal conductivity	0.5-2	High	W/m K
Thermal energy storage capacity			
Density	2.56-5.37	High	g/cm^3
Specific heat	621.75-923.36	High	J/kg K
Agglomeration			
Sphericity		High	
Size uniformity		High	
Melting point	1135	High	ºC
Particle size	150-200	High	µm
Absorptance		Low	
Sintering			
Melting point	>1000	High	ºC
Sphericity	0.9	High	parts per unit
Roundness	0.9	High	parts per unit
Size uniformity (mass median diameter)	As much as 0.26	High	parts per unit
Particle size	200-1000	High	µm
Agglomeration		Low	
Sintering heat *	>1000	High	ºC
Durability			
Sand erosion	0.0001-0.1	Low	%
Thermal shock degradation		Low	
Mechanical shock degradation	0.004-0.01	Low	%
Economic factors			
Price	0.01-17	Low	USD/kg
Sand erosion		Low	
Durability		High	

*ATD: according to the design.

Plant interaction

Main properties and parameters in *Table 4.2* are grouped according to the functional unit in which they intervene. Some parameters or properties are present more than once, since they are relevant in more than one aspect of the system.

Mechanical, thermal, geometric, optical and physical parameters and properties have been reported. Sometimes, they are related to a specific part of the plant (like optical properties in the receiver), but there are also considerations from a general view of the system.

For the receiver, alumina, silica sand, silicon carbide, zirconia and proppants have been considered and evaluated. For directly irradiated receiver optical properties are fundamental. Solar absorptance has been suggested to be the most important property, and in a second place the thermal emissivity. Therefore, a material with high solar absorptance and with high emissivity is more desired than another with low solar absorptance and low emissivity. In solid particle receivers, shape parameters have been found almost irrelevant for determining the solar absorptance efficiency, which can be determined by *Equation 4.1*.

$$\eta = \frac{(\alpha Q - \varepsilon \sigma T^4)}{Q} \qquad \text{(Eq 4.1)}$$

where α is the solar absorptance, Q is the irradiance in the receiver in W/m^2, ε is the thermal emissivity, σ is the Stefan-Boltzmann constant 5.67×10^{-8} $W/m^2 \cdot K^4$), and T is the temperature of the surface of the particles in Kelvin.

In reported analysis of suggested materials silicon carbide and proppants show the best results. However, these materials are not designed to withstand high temperature conditions but for high mechanical stress only. Therefore, thermal effect studies have been performed and reported from the optical properties point of view.

For thermal storage, thermal energy density is the main concern. This implies high density and high heat specific capacity. Two tank design is considered for solid particle CSP design. In the hot storage tank agglomeration and sintering should be avoided. High melting point and particle shape and size distribution are especially important to avoid sintering. Also the tank design can determine the way the particles are packed altering the real volumetric energy density and the sintering risk. *Equation 4.2* can be used to determine the thermal capacity, which is desired to be as high as possible from the TES perspective.

$$E = \rho c_p \qquad \text{(Eq 4.2)}$$

where E is the total energy stored in $J/m^3 \cdot K$, ρ is the density in kg/m^3 and C_p is the specific heat capacity in $J/kg \cdot K$.

Parameters and properties that influence in HEX performance depend fundamentally on the design. For fluidized bed, density, size distribution, sphericity, roundness and specific heat capacity are the main concerns for an acceptable fluidization efficiency. For packed bed HEX, agglomeration and thermal conductivity and diffusivity have strong influence on the overall exchanger efficiency. From the solid particle material perspective, for a fixed bed heat exchanger, the transfer heat rate depends on the thermal conductivity and the bed thickness as it can be appreciated in *Equation 4.3*:

$$Q = k \cdot \frac{\Delta T}{w} \qquad \text{(Eq 4.3)}$$

where Q is the thermal energy flow in W/m^2, k is the thermal conductivity in $W/m \cdot K$, w is the bed thickness and ΔT is the temperature difference between the beginning and the end of the conducting material.

When moving the particles thru the conveyance system, inter-particle collision (attrition) and interaction between the particle media and the system materials (mechanical wear or erosion) take place. The greater attrition effect is expected to take place in the HEX. However, the conveyance system can potentially get damaged as well. Shape factors, such as roundness and sphericity, have considerable influence in the erosion. Theoretically, hardness difference between the materials have a considerable effect in the erosion damage [13]. Yet, there has not been reported any study of the hardness of the particle media or the materials of the system. Erosion effect on the falling particle receiver has been reported, finding a relation between the particle velocity and the erosion caused to the receiver. Particle media of these studies were mainly proppants, which have a high sphericity and roundness, and high hardness. Mechanical wear in the HEX should be especially studied, since the majority of the proposed materials are ceramics, while the HEX usually is made of metals (for improving heat transference). Ceramic materials typically have a greater hardness than metals, particularly at high temperature.

Durability

Thermomechanical stability of the solid particles in the long term is fundamental for plant viability. The effect of the long term exposure to high temperatures, and the thermal cycle effect in the long term should be considered in the material selection.

Fundamentally, the changes on the particle media can be:

- Composition and allotropic changes, which can lead to changes in optical properties, thermal conductivity, size distribution, specific heat capacity and density.
- Sintering of the particles, which leads to a change in size distribution.
- Breaking of the particles, that will cause change in size distribution, as well as an increase of the chemical reactivity (because of the specific surface increase).

Solar absorptance variation with the effect of high temperature have been studied before with some of the materials that have been proposed. There has not been found any proper study about the thermal cycling effect in the long term.

Proposed materials

Some natural and synthetic materials have been proposed in the literature. A summary of these materials can be found in *Table 4.3* and *Table 4.4*. Thermal properties such as melting point, service temperature, thermal conductivity and specific heat are reported in *Table 4.4*. Composition, cost, density, solar absorptance and emissivity can be found in *Table 4.3*. Fly ash is the only potential byproduct that has been suggested in the reported research. Materials with low solar absorptance should only be considered as reference or for indirectly irradiated receiver systems.

Table 4.3. Summary of solid particle optical properties, cost and density to be used for CSP.

where, α - absorptance, ε – emissivity, ρ – bulk density.

Material	Composition	α	ε	Cost(€/kg)	ρ (g/cm³)
Silica Sand	92% - SiO_2 06% - Al_2O_3 <1% - Fe_2O_3 <1% - K_2O <1% - TiO_2	0.44 - 0.66	0.59 - 0.9	0.35 - 0.52	2.1 - 2.65
Hematite	98% - Fe_2O_3 01% - FeO <1% - Mn_2O_3	0.85	0.56	N/A	5.28
SiC	SiC	N/A	0.83 - 0.96	12.3 - 17.5	3 - 3.2
AccucastID ®	75% - Al_2O_3 11% - SiO_2 03% - TiO_2 09% - Fe_2O_3	0.906	0.754	N/A	N/A
CarboHSP®	83% - Al_2O_3 05% - SiO_2 04% - TiO_2 07% - Fe_2O_3	0.934	0.843	N/A	3.56
Alumina	Al_2O_3	0.1 - 0.25	0.3 - 0.5	28.1 - 35.1	3.94 - 3.96
Zirconia	95% - ZrO_2 04% - MgO	N/A	0.42 - 0.62	15.8 - 22.8	6.03 - 6.16
CarboProp®	72% - Al_2O_3 13% - SiO_2 04% - TiO_2 10% - Fe_2O_3	0.89 - 0.93	0.75 - 0.80	N/A	1.56
TiO_2	99% - TiO_2	0.4 - 0.7	0.5 - 0.8	21 - 31.6	3.97 - 4.05
MgO	MgO	N/A	0.2 - 0.5	29.8 - 43.8	3.54 - 3.58
Manganosite	98% - MnO 1.7% - MgO <1% Fe_2O_3 + FeO	N/A	N/A	N/A	5.43
Olivine	42% - MgO 39% - SiO_2 19% - FeO	N/A	N/A	35 - 43	2.8 - 3.37
Fly ash	88% - SiO_2 05% - CaO 02% - Al_2O_3 <1% - Fe_2O_3	N/A	N/A	0.03 - 0.14	1.83 - 2.2
Graphite	C	0.84	0.98	9.47 - 14.4	1.61 - 1.67
Basalt	48-59% - SiO_2 15-18% - Al_2O_3 07-12% - Fe_2O_3 06-09% - CaO 04-05% - Na_2O 03-05% - MgO 01-02% - TiO_2	N/A	0.72	2.01 - 2.22	2.5 - 2.89

Table 4.4. Summary of solid particle thermal properties to be used for CSP. where, k – thermal conductivity, C_p – specific heat capacity.

Material	Melting point (°C)	Service temp (°C)	k (W/m-°C)	C_p (J/kg-°C)
Silica Sand	1200 - 1400	400 - 600	1.14	742 - 1175
Hematite	1565 - 1597	N/A	N/A	650
Silicon Carbide	2150 - 2250	1470 - 1540	90 - 110	663 - 677
AccucastID®	N/A	N/A	0.7	1175
Carbo HSP®	N/A	N/A	2	1275
Alumina	2050	977 - 1030	20 - 25.6	790 - 800
Zirconia	2550 - 2700	2150 - 2250	1.7 - 2	418 - 436
CarboProp®	N/A	N/A	N/A	1175
Titanium Dioxide	1830 - 1850	1570 - 1640	4.8 - 9.2	683 - 697
Magnesium oxide	2810 - 2860	1980 - 2130	30 - 60	880 - 1030
Manganosite	1945	N/A	N/A	621- 788
Olivine	1870 - 1950	778 - 821	8 - 10	700 - 900
Fly ash	1270 - 1470	873 - 973	1.11 - 1.25	813 - 867
Graphite	3530 - 3680	2580 - 2690	44.2 - 48.3	852 - 941
Basalt	1410 - 1490	500 - 850	0,03 - 0,04	840

Conclusions

Material properties and parameters have a huge impact in the solid particle CSP plant viability. Each functional part of the system is influenced differently by the particle media.

Future work should include a proper material selection process, thermal stress tests due to high temperature in the long term and to the high number of thermal cycles, and mechanical stress test for attrition and erosion effects in the different parts of the system. Complete characterization of the materials should be carried out, not only for the particle media initial state, but to the aged materials as well.

Finally, material optimization can be developed based on the best material candidates to overcome possible drawbacks on stability of particle materials or the system materials.

4.2.3. JOURNAL PAPER

The journal paper named "Review of solid particle materials for heat transfer fluid and thermal energy storage in solar thermal power plants" was published in Energy Storage journal in 2019 with the manuscript number: doi.org/10.1002/est2.63.

Highlights

- Solid particle materials have potential for developing new CSP solar towers.
- Temperature limit can be improved making the power block more efficient.
- Further studies must be performed for conveyance and storage systems.
- Particle behavior requirements are different for each part of the system.
- Particle durability tests are needed, such as thermal stress (due to the high temperature and to charge/discharge cycles), and attrition/erosion tests.
- Particle characterization is needed to evaluate the evolution of properties.

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REVIEW

Review of solid particle materials for heat transfer fluid and thermal energy storage in solar thermal power plants

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Abstract

Current concentrated solar power (CSP) plants that operate at the highest temperature use molten salts as both heat transfer fluid (HTF) and thermal energy storage (TES) medium. Molten salts can reach up to 565°C before becoming chemically unstable and highly corrosive. This is one of the higher weaknesses of the technology. Solid particles have been proposed to overcome current working temperature limits, since the particle media can be stable for temperatures close to 1000°C. This work presents a review of solid particles candidates to be used as HTF and TES in CSP plants in open receivers. In addition, the interactions between solid particles with major system components are described in this review, for example, with TES system or heat exchanger. The parameters and properties of solid particles are identified from the material science point of view explaining their nature and the relation to the power plant efficiency and lifetime durability. Finally, future development is proposed; such as material selection according to each specific design, materials characterization, or durability test.

KEYWORDS

concentrated solar power, granular materials, sensible heat, solar tower, solid particles, thermal energy storage, thermal storage

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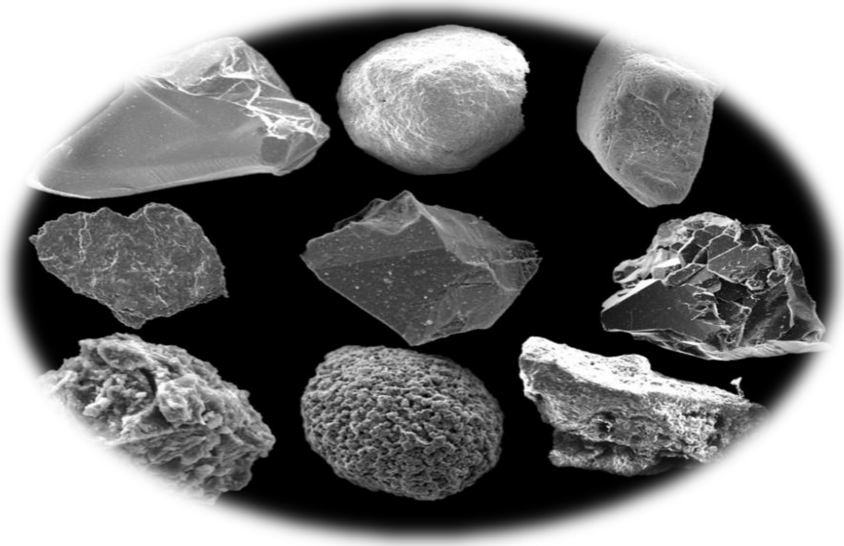
Material selection and evaluation

5



Chapter contents

5. MATERIAL SELECTION AND EVALUATION

5.1. P5: MATERIAL BASED DESIGN FOR SOLAR TOWER APPLICATIONS USING SOLID PARTICLE MATERIALS

5.1.1. INTRODUCTION

Solid particle CSP main aim is to user sensible heat storage in solar towers for temperatures over 600ºC [1,2]. Several materials have been previously considered, such as silica sand, alumina powder, fly ash, silicon graphite, among others; however, there has not being found any standardized materials selection [3] performed [2,4]. Nevertheless, properties and parameters have been previously identified by several authors, highlighting the main concerns for some of these materials [2,5].

During a standardized design procedure, the market need is translated to a concept which complies to a promising principle. Subsequently, the embodiment part of the design process defines the layout and assemblies the proof of concept. Finally, this design concept is optimized and evaluated.

The design-led approach [6] begins defining the requirements that allows an acceptable performance of the design concept. Properties and key parameters interactions, manufacturing processes and energy and environmental impacts must be evaluated to determine the relevance for the material selection. It will even be necessary to redesign process several times adapting it according to the best existing materials.

This redesign process which depends on the material selection is considered as a Materials-Based Design (MBD) process. This process is illustrated in *Figure 5.1*.

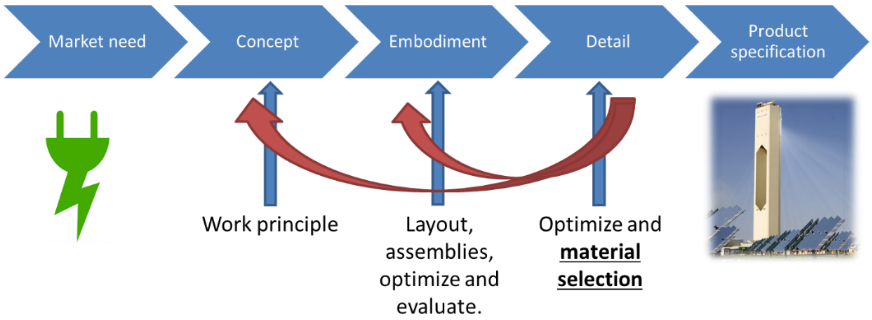


Figure 5.1. Material selection within system design process [7].

5.1.2. CONTRIBUTION

This MBD process scenario is applied to solid particle CSP granular media selection, since there are limited number of materials that can work at temperatures near 1000 °C.

The parameters and properties of the material impact on the performance, maintenance and durability of the whole concept. This analysis is focused on identifying those parameters and properties and relate them to the main design stages (receiver, thermal storage and HEX) and their particular objectives.

Key parameters and properties

Based on a reported literature, particle media parameters and properties that are considered important for solid particle CSP are shown in *Table 5.1*. In some cases, the desired values have been suggested by the researchers.

In this table, properties refer to the bulk material intrinsic properties, while parameters refer to physical design conditions, which in some cases may be modified.

According to the different stage objectives, properties and parameters relation were established and displayed in *Table 5.2*. These relations are critical for choosing the most appropriate material. Each stage objectives establishes the optimal behavior of the material for that individual stage. Therefore, Parameters and properties preferred behavior can differ from one stage to another.

Table 5.1. Properties and parameters of solid particle materials for CSP [2].

	Properties and parameters	Relevance	Desired value
Optical	Solar Absorptance	Determines the ability of the material to capture heat from solar energy.	α > 0.85
	Emissivity	Energy losses by heat radiation.	ε < 0.88
Physical	Sphericity	Effects on the particle material flow.	0.9
	Roundness	Effects on the particle material flow.	0.9
	Solid density	Determines the energy density and have influence the heat exchange process (fluidized or not)	High
	Particle size distribution	Determine the volume or number of particles of a certain diameter. Important to prevent the sintering and agglomeration of the material.	100-300 nm
Mechanical	Hardness	Determine the wear and mechanical degradation of the solid particle under stress conditions.	High
	Yield strength		High
	Fracture toughness		High
Thermal	Specific heat capacity	Determines de energy density of the material.	High
	Thermal conductivity	The ability of the particles to absorb heat and to transfer it to the heat exchanger.	High
	Melting point	Melting point have a close relationship with sintering, which must be avoided.	Higher than 1500°C
	Elongation	Ability to withstand of a material when temperature has big and fast changes. Thermal shock can cause dynamic crack propagation producing fatigue in the material structure. Also, material physical degradation can make the material more reactive.	High
	Thermal expansion coefficient		High
Chemical	Chemical composition	Determines chemical stability influence on the durability	Stable with temperature

Table 5.2. Material Stage Objectives and properties/parameters relation.

	Stage	Main objectives	Properties and parameters
System	Solar receiver	Improve solar field exploitation	Absorptivity, emissivity, specific heat, thermal conductivity, specific surface
	Thermal energy storage	Increase thermal storage, decrease thermal losses, avoid sintering and reduce material cost.	Specific heat, bulk and solid density, melting point
	Heat exchanger	Release thermal energy in short time	Particle size distribution, solid density, specific heat, thermal conductivity, specific surface, sphericity, roundness
Transversal	Thermo-mechanical stability	Improve durability of the particles and system materials	Chemical composition, sphericity, roundness, melting point, particle size distribution, hardness, yield strength, fracture toughness, elongation, thermal expansion coefficient
	Material compatibility	Avoid corrosion and wear	Corrosion enhancement of system components

Materials Based Design approach

For performing the MBD, a material index should be obtained. This material design and selection process has been previously established [3,6]. For current case of study, selection will be divided in the three main functional parts of the solid particle CSP plant: solar receiver, TES system and HEX.

Objective 1: Solar Absorptance efficiency

Solar absorptance of the materials is determined by several design and geometrical factors. However, only the intrinsic properties of the particle media are necessary for the material selection. Solar absorptance depends in the absorptivity of the particles weighted with the solar spectrum (usually AM 1.5). In this way, is important to emphasize that solar absorptance is also related to the solar spectrum expected in the design.

A second factor that influence the solar absorptance efficiency is the loss of heat due to radiative transfer by the particles and related to its temperature.

This radiative heat transfer is directly related to the emissivity property of the material under study.

Solar absorption efficiency can be determined by using the *Equation 5.1*. Where η is the absorptance efficiency, α is the material solar absorptance, $\dot{q}_i$ is the incoming irradiation into the receiver in $W\, m^{-2}$, Ɛ is the material emittance, σ is the Stefan-Boltzmann constant with a value of $5.61x10^{-8}\ W\, m^{-2}\, K^{-4}$ [8], *Ta* is the ambient temperature, and *Tr* is the temperature in the receiver.

$$\eta = \frac{\alpha \dot{q}_i - \varepsilon\sigma(Tr^4 - Ta^4)}{\dot{q}_i} \qquad \text{(Eq 5.1.)}$$

Since thermal losses depend on the maximum temperature of the receiver, influence under expected practical conditions had been illustrated in *Figure 5.2*. In this graphic, temperature effect in solar absorptance efficiency of four materials usually referenced by research groups is shown.

A relation of concentration 600 to 1 in order to reach $6x10^5$ W· m^{-2} in the incoming radiation $\dot{q}_i$ with an ambient temperature of 25 °C is assumed. Results show that, for the expected operating conditions, solar absorptance have bigger influence than emissivity in the receiver performance.

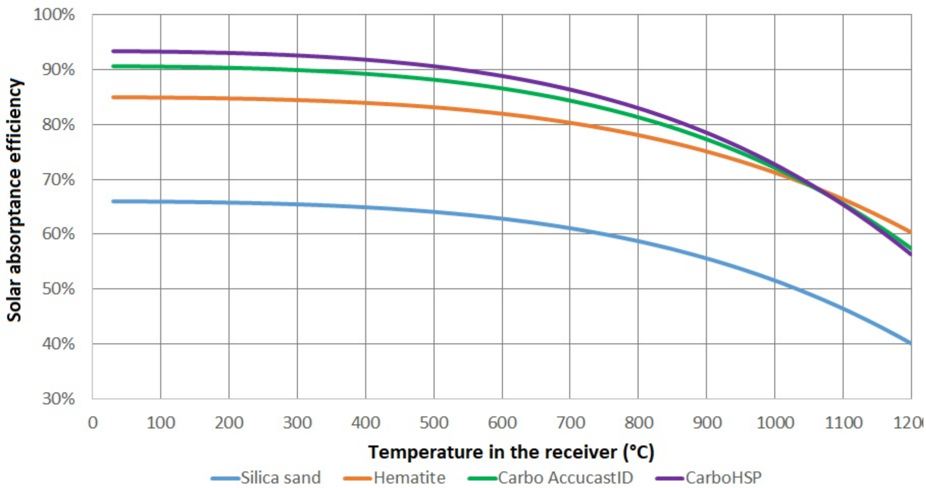


Figure 5.2. Effect of temperature in the solar absorptance efficiency according to the use of Silica sand, hematite, Carbo AccucastID or CarboHSP.

Table 5.3 summarized the function, constrains, free variables and objective for obtaining the material index in directly irradiated solar particle receivers.

Table 5.3. Material index definition of solar receiver.

SOLAR RECEIVER	Function	To absorb concentrated solar heat into the solid particle material
	Constrains	Mechanical properties Working service temperature
	Objective	To maximize the heat absorbed per m^2 of receiver aperture
	Free variables	Material choice Dimensions

Therefore, the objective equation can be obtained from the solar absorptance efficiency (*Equation 5.1*) into a heat flux $\dot{q}_a$ absorbed by the particle media flow, and that should be maximized as established in *Equation 5.2*.

$$\dot{q_a} = \alpha \dot{q}_i - \varepsilon\sigma({T_r}^4 - {T_a}^4) \qquad \text{(Eq 5.2.)}$$

Two material indices M_1 and M_2 were obtained and can be observed in *Equation 5.3* and *Equation 5.4*. Both indices should be maximized. *Figure 5.3* show this selection criteria for some of the materials previously reported in the literature [2]. Best materials are the ones closest to zero values. Nevertheless, $1/\alpha$ lower values have more relevance than lower ε values.

$$M_1 = \alpha \qquad \text{(Eq 5.3.)}$$

$$M_2 = 1/\varepsilon \qquad \text{(Eq 5.4.)}$$

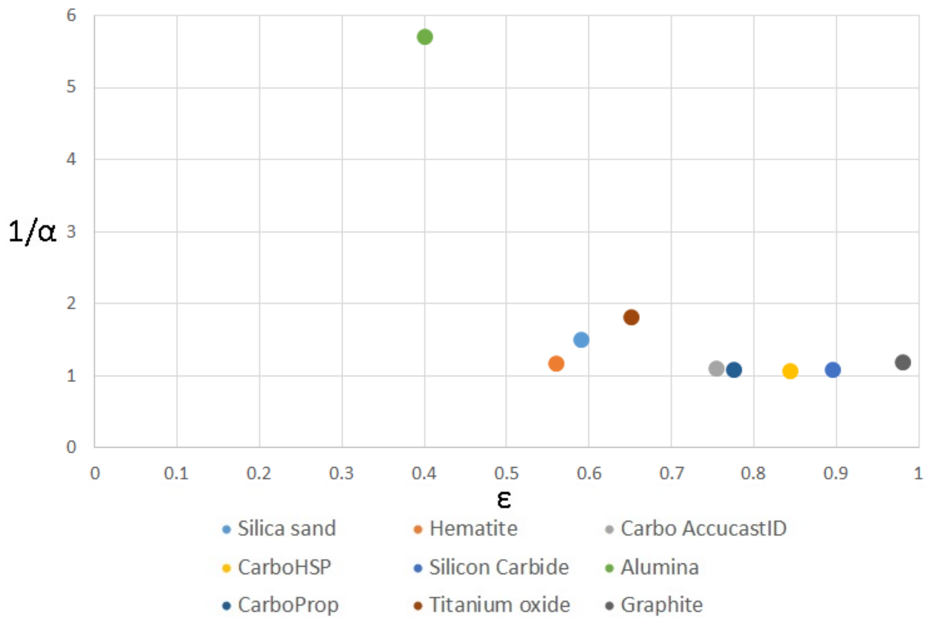


Figure 5.3. Materials to be used for storing solar thermal energy maximizing solar absorptance and minimizing emissivity.

Objective 2: Thermal Energy Storage

For the TES system stage there are two main objectives. First, to maximize the energy density per volume unit. This is necessary for reducing storage costs and for reducing thermal losses. The bigger the storage for the same amount of energy storage, the bigger the surface that loose thermal energy.

Thermal storage criteria can be observed in *Equation 5.5* as the objective function. Where Q is the amount of heat energy stored (Joules), V is the volume (m^3), ρ is the materials bulk density (kg/m^3), C_p is the heat capacity (Joules/kg K), and ΔT is the temperature increase between lower and higher operation temperatures.

$$\frac{Q}{V} = \rho \, C_p \, \Delta T \qquad \text{(Eq 5.5.)}$$

The second objective is related to the cost of the material. This parameter is related to the cost of storage capacity and to the amortization on the material.

For example, a material could have half durability compared to another if the price is significantly lower. *Equation 5.6* shows the objective function for this case, where C_m is cost of the material per mass unit and C is the total cost of the material.

$$\frac{Q}{C} = \frac{C_p}{C_m}\,\Delta T \qquad \text{(Eq 5.6.)}$$

Table 5 summarizes the function, constrains, objectives and free variables for the TES system.

Table 5.4. Material index definition of TES material.

STORAGE	Function	To store the solid particles in order to store the energy for later electricity production
	Constrains	High maximum service temperature Good thermal conductivity (above 1W/m K).
	Objective	Maximize the energy storage per volume (for reducing thermal loss rate) and per unit of material cost.
	Free variables	Material choice Dimensions

From this objectives, two material indices are obtained (*Equation 5.7* and *Equation 5.8*). M_3 and M_4 should then be maximized for a meeting the selection criteria. *Figure 5.4* shows this selection criteria for some of the materials previously reported in the literature [2].

$$M_3 = \rho\, \mathrm{C_p} \qquad \text{(Eq 5.7.)}$$

$$M_4 = \frac{C_p}{C_m} \qquad \text{(Eq 5.8.)}$$

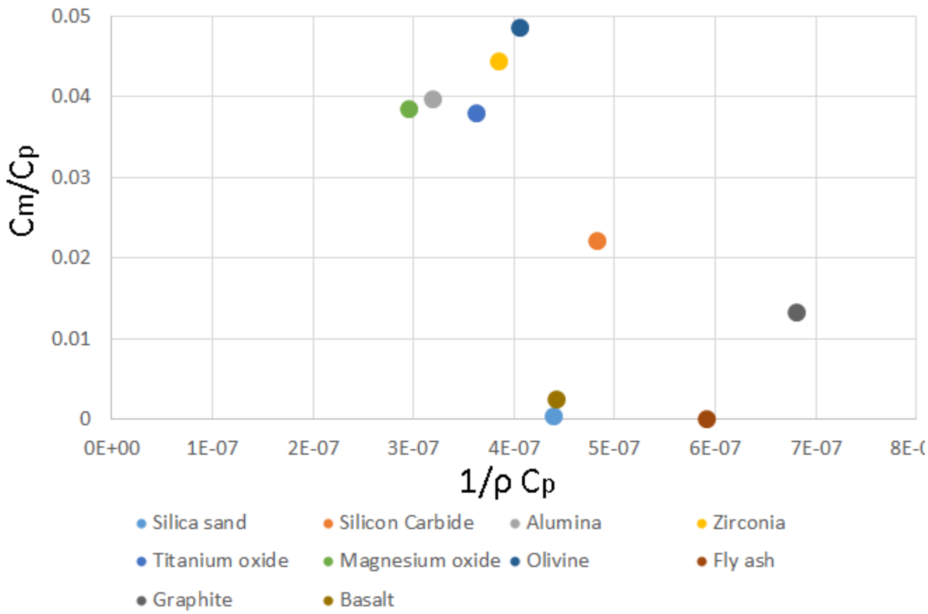


Figure 5.4. Materials to be used for storing solar thermal energy maximizing amount of heat per volume and per unit cost.

Objective 3: Heat transfer capacity

The heat transfer capacity is a main objective in terms of transmitting the heat that was stored previously in the solar receiver from the sun in the material and transferring the heat stored in the solid particle to a heat exchanger for power production.

From the solid particle material perspective, the heat transfer flux can be defined in relation to the thermal conductivity *k*, the width of the particle bed *w* and the temperature difference in both sides of the HEX T_1 and T_2 as shown in *Equation 5.9*.

$$\dot{q}_h = \frac{k}{w}(T_1 - T_2) \qquad \text{(Eq 5.9.)}$$

Table 5.5 summarizes the function, constrains, objective and free variables for heat transfer fluid used in the HEX.

Table 5.5. **Material index definition for solid particle HEX**

HEAT EXCHANGER	Stage function	Transfer the heat from the particles to the power block
	Constrains	Particle size distribution and shape
	objective	Maximize the energy flow per area of HEX
	free variables	Density Specific heat Material choice

In order to comply the design criteria, the material index M_5 is obtained and presented in *Equation 5.10*.

$$M_5 = k \quad \text{(Eq 5.10.)}$$

Thermomechanical stability and materials compatibility

Thermomechanical stability and materials compatibility are important for determining several aspects in a solid particle CSP plant. However, they depend in directly in the system design and materials used for building the system. Since current study is oriented for general selection no material index was developed according to these criteria.

Conclusions

Recognizing the design objectives, and not only the properties and parameters, has allowed building one or more material indexes, which allows to make a first screening and selection task.

However, in order to perform an optimal selection, the material performing the best should maximize all material indices together. This analysis can only be performed through a multi-variable optimization study.

Finally, durability of the materials should be added to the material selection. However, these criteria are related to each plant particular design. Next step after selecting the best available material will be to identify the properties that can be enhanced in order to improve one or several stages.

5.1.3. JOURNAL PAPER

The journal paper named "Material Based Design for solar tower applications using solid particle materials" will be sent to Materials and Design journal.

Material Based Design for solar tower applications using solid particle materials

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Abstract

Renewable energies have risen, all over the world, with the objective to reduce greenhouse gas emissions and the dependency in fossil fuels. Actual CSP renewable energy has a limitation of operation temperature due to solar salt operation temperature limit. Solid particle materials had been proposed for sensible heat storage in solar towers for temperatures over 600°C. Some materials have been previously suggested, some of their properties and parameters have been identified and measured. Nevertheless, no standardized materials selection has been performed. The aim of this study establish the base for finding a proper material for a specific design, taking into the account the properties and key parameters interactions between the different parts of the system. This methodology consists on re-designing according to the material selection, which is named as the *Materials-Based Design* (MBD) process. During this work key properties and parameters of materials were obtained and a MBD was performed, obtaining as a result the different material indices, for all the operation stages, that must be complied in order to make a formal material selection process. Recognizing the design objectives, and not only the properties, has allowed building one or more material indexes which allows to make a first screening and selection task.

Keywords: materials based design, solid particle, material index, concentrated solar power, thermal energy storage

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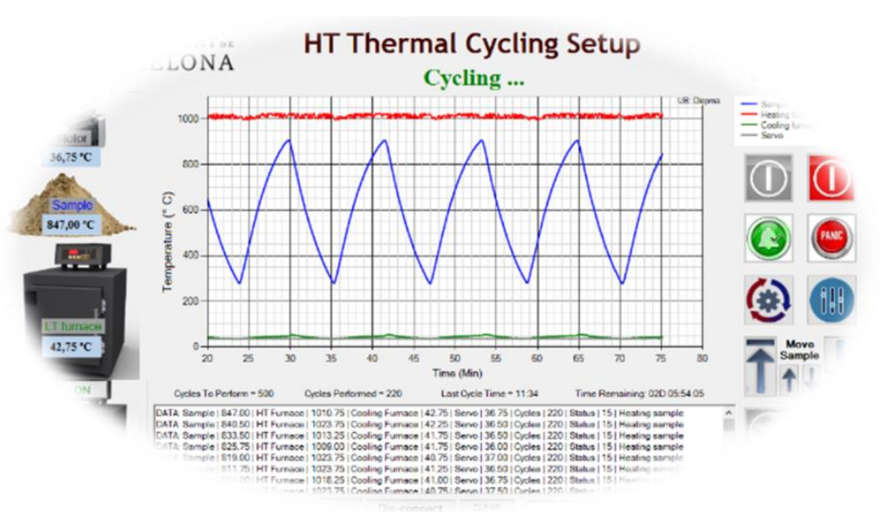
Thermal durability characterization 6



Chapter contents

6. THERMAL DURABILITY CHARACTERIZATION

Materials durability is an attribute difficult to characterize and quantify, since it depends on several thermal, mechanical and ambient conditions. However, durability is essential for system technical and economic viability [1], as chemical, thermal, mechanical and physical properties and parameters, used to design and evaluate plant lifetime, are affected by material degradation.

In solid particle CSP system, durability can be studied from the point of view of the system or of the particle media. In addition, material compatibility under mechanical and thermal stress conditions must be further studied for a proper material design and selection of both solid particles and system elements in contact with them (solar receiver, storage tanks, HEX and conveyance system).

Without a pilot plant with working conditions similar to the commercial proposed plant ones, predicting materials durability is extremely complex. Therefore, the effect of thermal conditions on durability is studied apart from the effect of mechanical stresses (wear, abrasion, attrition, etc.). During this dissertation thermal durability has been analyzed, leaving for future work the study of mechanical effects on durability.

Ceramic and metallic materials can become thermally degraded when exposed to heat, either for long periods of time (thermal aging) or by thermal fatigue. When the temperature is changed in a repetitive way with the same increase/decrease of temperature rate under the same conditions, we can consider that the material is being under thermal fatigue cycles. Thus, effect of thermal cycling during materials lifetime has a direct impact in materials durability. Multiple thermal shocks have shown that several mechanical properties get affected, such as hardness, Young modulus, plastic strain, and fracture toughness [2,3].

In this chapter, thermal aging and thermal cycling effects are studied. First, in section 6.1. thermally aged materials were characterized after several time spans. In section 6.2, previously thermal aged materials were further thermally cycled.

6.1. P6: Study on solar absorptance and thermal stability of solid particles materials used as TES at high temperature on different aging stages for CSP applications

6.1.1. Introduction

Effect of high temperature in the long term for solid particles can affect different properties and parameters, such as solar absorptance, emittance, specific heat capacity, thermal conductivity and density. As mentioned in the previous chapter, solar absorptance is critical for power plan viability and any change must be studied in detail. Current study was focused on the effect of high temperature over a long period of exposure. Three different solid particle materials were aged over different time spans. Two of these materials have been constantly suggested by other research groups as good candidates for CSP use at high temperature. Synthetic black silicon carbide from, silica sand and iron oxide (hematite) were the evaluated materials. Main parameters and properties found in literature can be observed in *Table 6.1*.

Table 6.1. Summary of properties and parameters.

Material	Source	Particle Size (mm)	Advantages / Disadvantages	Ref
Black silicon carbide	Synthetic	0.02–0.2	**Advantages:** Good mechanical properties, high wear resistance, high strength at high temperature, good thermal shock resistance. High thermal conductivity. Naturally black color. **Disadvantages:** High cost.	[4–6]
Silica sand	Mineral	0.2–0.5	**Advantages:** Very durable mineral, resistant to heat and chemical attack, high melting point, non-corrosive. **Disadvantages:** White color and polymorphic changes.	[4–7]
Iron oxide	Mineral	< 0.15	**Advantages:** Paramagnetic iron oxide. Naturally black color. **Disadvantages:** No noticeable disadvantages.	[7]

Thermal aging

Aging was performed without any atmosphere control, as it is expected on the open receiver configuration plant. A laboratory furnace was used with sintered alumina crucibles for containing the samples (*Figure 6.1*). New conversion cycles can be used with a 750 °C top temperature, however the ideal CO_2 supercritical thermal cycle becomes more efficient at 900 °C. Therefore, two aging temperatures were selected for thermal aging tests: 750 °C for a conservative approach and 900 °C for an ideal one.

Figure 6.1. Furnace and crucibles used for thermal aging.

Samples were collected from the material as received and after 24, 72, 168, 312, 405 and 500 hours. These samples were characterized by Thermogravimetrical Analysis (TGA) for chemical changes on an initial stage, Differential Scanning Calorimetry (DSC) for specific heat capacity, Spectrophotometry for solar absorptance, and X-ray Diffraction (XRD) for its composition. Among this, other analysis such as electronic microscopy, particle size distribution and density were performed although not reported in the publication.

Characterization

Specific heat capacity was measured using a DSC 822e Mettler Toledo calorimeter with around 15 mg of particles in an aluminum crucible with a 50ml/min N_2 flow. Equipment precision for these conditions is ±0.1 kJ/kg·K with a ±0.3 °C. X-ray diffraction analysis was performed in a PANalytical X'Pert Pro MPD Θ/Θ Bragg-Brentano powder diffractometer at ambient temperature.

Solar absorptance was measured in a Perkin Elmer Lambda 950 spectrophotometer with a 150 mm integrating sphere within 300 nm – 2500 nm wavelength range. This range was defined according to AM 1.5 solar spectrum. Since samples are particles under 1 mm, a sample holder (*Figure 6.2*) was developed in order to be able to perform the measurements and protect the integrating sphere sensor. This holder allowed to hold the particle media by using a plastic container with a sapphire crystal window. Sapphire was selected because its scratch resistance and the small influence on the reflectance/absorptivity measurements. In order to get remove the optical effect of the Sapphire window, the spectrophotometer calibration in black (0% reflection) and white (100% reflection) was carried out using a sapphire crystal between the calibration surface and the integrating sphere.

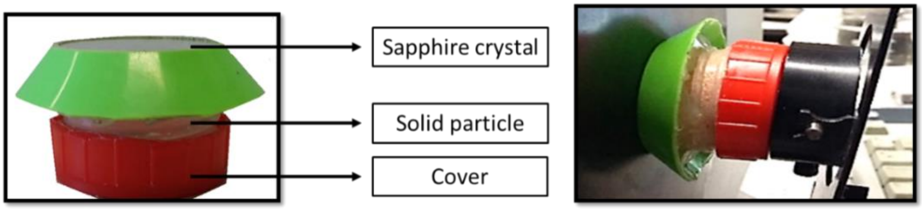


Figure 6.2. Sample holder for absorptivity measurement of particle media.

Absorptivity results from the spectrophotometer do not reflect the solar absorptance, but the absorptance with an ideal black body that emits the same quantity of energy on all the wavelengths. Therefore, results were weighted with AM 1.5 solar spectrum (*Figure 6.3*) and integrated to determine the percentage of the solar spectrum that the material absorbs.

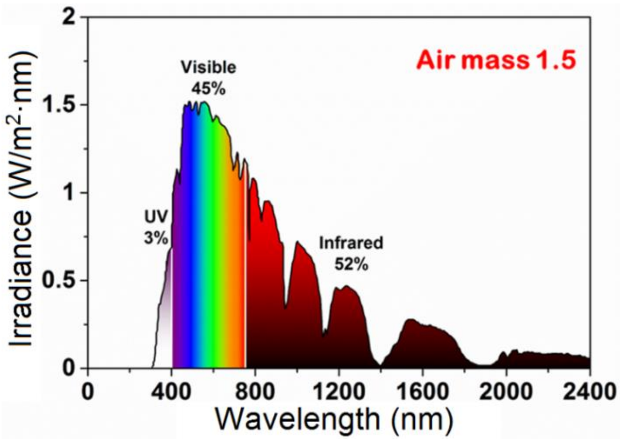


Figure 6.3. AM 1.5 solar irradiance on Earth [8].

A spectrophotometer measures the amount of energy in a determined wavelength that is reflected by the material. Since all the materials under analysis are opaque, there is no transmittance and it can be assumed that the energy that is not reflected is absorbed. *Figure 6.4* shows an example of the data before integration and weighting. Final solar absorptance of this example is 0.96 for sample as received, 0.94 after 168 hours of thermal aging, and 0.93 after 500 hours.

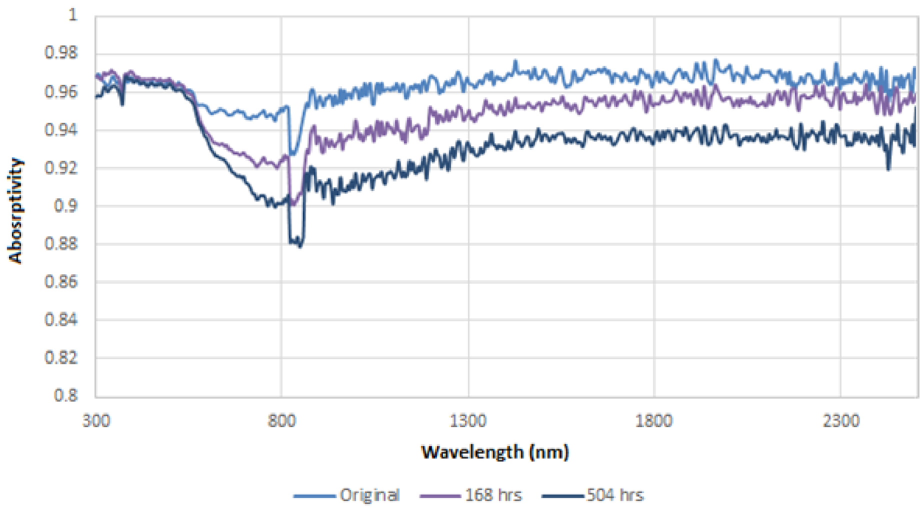


Figure 6.4. Absorptivity of Carbo HSP® proppant on original conditions and after 168 and 504 hours of thermal aging at 900 °C.

6.1.2. CONTRIBUTION

The performed material characterization helped to determine the most promising material among those evaluated. When measuring solar absorptance, the new sample holder allowed to test the materials under standard conditions and without special equipment.

The most relevant results about the specific heat capacity, solar absorptance and composition are presented. Since ceramic materials are mainly materials with crystalline structures (except for glass), X-ray diffraction was used for this analysis.

Specific heat capacity

Table 6.2 shows the specific heat capacity results for the as-received and 500 hour aged materials at two different temperatures. The first at 750 °C, which reflects a moderate increase of temperature compared with current molten salts (565 °C). The second temperature was of 900 °C, which considers a more ambitious approach that could give a clearer advantage to solid particle CSP technology over other systems.

Table 6.2. C_p results for the studied samples as received and after aging at 750°C and 900°C. Values measured at 100°C and 400°C by DSC.

Material	C_p initial (J/g·°C)		Aging temperature (°C)	C_p after 500 h of thermal aging (J/g·°C)	
Test temp	100 °C	400 °C		100 °C	400 °C
Black silicon carbide	1.3±0.1	1.5±0.1	900	1.6±0.1	1.8±0.1
			750	1.3±0.1	1.4±0.1
Silica sand	0.9±0.1	0.8±0.1	900	1.2±0.1	1.2±0.1
			750	-	-
Iron oxide	1.2±0.1	1.2±0.1	900	1.2±0.1	1.0±0.1
			750	0.9±0.1	0.7±0.1

Aging at 750 °C for silica sand was not performed, since its solar absorptance is significantly low. Only 900 °C aging was performed for reference, since this is a material reported by a considerable number of researchers [6,9,10].

Most important changes in specific heat capacity are the increase of C_p of black silicon carbide and silica sand after 900 °C aging, and the decrease for the iron oxide for the sample aged at 750 °C. Other results show no changes or changes within the measurement uncertainties.

Solar Absorptance

Reflectance analysis was performed for the same materials under the same aging conditions. However, in this case several intermediate samples between the as-received material and the 500-hour aging were considered to try to determine tendencies. Solar absorptance results for the three materials are presented in *Figure 6.5*, along with small pictures of the initial and last samples.

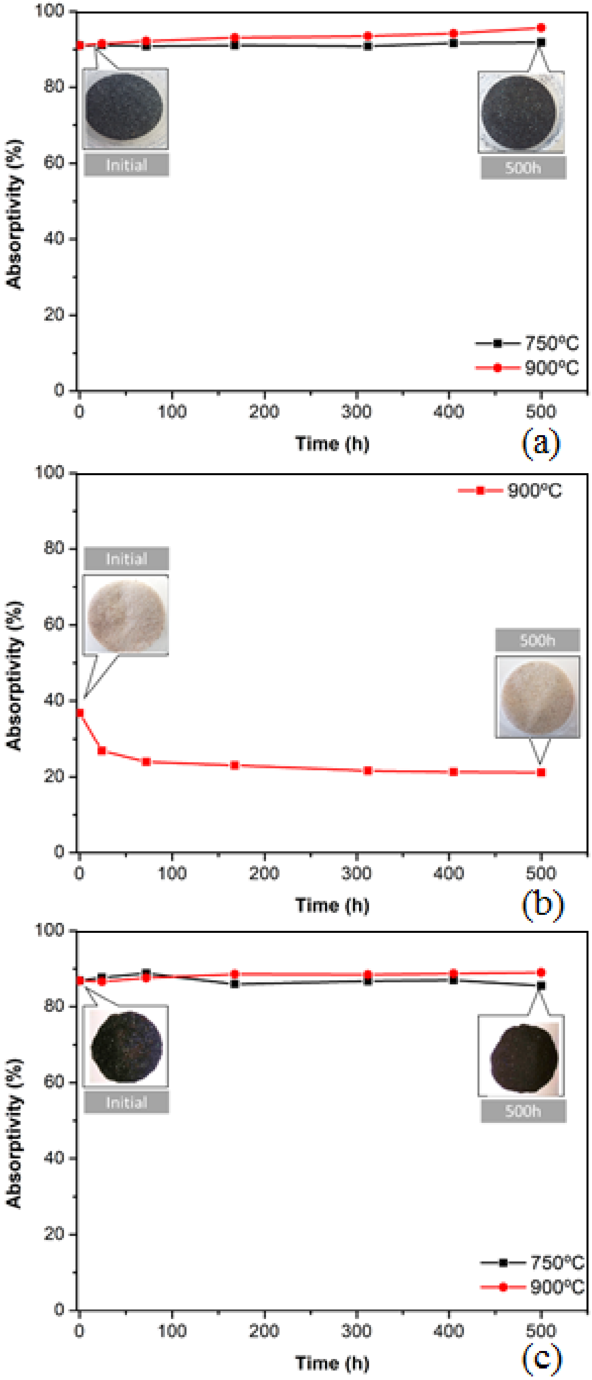


Figure 6.5. Solar absorptance for samples aged at 900°C (red) and 750°C (black): (a) black silicon carbide, (b) silica sand, and (c) iron oxide.

Black silicon carbide solar absorptance was stable and even increase 5% after 900 °C treatment. The tendency to increase absorptance is constant during the 500-hour aging process.

Silica sand presents the most significant change as its absorptance reduces almost to half with aging time. Most significant changes occurred during the first 50 hours of thermal treatment at 900 °C. This result shows that silica sand is definitively a bad candidate for directly irradiated designs.

Finally, Iron oxide solar absorptance shows to be stable for both aging temperatures. For 900 °C it even shows a slight enhance in this property.

Composition

X-ray diffraction analysis was performed to the as-received samples and to the 500-hour aged samples. Results are presented in *Figure 6.6*, in which samples are overlapped in blue for the as-received ones and in red for the aged ones.

Black silicon carbide XRD patterns do not present significant changes. This can be observed in *Figure 6.6a*. The slight differences between the patterns can be attributed to different stacking sequences.

Iron oxide patterns are presented in *Figure 6.6b* with no detectable changes. A peak detected at 42.8 degrees (marked with an arrow) can be assigned to $CaFe_3O_5$ impurities. Decomposition of dolomite could favor the formation of this oxide.

Finally, silica sand changes can be observed in *Figure 6.6c*. Structural changes can be clearly observed, since initial peaks can be assigned to an α-quartz (rhombohedral) major phase, while β/quartz (hexagonal) as major phase can be observed in the aged sample.

Conclusions

Overall analysis show that, among the three granular materials that were analyzed, silicon carbide is the best material from the long-term thermal stress point of view. Iron oxide is also a good candidate as it remains stable during thermal aging treatment. Also, temperature limit has a main role for selecting the most appropriate material for solid particles technology and must be considered for durability considerations.

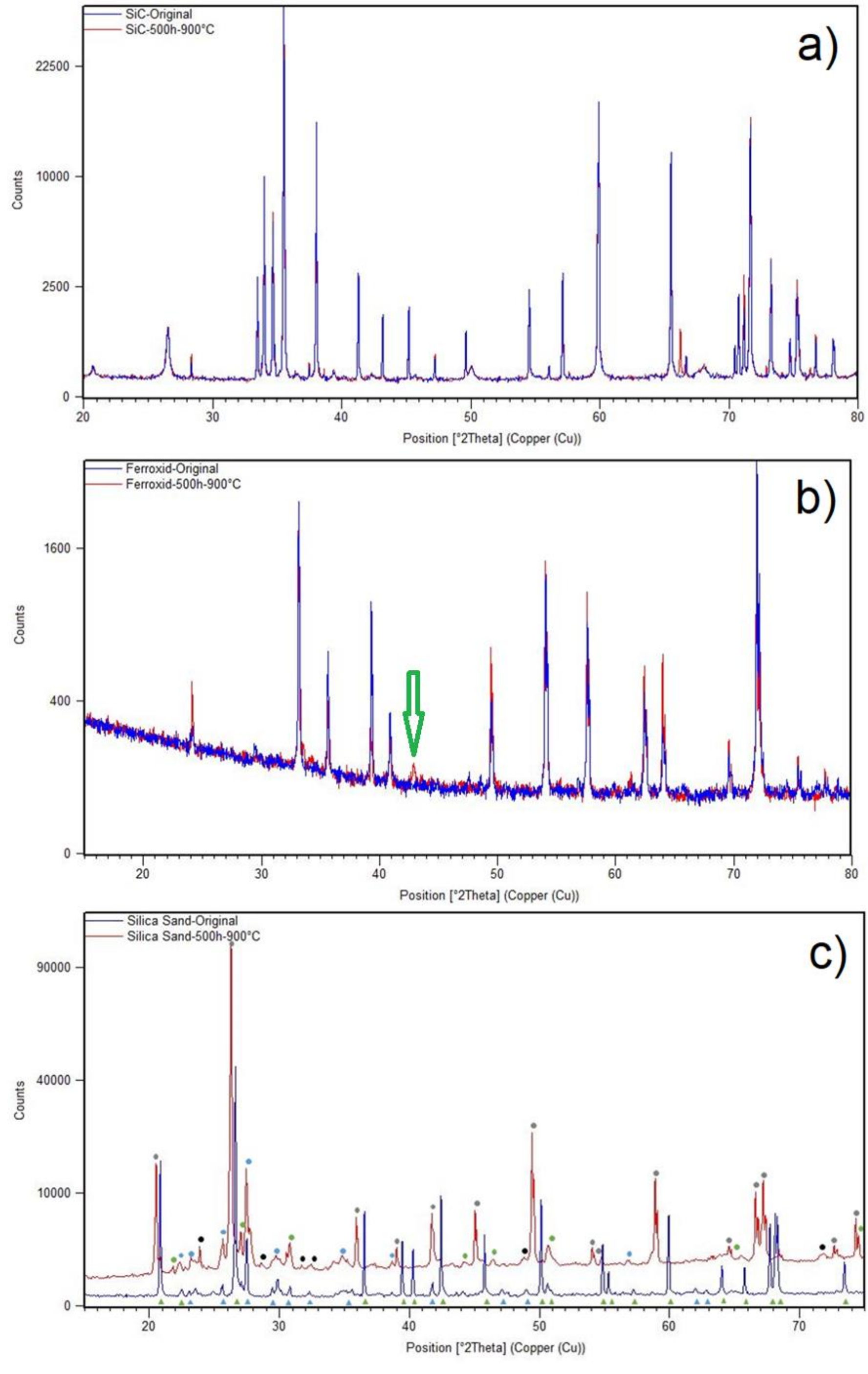


Figure 6.6. XRD for initial stage, and after aging at 900°C for a) black silicon carbide, b) iron oxide, and C) silica sand.

6.1.3. JOURNAL PAPER

The journal paper named “Study on solar absorptivity and thermal stability of solid particles materials used as TES at high temperature on different aging stages for CSP applications.” Was published in Solar Energy Materials and Solar Cells journal in 2019 in volume 201 and with the manuscript number: doi.org/10.1016/j.solmat.2019.110088.

Highlights

- Solid particles have great potential in concentrated solar power plants
- Efficiency of particles based systems depends on their optical properties
- This study provides experimental evidence of the particles candidates performance
- SiC, silica sand and Fe2O3 are aged tested & optically and thermally characterized
- SiC stand out as the most appropriate particulate material from optical perspective

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Study on solar absorptance and thermal stability of solid particles materials used as TES at high temperature on different aging stages for CSP applications

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ABSTRACT

The use of solid particles as heat transfer fluid (HTF) presents a great potential to overcome drawbacks addressed in commercial Concentrated Solar Power (CSP) plants. The solid particles thermal energy storage (TES) system allows achieving both high thermal performance at high temperature and low cost from the material perspective. The conversion efficiency of CSP solid particles-based systems at high temperatures strongly depends on the optical properties and thermophysical properties of materials used both as HTF and as storage medium. The present study is aimed to provide more experimental data and evidences of the potential in using particulate solids for CSP application. The solar absorptance and the specific heat capacity of silicon carbide (SiC), silica sand (SiO_2), and hematite (Fe_2O_3) are studied after different aging times at 750 °C and 900 °C. The solar absorptance slightly increases over the aging process except for the silica sand, which decreases its absorptance in the first 100 h, reaching a plateau. After the aging treatment, the specific heat capacity is increased for both SiC and silica sand. However, for the iron oxide the specific heat capacity is lower after aging. The black silicon carbide SiC is proven to be the best option to be used up to 900 °C as it shows the highest solar absorptance (96%) and the highest heat storage capacity.

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6.2. P7: THERMAL CYCLING TEST OF SOLID PARTICLES TO BE USED IN CONCENTRATING SOLAR POWER PLANTS

6.2.1. INTRODUCTION

As mentioned before, combination of thermal and mechanical stresses determines the particle media and system durability from the materials perspective. In order to analyze thermal stress individually, effect of high temperature exposure in the long term has previously been studied. Therefore, effect of thermal stress due to continuous heating and cooling of the material is reported in this section.

A thermal cycle could be defined as the process of getting a material from a temperature A to a temperature B and then back to temperature A. Different conditions can be defined for these thermal cycles: the upper and lower temperature limits; the time required to complete the cycle, defined as the sum of the heating time, the cooling time and any isotherm time (if applies).; in addition, special atmosphere conditions can be established for any particular pressure or when any reaction is to be favored or inhibited; finally, the number of thermal cycles must be defined according to the lifetime activity expected for the material under study.

For current solid particle CSP designs there are some conditions that can be established. Air atmosphere at standard pressure is adequate for open receivers. Also, the number of expected thermal cycles could be calculated for the expected plant lifetime based on current commercial state-of-the-art CSP plants. Molten salts CSP plants have a daily usage when they incorporate TES with a life time of 30 years [11–13]. These means that, at least, around 11,000 thermal cycles are expected to occur during facility lifespan. However, even with accelerated tests, this number is inviable to be performed for each material being evaluated. Thus, for current evaluation, up to 1,500 cycles were performed to the proposed materials.

Cycling speed is determined by the thermal cycling instrument design and by the material being cycled. From the solid particle CSP plant view, there is no heating (charging) or cooling (discharging) speed defined.

Finally, the low and high temperatures were defined to be 300 °C and 900 °C respectively. This temperature range was defined according to the ideal conditions of the CO_2 super critical Brayton thermal-to electric cycle, in which conversion efficiency can reach 60% under these conditions [14].

For performing thermal cycles in such conditions of speed, number of cycles and temperatures, no commercial or laboratory scale device was found. Therefore, a new device was designed and built for performing accelerated thermal cycling treatments.

The materials evaluated were Carbo HSP® and black silicon carbide. Carbo HSP® has been proposed by many researchers on this topic [5–7,15,16], while black silicon carbide showed the best results for thermal aging test, which was reported in *section 6.1*. Carbo HSP® is a composite granular material that was originally designed by Carboceramics Inc. as proppant for hydraulic fracture oil production. Hence, it was designed with good fluidization properties and good mechanical stress resistance [17], but not for high temperature thermal stress.

Table 6.3 show the main properties available for these materials. These values have been found in the literature and were not determined in any of the studies of this chapter. In addition, thermal conductivity values are in bulk conditions for black silicon carbide, while for Carbo HSP® reported values consider the granular shape, and therefore, the air between the particles. Similar bauxite materials show bulk thermal conductivity of around 25 W/m·K [18].

Table 6.3. Reported properties of SiC and Carbo HSP®.

MATERIAL	BLACK SILICON CARBIDE		CARBO HSP®	
MELTING POINT (°C)	2150 – 2250		2000 – 2100	
THERMAL CONDUCTIVITY (W/m·K)	90 – 110		2	
SPECIFIC HEAT (J/ kg ·K)	663 – 667		1275	
COMPOSITION	Min 99.3% SiC	max 0.4% C	83% Al_2O_3	5% SiO_2
	Max 0.4% SiO_2	max 0.2% Si	7% Fe_2O_3	4% TiO_2
ABSORPTANCE	–		0.93	
EMISSIVITY	0.83 – 0.96		0.84	
COST (€/kg)	12.3 – 17.5		0.6	
DENSITY (kg/m^3)	3000 – 3200		3560	
REFERENCES	[18–20]		[7,16,18,21]	

In order to evaluate any changes in material parameters and properties several characterization tests were performed to the samples in different stages of the aging process. For evaluating the effect of thermal cycling, materials were thermally aged at 900 °C during 500 hours before performing the 1500 cycle treatment. Samples as-received, thermally aged (at 900° for 500 hours) and thermally cycled (1,500 cycles between 300°C and 900°C) were characterized. Only for absorptivity measures intermediate samples were used.

Apart from the characterization techniques previously described in *section 6.*2, such as solar absorptance (using spectrophotometer), specific heat (using differential scanning calorimetry) and composition (with x-ray diffraction), other additional techniques have been used:

- Particle size distribution (PSD), in which a Beckman Coulter LSTM 13 320 laser diffraction analyzer with universal liquid module using electrical sensing zone method was used. Three measures were performed for each sample and the results were obtained by the average of them.
- Scanning electron microscopy (SEM), with a FEI Quanta 200 SEM. Obtained images were used to show changes in morphology of the materials before and after the thermal treatments.
- Energy dispersive spectroscopy (EDS) with the same FEI Quanta 200 SEM integrated with EDS detector. This technique was used to obtain a semi-quantitative elemental analysis of the samples.
- Helium pycnometer, with the use of a Micrometrics Accu-Pyc 1330 to determine real density changes.

6.2.2. CONTRIBUTION

A thermal cycling device has been developed in University of Barcelona in order to evaluate thermal stress durability of materials. The setup was the result of the effort of several researchers and took around a year to be completed. This setup can potentially perform a material thermal stress test, in around three months, equivalent to 30 years of a power plant operation (based on a single charge and discharge cycle per day). For the materials reported in this section each thermal cycle took between 11 (for black silicon carbide) and 14 minutes (for Carbo HSP®) with a temperature range between 300 °C and 900 °C.

The device, which can be appreciated in *Figure 6.7a*, consists of two furnaces vertically faced: the first one placed at the bottom of the device is the one used for heating the sample, and the second one at room temperature, used for cooling the sample, is placed above the heating furnace. Both furnaces have holes on top, and the one at room temperature has also a hole below so the alumina tube can move across one to the other. This is shown in two schematics in *Figure 6.7b* and *Figure 6.7c*.

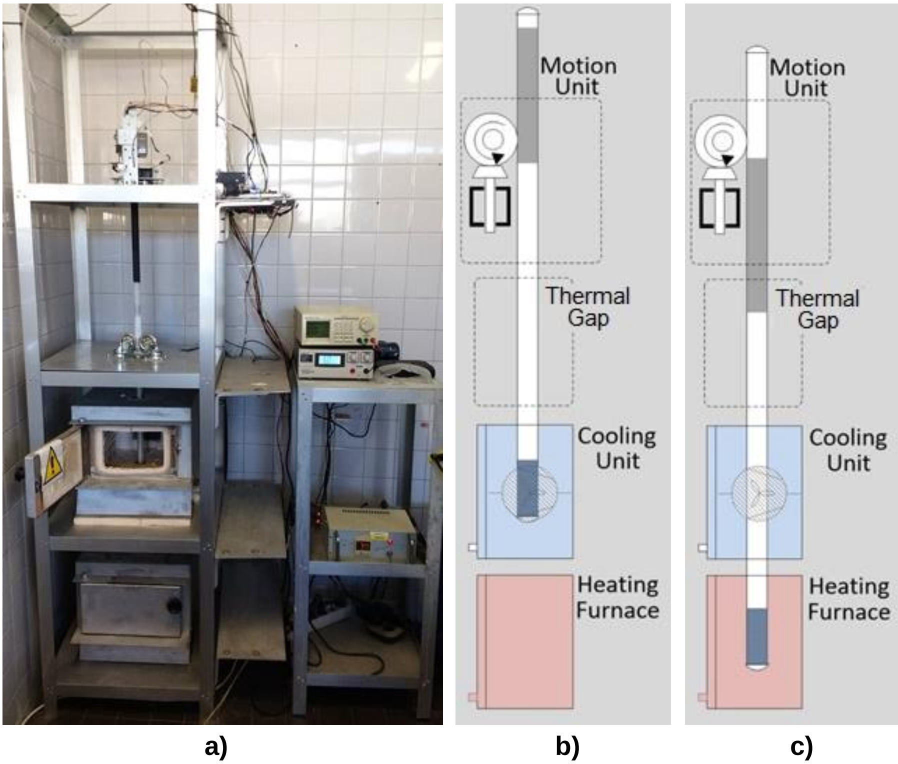


Figure 6.7. a) Thermal cycling device; b) Scheme of the thermal cycling device at cooling position; c) Scheme of the thermal cycling device at heating position.

The solid particle material sample is placed inside a sintered 20 mm diameter alumina tube. This tube is automatically moved between the two furnaces. The temperatures inside the furnaces are fixed: the hot furnace at 1050 °C and the cold furnace at room temperature (~23 °C). The upper part of the tube is painted in black and a color sensor helps to identify the position of the tube in the device.

When the device is working, the tube is automatically moved 24 hours a day and unattended. Different parts of the device are represented horizontally in

Figure 6.8. Besides the heating furnace and cooling unit previously described, a motion unit (*Figure 6.9a*) and a control unit (*Figure 6.9c*) were added in the device. The motion unit is responsible of moving the tube between the two furnaces. The sample remains in the same part of the tube (the lower part). It is the tube end which moves to the heating position (*Figure 6.7c*) until the sample reaches 900°C. Afterwards, the tube end is moved to the cooling position (*Figure 6.7b*) until the sample reaches 300°C, at which time it moves back down to the heating position, thus completing one thermal cycle, and starts again.

Temperature is monitored and controlled by four Type K thermocouples: inside the tube for monitoring the temperature of the sample, in the heating furnace, in the cooling unit, and in the motion unit. The temperature sensor inside the tube is the one in direct contact with the sample and is placed in the center of the volume occupied by the particles. This guarantees that the lowest and highest temperatures are reached by all the material. The inner diameter of the tube is 14.5 mm, which results in less than 7.25 mm in width of material between the thermocouple and the alumina tube. To improve sample cooling, an air fan was placed in the cooling unit, causing forced air convection over the outside of the tube when the sample is at the cooling position.

Several safety conditions were implemented in order to leave the device unattended and achieve 24 hours a day operation. When one of such conditions happens an alarm process is triggered. This alarm process includes interruption of the cycling process by turning off the power supply of both the heating furnace and the motion unit in case of alarm, while emitting an audible alarm sound.

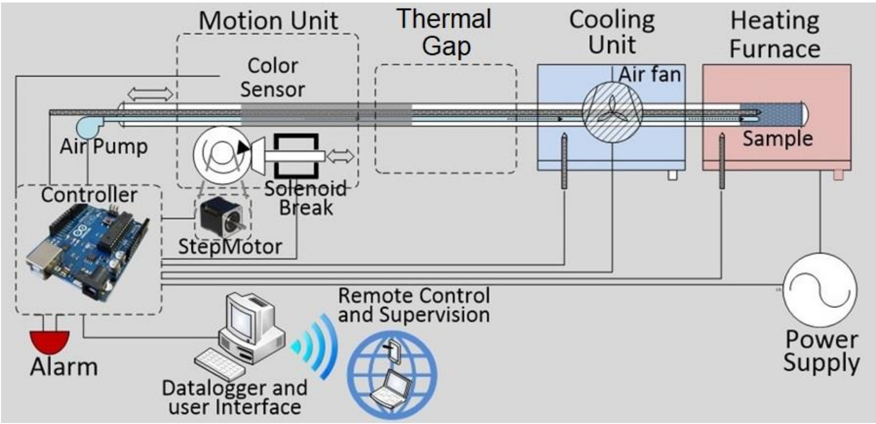
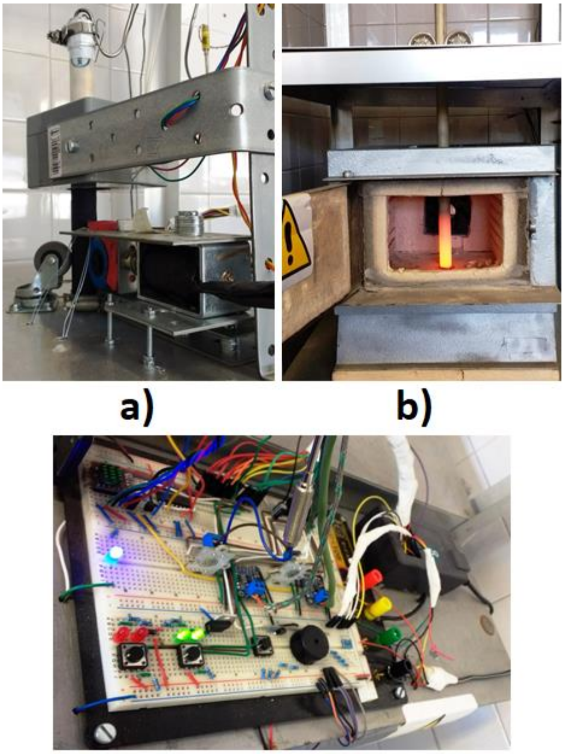


Figure 6.8. Thermal cycling device schematic distribution.

The controller unit was built using an Arduino Mega 2560® card and an electronic board for all the electronic interfaces (*Figure 6.9c*). This controller was programmed to handle the thermal cycles and the security triggers, as well as to communicate with the computer interface. For data collection and user control and monitoring, an interface was developed (*Figure 6.10*). This interface displays the recorded temperatures for the last hour on a graph, stores all the data on a database, and shows other parameters like the number of remaining cycles, the status of the device, etc. Functions and parameters can also be managed from the interface: starting/stopping the thermal cycles, defining the number of cycles to be performed, the set point for low and high temperatures, the alarm tolerance temperature, etc.



a) b)

c)

Figure 6.9. Thermal cycling device a) motion unit, b) cooling unit, and c) controller.

The stages of a cycle are illustrated in the graph in *Figure 6.10*: point A corresponds to the sample in the cooling position, point B when it has reached the maximum temperature, and point C when it returns to 300 °C. The time elapsed between A and B, and between B and C depends on the thermal diffusivity of the sample tested. Thus, the greater the energy density (that is the product of density by the heat capacity) of the material, and the lower the thermal conductivity, the more time the cycle will take.

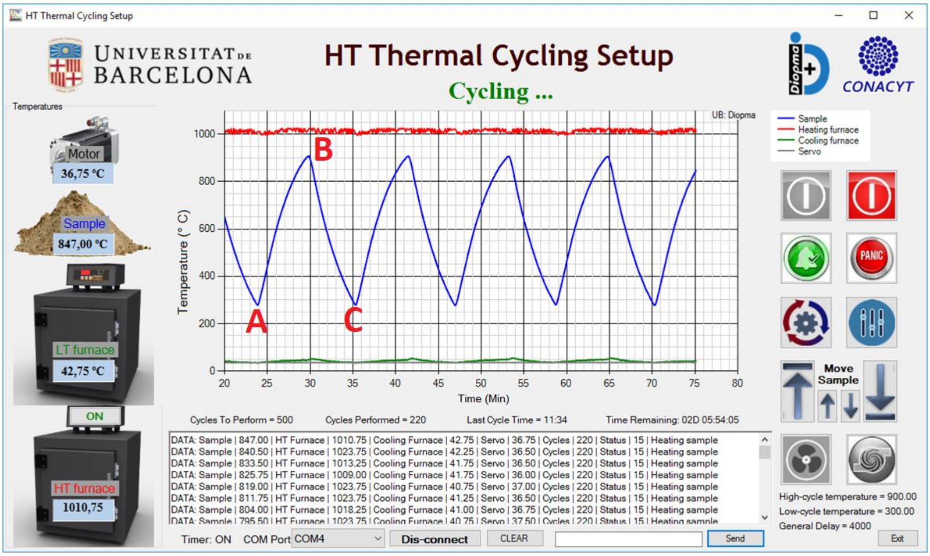


Figure 6.10. Thermal cycling device computer interface with charge and discharge highlighting (points A, B and C).

Results

Complete characterization of the Carbo HSP® and SiC samples was carried away. The most outstanding results are presented.

Physical and morphological analysis

Density data obtained by helium pycnometer are presented in *Table 6.4*. While Carbo HSP® shows no significant variation, SiC shows a slight decrease of around one percent after the thermal cycling test. This change may reflect a change in SiC due to thermal cycling treatment and should be taken into the account with other results for confirmation.

Table 6.4. Real density (kg/m^3) for SiC and Carbo HSP® as received and after thermal treatments.

Material	As received	After 500 hour aging	After 1500 cycles
Carbo HSP®	3645.1 ± 0.5	3635.5 ± 0.2	3637.4 ± 0.2
SiC	3206.4 ± 0.5	3202.4 ± 0.5	3176.5 ± 0.1

Particle size distributions, by volume and by number, can be observed for Carbo HSP® (*Figure 6.11*) and for SiC (*Figure 6.12*). A slight displacement can be observed related to a small increase in mean particle size due to thermal treatments. Since this displacement is present in both thermally treated samples it can be probably related to the long term thermal treatment rather than the thermal cycling itself.

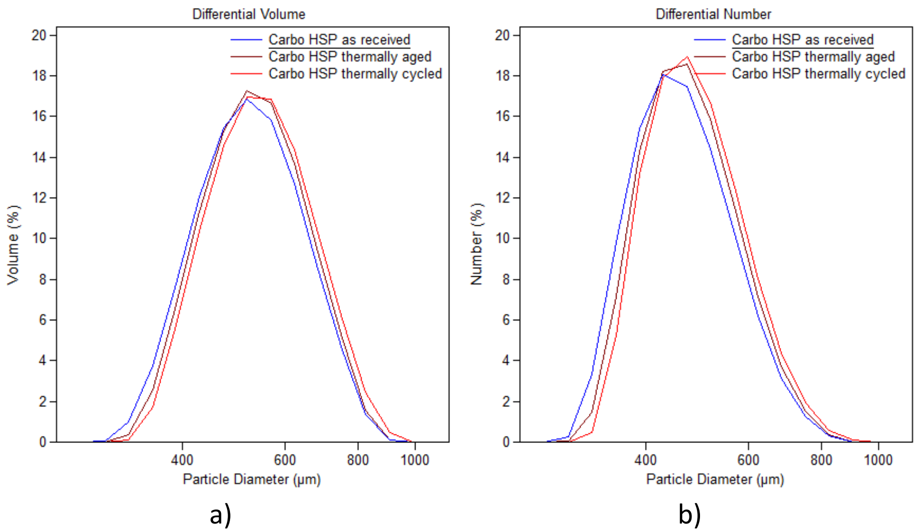


Figure 6.11. PSD for Carbo HSP® samples, a) by volume, and b) by number.

SiC size distribution shown in *Figure 6.*12 seems to be more affected by thermal shock than by aging. Volumetric distribution slightly changes for the thermally cycled sample, but the distribution by number shows an increase in the fraction corresponding to smaller particles, between 90 µm and 150 µm, thus reflecting that there has been an increase of fines probably originated by the fracture of the bigger particles due to thermal cycles.

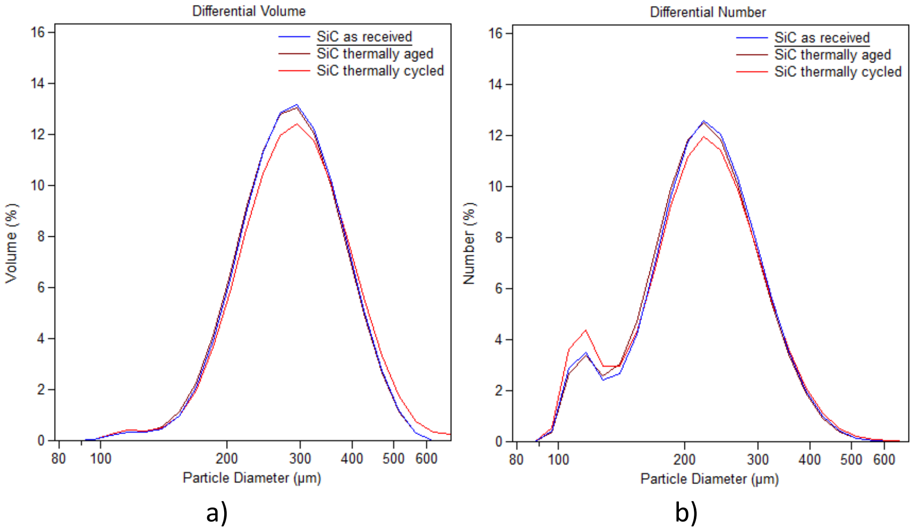


Figure 6.12. PSD for SiC samples, a) by volume, and b) by number.

Images obtained by SEM images of Carbo HSP® show that particles were not affected in its surface by the thermal stress tests. In the case of SiC (*Figure 6.13*) some changes can be appreciated on the surface of the particles, mainly after 1500 thermal cycles. These changes can be clearly observed in Figure 6.13c, where several cracks and fissures on the material surface appeared.

Chemical analysis

EDS analysis were performed on the most pronounced edges of the particles, since it is assumed that these are the most reactive parts of the particle surface. In addition, samples were graphite coated to increase electric conductivity, making any carbon analysis unreliable from EDS perspective.

Carbo HSP® EDS semi-quantitative elemental analysis showed that there are non-detectable changes. For SiC, EDS shows a slight change since oxygen appears in thermally aged sample and in the thermally cycled sample (*Figure 6.14*). This suggests that SiC surface reacted with oxygen in the air during the test and formed SiO_2 while releasing CO_2.

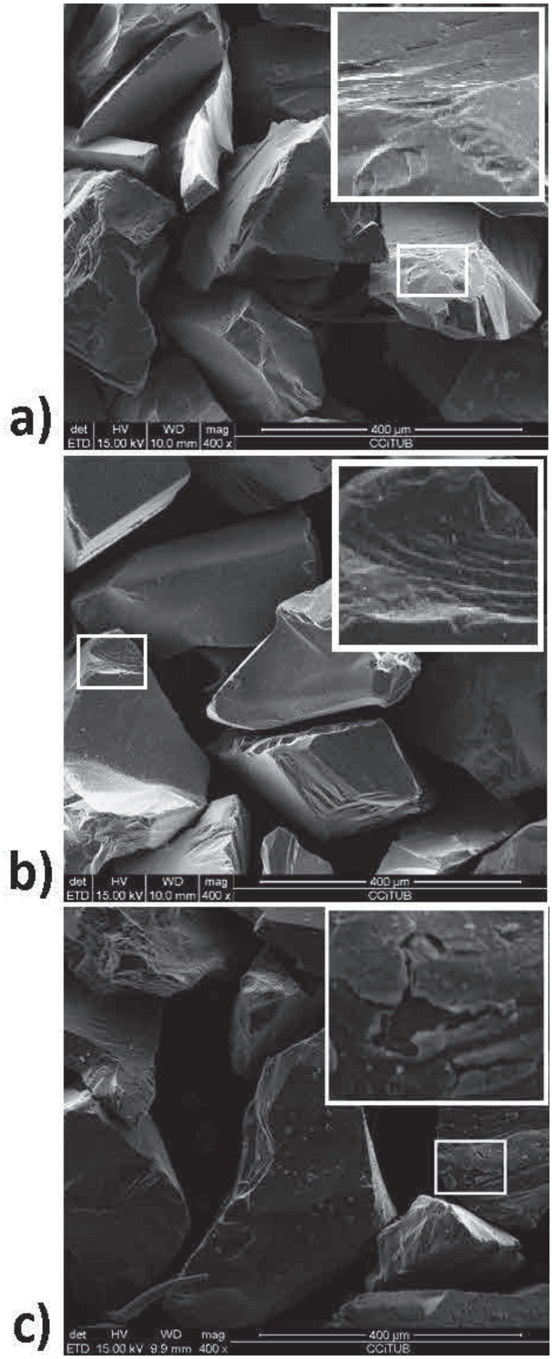


Figure 6.13. SEM images of SiC with inserted magnification a) as received; b) after 500 hours at 900°C; c) after 1500 thermal cycles between 300°C and 900°C.

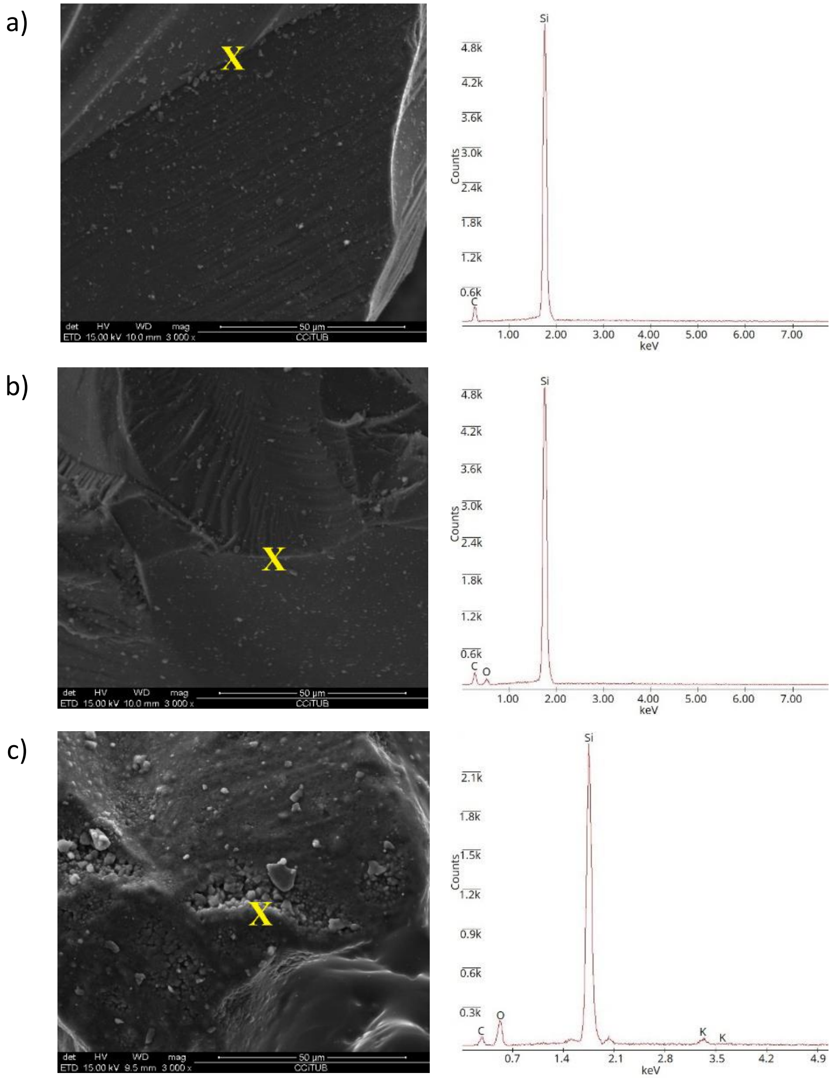


Figure 6.14. SEM images of SiC and corresponding EDS analysis performed at X points in the images of samples a) as received; b) thermally aged; c) thermally cycled.

Carbo HSP® XRD analysis shows that the main crystalline phases are Al_2O_3, SiO_2 and Fe_2O_3. There were no visible composition changes between the three samples (as received, thermally aged and thermally cycled).

SiC XRD results can be observed in *Figure 6.15*, in which original and aged samples only SiC was detected, since only fractions with more than 4% w/w can be securely identified.

Figure 6.15a shows XRD analysis for a SiC sample after 1500 thermal cycles, which differs only in one peak (marked with a triangle in *Figure 6.15 b*) from the corresponding XRD for as received and thermally aged samples. It has been reported that pure SiC sample do not react with oxygen at temperatures under 1200°C. However, there has been reported that the SiC develops a protective surface layer of SiO_2 which prevents SiC decomposition at temperatures under 1200°C [22].

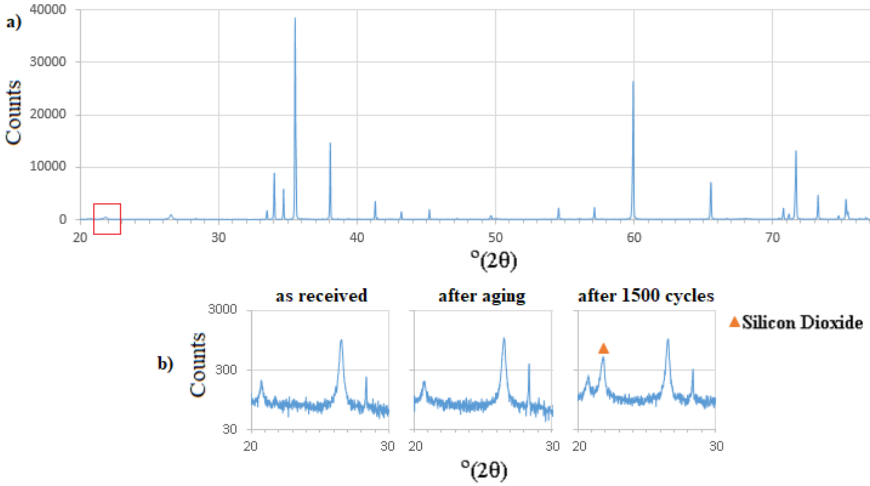


Figure 6.15. XRD spectra for SiC a) after 1500 cycles between 300°C and 900°C, b) expansion of the spectrum between 20 and 30° angle for as received, after aging at 900°C for 500 hours, and after 1500 cycles between 300°C and 900°C.

Optical analysis

Solar absorptance (*Figure 6.16*) was determined by the measured absorptivity weighted with AM1.5 solar spectra. Results of Carbo HSP® show that, during the first hours of thermal aging, the absorptance decreases constantly. Nevertheless, this decrease is not severe enough to get to absorptance levels as other proposed materials like silica sand, olivine, slate, alumina, etc. [23,24]. Later, the thermal cycling after the thermal aging seems to stabilize solar absorptance. It is advised to perform long thermal aging and thermal cycling tests to guarantee the material stability during the expected lifetime.

For SiC, solar absorptance is slightly incremented during both thermal treatments. Results for SiC are shown in *Figure 6.16c* and *Figure 6.16d*. It appears that thermal aging and thermal cycling benefits the solar absorptance of the silicon carbide particles.

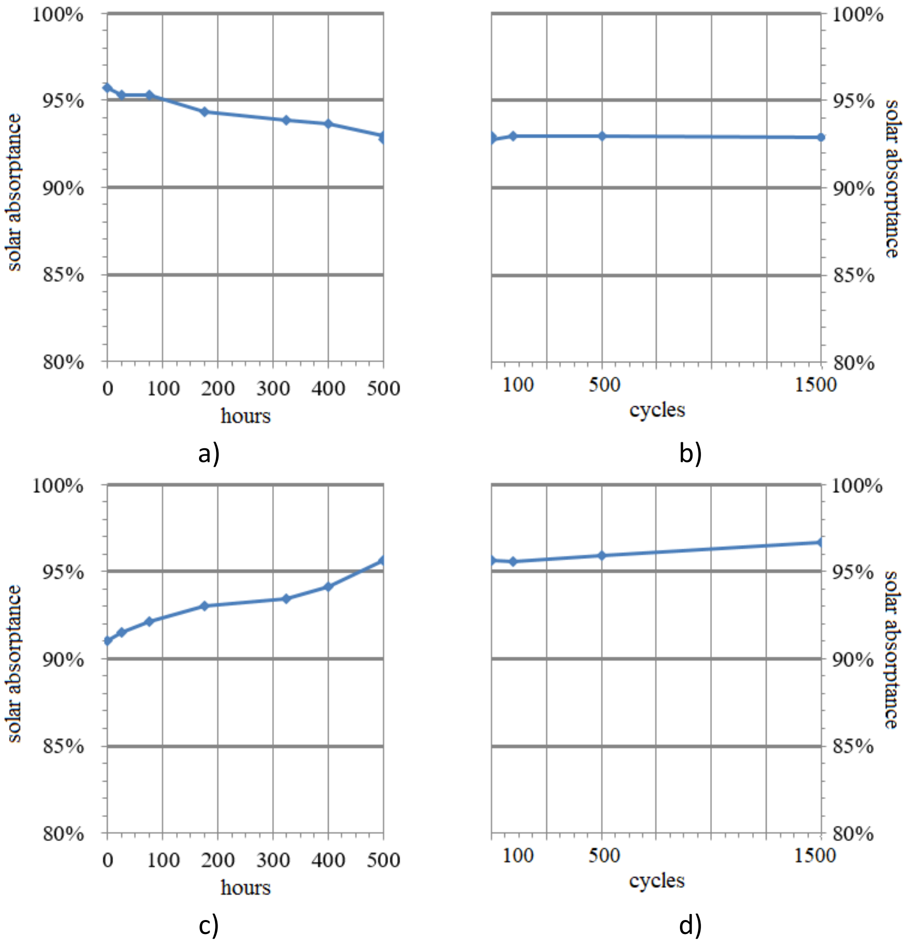


Figure 6.16. a) Solar absorptance of Carbo HSP® after thermal aging, and b) thermal cycling; c) solar absorptance of SiC after thermal aging, and d) thermal cycling.

Thermal properties

Heat capacity analysis by DSC can be appreciated in *Table 6.5*. Both materials reduce their heat capacity after thermal treatments. This reduction is more significant for SiC. This is in accordance with the optical and chemical characterization.

The thermal energy storage capacity reduction measured in this study is significant, for Carbo HSP® around 7.5% and for SiC of around 20%.

Table 6.5. Heat capacity results (J/kg·K) for SiC and Carbo HSP® as received and after thermal treatments.

MATERIAL	AS RECEIVED	AFTER 500 HOUR AGING	AFTER 1500 CYCLES
Carbo HSP®	1.19 ± 0.01	1.14 ± 0.01	1.10 ± 0.01
SiC	1.31 ± 0.01	1.05 ± 0.01	1.00 ± 0.01

Conclusions

The thermal aging tests reveal that thermal stress have a considerable effect in the material durability. Two materials were selected by their relevance given by research groups that develop solid particle CSP technology.

SiC, which was the best material on the previous section, seems to be more affected by thermal cycling treatment. Results analysis has shown that black silicon carbide had mayor problems when dealing with long-term thermal cycling. Evidences have shown that the mean particle size lowers, and that the particles increase their reactivity with air. Particles damage can be observed by SEM, EDS and changes in the measured particle size. Previously reported SiO_2 surface layer protects the rest of SiC particle from reacting with oxygen present in air, but experimental evidence in this study has shown that thermal cycling causes thermal stress that breaks the SiO_2 coating, exposing new surface of SiC particle to oxygen.

Carbo HSP® showed more stability after thermal aging and thermal cycling treatments. Carbo HSP® solar absorptance remains in high values, but not as much as for black silicon carbide. Slight changes in its chemical structure origins an specific heat small decrease. XRD and SEM results show a great stability in the long term. Carbo HSP® has higher resistance to thermal cycling and seems to be stable for longer thermal cycling evaluation, thus becoming a good candidate for CSP plants.

Thermal cycling has proved to be relevant for selecting the best material for solid particle CSP plants with directly irradiation receivers. The novel thermal cycling device was effective to evaluate the thermal stress durability.

Future research should include combined thermal and mechanical stress tests for a more accurate durability prediction study. In addition, mechanical and thermal conditions should be the most similar as possible to the ones in the specific solid particle CSP plant design.

6.2.3. JOURNAL PAPER

The journal paper named "Thermal cycling test of solid particles to be used in concentrating solar power plants." was sent to Solar Energy Materials and Solar Cells journal in July 2019 with manuscript number SOLMAT-D-19-01211 and it is currently under revision.

Highlights

- Durability of solid particles used in CSP is critical to ensure a low-cost material
- Thermal aging and thermal cycling stability were evaluated at high T
- New setup has been developed to perform thermal cycling accelerate-durability tests
- Optical, chemical, physical and thermal test were performed to evaluate durability
- Cycling device has shown to be effective to evaluate the thermal stress durability

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Manuscript Draft

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Title: Thermal cycling test of solid particles to be used in concentrating solar power plants

Article Type: Full Length Article

Keywords: solid particles; thermal energy storage; concentrated solar power; solar tower; heat transfer fluid; accelerated thermal cycling

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Abstract: Material durability and reliability of solid particles to be used in concentrating solar power tower plants is critical for all project viability. This study is focused on thermal aging and thermal cycling stability evaluation of solid particles at high temperatures. A new device has been developed to perform accelerated-durability tests, that allows to emulate thermal cycling stress from years to days, and even evaluate the 11,000 cycles expected to be reached during 20 years' plant's lifetime in less than four months. A description and explanation of the operation of this device is included in this paper. In addition, current solar absorptance, chemical composition, physical properties, thermal characteristics and morphologic analysis of the samples before and after thermal treatments and cycling have been performed. The materials under the scope of this study are the most reliable solid particles reported in CSP field: silicon carbide and CarboHSP® 30/60. Characterization results show that SiC is more affected on its durability by thermal cycling than by constant temperature aging, while CarboHSP® is affected by temperature aging rather than thermal cycling. SiC reacts with oxygen in the air to form SiO2 on the surface, with a positive effect in its solar absorptance. Nevertheless, with thermal cycles, SiC particle surface becomes damaged and the reaction continues with more new exposed surface. Meanwhile, CarboHSP® reduces its solar absorptance with high temperature only due to changes in its surface chemical composition. However, thermal cycling shows no negative effect in CarboHSP® properties.

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Conclusions and future work 7

Chapter contents

7. CONCLUSIONS AND FUTURE WORK

Throughout this PhD Thesis several conclusions and future work recommendations can be found through the chapters and scientific articles. In this section these conclusions and recommendations will be recapitulated and some other more transversal will be discussed.

7.1. CONCLUSIONS

Solid particle concentrating solar power is currently under development. Several research groups are making advances in the main different aspects of this technology, such as solar receivers, thermal energy storage systems, heat exchangers, conveyance systems, generation cycles, and the particle media. Some pilot tests had been already performed on some of these stages. From the materials perspective the research found is focused on proposing some materials and evaluate their performance with different techniques on each research group, since there are few standardized rules for evaluating performance and durability of the materials. In addition, there is no materials reported that are created for this specific application.

According to the scope of this PhD Thesis, the following specific conclusions have been carried out:

- Evolution of concentrating solar power requires that the service temperature is increased in order to use more efficient thermal-to-electricity generation cycles. Increasing the conversion efficiency translates into lower cost of production of electricity. Developing a solid particle concentrating solar power technology with thermal energy storage capability will lead to a clean, renewable, cost competitive and flexible power generation technology.
- Scientific relevance of concentrating solar power and thermal energy storage was carried out by performing two bibliometric studies, in which also researchers, research communities and main country and regional efforts were identified in terms of scientific output productivity and relevance in the scientific community.
- A methodology was designed to carry out the bibliometric studies, as well as new software was created to analyze this research output.

- State-of-the-art analysis was divided into system and particle media analyses. System state of the art revealed that solar receiver technology is focused in controlling particle exposure time to sunlight thermal input. Heat exchangers had also been studied, while conveyance and thermal storage systems aspects remain to me fully developed.
- Particle media state-of- the-art revealed several materials proposed and the most important properties and parameters to be evaluated. Experimental and theoretical information of these materials have been collected and summarized for evaluation and comparison.
- Solid particle design and selection bases were established according to main objectives in each functional stage of the plant. Material indices were obtained and some of the proposed materials were evaluated under the design objectives consideration.
- Thermal stress test was developed for long time high temperature exposure (thermal aging) and due to largo number of charge-discharge cycles (thermal cycling).
- Thermal aging performed for 500 hours found to affect mainly the several properties of some of the materials evaluated, being the most relevant the solar absorptance. However, these changes seem to stabilize during the first hours.
- For performing the thermal cycling test, a novel device was developed in order to make an accelerated thermal cycling at temperatures between 300 °C and 900 °C. This device was necessary to heat and cool the fastest as possible and to perform large number of cycles in short time.
- Thermal cycling test results showed that some materials become unstable under such conditions and it does not have any tendency to stabilize with time. Making indispensable to evaluate this effect for considering materials durability in the long term.

7.2. FUTURE WORK

In order to continue the development of solid particle concentrating solar power technology, the following recommendations are made based in the current PhD dissertation.

- From the power plant system view, parasitic loads related to holding particle media in the receiver and to moving the solid particle material through the conveyance system must be reduced, so that there is minimum impact in plant viability.

- A unified plant design is needed for achieving a commercial viable plant and to select the best available material. After this, this design must be adapted for optimal operation.
- For the material selection, a multi-variable analysis must be performed. In order to perform an optimal selection, the material performing the best should maximize all material indices together.
- Combined material selection between the particle media material and the materials used in building the system, must be carried out. Durability of these materials depends in great part of this analysis.
- Thermomechanical durability test must be carried out, since the interactions of mechanical stress and thermal stress will occur simultaneously.
- For ensuring good an optimal material, making new enhanced materials should be considered. Best current available materials can be used as base, enhancing their best capabilities and overcoming their main drawbacks.

Part II

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Manuscript Draft

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Title: Bibliometric study in Concentrating Solar Power technologies

Article Type: Research Paper

Keywords: Bibliometric; Solar Energy; Concentrating Solar Power; solar tower; parabolic trough; Stirling dish

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Abstract: Bibliometric analysis is a key study in order to elucidate the relevance of a research field. This study will point out the main evolution of a research performed in a topic considering the significance of each sub-topic. This study aims to perform a bibliometric analysis in concentrating solar power (CSP) technology. CSP had a first commercial wave between 1984 and 1995. Between 1995 and 2005 there was a period of commercial inactivity. Nevertheless, since 2005 CSP commercial implementation has been accelerating. This topic accounts almost 6,300 publications on relevant journals and conference proceedings. Regional analysis showed that China is becoming the most relevant country for CSP research. European Union still leads the development and will continue that way at least in the short term. Authors' keyword evolution analysis has been useful as an indirect measure of technological maturity. It was found that conference proceedings have an important effect in the overall CSP publications and need to be consider when working within this field. However, the journal publications use to have more impact since they are more frequently cited. Funding analysis had shown a direct relationship between funding and research output. Finally, it was concluded that inside CSP field, parabolic trough has shown to have great relevance in the research output.

Highlights

- This work use bibliometric techniques to study CSP written publications.
- Countries, authors, journals and communities have been identified for CSP field.
- CSP technologies were analyzed by parabolic trough, tower, dish and Fresnel.
- All CSP scientific research has been growing exponentially over the last decade.
- US, China and Spain led CSP research with China increasing rapidly.

Bibliometric study in Concentrating Solar Power technologies

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ABSTRACT

Bibliometric analysis is a key study in order to elucidate the relevance of a research field. This study will point out the main evolution of a research performed in a topic considering the significance of each sub-topic. This study aims to perform a bibliometric analysis in concentrating solar power (CSP) technology. CSP had a first commercial wave between 1984 and 1995. Between 1995 and 2005 there was a period of commercial inactivity. Nevertheless, since 2005 CSP commercial implementation has been accelerating. This topic accounts almost 6,300 publications on relevant journals and conference proceedings. Regional analysis showed that China is becoming the most relevant country for CSP research. European Union still leads the development and will continue that way at least in the short term. Authors' keyword evolution analysis has been useful as an indirect measure of technological maturity. It was found that conference proceedings have an important effect in the overall CSP publications and need to be consider when working within this field. However, the journal publications use to have more impact since they are more frequently cited. Funding analysis had shown a direct relationship between funding and research output. Finally, it was concluded that inside CSP field, parabolic trough has shown to have great relevance in the research output.

Keywords: Bibliometric; concentrating solar power; solar tower; parabolic trough; Stirling dish

1. INTRODUCTION

Meeting world energy demand constitutes one of the greatest challenges of our generation, just in 2017 demand increased by 2.1%. For developed countries as well as for developing ones' energy has a major role for achieving the desired wellness; 40% energy demand growth in 2017 was driven by China and India [1,2]. Use of fossil fuels as main source of energy to reach energy demand has resulted on a continuous CO_2 emissions growth related to it; just in 2017 CO_2 emissions grew by 1.4% [1,3]. However, the emissions concern has result on the implementation of renewable energy and low emissions policies for several decades, and as a consequence has contributed towards the reduction of emissions per the amount of energy produced [3,4].

Renewable energies have a main role on today's global energy strategy. Nowadays photovoltaic and wind power have become the main drivers on renewable energy implementation [5]. Nevertheless, their development is limited by the mismatch between resource availability and energy demand. This mismatch cannot be fully countervailed, for now, with economically and technical viable solutions (like energy storage or interconnection) [6].

Solar thermal energy offers the advantage of storing heat and/or cold, which is much simpler than storing electricity; even if the thermal energy is converted later to electricity. Concentrated Solar Power (CSP) offers a solution for harvesting solar energy and integrate it with thermal storage for high enthalpy applications (such as industrial heat or electricity generation) [7]. CSP technologies have been under constant development in recent years; it is expected that, with the adequate support, thermal CSP can constitute up to 11% of electricity generation by 2050 [7,8]. Notice that 11 TWh were produced by CSP during 2017 compared with 1 TWh in 2000 and this numbers are expected to grow till 68,000 MW in 2040 [5,9].

Different strategies are under research stage in order to make more technologically and economically viable thermal solar power; such as increasing the low and high temperatures [10–12], using latent heat on heat transfer fluid (HTF) and thermal energy storage (TES) media [13], studying thermochemical reactions for long term energy storage capabilities [14], studying ways to improve current HTF-TES and power plant operation conditions [15,16], new supercritical power conversion cycles with improved efficiency, solar field components optimization for cost reductions [17,18], etc. Over the years, CSP progress has been closely related to scientific research, to finally impact CSP commercial applications, until each technology research have enough technological maturity [19–21]. By studying research efforts and trends in order to monitor topic relevance and management of knowledge, Bibliometrics had become an important part of information sciences. Several studies have been made during years for several fields, such as health, marketing, entrepreneurship, production and operations management, innovation, etc. [22]. In the same way, bibliometric studies have been recently published for wind power price [23], for alternative energy research during 1994 and 2013 [24], and for TES technologies [25]. For CSP field, there are no deep bibliometric analysis that studied CSP technologies.

The aim of this bibliometric study is to provide an overview of CSP research and development evolution by using bibliometric methods. Finding research and development trends can be of great interest for CSP developers and researchers, for energy policy stakeholders, and for everyone involved or starting on this field. Several regional efforts, policies and financing were identified over the years from the knowledge creation perspective. Finally, advancements and technological maturity were studied for the main CSP harvesting configurations: parabolic trough, solar tower, Stirling dish and Fresnel systems.

2. Methodology

The procedures and tools used for performing the analysis of CSP research evolution are described in this section. Formally, Bibliometrics is a science dedicated to study the scientific publications of a specific research field by using statistical tools; this studies can be extended to a wide number of scientific fields [26]. Bibliometrics had been considered as a way to bring a general picture of the progress of a particular research field, detect the top researchers as individual or as communities, find the most outstanding journals on that specific field, the interactions between authors and countries, among other specific analyses [27].

In order to use the most significant information sources and indicators, Web of Science (WoS) Core Collection was used as the source of data. This database includes more than 14,000 high-quality journals and provides enough information about the publications, such as authors name, affiliations, abstract, keywords, references, funding information, etc. All this information allowed us to extract high value analyses that could not be performed using other databases.

For creating the database, authors searched in the topic, abstract or keywords sections the research query: ("solar tower") OR ("solar field" AND ("concentrated")) NOT ("PV" OR "photovoltaic") OR ("parabolic trough") OR ("concentrated solar" AND ("power" OR "thermal")) OR ("fresnel reflector") OR ("dish stirling") OR ("molten salts" AND ("solar" OR "power plant" OR "storage")) NOT ("PV" OR "photovoltaic" OR "polymer" OR "barrier" OR "lithium") OR ("heat transfer fluid" AND ("concentrated")) OR ("heliostats").

A common problem for building up a database for bibliometric analysis is that terminology selected by authors is different according to the specific approach they are using. This occurs also in CSP field. Therefore, a keyword map was used in order to make more complex and inclusive search, allowing as well as omitting several keywords from the result to avoid all subjects not related to CSP. Establishing boundaries and selecting the best keyword combination was challenging, since there is no convention on CSP classification by stages or by components or even into the terminology.

Table 1 shows these keywords that were used to collect the CSP database. In this keyword map a main phrase search is only included if at least one of the complement phrases in the same row are present in the different searched sections (title, keywords, abstract, etc.), with the exception of those publications that have at least one of the exclusion phrases in that same row. As a result, keyword map allowed getting, in an improved way, a reliable database of CSP publications. The total scientific articles selected by each row search are also shown in Table 1. It is remarkable that several publications were selected by more than one row search and the sum of all the articles selected per row is higher than the total publications.

6,298 publications were found between 1969 and 2019. For yearly analyses only periods until 2018 were considered because the database was created at early 2019.

Table 1. CSP keyword map search.

EXCLUSION PHRASES					MAIN PHRASES	COMPLEMENT PHRASES			TOTAL
					solar tower				668
pv	photovoltaic				solar field	concentrated			150
					parabolic trough				2328
					concentrated solar	power	thermal		2675
					fresnel reflector				211
					dish stirling				205
pv	photovoltaic	polymer	barrier	lithium	molten salts	power plant	storage	solar	662
					heat transfer fluid	concentrated			338
					heliostats				501

Note that proceedings were included in the extraction because authors noticed the relevance this kind of publications has in the field.

For deeper analysis, the database extracted from WoS was analyzed for studying specific CSP technologies which included parabolic trough, solar tower, Stirling dish and Fresnel collectors. Most of relevant authors, journals, regional cooperation and other relevant information was assessed and is presented in the following sections.

Bibliometric analyses were carried out by python coding and graphic tools. Additional reports were done using VOS Viewer® scientific visualization tools [28] used for bibliometric network analysis and Complexity Lab Barcelona (CLabB) [29] software.

3. Results

3.1. Publication bibliometric analyses

Based on the publications included in this new bibliometric database search, the total of publications per year regarding the whole concentrating solar power field are presented as bars in Figure 1 for the last 20 years. Also, the number of citations can be appreciated by the green line in Figure 1. Therefore, the number of publications has grown considerably during the last decade, even that not every year increases the number of publications. Since proceeding papers have been included, they influenced the change of tendency from one year to another but not to the tendency on a greater time span. Citations of the publications are low for the last years; nevertheless, this was expected since the most recent papers have not been cited yet. Indeed, publication will not reach their full citable potential until some years after their publication date. General tendency remarks that CSP field is growing up along with their market development in the near future [5].

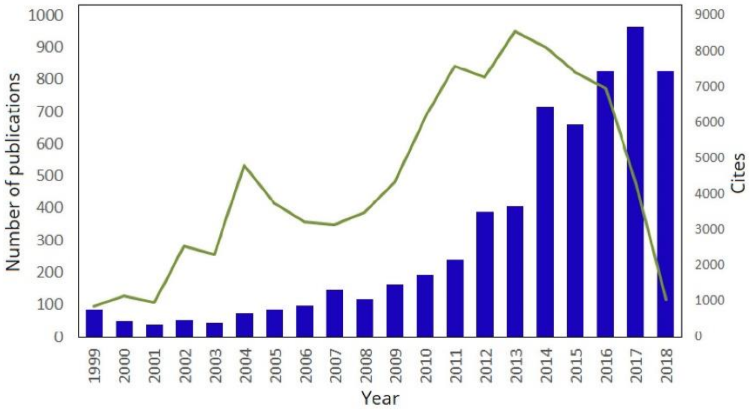


Figure 1. CSP publications and cites during the last two decades.

Figure 2 shows the top trend keywords for CSP field. It can be seen that the most used keywords are “performance”, “design”, “solar energy”, “energy”, “optimization”, “systems”, “parabolic trough” and “concentrated solar power”. Moreover, “optimization” and “concentrated solar power” have been used more recently in 2016 compared with “performance”, “design” or “system” in 2014-2015; this reflects the maturity of the technology, since these keywords are most commonly used for optimization of commercial solutions. As a visible example is that the optimization prevails over the design learning process, since CSP is a mature technology, even that is under constant improvement. Oldest top keywords are “solar energy”, “energy” and “parabolic trough” which were more used in 2013.

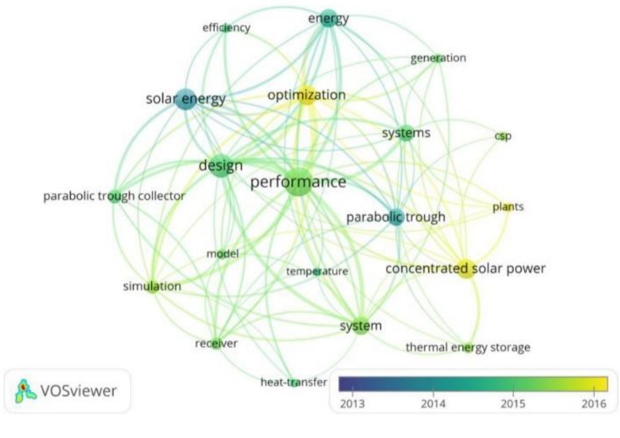


Figure 2. Evolution of trend keywords on CSP publications.

Table 2. CSP Most cited publications.

AUTHORS	TITLE	JOURNAL	TYPE	COUNTRIES	CITES	YEAR
Kalogirou, SA	Solar thermal collectors and applications	PROGRESS IN ENERGY AND COMBUSTION SCIENCE	Review	Cyprus	1111	2004
Steinfeld, A	Solar thermochemical production of hydrogen - a review	SOLAR ENERGY	Review	Switzerland	723	2005
Jacobson, Mark Z.	Review of solutions to global warming, air pollution, and energy security	ENERGY & ENVIRONMENTAL SCIENCE	Review	USA	680	2009
Papageorgiou, N; Athanassov, Y; Armand, M; Bonhote, P; Pettersson, H; Azam, A; Gratzel, M	The performance and stability of ambient temperature molten salts for solar cell applications	JOURNAL OF THE ELECTROCHEMICAL SOCIETY	Article	France, Switzerland	638	1996
Gil, Antoni; Medrano, Marc; Martorell, Ingrid; Lazaro, Ana; Dolado, Pablo; Zalba, Belen; Cabeza, Luisa F.	State of the art on high temperature thermal energy storage for power generation. part 1-concepts, materials and modellization	RENEWABLE & SUSTAINABLE ENERGY REVIEWS	Review	Spain	634	2010
Jacobson, Mark Z.; Delucchi, Mark A.	Providing all global energy with wind, water, and solar power, part i: technologies, energy resources, quantities and areas of infrastructure, and materials	ENERGY POLICY	Article	USA	529	2011
Tian, Y.; Zhao, C. Y.	A review of solar collectors and thermal energy storage in solar thermal applications	APPLIED ENERGY	Review	China, UK	475	2013
Kalogirou, SA	Applications of artificial neural-networks for energy systems	APPLIED ENERGY	Article	Cyprus	470	2000
Kalogirou, SA	Artificial neural networks in renewable energy systems applications: a review	RENEWABLE & SUSTAINABLE ENERGY REVIEWS	Review	Cyprus	440	2001
Fernandez-Garcia, A.; Zarza, E.; Valenzuela, L.; Perez, M.	Parabolic-trough solar collectors and their applications	RENEWABLE & SUSTAINABLE ENERGY REVIEWS	Review	Spain	437	2010
Steinfeld, A	Solar hydrogen production via a two-step water-splitting thermochemical cycle based on zn/zno redox reactions	INTERNATIONAL JOURNAL OF HYDROGEN ENERGY	Article	Switzerland	435	2002
Price, H; Lupfert, E; Kearney, D; Zarza, E; Cohen, G; Gee, R; Mahoney, R	Advances in parabolic trough solar power technology	JOURNAL OF SOLAR ENERGY ENGINEERING	Article	USA, Spain	434	2002
Kuravi, Sarada; Trahan, Jamie; Goswami, D. Yogi; Rahman, Muhammad M.; Stefanakos, Elias K.	Thermal energy storage technologies and systems for concentrating solar power plants	PROGRESS IN ENERGY AND COMBUSTION SCIENCE	Review	USA	419	2013
Mills, D	Advances in solar thermal electricity technology	SOLAR ENERGY	Article	Australia	412	2004
Kenisarin, Murat M.	High-temperature phase change materials for thermal energy storage	RENEWABLE & SUSTAINABLE ENERGY REVIEWS	Review	Uzbekistan	347	2010
Van Valkenburg, ME; Vaughn, RL; Williams, M; Wilkes, JS	Thermochemistry of ionic liquid heat-transfer fluids	THERMOCHIMICA ACTA	Article	USA	316	2005
Medrano, Marc; Gil, Antoni; Martorell, Ingrid; Potau, Xavi; Cabeza, Luisa F.	State of the art on high-temperature thermal energy storage for power generation. part 2-case studies	RENEWABLE & SUSTAINABLE ENERGY REVIEWS	Review	Spain	297	2010
Zhang, H. L.; Baeyens, J.; Degreve, J.; Caceres, G.	Concentrated solar power plants: review and design methodology	RENEWABLE & SUSTAINABLE ENERGY REVIEWS	Review	Belgium, UK, Chile	273	2013
Herrmann, U; Kelly, B; Price, H	Two-tank molten salt storage for parabolic trough solar power plants	ENERGY	Article	Germany, USA	267	2004
Selvakumar, N.; Barshilia, Harish C.	Review of physical vapor deposited (pvd) spectrally selective coatings for mid- and high-temperature solar thermal applications	SOLAR ENERGY MATERIALS AND SOLAR CELLS	Review	India	266	2012

In Table 2 the 20 most cited articles can be appreciated. It is understandable that 12 of the top 20 articles are reviews. Also, several molten salts publications are in the top 20 since is very attractive as HTF and TES media for its high service temperature limit. Kalogirou also denotes as one of the most cited authors as well as Steinfeld. This stays in line with current CSP tendency to incorporate TES for optimizing CSP plants, which allows considering the high manageability of CSP as a main attribute that adds flexibility to electric network and to the energy mix.

3.2. Country bibliometric evolution

Regional evolution is of great interest for design and evaluation of research policies focused on particular technologies. In Figure 3, total publications over time for the top 20 countries are presented. USA stands at the top as the country with more publications, followed by China, Spain and Germany. When considering regional efforts Spain, Germany, Italy, France, United Kingdom, Greece and Portugal suggest that the biggest effort has been made by European Union. Also, emerging economies such as India and China outstand in this list.

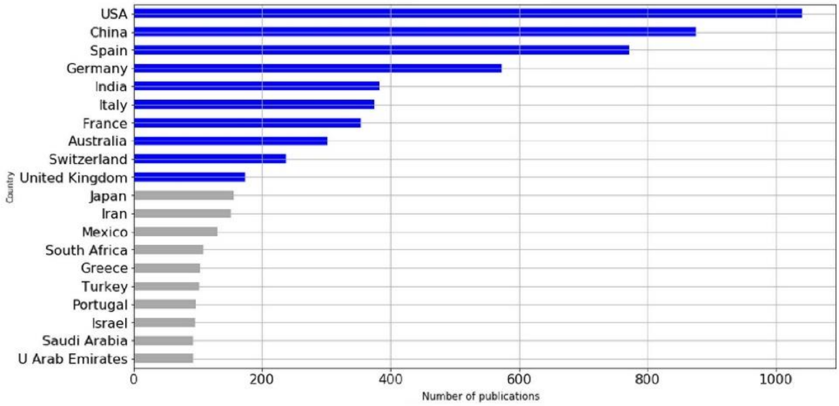


Figure 3. Top 20 publishing countries in the CSP field.

Figure 4a) shows the publication evolution per country over the last two decades. Notice that high number of publications per country does not implies that countries produce top research in recent years. USA and almost every European countries research literature were constant over the last five years, while growth during these years was mainly driven by China, India, United Kingdom and Australia. This is related with different strong programs that have been implemented by the European Union, the Department of Energy (DoE) of USA and China government [30,31].

Based on current trends, it is expected that China will lead CSP research over the next years, followed by a significant increase of India participation in CSP deployment. China technological development policy is being implemented in CSP field as it has been implemented in other technological areas, which includes use of foreign experts in order to achieve expertise combined with strong and well-funded homeland research and innovation programs [32,33]. This in the long term will potentially allow China to be the most developed country in CSP. This tendency is replicated in Table 3 where publication rate is compared to their total papers accumulated up to the previous year. This information clearly elucidates that China, India, United Kingdom and Australia were growing during recent years. Also, Spain, Italy and France maintained their publications trend at a constant rate.

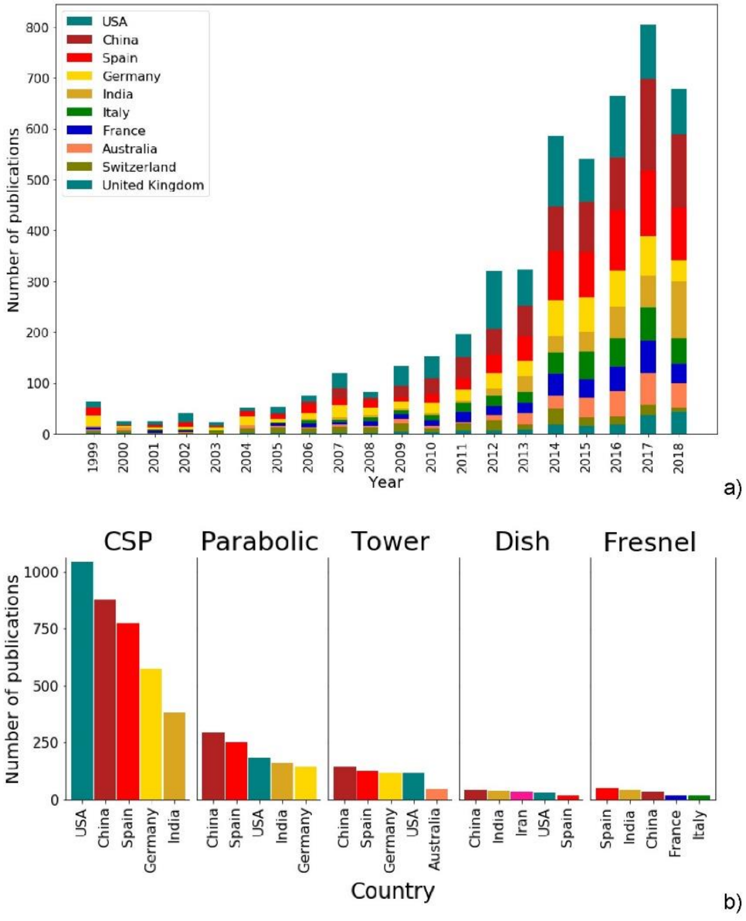


Figure 4. a) Publication evolution regarding CSP field in the last 2 decades by countries; b) Total publications in CSP field of top 5 countries and EU, and parabolic trough, solar tower, Stirling dish and Fresnel publication of those countries/zones.

Furthermore, Figure 4b) presents the total publications for the top five countries divided by CSP technologies. Main ways to harvest concentrated sunlight considered are parabolic trough, solar tower, Stirling dish and Fresnel lens. Total publications for each of these technologies are presented in Figure 4b) and compared to the total publications of CSP field. It can be observed that China leads the total publications for parabolic trough, solar tower and Stirling dish, while Spain remains as the first one for Fresnel and second one in parabolic trough and solar tower.

Table 3. Country increment of CSP publications compared to the accumulated from previous year.

Country	2018	2017	2016	2015	2014	2013	2012	2011	2010	2009
USA	9.5%	12.6%	17.0%	13.3%	28.1%	16.8%	36.5%	17.0%	19.9%	21.4%
China	19.9%	33.5%	23.5%	28.8%	34.9%	31.9%	37.4%	43.3%	47.0%	53.5%
Spain	15.8%	24.3%	28.6%	27.6%	42.9%	27.0%	24.5%	18.2%	16.3%	8.3%
Germany	7.8%	17.1%	19.0%	22.3%	29.3%	13.8%	17.3%	13.3%	14.5%	12.2%
India	41.9%	30.9%	43.7%	36.5%	44.4%	75.6%	51.9%	22.7%	15.8%	11.8%
Italy	15.2%	24.7%	27.6%	36.2%	39.3%	27.4%	33.3%	40.0%	36.4%	32.0%
France	12.8%	26.3%	24.1%	22.1%	35.8%	18.8%	18.8%	28.8%	20.0%	22.2%
Australia	18.8%	33.0%	35.3%	39.0%	35.1%	45.1%	27.5%	11.1%	12.5%	33.3%
Switzerland	4.0%	9.7%	8.4%	9.8%	21.7%	7.5%	17.7%	13.0%	8.7%	22.7%
U K	33.3%	40.2%	26.0%	28.1%	46.2%	25.8%	29.2%	41.2%	21.4%	40.0%

Figure 4.b) also reflects the higher interest on parabolic trough and solar tower compared to both remaining technologies. This is understandable since parabolic trough and solar tower are the first and second more implemented CSP technologies, respectively.

Citations are very interesting to analyse, since it can reflect relevance of the published work. In Table 4 performance ratio, defined as the total number of citations divided by the number of publications, is presented for the top 20 countries. Again, the performance ratio is low for recent years' papers. Most productive period was registered for Spain between 2009-2011; nevertheless, it was reduced during recent year publications compared to other countries like Switzerland, Iran or Greece. The case of Spain could be explained due to changes in the public regulations regarding solar energy in that country during 2013-2018 [34–36]. In addition, it is remarkable the case of Switzerland performance ratio over the last ten years, since it was the most prolific one, achieving about 35 cites per paper for the whole decade. Together with Spain, USA decreased citations per paper over the last decade. Finally, India performance ratio was the lowest during the last decade overall the top ten countries caused mainly by the low citations during 2014-2016 period.

Table 4. Country performance ratio of CSP publications per year for the last 10 years.

Country	2018	2017	2016	2015	2014	2013	2012	2011	2010	2009	Publications	Cites
USA	1.2	4.6	5.5	13.4	10.7	26.5	13.5	51.6	15.8	34.3	1041	16666
China	1.6	6.3	10.3	11.6	14.4	21.0	15.1	32.4	28.3	15.7	876	10763
Spain	1.3	4.2	7.6	10.7	13.4	23.8	24.7	44.3	94.8	57.5	772	12563
Germany	1.0	3.4	4.8	8.8	14.4	21.6	20.2	33.9	19.0	14.7	573	9347
India	0.7	3.8	6.9	10.9	8.2	23.2	38.8	15.8	52.3	63.5	382	3553
Italy	1.1	3.0	10.3	9.9	12.1	19.5	24.1	47.1	36.0	14.6	374	4822
France	1.2	3.7	8.2	8.7	14.1	32.2	19.9	25.2	20.3	21.7	354	5016
Australia	1.6	4.3	10.5	14.3	14.7	18.2	58.3	13.3	82.8	60.8	302	5417
Switzerland	2.2	3.6	8.9	15.8	12.9	16.9	41.7	34.3	37.8	35.1	237	8373
United Kingdom	1.6	6.1	11.4	14.7	13.5	108.9	23.0	49.9	83.3	95.3	173	3912
Japan	0.9	3.1	8.8	8.4	6.3	39.3	9.2	46.4	29.4	0.0	155	4195
Iran	2.5	6.6	16.7	31.6	18.9	31.8	28.5	0.0	48.3	0.0	151	2118
Mexico	0.6	5.7	4.9	12.3	4.0	36.2	4.3	23.5	19.0	29.0	130	1372
South Africa	0.8	4.0	6.2	14.0	10.8	29.8	11.7	1.0	1.0	63.0	108	1119
Greece	3.2	9.1	23.9	19.2	26.3	20.2	23.0	45.3	33.0	0.0	103	1669
Turkey	1.2	5.4	11.4	5.3	16.6	6.8	10.0	24.5	6.0	16.3	102	725
Portugal	0.5	2.9	8.0	4.8	10.5	10.4	12.3	20.8	39.8	3.3	97	856
Israel	0.3	2.3	6.8	9.7	4.3	4.6	18.3	12.4	21.0	16.5	95	1978
U Arab Emirates	1.4	2.2	4.3	10.6	5.0	10.3	5.0	10.5	18.5	27.0	92	500
Saudi Arabia	1.1	6.1	9.4	15.4	10.3	25.0	21.3	41.3	0.0	0.0	92	1042

Co-authorship between countries has also been studied on CSP field (see Figure 5). Each country is represented by a circle in this figure; the size of the circle represents the number of publications, while thickness of the curved lines represents the interaction strength between countries. Colours represent the most relevant year interaction between countries. Thereby, the oldest research cooperation relies between USA and Germany, followed by a newer relation between Spain and Italy. Also, Spain and Germany have the biggest relationship of all, leading the European cluster; followed by USA-China relationship. This is consistent with known research cooperation between CIEMAT (Spain) and DLR (Germany) with the PSA (Plataforma Solar de Almeria), and ENEA Group (Spain) and DLR molten slat trough projects. Also, China-USA co-authorship is in line with NREL (USA) and Sandia National Laboratories(USA) cooperation with China. Other known cooperative projects that are coherent with the bibliometric data are the MIT (USA) – Masdar (UAE) projects as well as solid particle technologies for solar tower between DLR (Germany), Sandia National Laboratories (USA) and CNRS (France) [11,31,37]. One outstanding cooperation opportunity relies of the cooperation between China and Germany-Spain cluster.

Besides, Middle Eastern countries were the newest relevance and cooperation of the top countries, showing a growing relevance in the world's stage. Finally, lack of African and South American countries shows an area of opportunity for deployment, since a lot of those countries can find CSP implementation very favourable [8]. A special highlight is the case of Chile. This country did a huge step forward in renewables implementation around the country and built the biggest CSP plant in South America in 2018 (110 MW and 17.5 hours of storage) being one of the most ambitious projects looking within the future regarding CSP field[38].

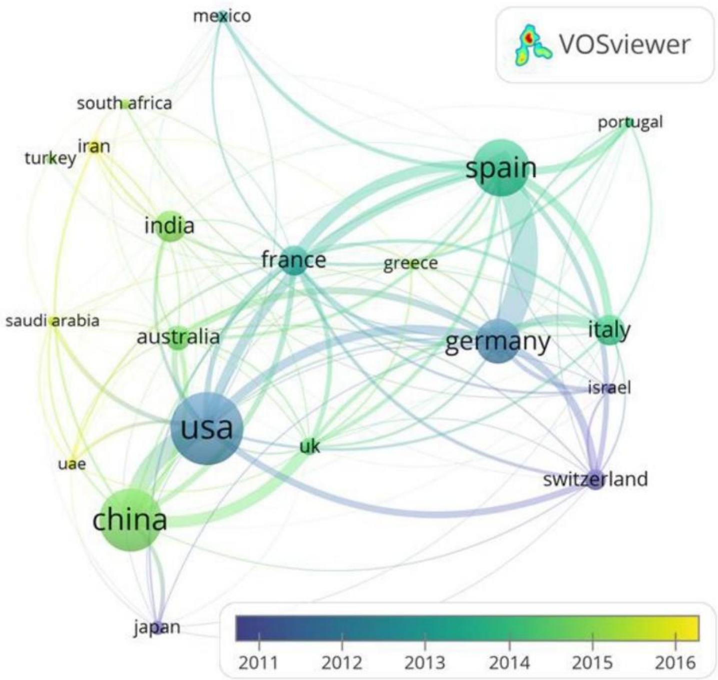


Figure 5. Country co-authorship interaction collaboration of the Top20 countries.

3.3. Authorship bibliometric evolution

The accumulated author publications profile is shown in Figure 6 by taking into account the grouped publication of each author profile available in the WoS - core collection database, and authors were checked for repeated WoS profiles although it is difficult to do this revision in every single profile. This analysis does not remark the authorship order, only if they are in the author list.

As Figure 6 shows, Dr. Aldo Steinfeld is the top-one researcher publishing in CSP field followed by Dr. Zhifeng, Dr. Pitz-Paal and Dr. Flamant, who are the most representative prestigious researchers in the CSP field. CSP h index can also be appreciated, this h index was calculated by talking only CSP database. H index was defined by Prof. J.E. Hirsch from University of California as *"The number of papers with citation number higher or equal to h, as a useful index to characterize the scientific output of a researcher"* [39]. In CSP field, Dr. Aldo Steinfeld obtained an h index of 42, while Dr. Zhifeng Wang and Dr. Giles Flamant was 22 each. This results must be interpreted with caution, since some research centers include the scientific directors of the centers into the publication's author list. While in other centers only the persons involved directly in the projects use to be in the publication author list. Some known experts in CSP field that are present in the current top 20-author list include Dr. Clifford Ho, Dr. Eduardo Zarza, among others.

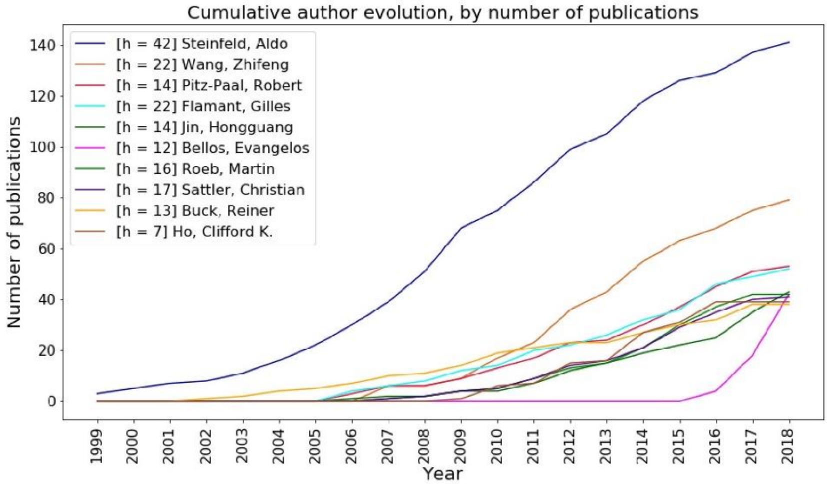


Figure 6. Cumulative author evolution by publications for the last two decades.

In Table 5, top 20 authors by number of CSP publications are listed with the number of citations and CSP h-index The most cited author and the one with higher CSP h-index is Dr. Aldo Steinfeld. Other relevant authors that can be denoted are Dr. Zhifeng Wang and Dr. Giles Flamant with a CSP h-index of 22. When considering countries of the top 20 authors, Germany, Spain, USA and China show to be the most relevant. Finally, German Aerospace Centre (DLR) outstands since four of the top 10 authors are affiliated there.

Table 5. Top 20 authors in CSP field.

Author	Affiliation	CSP publications	Total CSP cites	CSP h-index
Steinfeld, Aldo	ETH Zurich. Switzerland.	146	5581	42
Wang, Zhifeng	Hebei University of Technology. China.	79	1176	22
Pitz-Paal, Robert	German Aerospace Centre (DLR). Germany.	53	796	14
Flamant, Gilles	Centre National de la Recherche Scientifique (CNRS). France.	52	1421	22
Jin, Hongguang	Institute of Engineering Thermophysics, CAS. China.	43	538	14
Bellos, Evangelos	National Technical University of Athens. Greece.	42	392	12
Roeb, Martin	German Aerospace Centre (DLR). Germany.	42	888	16
Sattler, Christian	German Aerospace Centre (DLR). Germany.	41	884	17
Buck, Reiner	German Aerospace Centre (DLR). Germany.	40	802	13
Ho, Clifford K.	Sandia National Laboratory, Department of Energy. USA.	39	373	7
Tzivanidis, Christos	National Technical University of Athens. Greece.	39	380	12
Valenzuela, Loreto	Plataforma Solar Almeria. Spain.	39	837	12
Romero, Manuel	IMDEA Energy Institute. Spain.	32	1036	12
Taylor, Robert A.	University of New South Wales Sydney. Australia.	32	513	13
Liu, Qibin	Institute of Soil Science, CAS. China.	31	480	14
Yang, Yongping	North China Electric Power University. China.	31	264	11
Zarza, Eduardo	CIEMAT. Spain.	30	1714	17
Abanades, Stephane	Centre National de la Recherche Scientifique (CNRS). France.	29	875	16
Epstein, Michael	University of Nebraska Lincoln. USA.	29	690	13
Covault, C. E.	Case Western Reserve University. USA.	29	202	8

Identifying the author communities besides their affiliation or geographical location can be very useful. Figure 7 shows group of authors based on the number of co-authorship. Top 100 authors were analysed and the top 20 are identified in the figure. This analysis was performed by using CLabB software tool which define the attraction forces between the authors are order them in communities.

International cooperation outstands in the two main groups showing even strong link cooperation between them. The first group include organizations such as ETH Zurich, CNRS, DLR, IMDEA (with thermochemical solar tower and solid particle solar tower) and University of Nebraska and groups 7 of the top 20 authors. In the second group organizations such as DLR, Plataforma Solar de Almeria and CIEMAT are represented by 5 of the top 20 authors. Between these two groups 12 of the top 20 authors had cooperated actively. Another group led by Dr. Wang from the Chinese Academy of Sciences, had some cooperation with other communities but not with such intensity as others. This can be explained because of Dr. Wang role as government technical advisor for commercial CSP projects. Finally, a strong cooperation opportunity outstands with the community led by Dr. Covault, which show no co-authorship with any other group, even that they have 11 of the top 100 authors in CSP field.

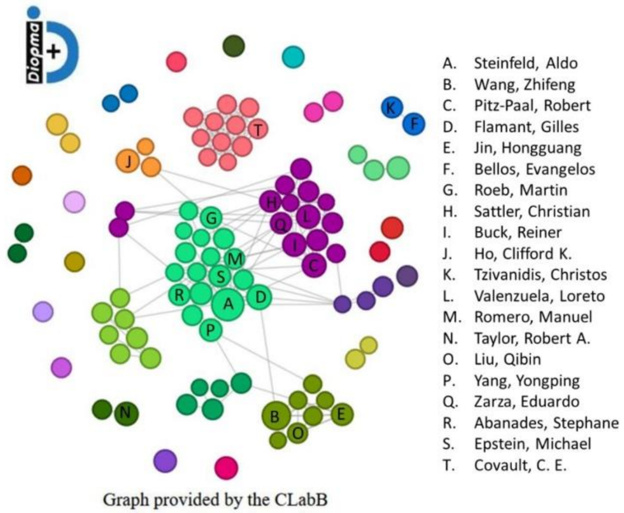


Figure 7. Authorship communities based on the interaction of published papers in CSP field [40].

3.4. Journal bibliometric study

Main journals evolution in CSP field are presented in Figure 8 by number of publications. Journals and conference proceedings are included together in this analysis. Also a h-index was calculated for CSP field only. Solar Energy journal had been leading by far CSP publications during the last decade with the highest h-index of 55. Other journals such as Applied Energy, Energy Conversion and Management and Energy had been increasing their publications during the last years, while Renewable Energy and Journal of Solar Energy Engineering had stagnated during more recent years.

Conference proceedings has shown to be of big relevance, especially Solar Paces Conference with a number of publications similar to Solar Energy journal. Nevertheless, h-index is significantly low for conference proceeding compared to journals. This can be explained since availability of conference proceedings is more limited compared to journal publications.

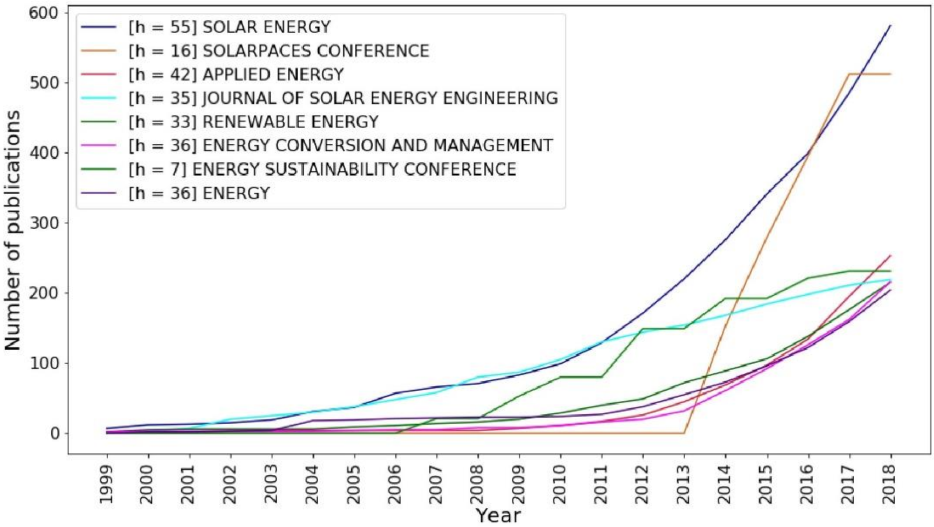


Figure 8. Cumulative journal evolution, by number of publications

In Table 6, top 20 journal and conference proceedings CSP performance ratio is presented, as well as impact factor and quartile score (only for journals). The performance ratio is obtained by dividing the number of CSP cites over the total publications. Energy Policy journal has the better performance ration followed closely by Renewable & Sustainable Energy Reviews journal, which was expected since it's a reviews journal. Applied Energy journal has the third better performance ratio, reflecting more relevance in their publications in CSP field. Other journals such as Solar Energy, Energy, and International Journal of Hydrogen Energy, have a higher impact factor regardless that they are not leading on number of publications. This suggests a good quality on their contents.

Table 6. Top 20 journals in CSP field.

Journal	CSP publications	Total CSP cites	Performance ratio	Impact factor	Quartile Scores
SOLAR ENERGY	609	13956	23	4.374	Q1
SOLARPACES CONFERENCE (PROCEEDINGS)	512	1859	4	N/A	N/A
APPLIED ENERGY	259	7171	28	7.9	Q1
JOURNAL OF SOLAR ENERGY ENGINEERING	240	5143	21	1.367	Q2
RENEWABLE ENERGY	237	3944	17	4.9	Q1
ENERGY CONVERSION AND MANAGEMENT	233	4279	18	6.377	Q1
ENERGY SUSTAINABILITY CONFERENCE (PROCEEDINGS)	231	150	1	N/A	N/A
ENERGY	208	4696	23	4.968	Q1

APPLIED THERMAL ENGINEERING	195	3248	17	3.771	Q1
RENEWABLE & SUSTAINABLE ENERGY REVIEWS	175	7553	43	9.184	Q1
SOLAR ENERGY MATERIALS AND SOLAR CELLS	127	2488	20	5.018	Q1
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY	104	2689	26	4.229	Q1-Q2
SOLAR WORLD CONGRESS (PROCEEDINGS)	88	190	2	N/A	N/A
ENERGIES	53	239	5	2.676	Q2
INTERNATIONAL JOURNAL OF ENERGY RESEARCH	47	300	6	3.009	Q2
INTERNATIONAL JOURNAL OF HEAT AND MASS TRANSFER	44	820	19	3.891	Q1
DESALINATION	42	898	21	6.603	Q1
JOURNAL DE PHYSIQUE IV (PROCEEDINGS)	37	68	2	N/A	N/A
ENERGY POLICY	32	1579	49	4.039	Q1
DESALINATION AND WATER TREATMENT	30	93	3	1.383	Q2-Q3

In Figure 9 journal citation relevance is showed graphically. This analysis was performed using VOS Viewer® software tool. It can be appreciated that Applied Energy journal has the higher citation relevance even with their small amount of publications. Solar Energy journal is clearly the most relevant and influent in CSP field. Also Solar Paces conference importance is confirmed even that citations are low.

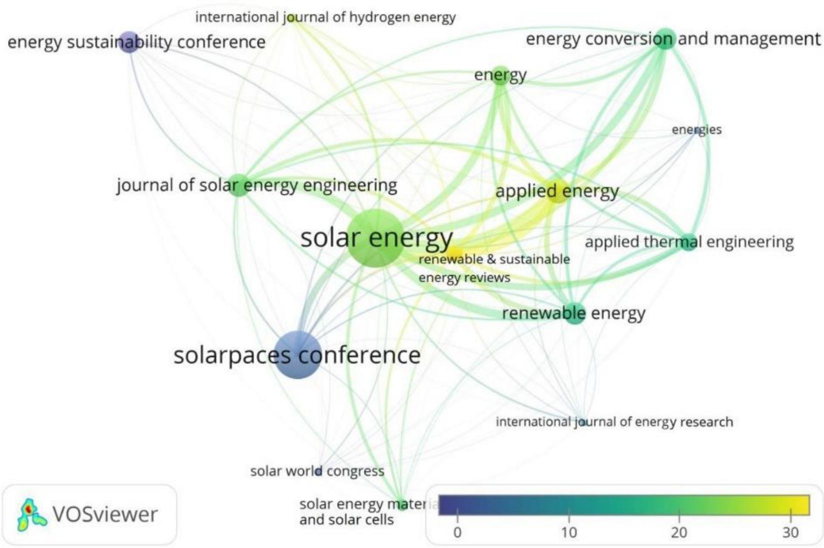
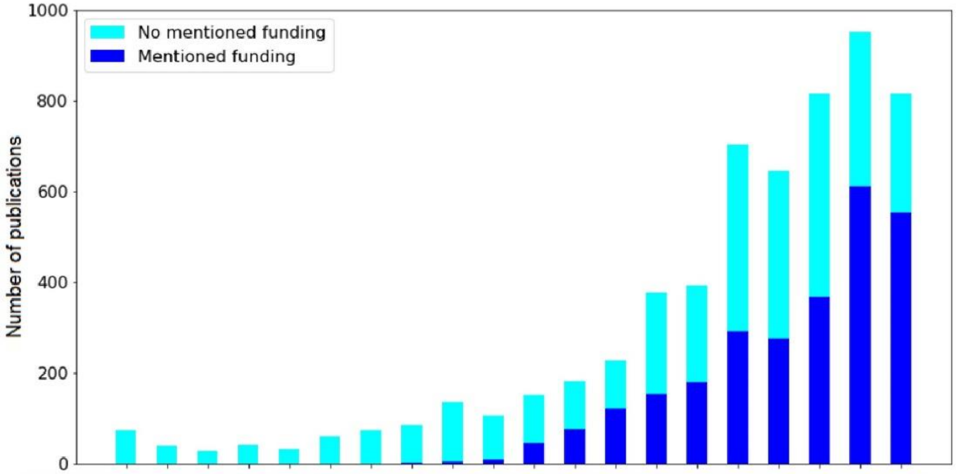


Figure 9. Journal citation relevance and co-citation interaction.

3.5. Funding

The funding achieved to perform research is CSP field were properly reported over the last decade, therefore, this information is highlighted in Figure 10. Thereby, the relation between the special funding and research publications is shown in this Figure. Half of the works regarding CSP field mentioned any funding agent. USA, China and the European Union countries have strong funding programs (by Department of Energy, EU Commission and Chinese Academy of Sciences, respectively).



Year	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018
Not funded	73	39	27	42	32	61	74	84	131	95	106	107	106	221	215	411	369	448	341	261
Funded	0	0	0	0	0	0	0	2	4	10	46	75	122	155	179	293	277	367	611	554
% funded	0%	0%	0%	0%	0%	0%	0%	2%	3%	10%	30%	41%	54%	41%	45%	42%	43%	45%	64%	68%

Figure 10. Funding evolution for CSP publications.

3.6. CSP technology bibliometric evolution

CSP plants have several plant configurations. These are the following: parabolic trough, solar tower[41], Stirling dish [42], and Fresnel reflector [43] within other that are not considered in commercial or pilot scale as the open receiver curtain [44]. All these CSP configuration are analyzed in this section. Figure 11 shows the number of publications in CSP field divided by CSP configurations published over the last 2 decades. This is one of the most important part of the bibliometric analyses shown in this study since elucidate the importance of each technology in the research field. Therefore, the most important to the less in order are as follows: parabolic trough, solar tower, Stirling dish and Fresnel reflectors. However, it is well known that the most commercially installed configuration is the solar tower one [45]. Therefore, the publishing trend do not follow the market trend in this case.

The papers evolution, in general, exponential but there are some peaks in the last years as 2017 and 2014.

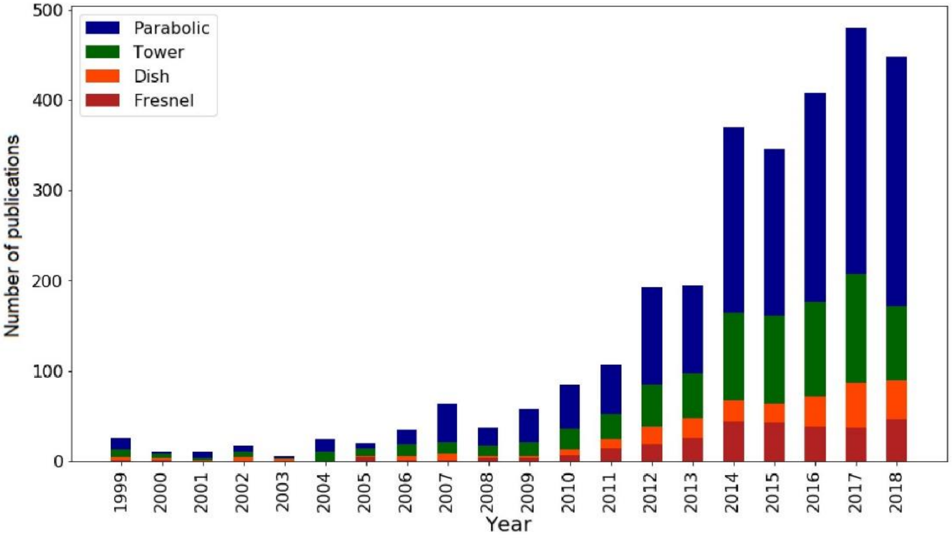


Figure 11. Number of publications per year for each CSP technology

3.6.1. Parabolic trough

Parabolic trough configuration papers per year are presented in Figure 12.a. These papers represent almost half part of the total papers published in CSP field when the CSP configuration is mentioned in the paper. The evolution is similar than the one shown in Figure 11, therefore, In general follows an exponential growing but there is a peak in 2014.Thereby, this trend is still growing after 20 years becoming more and more highlighted during the last decade.

Figure 12.b presents the total parabolic trough configuration publications per country (top ten countries) and Table 7 lists all the data regarding this information for the top ten countries. Since In 2015, the most publishing country about parabolic trough CSP configuration is China. The increment of publishing is in agreement with the economic growth that China is performing in the last years. Before this year, this position was occupied by Spain together with USA. Moreover, it is remarkable that countries as Algeria and Mexico are within the top 10 publishing countries in this field.

Figure 12.c. and Table 8 show the evolution of the last 20 years of the top 10 authors publishing papers regarding parabolic trough configuration in CSP plants. The author with higher number of publication is Evangelos Bellos. Moreover, the h index was calculated for each author in the parabolic trough CSP field and the h index of each authors are also listed in Figure 12.c.

Figure 12.d. presents the evolution of the published papers over the last 2 decades considering the journal where these papers were published and Table 9 summarizes this data. Thereby, the journal that has more publication about parabolic trough in CSP configuration is Solar Energy followed by the Solar Paces proceedings (https://www.solarpaces-conference.org/home/). This is very remarkable since a conference is the second publishing source in the field. That means that the conference is the most highlighted scenario related with this field and all people working on this field is presenting their works on it.

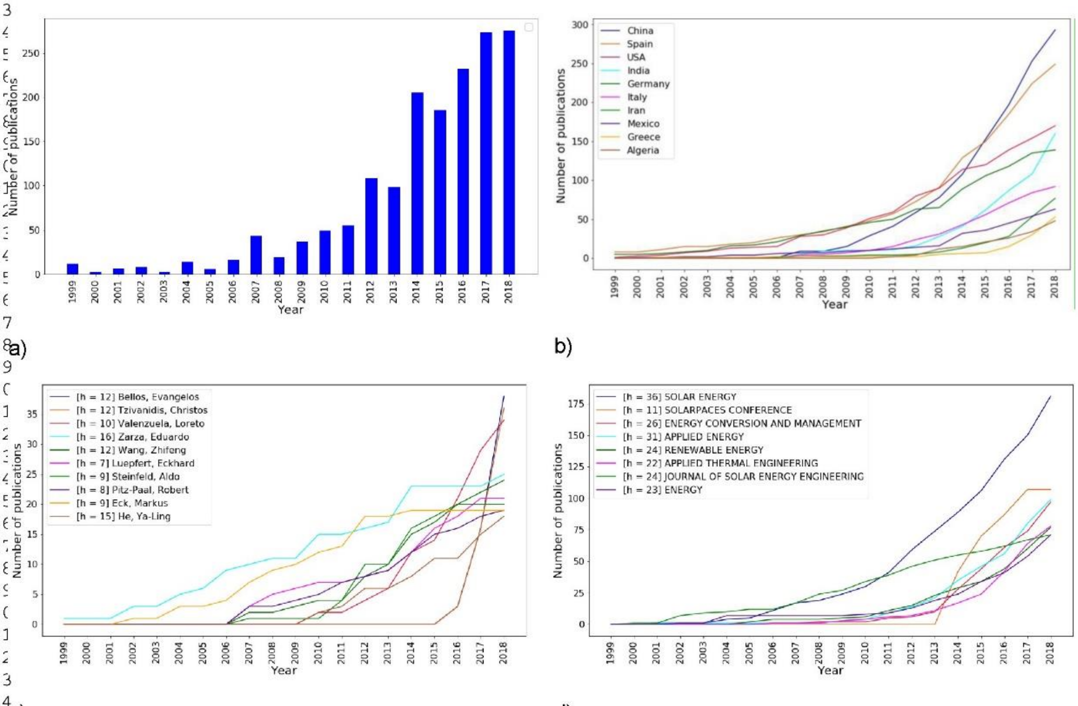


Figure 12. a) Total publications evolution in Parabolic Trough field per year; b) Total publications in parabolic trough field per country; c) Publication evolution of parabolic trough field per country; d) Cumulative author evolution in parabolic trough field by number of publications.

Table 7. Country increment of parabolic trough field publications compared to the accumulated from previous year.

Country	2018	2017	2016	2015	2014	2013	2012	2011	2010	2009
China	15.8%	28.4%	28.8%	41.7%	38.5%	32.2%	43.9%	41.4%	93.3%	66.7%
Spain	11.2%	21.1%	23.3%	16.3%	41.8%	24.7%	28.1%	18.8%	17.1%	20.6%
USA	9.5%	9.7%	14.1%	4.7%	22.9%	10.5%	28.4%	12.1%	22.2%	20.0%
India	48.1%	24.1%	40.3%	51.2%	46.4%	75.0%	45.5%	10.0%	0.0%	11.1%
Germany	2.9%	14.2%	11.1%	18.7%	35.8%	3.1%	25.0%	8.3%	14.3%	13.5%
Italy	9.5%	18.3%	26.8%	30.2%	38.7%	29.2%	60.0%	50.0%	42.9%	40.0%
Iran	45.3%	89.3%	40.0%	53.8%	62.5%	60.0%	25.0%	0.0%	33.3%	0.0%
Mexico	16.4%	19.6%	24.3%	12.1%	94.1%	13.3%	15.4%	18.2%	10.0%	25.0%
Greece	76.7%	100.0%	114.3%	16.7%	20.0%	150.0%	0.0%	0.0%	0.0%	0.0%
Algeria	41.2%	30.8%	23.8%	40.0%	25.0%	200.0%	100.0%	-	-	-

Table 8. Top 10 authors in Parabolic Trough field.

Author	Affiliation	Parabolic publications	Total Parbolic cites	CSP h-index
Bellos, Evangelos	National Technical University of Athens. Greece.	38	337	12
Tzivanidis, Christos	National Technical University of Athens. Greece.	36	327	12
Valenzuela, Loreto	Plataforma Solar Almeria. Spain.	35	808	10
Zarza, Eduardo	CIEMAT. Spain.	25	1663	16
Wang, Zhifeng	Hebei University of Technology. China.	24	340	12
Luepfert, Eckhard	German Aerospace Centre (DLR). Germany.	21	135	7
Steinfeld, Aldo	ETH Zurich. Switzerland.	20	320	9
Pitz-Paal, Robert	German Aerospace Centre (DLR). Germany.	19	345	8
Eck, Markus	German Aerospace Centre (DLR). Germany.	19	610	9
He, Ya-Ling	Xian Jiaotong University. China.	18	875	15

Table 9. Top 10 journals or publishing sources for parabolic trough field.

Journal	Parabolic publications	Total Parabolic cites	Perf. ratio	Impact factor	Quartile Scores
SOLAR ENERGY	189	4662	25	4.374	Q1
SOLARPACES CONFERENCE (PROCEEDINGS)	107	515	5	N/A	N/A
ENERGY CONVERSION AND MANAGEMENT	106	1834	17	6.377	Q1
APPLIED ENERGY	102	3264	32	7.9	Q1
RENEWABLE ENERGY	85	1543	18	4.9	Q1
APPLIED THERMAL ENGINEERING	79	1211	15	3.771	Q1
JOURNAL OF SOLAR ENERGY ENGINEERING	72	2279	32	1.367	Q2
ENERGY	72	1740	24	4.968	Q1
RENEWABLE & SUSTAINABLE ENERGY REVIEWS	67	3758	56	9.184	Q1
ENERGY SUSTAINABILITY CONFERENCE (PROCEEDINGS)	59	58	1	N/A	N/A

3.6.2. Solar tower

In the case of solar tower configuration, the evolution over the last 2 decades is shown in Figure 13.a. The trend is clearly exponential since 2018 where a decrement is shown. There is not a clear stagnation but the evolution needs to be followed in order to understand if it is changing or it is just an exception. Solar tower technology was expected to be the best CSP technology driver. However, problems in current commercial plants and the cost reduction of parabolic trough has slowed down solar tower growth. This also have consequences in the research output, leaving solid particle solar tower and thermochemical solar tower as the main research.

Figure 13.b shows the total solar tower configuration papers by countries over the last 2 decades. The top 10 countries are represented and the evolution country in percentage per year is listed in Table 10. China, Spain, USA and Germany are the most publishing papers and their publishing trends have changed a lot since 2012.

Figure 13.c. shows publication cumulative evolution of published papers over the last 20 years and again considering the top 10 authors. Table 11 listed this information. The most publishing author is Dr. Wang followed by Dr. Buck and Dr. Ho. The h index of each author in the solar tower in CSP field is calculated and listed in this figure as well.

Figure 13.d shows the journal evolution of publications in solar tower CSP configuration. The most publishing source is Solar PACES proceedings followed by Solar Energy journal. Again, the Solar PACES conference is the most important scenario where authors present their papers related to solar tower in CSP field.

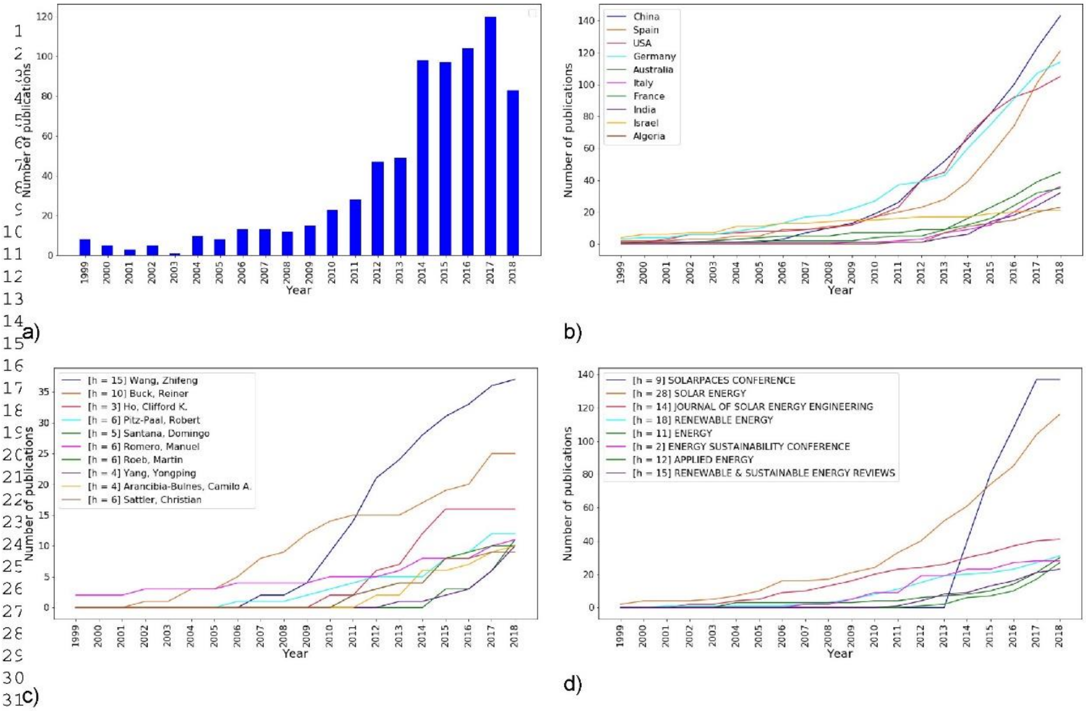


Figure 13. a) Total publications evolution in solar tower field per year; b) Total publications in solar tower per country; c) Publication evolution per authors for solar tower; d) Cumulative author evolution in solar tower field by number of publications.

The increment of the number of publications of solar tower compared to the total from previous years is presented on Table 10.

Table 10. Country/region increment of solar tower publications compared to the accumulated from previous year.

Country	2018	2017	2016	2015	2014	2013	2012	2011	2010	2009
China	16.3%	23.0%	22.0%	24.2%	26.9%	30.0%	53.8%	36.8%	46.2%	30.0%
Spain	19.8%	36.5%	32.1%	43.6%	39.3%	21.7%	15.0%	17.6%	41.7%	9.1%
Germany	6.4%	17.0%	20.5%	23.8%	37.0%	9.5%	5.0%	33.3%	20.0%	19.0%
USA	7.3%	4.8%	10.6%	17.5%	40.4%	9.6%	48.6%	20.7%	20.8%	9.1%
Australia	15.4%	30.0%	30.4%	43.8%	77.8%	0.0%	28.6%	0.0%	0.0%	40.0%
France	9.4%	33.3%	50.0%	33.3%	33.3%	80.0%	0.0%	25.0%	100.0%	0.0%
Italy	24.1%	45.0%	66.7%	33.3%	28.6%	133.3%	50.0%	100.0%	0.0%	-
India	33.3%	33.3%	28.6%	133.3%	50.0%	300.0%	0.0%	0.0%	0.0%	0.0%

Algeria	15.0%	33.3%	15.4%	18.2%	57.1%	600.0%	0.0%	-	-	-
Israel	0.0%	4.3%	4.5%	10.0%	0.0%	0.0%	5.3%	5.6%	0.0%	5.9%

The most relevant authors in solar tower CSP configuration field and their affiliations are listed in Table 11 where the total publications, the total cites and the h-index of these top 10 authors are also included.

Table 11. Top 10 authors in Solar Tower field.

Author	Affiliation	Total publications	Total cites	h-index
Wang, Zhifeng	Hebei University of Technology. China.	37	649	15
Buck, Reiner	German Aerospace Centre (DLR). Germany.	25	582	10
Ho, Clifford K.	Sandia National Laboratory, Department of Energy. USA.	16	29	3
Kribus, Abraham	Tel Aviv University. Israel.	14	192	6
Pitz-Paal, Robert	German Aerospace Centre (DLR). Germany.	12	238	6
Santana, Domingo	Universidad Carlos III de Madrid. Spain.	11	87	5
Romero, Manuel	IMDEA Energy Institute. Spain.	11	329	6
Roeb, Martin	German Aerospace Centre (DLR). Germany.	10	149	6
Yang, Yongping	North China Electric Power University. China.	10	46	4
Arancibia-Bulnes, Camilo A.	Universidad Nacional Autonoma de Mexico. Mexico.	10	40	4

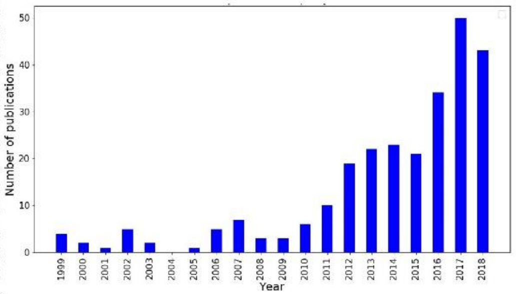
Finally, Table 11 shows the most relevant journals in solar tower topic along with the total publications per journal, the total cites, the performance ration, the impact factor of each journal and the quartile scores.

Table 12. Top 10 journals in solar tower field.

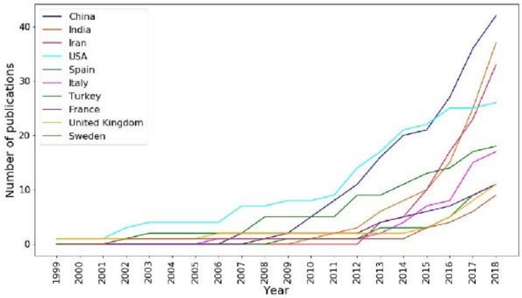
Journal	Total publications	Total cites	Perf. ratio	Impact factor	Quartile Scores
SOLARPACES CONFERENCE (PROCEEDINGS)	137	333	2	N/A	N/A
SOLAR ENERGY	118	2382	20	4.374	Q1
JOURNAL OF SOLAR ENERGY ENGINEERING	45	809	18	1.367	Q2
RENEWABLE ENERGY	37	831	22	4.9	Q1
ENERGY	30	414	14	4.968	Q1
ENERGY SUSTAINABILITY CONFERENCE (PROCEEDINGS)	28	19	1	N/A	N/A
APPLIED ENERGY	28	304	11	7.9	Q1
RENEWABLE & SUSTAINABLE ENERGY REVIEWS	23	1215	53	9.184	Q1
APPLIED THERMAL ENGINEERING	20	379	19	3.771	Q1
SOLAR WORLD CONGRESS (PROCEEDINGS)	18	26	1	N/A	N/A

3.6.3. Stirling dish

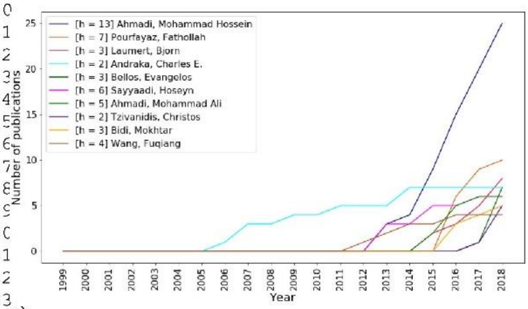
In the case of the Stirling dish, the evolution per year over the last 20 years is presented in Figure 14.a. The trend is exponential until 2018 where a decrement is accounted. The trend needs to be studied in the next years in order to understand if it is an exception or it is stagnation in the field. Figure 14.b. shows the total Stirling dish papers by country over the last 20 years. China, India and Iran are standing out since 2014-2015. This is remarkable since before this period USA or Spain occupied these top positions. Table 13 summarizes the country increment in Stirling dish field over the last decade in percentages. Figure 14.c. shows publication evolution over the last 20 years by authors in Stirling dish CSP field. The publication evolution was linear since Charles E. Andraka started detaching in 2005. However, the most significant standing up author is Mohammad Hossein Ahmadi that started in 2013 the scaling up until today. Figure 14.d. shows the most publishing resources regarding the Stirling dish CSP configuration. The most publishing source is Energy conversion and management journal since 2015. The second one again is Solar PACES proceedings followed by Journal of Solar Energy Engineering.



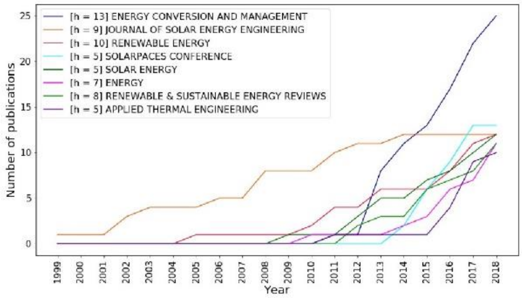
a)



b)



c)



d)

Figure 14. a) Total publications evolution in Stirling dish field per year; b) Total publications in Stirling dish per country; c) Cumulative publication evolution per year of the top ten authors in Stirling dish field; d) Publication evolution per journal/source in Stirling dish field by number of publications

Table 13. Country/region increment of Stirling dish publications compared to the accumulated from previous year.

Country	2018	2017	2016	2015	2014	2013	2012	2011	2010	2009
China	16.7%	33.3%	28.6%	5.0%	25.0%	45.5%	37.5%	60.0%	150.0%	0.0%
India	48.0%	66.7%	50.0%	25.0%	33.3%	100.0%	50.0%	100.0%	-	-
Iran	43.5%	35.3%	70.0%	100.0%	25.0%	-	-	-	-	-
USA	3.4%	0.0%	11.5%	4.0%	19.0%	16.7%	38.5%	8.3%	0.0%	9.1%
Spain	5.9%	21.4%	7.7%	18.2%	22.2%	0.0%	80.0%	0.0%	0.0%	0.0%
Italy	13.3%	87.5%	14.3%	75.0%	100.0%	100.0%	0.0%	0.0%	0.0%	0.0%
United Kingdom	37.5%	60.0%	66.7%	50.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Turkey	22.2%	80.0%	66.7%	0.0%	0.0%	200.0%	0.0%	0.0%	0.0%	-
France	22.2%	28.6%	16.7%	20.0%	25.0%	100.0%	0.0%	0.0%	0.0%	100.0%
Sweden	50.0%	50.0%	33.3%	200.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

The top 10 authors in Stirling dish field are listed in Table 14. Moreover, the total publication of each author as well as the cites and calculated h-index for Stirling dish field are also included in this table.

Table 14. Top 10 authors in Stirling Dish field.

Author	Affiliation	Dish publications	Total Dish cites	Dish h-index
Ahmadi, Mohammad Hossein	University of Derby. United Kingdom.	25	655	13
Pourfayaz, Fathollah	University of Tehran. Iran.	10	185	7
Laumert, Bjorn	Royal Institute of Technology. Sweden.	8	31	3
Andraka, Charles E.	Sandia National Laboratory, Department of Energy. USA.	7	28	2
Bellos, Evangelos	National Technical University of Athens. Greece.	7	27	3
Sayyaadi, Hoseyn	K. N. Toosi University of Technology. Iran.	6	284	6
Ahmadi, Mohammad Ali	Amirkabir University of Technology. Iran.	6	164	5
Tzivanidis, Christos	National Technical University of Athens. Greece.	5	17	2
Bidi, Mokhtar	Shahid Beheshti University. Iran.	5	47	3
Wang, Fuqiang	Harbin Institute of Technology, China.	4	136	4

Table 15 lists the most relevant journals for Stirling dish field. Moreover, this table includes the total publication per journal, the total citations of each journal, the performance ration, the impact factor, and the quartile of each journal.

Table 15. Top 10 journals in TCS field.

Journal	Total publications	Total cites	Perf. ratio	Impact factor	Quartile Scores
ENERGY CONVERSION AND MANAGEMENT	25	648	26	6.377	Q1
JOURNAL OF SOLAR ENERGY ENGINEERING	16	336	21	1.367	Q2
RENEWABLE ENERGY	14	230	16	4.9	Q1
SOLARPACES CONFERENCE (PROCEEDINGS)	13	56	4	N/A	N/A
SOLAR ENERGY	12	168	14	4.374	Q1
ENERGY	11	149	14	4.968	Q1
RENEWABLE & SUSTAINABLE ENERGY REVIEWS	11	438	40	9.184	Q1
APPLIED THERMAL ENGINEERING	10	160	16	3.771	Q1
APPLIED ENERGY	7	193	28	7.9	Q1
ENERGY SUSTAINABILITY CONFERENCE (PROCEEDINGS)	6	2	0	N/A	N/A

3.6.4. Fresnel reflector

In the case of Fresnel reflector, the evolution per year since 1999 is presented in Figure 15.a. The trend was clearly exponential until 2014 and stagnation trend followed until 2017. This was mainly caused because the development and advantages of parabolic trough collectors. Nevertheless, in 2018 linear Fresnel gained interest for process steam generation.

Figure 15.b shows the total number of publications per country over the last 20 years. It is shown a standing up growth presented by China since 2011 in concordance with Chine gross domestic product (GDP) growth.

Figure 15.c shows the publication evolution over the last 20 years regarding the top 10 authors in the Fresnel reflector field. The most publishing author is Ruben Abbas that has a outstanding publication trend followed by Jose M. Martínez-Val. The h-index of each author are also listed in this figure.

The most publishing journal in Fresnel reflector field is Solar Energy followed by Solar PACES proceding. Solar Energy journal has an outstanding trend for the last 10 years. Figure 15.d shows the journal publications evolution over the last 2 decades considering the h-index of each journal

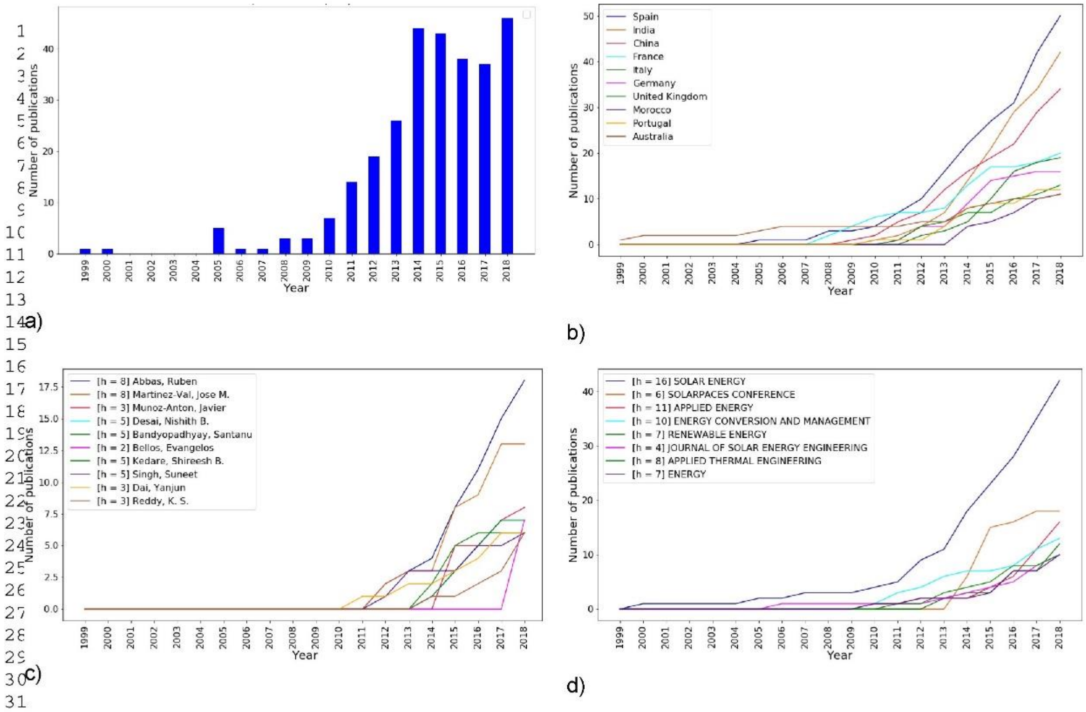


Figure 15. a) Total publications evolution in Fresnel reflector field per year; b) Total publications in Fresnel reflector field per country; c) Cumulative publication evolution per authors of the top ten authors in Fresnel reflector field; d) Publication evolution per year of journals publishing in Fresnel reflector field.

Increment of the publications on Fresnel reflector field compared to the previous 10 years is presented in Table 16. The amount of publication are presented in percentages and the most publishing paper in 2018 was India, followed by Spain and UK.

Leaders like EU, China or USA are growing at important rates. Other minor leaders such as Canada, India, Australia and Saudi Arabia are growing at rates that can make them top leaders in the following years.

Table 16. Country/region increment of TCS publications compared to the accumulated from previous year.

Country	2018	2017	2016	2015	2014	2013	2012	2011	2010	2009
Spain	19.0%	35.5%	14.8%	22.7%	37.5%	60.0%	42.9%	75.0%	33.3%	0.0%
India	23.5%	17.2%	38.1%	50.0%	100.0%	75.0%	100.0%	100.0%	-	-
China	17.2%	31.8%	15.8%	18.8%	33.3%	71.4%	40.0%	150.0%	100.0%	-
France	11.1%	5.9%	0.0%	30.8%	62.5%	14.3%	0.0%	16.7%	50.0%	100.0%
Italy	5.6%	12.5%	60.0%	100.0%	66.7%	50.0%	-	-	-	-
Germany	0.0%	6.7%	7.1%	55.6%	125.0%	0.0%	300.0%	-	-	-
United Kingdom	18.2%	10.0%	42.9%	0.0%	40.0%	25.0%	300.0%	-	-	-
Morocco	10.0%	42.9%	40.0%	25.0%	-	-	-	-	-	-
Portugal	0.0%	33.3%	0.0%	12.5%	100.0%	300.0%	0.0%	0.0%	-	-
Australia	10.0%	0.0%	11.1%	12.5%	60.0%	0.0%	25.0%	0.0%	0.0%	0.0%

The top ten authors in Fresnel reflector field are listed in Table 17 as well as their affiliations. The most publishing authors are from the Polytechnic University of Madrid. Spain. In addition, the total publication, the total citations and the h-index of each author calculated in Fresnel reflector field is also listed in Table 17.

Table 17. Top 10 authors in Fresnel field.

Author	Affiliation	Total publications	Total cites	h-index
Abbas, Ruben	Polytechnic University of Madrid. Spain.	18	293	8
Martinez-Val, Jose M.	Polytechnic University of Madrid. Spain.	13	257	8
Munoz-Anton, Javier	Polytechnic University of Madrid. Spain.	8	56	3
Desai, Nishith B.	Pandit Deendayal Petroleum University. India.	7	104	5
Bandyopadhyay, Santanu	Indian Institute of Technology (IIT) - Bombay. India.	7	107	5
Bellos, Evangelos	National Technical University of Athens. Greece.	7	19	2
Kedare, Shireesh B.	Indian Institute of Technology (IIT) - Bombay. India.	6	82	5
Singh, Suneet	Indian Institute of Technology (IIT) - Bombay. India.	6	76	5
Dai, Yanjun	Shanghai Jiao Tong University. China.	6	92	3
Reddy, K. S.	Indian Institute of Technology (IIT) - Madras. India.	6	50	3

Table 18 shows the most relevant journals for Fresnel reflector field along with their Fresnel reflector performance index, showing that Solar Energy journal is the leader with a good performance. Nevertheless, Renewable and Sustainable Energy Reviews has the highest performance for non-review journals showing higher quality on their publications in Fresnel reflector. In addition, the total publication, the total citation, the performance ration, the impact factor of the journal as well as the quartile score are listed in Table 18.

Table 18. Top 10 journals in TCS field.

Journal	Total publications	Total cites	Perf. ratio	Impact factor	Quartile Scores
SOLAR ENERGY	42	929	22	4.374	Q1
SOLARPACES CONFERENCE (PROCEEDINGS)	18	96	5	N/A	N/A
APPLIED ENERGY	16	351	22	7.9	Q1
ENERGY CONVERSION AND MANAGEMENT	16	319	20	6.377	Q1
RENEWABLE ENERGY	14	117	8	4.9	Q1
JOURNAL OF SOLAR ENERGY ENGINEERING	11	103	9	1.367	Q2
APPLIED THERMAL ENGINEERING	10	245	25	3.771	Q1
ENERGY	10	187	19	4.968	Q1
RENEWABLE & SUSTAINABLE ENERGY REVIEWS	9	310	34	9.184	Q1
SOLAR WORLD CONGRESS (PROCEEDINGS)	7	24	3	N/A	N/A

4. Conclusions

CSP scientific research field bibliometric revision has studied almost 6,300 publications on relevant journals and conference proceedings. This is the first time a bibliometric study of CSP has been performed with current scope and detail.

This study presents the publication evolution in CSP field over the last two decades. Several metrics were used to analyze regional efforts, relevant authors, author communities, relevant journals, keywords evolution and funding effort effect on the research output. Different parameters were used to measure the grade of cooperation between countries/authors and the relevance of authors/journals (h-index and impact factor). Some of these metrics were applied also within the main four CSP technologies: parabolic trough, solar tower, Stirling dish and linear Fresnel.

Regional analysis showed that China is becoming the most relevant country for CSP research. Nevertheless, European Union still leads the development and will continue that way at least in the short term. Also, USA have an important role in CSP development, as it has occurred in the past, in the foreseen future.

Research communities study allowed to identify cooperation opportunities. Also, regional and research communities' cooperation are in line with known cooperation agreements between countries and institutions. Author analysis helped to identify individual CSP research stakeholders.

However, each author should be considered individually, since several institutions use to add center managers into the author lists. This is actually not a negative issue, since usually these managers are important technology stakeholders, but it gets mixed with the technological and technical experts. Authors keyword evolution analysis has been useful as an indirect measure of technological maturity.

Main journals and conferences were identified and contrasted. It was found that conference proceedings have an important effect in the overall CSP publications. However, the journal publications use to have more impact since they are more frequently cited.

Funding analysis had shown a direct relationship between funding and research output. This first approach could help to make deeper analysis in the future to measure the effectiveness by country or by funding agency.

Inside CSP field, parabolic trough has shown to have great relevance in the research output. This also has been reflected in the cost reductions achieved by this technology. Solar tower technology is under constant research evolution. Nevertheless, it needs to be optimized to compete with parabolic trough, as well to solve current technical difficulties. New approaches on this technology like the solid particle solar tower are currently under very active research activity. Finally, Stirling dish and linear Fresnel are still emerging with CSP research field with an accelerated research output.

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Where is Thermal Energy Storage (TES) research going? – A bibliometric analysis

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Thermochemical

ABSTRACT

Energy storage technologies can provide energy security, fight climate change, and improve the value of current or future energy systems. Thermal Energy Storage (TES) is a key enable technology, it allows to stock thermal energy that can be further used for heating and cooling applications and power generation. The methods and tools used to analyse all the literature about the evolution of TES systems research are described in this paper. Bibliometrics is the science that studies, in a statistical way, the written publications of a certain field of research, and it is considered one of the few interdisciplinary research fields that can be extended to almost all scientific areas. The bibliometric analysis of the database Web-of-science (core collection) shows highlighted information in order to figure out the scientific outputs. The importance of the bibliometrics is to analyse a knowledge development from a strategic point of view in order to detect its evolution regarding the research in such a field and to detect which are the opportunities within this area. This study presents the publication evolution in TES field over the last two decades, per year, per country, per authors, per journal, and per TES technology, taking into account sensible heat TES (SHTES), latent heat TES (LHTES), and thermochemical energy storage (TCS), and considering the connection between authorship communities and country interactions. The communities are obtained from the co/authorships, regardless of the country or affiliation; this permits to view the size of the communities, as well as to identify collaboration opportunities between communities with low or no interaction. Furthermore, studies are included regarding detailed analysis on each TES technology, as well as other factors (such as funding) that can influence the current and future research.

1. Introduction

Nowadays, the global energy supply is one of the most important concerns for developed countries. Trends in energy supply and use are economically, environmentally and socially unsustainable. Both population growth and industrial development have led to a continuous increase of energy consumption (Nejat et al., 2015; Bhattacharya et al., 2004). This usually results in an increased use of fossil fuels that today remain as the main source of energy generation. However, the high pollution associated with their use is a major concern for the producers and consumers of fossil fuels. For several decades, the implementation of renewable energy that helps supply the large energy demand has contributed towards the reduction in the consumption of conventional polluting energy (Ürge-Vorsatz et al., 2015; Dincer, 2000).

Energy storage technologies can provide energy security, fight climate change, and improve the value of current or future energy systems (International Energy Agency, 2014). Thermal Energy Storage (TES) is a key enable technology, as it allows to stock thermal energy that can be further used for heating and cooling applications and power generation.

Because of its relevance for the monitoring of information and management of knowledge, bibliometrics has become an important field of information science. In recent years, many studies have provided a bibliometric overview of their research fields, such as management, econometrics, health economics, marketing, statistics, ecological economics, entrepreneurship, production and operations management, data envelopment, gray systems, and innovation, among others (Merigó et al., 2015).

In this way, Gao et al. published a bibliometrics study targeted to the field of wind power price (Gao et al., 2016) and conducted a

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bibliometric and network analysis based on the data from Scopus. The results show that the numbers of total related publications are gradually increasing, with the US as the leading country. In addition, Mao et al. published a bibliometric analysis regarding the forward for alternative energy research during 1994–2013 (Mao et al., 2015). Thereby, the stated that the conversion devices such as the wind turbines and solar cell were paid most attention in order to improve the production efficiency. These are examples of the very few bibliometric studies available in SCOPUS database. There are not bibliometric studies regarding thermal energy storage (TES) field.

The aim of this study is to provide an overview of the history of TES research and development, by using bibliometric methods. Identifying different technology tendencies and developments, as well as the most productive and influential research, can be interesting for everyone involved on TES development. Regional particularities, policies, financing efforts and economic growth have been evaluated from the point of view of knowledge production. In addition, technological maturity has been observed according to the most dynamic knowledge areas for each specific technology.

2. Methodology

The methods and tools used to analyze all the literature about the evolution of TES systems research are described in this section. Bibliometrics is the science that studies, in a statistical way, the written publications of certain field of research, and is considered one of the few interdisciplinary research fields that can be extended to almost all scientific fields (Pritchard, 1969). Björk and Hedlund (2015) defined that the main purpose of bibliometric studies is to bring the general picture of the development of a certain research field, as well as the analysis of the leading researchers (authors, journals, institutions and countries) in such area of knowledge (Björk and Hedlund, 2015). Therefore, this important information science has become more and more relevant for the monitoring of information and management of knowledge. In recent years, many are the studies that have provided a bibliometric overview of their research fields such as management, econometrics, health economics, marketing, statistics, ecological economics, entrepreneurship, production and operations management, data envelopment, gray systems, and innovation, among others (Merigó et al., 2015).

However, over the years, several issues have emerged in order to provide nurturing bibliometric information, mainly behind the determination of the most significant information sources and indicators for measuring the bibliographic material. Therefore, in order to be the more informative and neutral with the information, Web of Science (WoS) Core Collection database was used to search the most relevant scientific articles related to TES. The Web of Science Core Collection includes more than 14,000 high-quality journals indexed with the most complete information for all the articles, including all the authors' names, authors' affiliations, abstracts, keywords, funding information, etc. This rich database allowed us extracting very valuable information unavailable with other databases.

To develop the search process, authors have used the keywords "thermal storage" OR "thermal energy" OR "cold storage" OR "concentrated solar power" OR "phase change material" OR "thermochemical storage" OR "molten salts" OR "CSP" OR "heat storage" OR "latent heat" OR "sensible heat" OR "thermochemical" OR "PCM" searched in the topic, abstract or keywords sections. One of the main challenges faced was that, through the years, papers that addressed TES systems do not use the same keywords to refer to this technology. In fact, from our first attempts of data gathering, several important documents were missing behind this keyword "incongruence". Within this scenario, a more complex and inclusive keyword map, which includes not only the main keywords used in the literature of TES, but also a combination of these keywords with other complement phrases was developed (see Table 1). Additionally, some exclusion phrases were included, behind the elevated number of papers that emerged from our first search that, even they use some of our selected keywords, they were not related to TES systems (i.e. Photovoltaic systems). This improved roadmap allowed us to reach, in a more efficient manner, almost all the papers in TES systems.

From the Table 1, it is important to note that only articles and reviews were considered in this analysis, resulting on 14,754 papers published during 109 years (papers can be considered in more than one main category).

Finally, with this database, more specific analysis has been performed according to sensible, latent and thermochemical technologies showing interesting and promising results. Relevant authors, journals, funding initiatives, regional cooperation and other relevant information will be showed in the following sections.

Analyses were made using python coding and graphic tools. Other reports were provided using VOS viewer (L.U. Centre for Science and Technology Studies, 2018) and Complexity Lab Barcelona (CLabB) (Departament de Física Fonamental, 2018) software. VOS viewer is a tool for visualizing bibliometric networks. Communities analysis was made using CLabB tool in order to identify scientific communities working together, regardless their country or affiliation.

3. Results

3.1. Number of publications

Based on the available data in this new bibliometric database, the total of publications per year regarding thermal energy storage field is presented in Fig. 1 for the last 20 years. The TES field in the scientific sector is growing up in the last 10 years as can be observed in Fig. 1, and this fact remarks that this field is in a highlighted growth, which is supposed to become as a huge market deployment in the near future.

3.2. Countries bibliometric evolution

In addition, Fig. 2 shows the analysis of the data available in the new bibliometric database regarding the publications by countries in the TES field. European Union publications are grouped, and it is the top one publishing zone in the world, followed by China, USA, and Japan. Furthermore, the European countries are also accounted separately. Germany is the country that published more papers in TES research field, followed by France, Spain and England. Canada, India and Italy are also included in the top 10 TES publishing countries.

Furthermore, the publication evolution per country over the last two decades is shown in Fig. 3. Indeed, the increment evolution related with the TES publication is shown as an exponential increment which is accentuated in European Union and China. USA publication evolution regarding the TES field is stagnated since 3–4 years ago. The other top 10 countries publishing evolutions are similar over the last decades. Based on current tendency, China is expected to be leading TES research over the next years, followed closely by European Union.

The constant growth can be also appreciated in Table 2, in which growth compared to the total publications accumulated until the previous year is presented. It can be observed that EU has an exponential growth but less accelerated when compared to China and India. Then, it can be expected that in the following years China and India will lead TES research. Even though Iran is now on the 10th place its growing rates show that can become an important actor on TES research on the following year. USA stagnation is confirmed also when considering growing rates.

Furthermore, Fig. 3(b) presents the total publications per country and EU divided by technology to store thermal energy. It is well known that TES systems are able to store energy by three different technologies: sensible heat (SHTES), latent heat (LHTES), and thermochemical storage (TCS). These three categories are the ones used in Fig. 3(b).

Notice that EU has published more than 5000 papers in this field

Table 1
TES keyword search roadmap.

Exclusion phrases			Main phrases	Complement phrases					Total papers
			Thermal storage						2620
			Thermal energy	Storage					5703
			Cool storage	Thermal					80
			Concentrated solar power						703
			Phase change material						4503
			Thermochemical storage						75
PV	Photovoltaic		Molten salts	Solar	Energy	Power plant	Storage		1108
Cloud	Internet	Software	CSP	Solar	Energy	Renewable	Power	Storage	1528
			Heat storage						4368
			Latent heat	Storage					2911
			Sensible heat	Storage					646
			Thermochemical	Energy storage					361
			PCM	Energy storage					2765

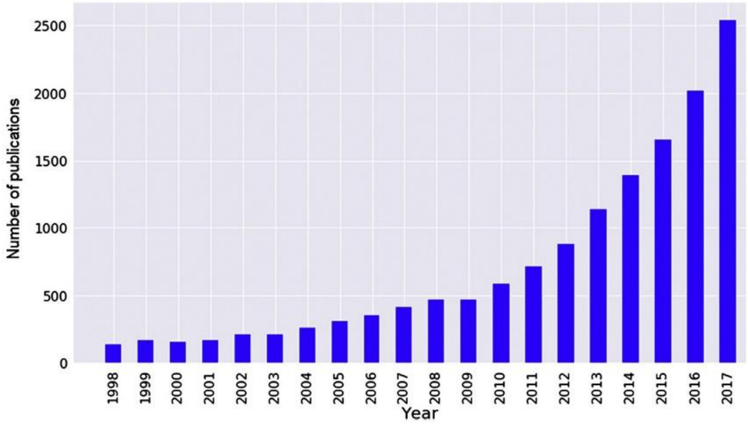

Fig. 1. Thermal energy storage publications during the last two decades.

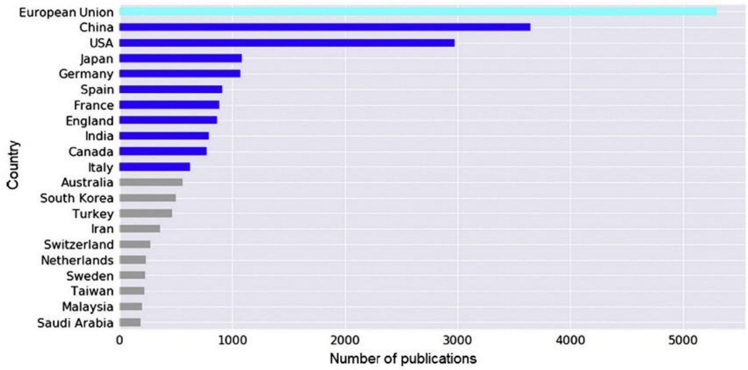

Fig. 2. Top 20 publishing countries in the TES field.

followed by China that currently has more than 3500 scientific publications.

On the other hand, the TES technology that accounts more amounts of scientific publications based on the data available is LHTES, followed by SHTES and TCS that presents the lower amounts of publication. This is a remarkable point what means that TCS has highest potential to perform scientific research. Notice that EU is the zone that published more papers in SHTES and TCS but China is the one that published more in LHTES technology.

Fig. 4 shows the publication evolution over the last 20 years for the top 10 publishing European countries (Germany followed by Spain, France, UK, Italy, Netherlands, Poland, Portugal, Denmark, and Belgium). The TES publication trends in Europe is still growing up and this trend is followed by all the countries represented in this figure. The publishing stagnation is far to be reached in EU TES as this figure clarifies.

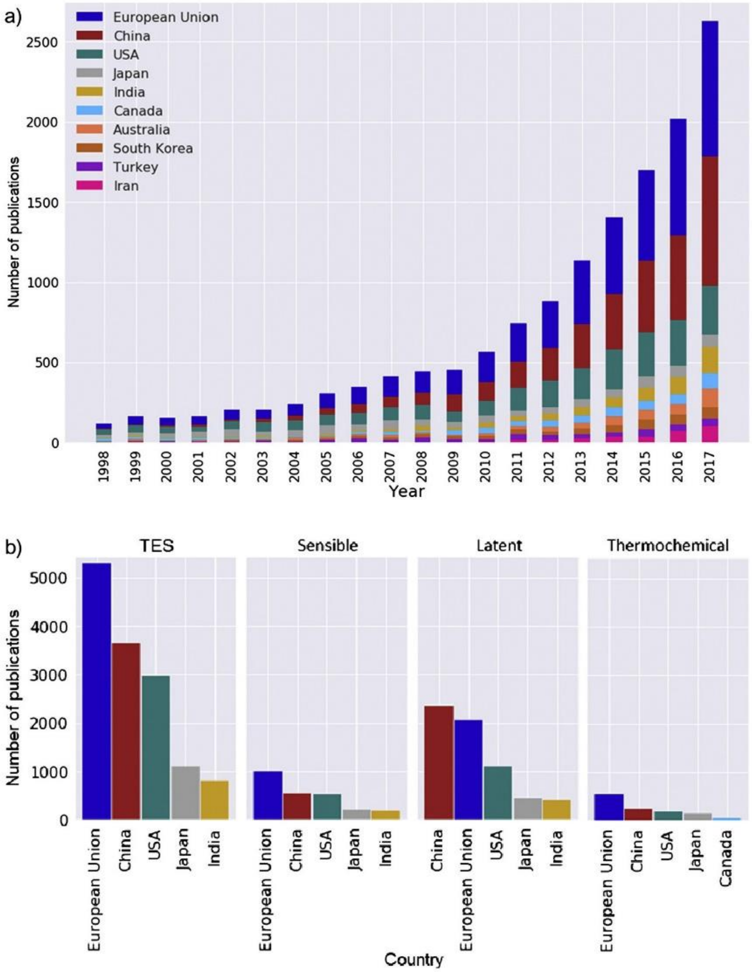

Fig. 3. (a) Publication evolution regarding TES field in the last 2 decades by countries; (b) Total publications in TES field of top 5 countries and EU, and SHTES, LHTES, TCS publication of those countries/zones.

Table 2
Country/region increment of TES publications compared to the accumulated from previous year.

Country	2017	2016	2015	2014	2013	2012	2011	2010	2009	2008
EU	20.3%	21.1%	19.6%	19.9%	19.8%	17.1%	16.2%	14.3%	13.2%	13.1%
China	31.7%	26.1%	28.8%	28.7%	29.4%	27.2%	28.3%	26.3%	31.0%	29.9%
USA	12.1%	12.6%	13.6%	14.0%	12.4%	12.2%	11.2%	7.9%	6.1%	9.2%
Japan	7.6%	7.8%	8.9%	6.8%	7.1%	5.8%	5.3%	7.5%	6.3%	7.3%
India	28.4%	23.4%	20.9%	18.5%	19.5%	17.1%	14.6%	18.5%	8.4%	22.0%
Canada	15.7%	11.2%	11.0%	12.2%	10.8%	10.7%	9.3%	11.7%	10.8%	4.5%
Australia	28.3%	19.4%	22.2%	25.1%	18.6%	19.0%	16.2%	11.5%	6.1%	9.5%
South Korea	17.6%	16.6%	20.7%	18.9%	17.3%	10.6%	17.5%	15.9%	14.0%	22.2%
Turkey	12.0%	11.0%	14.6%	9.6%	9.7%	14.7%	19.8%	6.9%	13.6%	23.2%
Iran	43.9%	48.4%	32.5%	44.4%	47.3%	41.0%	77.3%	57.1%	27.3%	22.2%

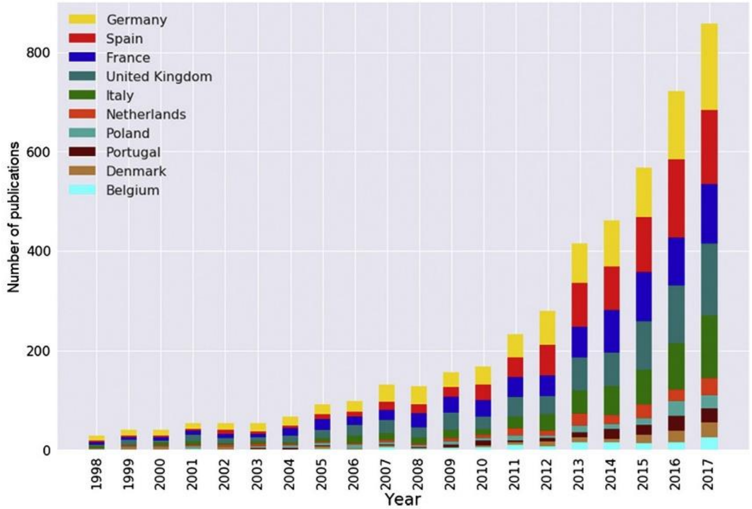

Fig. 4. Publication evolution regarding TES field in the last 2 decades divided by top 10 European countries.

Table 3
EU countries increment of TES publications compared to the accumulated from previous year.

Country	2017	2016	2015	2014	2013	2012	2011	2010	2009	2008
Germany	17.1%	16.2%	13.9%	15.1%	15.2%	15.5%	12.6%	11.4%	10.8%	14.4%
Spain	17.5%	22.5%	20.6%	20.6%	26.6%	24.3%	20.5%	20.5%	16.7%	17.0%
France	14.2%	13.2%	15.6%	15.8%	13.2%	10.8%	11.8%	11.1%	11.4%	11.6%
U K	17.9%	17.4%	17.5%	15.0%	17.1%	11.3%	14.1%	9.8%	15.9%	10.8%
Italy	20.9%	19.6%	18.8%	19.0%	18.5%	16.8%	13.7%	7.6%	12.7%	12.0%
Netherlands	15.4%	12.5%	16.1%	12.8%	21.1%	9.3%	17.0%	11.0%	9.2%	5.1%
Poland	15.6%	21.3%	11.7%	10.2%	14.8%	8.0%	13.0%	8.3%	10.9%	8.2%
Portugal	19.4%	25.9%	23.3%	30.3%	21.7%	16.7%	13.3%	34.6%	35.3%	9.1%
Denmark	22.2%	21.0%	20.5%	10.6%	15.3%	20.0%	12.5%	11.4%	6.5%	6.9%
Belgium	19.7%	15.1%	15.6%	19.7%	26.2%	15.6%	26.3%	17.9%	13.0%	10.0%

Table 3 represents growing rates for the top 10 EU members on TES. It can be noted that Denmark, Italy and Germany constantly have been incrementing their research when compared to previous total publications. On the other hand, Spain constantly decreased their research output over the last years, having the lower one in 2017 since 2009.

The interactions through joint publications by different countries where also identified in this bibliometric study based on the affiliations of the authors in the papers available in the database. Notice that there are countries that are not considered in this map since only the most publishing countries are highlighted in Fig. 5 (top 15 TES publishing countries). Interaction strength is represented by the thickness of the line between the countries. Therefore, the main interaction of European countries is with China in the TES field (thicker blue). The second more remarkable interaction is between EU and USA, and both USA and China have a highlighted interaction too. In addition, Europe has remarkable interaction with Australia, Switzerland, and Canada. These countries form the first group of interaction in TES field (in blue). Moreover, there is a huge interaction between Japan, South Korea, Taiwan, which form the second group (in green). Last, India, Iran, Turkey, Malaysia, Egypt, Saudi Arabia and Canada form the third main group (in red).

Note that countries from South America and Africa are not included in this interaction map since these countries are less active in publishing papers in TES field.

Fig. 6 shows the interaction between European countries publishing in TES field. It can be seen that there are five main publishing countries in TES field, which are Germany, Spain, England, France and Italy. Indeed, these countries highly interact between them as this figure shows. Moreover, these five countries interact and share authorship with all the other countries of this figure.

3.3. Authorship bibliometric evolution

The cumulative author evolution by number of publications is shown in Fig. 5. This takes into account the grouped publication of each author profile available in the web of science (WoS) – core collection database, and authors were checked for repeated WoS profiles although it is difficult to do this revision in every single profile. This analysis does not take into account in which order the authors appear on the articles, only that they participate on them. As Fig. 7 shows, Prof. Luisa Cabeza is the top-one researcher publishing in TES field followed by Dr. Song, Dr. Sari and Prof. Farid, who are the most representative prestigious researchers in the TES field. Furthermore, the *h index* was calculated only taking into account papers published in TES field for each of the top 10 authors and these indices are presented in Fig. 7. Prof. J.E. Hirsch from University of California (San Diego) defined *h index* (Hirsch, 2010) as *"The number of papers with citation number higher or equal to h, as a useful index to characterize the scientific output of a researcher"*. Thereby, all top 10 authors have *h index* higher than 15, being Prof. Cabeza the top one ($h = 38$).

Besides, Table 4 shows the citations of the top 20 authors in TES field, what is even more important than the amount of publications

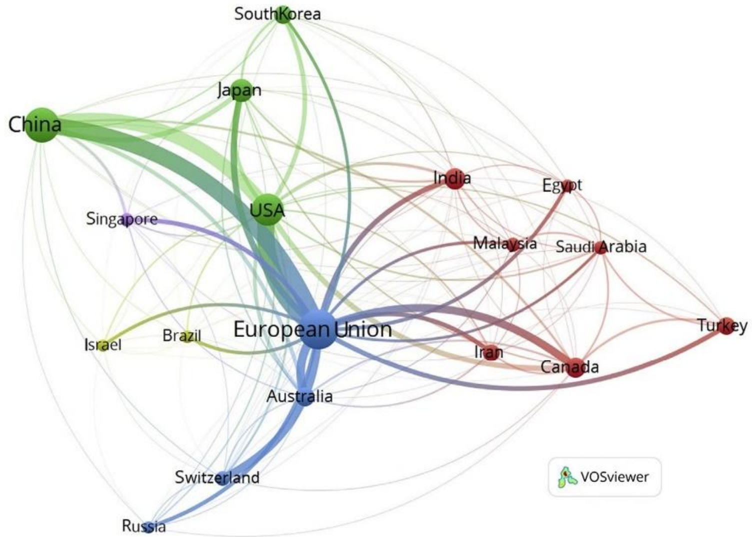

Fig. 5. Affiliation and co-authorship interaction taking into account the countries collaboration of the Top15 countries and EU.

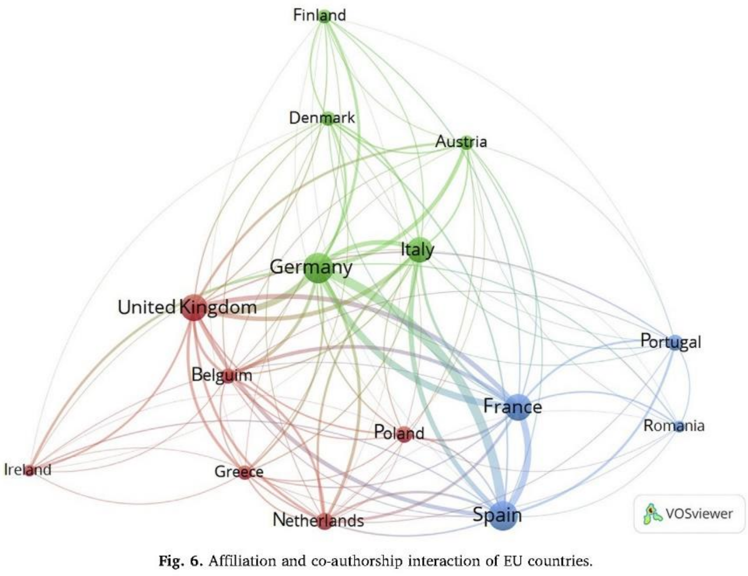

Fig. 6. Affiliation and co-authorship interaction of EU countries.

since it is also a quality-publishing indicator, or the TES h index, which is calculated only for the TES field articles and reviews. The top one in citation is also Prof. Cabeza who accounts more than 8000 citations, followed by Dr. Song and Dr. Sari. Notice that almost all top 10 authors of Fig. 5 are also included in Table 4.

Finally, one of the most highlighted analysis of the bibliometric analysis here presented is the Fig. 8, where the authorship communities in TES field are shown. A list of the publications in the TES database was analyzed by CLabB software tool in order to define the attraction forces between the authors (represented by the circles) and order them, using an algorithm, to identify the communities they belong to.

Notice that the top 10 publishing authors (listed in Fig. 7) are highlighted in Fig. 8. Prof. Cabeza and Prof. Farid are members of the biggest research community (in olive green). Prof. Zhang leads the second one (in indigo), followed by Prof. Song and Prof. Bo who integrate the third one (in green). There are other 12 detected research communities in TES field (marked in different colors in Fig. 8).

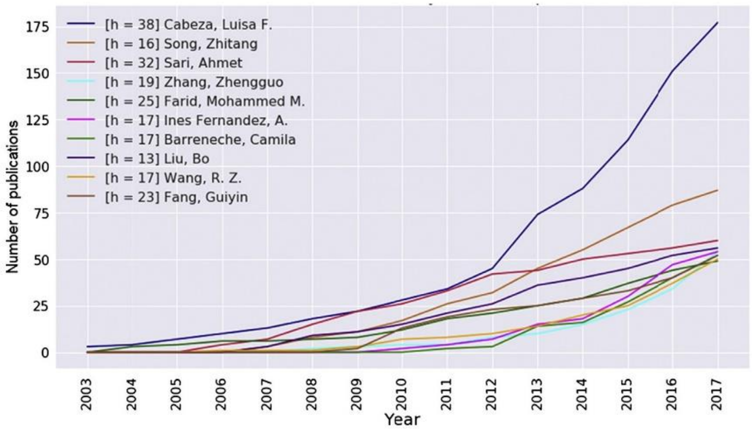

Fig. 7. Cumulative author evolution by number of publications over the last two decades.

Table 4
Top 20 authors in TES field.

Author	Affiliation	TES publications	Total TES cites	TES h index
Cabeza, Luisa F.	Universitat de Lleida, Spain	196	8400	38
Song, Zhitang	Shanghai Institute of Microsystem & Information Technology, China	87	778	16
Sari, Ahmet	Gaziosmanpasa University, Turkey	66	3755	32
Zhang, Zhengguo	South China University of Technology, China	62	1178	19
Farid, Mohammed M.	University of Auckland, New Zealand	60	4079	25
Ines Fernandez, A.	Universitat de Barcelona, Spain	59	1284	17
Barreneche, Camila	Universitat de Barcelona, Spain	56	1139	17
Liu, Bo	National Institute of Advanced Industrial Science & Technology, Japan	56	558	13
Fang, Guiyin	Nanjing University, China	54	1385	23
Wang, R. Z.	Shanghai Jiao Tong University, China	54	1288	17
Velraj, R.	Anna University Chennai, India	53	1879	23
Feng, Songlin	Shanghai Institute of Microsystem & Information Technology, China	52	586	14
Dincer, Ibrahim	University of Ontario Institute Technology, Canada	49	762	16
Alkan, Cemil	Gaziosmanpasa University, Turkey	48	1972	25
Li, Wei	Peking University, China	48	1030	16
Rao, Zhonghao	China University of Mining & Technology, China	47	1019	18
Zhao, C. Y.	Shanghai Jiao Tong University, China	46	2228	20
Akiyama, Tomohiro	Hokkaido University, Japan	44	1545	20
Ding, Yulong	University of Birmingham, United Kingdom	43	1341	14
de Gracia, Alvaro	Universitat Rovira i Virgili, Spain	39	1355	17

3.4. Journal bibliometrics

The cumulative journal evolution that TES researchers use to publish their research is presented in Fig. 9, by number of publications. Thereby, the journal that publish more TES papers is Applied Thermal Engineering, followed by Applied Energy, Solar Energy and Energy Conversion and Management.

This trend is the current but it has been changing over the years. For example, until 2000 the journal that published more TES papers was Energy Conversion and Management followed by Energy and International Journal of Heat and Mass Transfer, and the current trend is susceptible to be changed again.

In Table 5, TES performance ratio is shown, as well as journal impact factor and quartile score for each of the top 20 TES journals. The performance ratio is calculated by dividing the number of TES cites over the total TES publications. Renewable & Sustainable Energy Reviews journal has the better performance ratio, which was expected since it's a reviews journal. Other journals such as Solar Energy, Energy Conversion and Management, Applied Energy, and Solar Energy Materials and Solar Cells, have a higher impact factor regardless that they are not leading on number of publications. This suggests a greater quality on their contents.

3.5. Funding

Special programs to encourage research performance include funding efforts. These fundings have been properly reported on the last decade. In Fig. 10 the relation between the special fundings and research publications is shown. It is undeniable that fundings have a main role on current TES research exponential growth; the main two world TES actors, EU and China, have strong funding programs (by EU Commission and Chinese Academy of Sciences, respectively).

3.6. TES technology bibliometrics evolution

The publications classified by TES technologies (SHTES, LHTES, TCS) are analysed in this section.

One of the most important analyses of this bibliometric study is the one shown in Fig. 11. This figure displays the total number of publication per years and per TES technology during the last 20 years.

The publishing evolution over years is clearly exponential. The technology that accounts for the highest amount of publications per

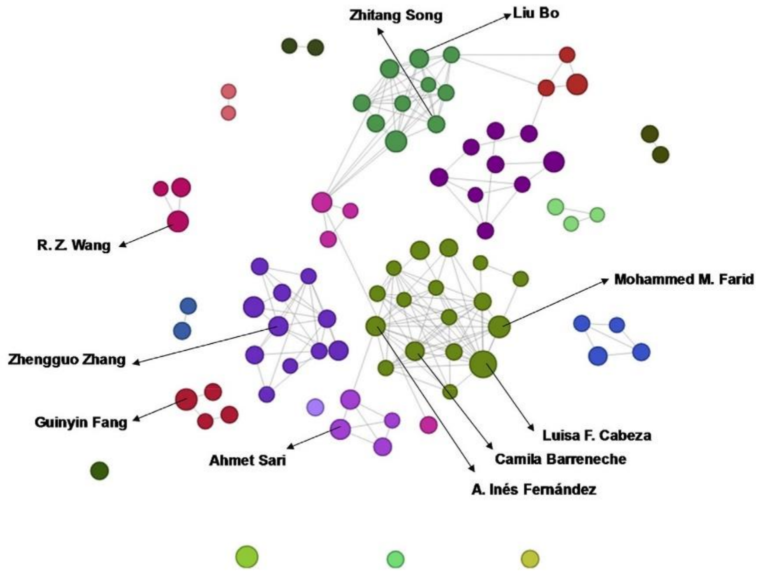

Fig. 8. Authorship communities based on the affiliation interaction of published papers in TES field (Calderón, 2018).

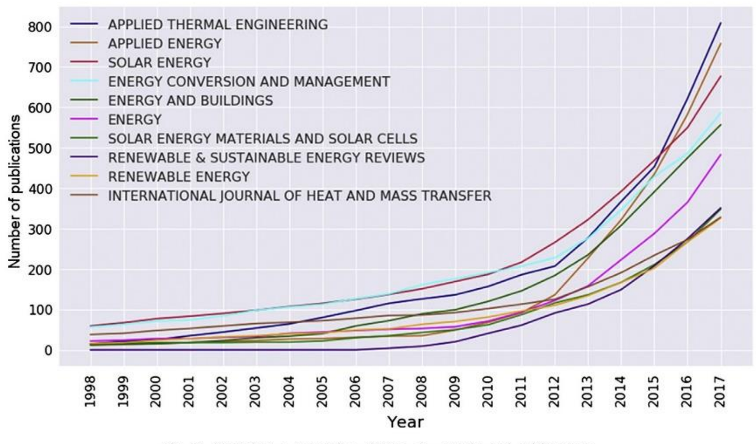

Fig. 9. Cumulative journal evolution, by number of publications.

year is LHTES. Moreover, the technology whose publication increment per year is higher during the last year is SHTES, accounting for a 43% increment. The amount of publications regarding TCS is increasing although following a slow trend. This is highlighted for TES field since it is the most promising technology that allows achieving compact storage systems to be implemented in several fields as renewables, heating and cooling for buildings, etc.

SHTES publications per year are presented in Fig. 12(a). The trend has passed over some attempt of stagnation during the last 20 years but it is still increasing every year.

Fig. 12(b) shows the total SHTES publications by countries and Europe. Europe is by far the most publishing zone in the worldwide accounting around 1000 publications in SHTES, followed by China and USA, and Germany is the most publishing country in Europe.

Fig. 12(c) shows publication evolution over the last 20 years and the very high increase trend for China in the last 3 years is remarkable. The increment of publishing is in accordance with the economic growth that China is showing in the last years.

Fig. 12(d) and Table 6 present the top 10 authors publishing in SHTES sub-field and their cumulative evolution by number of publications. Again, Prof. Cabeza is the author with highest amount of publications in SHTES.

Increment of the number of publications on SHTES compared to the previous year is presented in Table 7, showing that China, India and Iran are making important growing efforts, while the other top 10 countries are making slightly but constant progress.

Finally, Table 8 shows the most relevant journals for SHTES along with their TES performance ratio, showing Applied Energy and Energy Conversion and Management as a non-review journal leaders on this area from this point of view.

Table 5
Top 20 journals in TES field.

JOURNAL	TES publications	TES cites	Performance ratio	Impact factor	Quartile scores
APPLIED THERMAL ENGINEERING	876	16,262	18.6	3.77	Q1-Q2
APPLIED ENERGY	829	19,619	23.7	7.90	Q1
SOLAR ENERGY	703	16,219	23.1	4.37	Q1
ENERGY CONVERSION AND MANAGEMENT	608	16,824	27.7	6.38	Q1
ENERGY AND BUILDINGS	589	13,522	23.0	4.46	Q1
ENERGY	513	9595	18.7	4.97	Q1
SOLAR ENERGY MATERIALS AND SOLAR CELLS	397	10,577	26.6	5.02	Q1
RENEWABLE & SUSTAINABLE ENERGY REVIEWS	393	20,194	51.4	9.18	Q1
RENEWABLE ENERGY	360	6601	18.3	4.90	Q1
INTERNATIONAL JOURNAL OF HEAT AND MASS TRANSFER	352	9031	25.7	3.89	Q1
JOURNAL OF SOLAR ENERGY ENGINEERING-TRANSACTIONS OF THE ASME	223	3677	16.5	1.37	Q3
INTERNATIONAL JOURNAL OF ENERGY RESEARCH	199	3098	15.6	3.01	Q2
THERMOCHIMICA ACTA	169	3623	21.4	2.19	Q2-Q3
INTERNATIONAL JOURNAL OF REFRIGERATION-REVUE INTERNATIONALE DU FROID	149	2737	18.4	3.23	Q1
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY	141	1608	11.4	4.23	Q1-Q2
ENERGIES	130	478	3.7	2.68	Q2
JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY	112	1198	10.7	2.21	Q2-Q3
INTERNATIONAL JOURNAL OF THERMAL SCIENCES	96	1948	20.3	3.36	Q1
RSC ADVANCES	92	641	7.0	2.94	Q2
JOURNAL OF HEAT TRANSFER-TRANSACTIONS OF THE ASME	88	1100	12.5	1.6	Q3

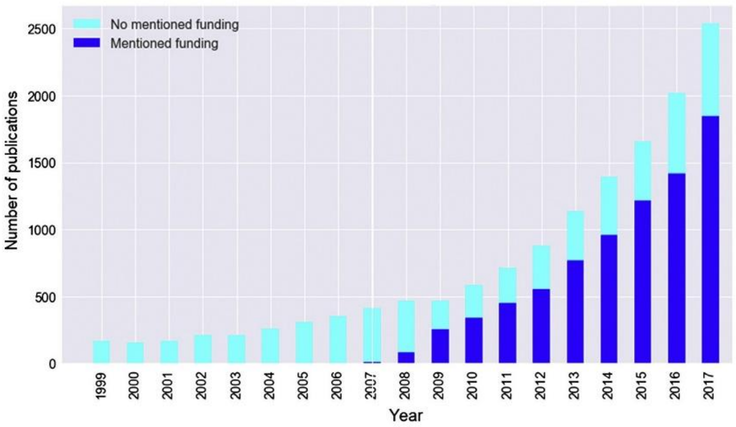

Fig. 10. Funding evolution for TES publications.

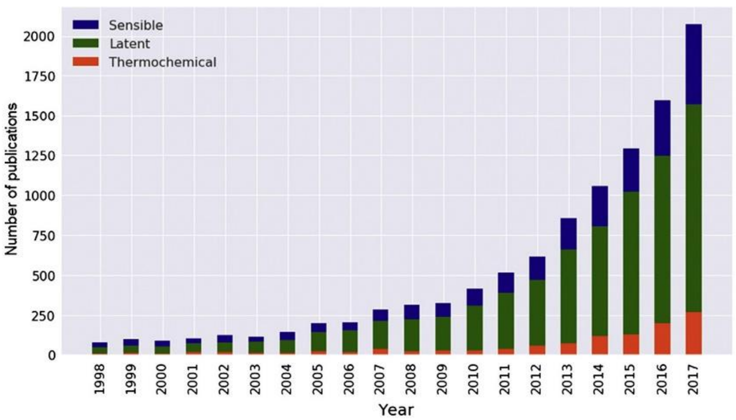

Fig. 11. Number of publications per year for each TES technology and forecast technology calculation for 2017.

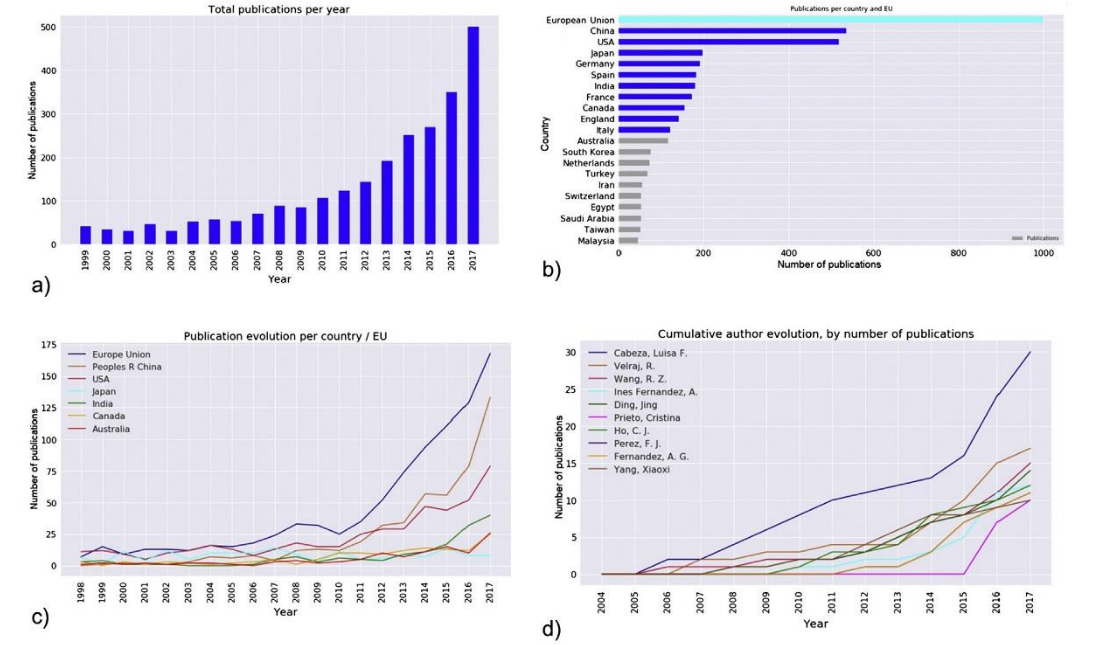

Fig. 12. (a) Total publications evolution in SHTES field per year; (b) Total publications in SHTES per country and EU; (c) Publication evolution per country and EU for SHTES; (d) Cumulative author evolution in SHTES field by number of publications.

Table 6
Top 10 authors in SHTES field.

Author	Afiliation	SHTES publications	Total SHTES cites	SHTES h index
Cabeza, Luisa F.	Universitat de Lleida, Spain	35	1004	16
Velraj, R.	Anna University Chennai, India	17	379	8
Wang, R. Z.	Shanghai Jiao Tong University, China	15	455	8
Ines Fernandez, A.	Universitat de Barcelona, Spain	15	225	7
Ding, Jing	Sun Yat Sen University, China	14	179	6
Prieto, Cristina	Abengoa Solar New Technologies S.A., Spain	14	85	6
Ho, C. J.	Sandia National Laboratories, USA	12	173	8
Perez, F. J.	Complutense University of Madrid, Spain	11	154	6
Fernandez, A. G.	Complutense University of Madrid, Spain	11	159	7
Yang, Xiaoxi	Dongguan University of Technology	10	189	6

Table 7
Country/region increment of SHTES publications compared to the accumulated from previous year.

Country	2017	2016	2015	2014	2013	2012	2011	2010	2009	2008
EU	21.8%	20.1%	20.9%	21.5%	20.3%	16.7%	12.6%	9.9%	14.5%	17.6%
China	38.1%	29.3%	26.2%	36.3%	27.6%	35.2%	26.4%	20.0%	27.7%	34.3%
USA	18.5%	13.9%	13.3%	16.5%	11.4%	12.8%	12.4%	8.1%	8.8%	11.8%
Japan	4.4%	4.6%	8.7%	4.5%	5.5%	4.3%	3.7%	8.9%	2.5%	8.0%
India	33.3%	36.4%	23.9%	18.3%	17.6%	8.5%	11.9%	16.7%	9.1%	26.9%
Canada	20.7%	11.0%	13.5%	17.1%	17.1%	14.8%	19.6%	24.4%	13.9%	2.9%
Australia	30.6%	13.3%	25.0%	22.4%	16.7%	31.3%	18.5%	12.5%	9.1%	22.2%
South Korea	18.6%	9.3%	17.4%	21.1%	15.2%	22.2%	22.7%	46.7%	7.1%	16.7%
Turkey	6.8%	13.5%	8.3%	4.3%	12.2%	7.9%	18.8%	10.3%	7.4%	22.7%
Iran	74.1%	28.6%	10.5%	26.7%	50.0%	11.1%	125.0%	33.3%	0.0%	–

In the case of LHTES publications, the evolution per year during the last 20 years is presented in Fig. 13(a). The trend is clearly exponential without stagnation during the last 2 decades.

Fig. 13(b) shows the total LHTES publications by countries and Europe. Europe is by far the most publishing zone in the worldwide accounting around 2300 publication in LHTES, followed by China and USA and France is the most publishing country in Europe.

Fig. 13(c) shows publication evolution over the last 20 years and again, it, the very high increase trend that followed China between 2014 and 2016 is remarkable in concordance with the high economic

Table 8
Top 10 journals in SHTES field.

JOURNAL	SHTES publications	SHTES Cites	Performance Ratio	Impact factor	Quartile scores
APPLIED THERMAL ENGINEERING	171	2543	14.9	3.77	Q1-Q2
SOLAR ENERGY	164	3358	20.5	4.37	Q1
APPLIED ENERGY	144	3141	21.8	7.90	Q1
ENERGY CONVERSION AND MANAGEMENT	109	2372	21.8	6.38	Q1
RENEWABLE & SUSTAINABLE ENERGY REVIEWS	93	3367	36.2	9.18	Q1
ENERGY	83	1603	19.3	4.97	Q1
SOLAR ENERGY MATERIALS AND SOLAR CELLS	75	1147	15.3	5.02	Q1
ENERGY AND BUILDINGS	63	837	13.3	4.46	Q1
RENEWABLE ENERGY	63	838	13.3	4.90	Q1
JOURNAL OF SOLAR ENERGY ENGINEERING-TRANSACTIONS OF THE ASME	56	868	15.5	1.37	Q3

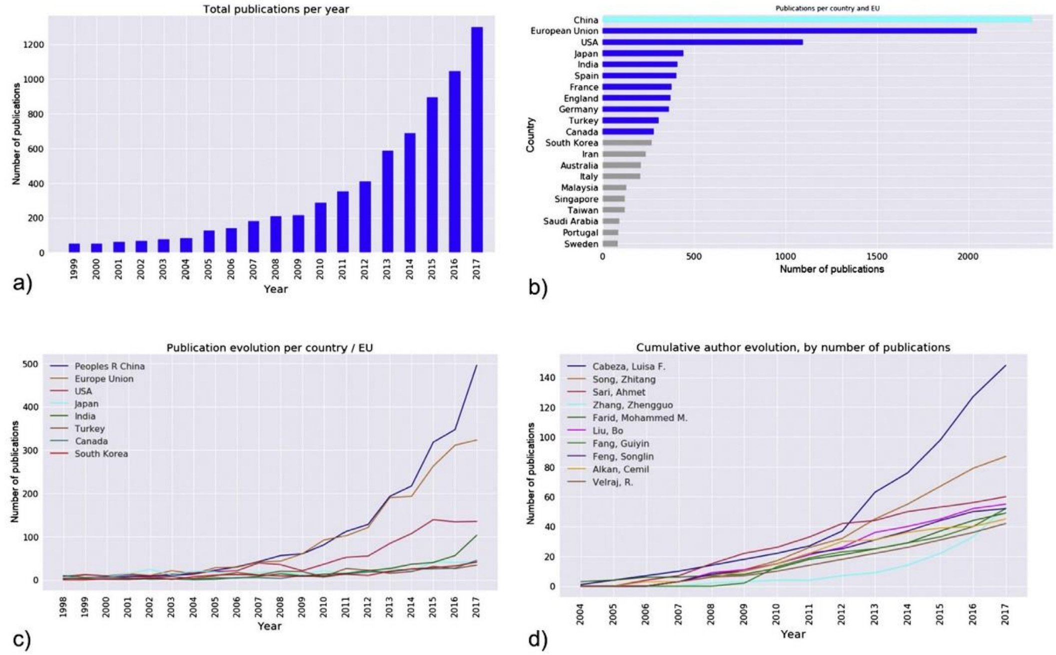

Fig. 13. (a) Total publications evolution in LHTES field per year; (b) Total publications in LHTES per country and EU; (c) Publication evolution per country and EU for LHTES; (d) Cumulative author evolution in LHTES field by number of publications.

Table 9
Top 10 authors in LHTES field.

Author	Affiliation	LHTES publications	Total LHTES cites	LHTES h index
Cabeza, Luisa F.	Universitat de Lleida, Spain	167	7306	36
Song, Zhitang	Shanghai Institute of Microsystem & Information Technology, China	87	778	16
Sari, Ahmet	Gaziosmanpasa University, Turkey	66	3755	32
Zhang, Zhengguo	South China University of Technology, China	61	1154	18
Farid, Mohammed M.	University of Auckland, New Zealand	57	4020	25
Liu, Bo	National Institute of Advanced Industrial Science & Technology, Japan	55	554	13
Fang, Guiyin	Nanjing University, China	54	1385	23
Feng, Songlin	Shanghai Institute of Microsystem & Information Technology, China	52	586	14
Alkan, Cemil	Gaziosmanpasa University, Turkey	48	1972	25
Velraj, R.	Anna University Chennai, India	48	1797	21

growth that China is showing the last years.

Fig. 13(d) and Table 9 present the top 10 authors publishing in LHTES sub-field and their cumulative evolution by number of publications. Again, Prof. Cabeza is the author with the highest amount of publications in LHTES.

Increment of the number of publications of LHTES compared to the total from previous year is presented on Table 10, showing that EU, USA and Japan are slowing down their research growth, while the

Table 10
Country/region increment of LHTES publications compared to the accumulated from previous year.

Country	2017	2016	2015	2014	2013	2012	2011	2010	2009	2008
China	29.9%	26.5%	32.0%	28.0%	33.1%	28.1%	32.7%	30.9%	29.7%	38.4%
EU	20.2%	24.1%	25.6%	23.2%	29.5%	23.2%	24.3%	28.0%	22.4%	19.1%
USA	14.9%	17.4%	22.0%	20.3%	19.0%	14.2%	15.5%	12.0%	7.6%	14.4%
Japan	10.8%	11.5%	13.4%	7.0%	10.8%	7.0%	5.2%	10.0%	6.1%	10.1%
India	38.0%	26.0%	22.9%	25.9%	23.0%	22.8%	19.5%	20.3%	16.4%	34.1%
Turkey	13.4%	11.5%	15.8%	10.7%	9.3%	15.7%	22.8%	6.5%	21.6%	29.4%
Canada	20.5%	14.1%	15.0%	17.6%	14.5%	17.0%	15.2%	7.0%	13.2%	4.1%
South Korea	19.2%	17.6%	18.2%	19.4%	18.3%	10.1%	15.1%	11.7%	11.6%	15.0%
Iran	43.7%	45.2%	30.0%	50.9%	51.4%	59.1%	69.2%	85.7%	40.0%	0.0%
Australia	35.2%	29.1%	34.1%	49.1%	44.7%	46.2%	36.8%	18.8%	0.0%	14.3%

Table 11
Top 10 journals in LHTES field.

JOURNAL	LHTES publications	LHTES cites	Performance ratio	Impact factor	Quartile scores
APPLIED THERMAL ENGINEERING	566	11,948	21.1	3.77	Q1-Q2
APPLIED ENERGY	419	11,771	28.1	7.90	Q1
ENERGY AND BUILDINGS	386	9482	24.6	4.46	Q1
ENERGY CONVERSION AND MANAGEMENT	371	13,089	35.3	6.38	Q1
SOLAR ENERGY MATERIALS AND SOLAR CELLS	284	8750	30.8	5.02	Q1
INTERNATIONAL JOURNAL OF HEAT AND MASS TRANSFER	266	6732	25.3	3.89	Q1
SOLAR ENERGY	244	7461	30.6	4.37	Q1
ENERGY	198	4003	20.2	4.97	Q1
RENEWABLE & SUSTAINABLE ENERGY REVIEWS	191	14,417	75.5	9.18	Q1
RENEWABLE ENERGY	149	3853	25.9	4.90	Q1

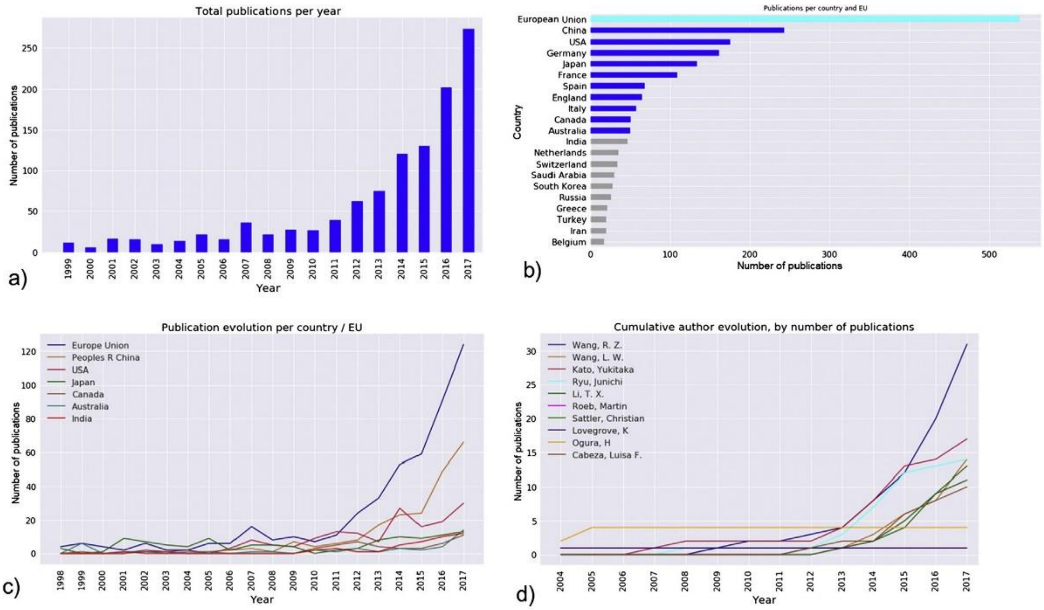

Fig. 14. (a) Total publications evolution in TCS field per year; (b) Total publications in TCS per country and EU; (c) Publication evolution per country and EU for TCS; (d) Cumulative author evolution in TCS field by number of publications.

other, mainly China, India, Iran and Australia are still on a strong growing rate.

Finally, Table 11 shows the most relevant journals for LHTES along with their TES performance index, showing that Applied Energy, and Energy Conversion and Management journals have the highest performance ratio, as defined in this work, as non-review journal leaders on LHTES.

In the case of TCS publications, the evolution per year during the last 20 years is presented in Fig. 14(a). The trend is clearly exponential without stagnation during the last 7 years.

Fig. 14(b) shows the total TCS publications by countries and Europe. Europe is also by far the most publishing zone in the worldwide

Table 12
Top 10 authors in TCS field.

Author	Afiliation	TCS publications	Total TCS cites	TCS h index
Wang, R.Z.	Shanghai Jiao Tong University, China	35	553	12
Wang, L.W.	Hebei University of Science & Technology, China	18	274	7
Kato, Yukitaka	Tokyo Institute of Technology, Japan	17	155	7
Ryu, Junichi	Chiba University, Japan	14	129	6
Li, T.X.	Shanghai Jiao Tong University, China	14	143	7
Roeb, Martin	German Aerospace Centre (DLR), Germany	11	228	7
Sattler, Christian	German Aerospace Centre (DLR), Germany	11	228	7
Lovegrove, K	IT Power, Australia	11	267	8
Ogura, H	Chiba University, Japan	11	143	7
Cabeza, Luisa F.	Universitat de Lleida, Spain	10	269	9

Table 13
Country/region increment of TCS publications compared to the accumulated from previous year.

Country	2017	2016	2015	2014	2013	2012	2011	2010	2009	2008
EU	33.1%	32.0%	26.2%	30.8%	23.7%	20.9%	10.6%	7.2%	11.5%	10.1%
China	44.9%	50.0%	32.4%	45.1%	50.0%	30.8%	30.0%	25.0%	77.8%	12.5%
USA	22.2%	16.4%	16.0%	37.0%	10.6%	22.2%	31.7%	28.1%	14.3%	21.7%
Japan	11.1%	10.4%	9.3%	11.5%	10.1%	3.9%	2.7%	0.0%	5.7%	7.7%
Canada	28.9%	18.8%	10.3%	11.5%	18.2%	46.7%	50.0%	42.9%	0.0%	0.0%
Australia	41.2%	13.3%	7.1%	12.0%	4.2%	14.3%	5.0%	11.1%	0.0%	5.9%
India	38.7%	47.6%	50.0%	55.6%	12.5%	14.3%	75.0%	100.0%	0.0%	0.0%
Switzerland	22.2%	28.6%	16.7%	12.5%	6.7%	15.4%	0.0%	0.0%	0.0%	8.3%
Saudi Arabia	31.8%	83.3%	71.4%	40.0%	25.0%	100.0%	0.0%	100.0%	0.0%	0.0%
South Korea	25.0%	53.8%	30.0%	25.0%	60.0%	66.7%	50.0%	0.0%	0.0%	0.0%

Table 14
Top 10 journals in TCS field.

JOURNAL	TCS publications	TCS cites	Performance ratio	Impact factor	Quartile scores
SOLAR ENERGY	89	1686	18.9	4.37	Q1
APPLIED ENERGY	89	1264	14.2	7.90	Q1
APPLIED THERMAL ENGINEERING	88	1022	11.6	3.77	Q1-Q2
ENERGY CONVERSION AND MANAGEMENT	53	538	10.2	6.38	Q1
ENERGY	51	822	16.1	4.97	Q1
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY	46	419	9.1	4.23	Q1-Q2
RENEWABLE & SUSTAINABLE ENERGY REVIEWS	44	1878	42.7	9.18	Q1
SOLAR ENERGY MATERIALS AND SOLAR CELLS	28	758	27.1	5.02	Q1
JOURNAL OF PHYSICAL CHEMISTRY C	20	368	18.4	4.48	Q1-Q2
ENERGY AND BUILDINGS	20	294	14.7	4.46	Q1

accounting around 550 publications in TCS, followed by China and USA and Germany is the most publishing country in Europe.

Fig. 14(c) shows publication evolution over the last 20 years. The publication evolution was linear until 2012 when Europe started a high increment trend that is still growing. China started this growth trend in 2015 and it has a remarkable increment during this last period (2015–2017).

Fig. 14(d) and Table 12 present the top 10 authors publishing in TCS sub-field and their cumulative evolution by number of publications. In this case, Prof. Wang is who has published more articles in TCS sub-field, and Prof. Cabeza has the 10th position in this sub-field.

Increment of the publications on TCS compared to the previous year is presented in Table 13, showing that every country in the list is making a remarkable effort to develop TCS technology. Leaders like EU, China or USA are growing at important rates. Other minor leaders such as Canada, India, Australia and Saudi Arabia are growing at rates that can make them top leaders in the following years.

Table 14 shows the most relevant journals for TCS along with their TCS performance index, showing that Solar Energy journal is the leader with a good performance. Nevertheless, Solar Energy Materials and Solar Cells journal has the highest performance for non-review journals showing higher quality on their publications in TCS.

4. Conclusions

TES scientific research field is a very important one accounting for more than 14,000 publications on relevant journals during the last decades. It is the first time that bibliometric analysis tool is applied in TES field.

This study presents the publication evolution in TES field over the last two decades, per year, per country, per authors, per journal, and per TES technology taking into account SHTES, LHTES, and TCS. Moreover, the interaction between co-authorship countries have been studied as well as author's community based on the co-authorship connections.

Furthermore, 14 research communities in TES field were detected by this bibliometric analysis, and the top 10 authors in this field leading most of these research communities.

Europe is leading the research in TES field since is the zone of the world that accounts for more amount of publications, more authors, and the main interactions are between Europe and all the countries of the world. In addition, China has suddenly increased the amount of TES publications per year, and this fact is directly related to the economic growth of this country. Therefore, the maturity of this technology is high but there is still place to continue performing research in TES field. Especially in TCS, this accounts for the lowest amount of published papers. Besides, the growth of number of publications, in this sub-field has appeared during the last years of this decade.

Acknowledgements

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High temperature systems using solid particles as TES and HTF material: A review

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HIGHLIGHTS

- Several issues must be solved to transfer to the market solid particle CSP plants.
- Solid particles combine roles: as TES media and HTF within CSP plants configuration.
- Review of operating conditions and parameters that make solid particles attractive.
- Review about whole system: the storage, heat exchangers and material conveyance.
- Solid particle systems can increase heat conversion efficiency to electric power.

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ABSTRACT

Thermal energy constitutes up to 90% of global energy budget, centering on heat conversion, transmission, and storage; therefore, the technology for harvesting solar energy worth to be developed. One of them is the concentrated solar power (CSP) solar towers where sun-tracking heliostats reflect solar radiation to the top of a tower where the receiver is located. The great advantage of CSP over other renewable energy sources is that energy storage is feasible, particularly when the heat transfer fluid (HTF) is also used as thermal energy storage (TES) material which is the case of solid particles. A lot of development efforts are under way for achieving commercial direct solar solid-particle systems. Solid particle systems for transferring high temperature thermal energy are purposed for increasing the efficiency of these systems when converting heat into electric power. This review recapitulates the concept of these systems taking into account the main receiver designs, particle conveyance, particle storage systems and components, the heat exchanger, and the main challenges that must be overcome to split this technology as a commercial one, especially from the materials availability point of view. This review summarizes the actual status of the use of solid particles for TES and as HTF for CSP Tower, and condenses all the available information and classifies them considering the main functional parts and remarking the current research in each part as well as the future challenging issues.

1. Introduction

Thermal energy constitutes up to 90% of global energy budget, centering around heat conversion, transmission, and storage [1]. Almost all this thermal energy comes directly or indirectly from sunlight. Therefore, the technology for harvesting solar energy is worth to be developed. Concentrating sunlight technologies allow increasing the operation temperature by increasing the type of applications and their efficiency.

Concentrating Solar Power (CSP) potential changes according to the region where is developed. Moreover, CSP can reach up to 11.3% of global electricity production with the appropriate support [2]. The installed capacity of CSP in 2015 reached 4650 MW compared with 1256 MW on 2010 [3]. Global technical potential of CSP amounts to almost 3,000,000 TWh/y against 22,000 TWh/y consumed globally on electricity [4,5]. It is expected that CSP will reach more installed capacity that geothermal [6]. CSP technologies have most favorable potential for North Africa, the Middle East, northwestern India, the southwestern United States, Mexico, Peru, Chile, the western part of China and Australia; and more moderate potential on extreme southern

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Europe, Turkey, central Asian countries, Brazil, Argentina and other locations on USD and China [2,7]. Initially CSP were more developed on Spain and the United States, but recently other markets are developing CSP plants such as de 160 MW plant on Auarzazete, Morocco [6].

Solar energy can be harnessed by different technologies [8,9]. Particularly, CSP with central tower is a promising option because of the high power that can be reached, high efficiency of the power block (due to the high temperatures that can be reached), high land efficiency and large scale heat storage [2,4]. On CSP towers, sun-tracking heliostats reflect solar radiation to the top of a tower where the receiver, or solar absorber, is located [10]. Then, solar heat is transferred to a heat transfer fluid (HTF) in the receiver [11], in order to get the heat energy input into the system. After the receiver captures the heat on the HTF, thermal energy is transported either for conversion or for storage. The energy transport consists on moving the HTF through the system pipe network that connects the storage and energy exchange systems. If the energy conversion takes place on a different cycle, the collected thermal energy is carried away by the HTF that will transfer heat to the electricity conversion cycle (or power block) using a heat exchanger (HEX) [12]. Nevertheless, when the energy is stored for further use on conversion, there are two options to store it: the first is to keep the HTF in a storage device, and the second to use a HEX to store heat in a different media.

Unlike other renewable energy sources (except hydro), solar thermal CSP plants have the inherent capacity to store high inventory of energy (in form of heat) for later conversion to electricity [2] at low cost. In this case, it is desirable that the HTF and thermal energy storage (TES) material is the same.

CSP-TES systems are classified depending on whether it has an active or passive TES, a direct or indirect storage unit, or if the system is open or closed (only for active) [5]. Active TES is divided into direct storage, which refers when the HTF is used as the heat storage medium, and indirect storage, when other material is heated using a heat exchanger in order to save heat [13]. CSP-TES closed systems use controlled pressure and environment inside the system, while open systems use the same outside ambient atmospheric conditions for the control. Finally, these systems can also be classified depending on the kind of receiver used and if the HTF is directly or indirectly (using another material/structure as HEX) irradiated by the concentrated sunlight [14].

The main motivations for developing and enhancing CSP systems are: increasing the temperature (thus making thermal energy to electricity conversion more efficient), decreasing energy losses from receivers (and therefore using a smaller solar field), and using low cost materials that could meet the optimal operating conditions [12]. The current state of the art of the technology that has better commercial application for CSP towers is the one that uses molten salts as HTF [15], and has the advantage that it is also a good energy storage medium [12,16]. The major drawback of molten salt systems is the allowable operating temperature range, which is limited by the temperature of solidification of the solar salt at the low end, and the onset of thermal decomposition and corrosiveness at the high end [17]. Because of this, conventional central receiver technologies are limited to temperatures of around 565 °C [15]. For higher temperatures, molten nitrate salt (the most common salt used) becomes chemically unstable, producing oxide ions that are highly corrosive, which results in significant mass loss [18], and corrosion thru the storage, HEX, receiver and conveyance system [16].

One solution to overcome these drawbacks is using solid particles as TES material and HTF [11]. The solid particle TES system achieves both high performance at high temperature, and low cost from the material perspective [19]. Direct absorption receivers using solid particles that fall through a beam of concentrated solar radiation for direct heat absorption and storage have the potential to increase the maximum temperature of the heat transfer media to more than 1000 °C [20]. A CSP system that operates from 600 °C to more than 1000 °C is possible because of the use of stable materials and the minimized thermal losses due to thermal self-insulation of particles in the storage medium [21]. The material and maintenance costs are expected to be lower for solid media storage systems [17].

Thus, solid particles have three main advantages as storage media, relative to more conventional materials such as molten salts:

- They are chemically inert and stable beyond 1100 °C.
- They are capable of storing energy over a greater temperature span (effectively increasing storage density in a sensible energy-based system)
- They are expected to be relatively low cost.

The first studies on direct absorption solar receivers started in the early 1980 s with two concepts, the fluidized bed receiver and the free falling particles receiver. In the first concept, the solid particles were fluidized in a transparent tube but did not flow outside, there was no solid circulation. In the free-falling particles curtain concept, the solid drop directly into the concentrated solar beam from the top of the receiver, and is heated during the time of its pass through the concentrated radiation. Particle selection and radiative heat transfer modeling have been proposed [22,23]. After about twenty years without significant new developments, this concept has been again proposed as a promising option for a new generation of high temperature solar thermal concentrating plants. Improved models have been developed and validated by on-sun experiments at pilot scale [11,24–28].

This review summarizes the actual status of the use of solid particles for TES and as HTF for CSP Tower applications taking into consideration the main components of the technology: the receiver, the heat exchanger and the TES unit. Moreover, the review condenses all the available information and classifies them considering the main functional parts and remarking the current research in that part as well as the future challenging issues.

2. Solid particle for use on Concentrating Solar Power (CSP)

Several development efforts are under way for achieving commercial direct solar solid-particle open systems. Several studies, simulations, experiments and pilot plant tests have been or are being performed including receiver design, conveyance systems, material storage and heat exchangers. Nevertheless, the solid-particle material itself has been studied according to the plant engineering specifications, and the availability of materials or a formal material selection has not been performed.

The main approach consists in concentrating solar power reflected by heliostats in a central tower, which has a receiver for capturing concentrated sunlight into the solid particles. This particles are moved across a specially designed conveyance system to a first storage, in which material is stored until its moved (by a fluidized bed system) into a heat exchanger (HEX) in order to transfer the heat to a generation cycle. After losing heat, the particle material is stored in a second silo before getting moved again to the receiver [19]. Solid Particle CSP general concept is shown in Fig. 1. This system is similar to the current state-of-the-art molten salts system [29], but almost all the components must be specially designed for working with solid particles.

Current CSP central tower receiver systems are limited to power-cycle efficiencies up to 40%. By reaching temperatures over 650 °C, power-cycle efficiency can increase up to 50–60% by using more efficient thermodynamic cycles that require higher operation temperature (like Brayton cycle) [20,30–32]. Additional to this, cheaper thermal storage will be allowed, lowering the leveled cost of electricity [20].

3. Solar receiver

There are several studies suggesting different designs for particle

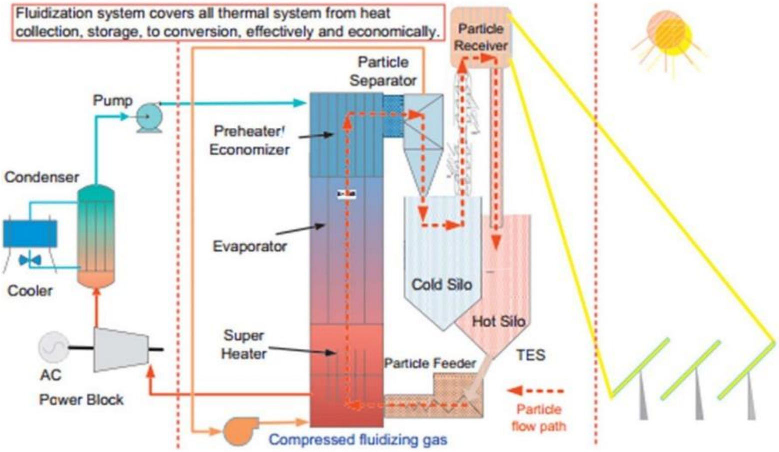

Fig. 1. CSP solid particle system with TES and fluidized bed [21].

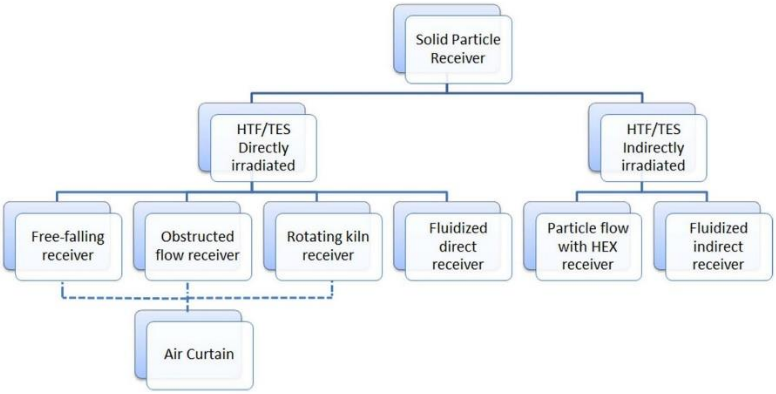

Fig. 2. Solid particle receiver classification.

receivers [14,18,21,26,33–41]. Nonetheless, there are some receivers more developed that can be categorized as shown in Fig. 2. A receiver that is designed to allow the HTF to absorb directly the solar irradiance is called Direct Receiver; therefore, a receiver in which the HTF receives the heat from another material that has received the solar irradiance is called an Indirect Receiver.

The receivers are subcategorized according to their work principle. The most remarkable Direct Receivers are the Free-falling particle receiver, the Obstructed flow receiver, the Rotating kiln receiver and the Fluidized receiver. For the Indirect Receivers Particle flow with HEX receiver and the fluidized indirect receiver are the most developed.

Other related particle receiver designs and experimental evaluations have been performed, but they are not under the mentioned classification. Bertocchi [34] reported an experimental evaluation of a receiver which achieved temperatures over 2100 K. It consisted in a conical cavity isolated from ambient conditions by a quartz window. On this design, a gas/particle suspension was conducted at the focal plane near the window [42]. Another approach proposes to incorporate gas-based Brayton cycles, with the objective of increasing overall efficiency, and eliminate cooling water requirements [32,39].

A way to evaluate the performance of a receiver is the absorptance efficiency (also called collection efficiency). It is calculated by obtaining the ratio of the heat captured by the particles to the solar energy received, and it has a dependent relation to the solar absorption captured by the receiver [43]. Nonetheless the material has an important role to determine the absorptivity efficiency; it allows measuring the efficiency due to the receiver principle of work and design.

Nevertheless different approaches have been proposed, there are no studies available about the material compatibility between the HTF-TES material and the material in used to build the receivers. Also, the designs don't consider any of the interactions with the HTF-TES material properties and stability. Some of these interactions have been observed until prototype plant development [27] but there has not been reported any proper material selection.

Free falling receiver design was the first particle receiver conceived on the early 1980s by Sandia National Laboratories [44–46]. Despite the original interest on the 1980s [44–48], the research stopped until late 2000s, when solid particle receivers gain attention because of the molten salts central tower CSP efficiency-temperature limitations; and it has been under continuous development since then. Fig. 3 illustrates this increasing development based on the publications related showed on 5 year periods. Also, a projection is showed based on the number of publications reached in 2016 and the beginning of 2017 (dotted line). The projection was performed accounting the amount of publications during these two years. Then, this value was divided per month and extrapolating the result was the calculation use to produce this projection.

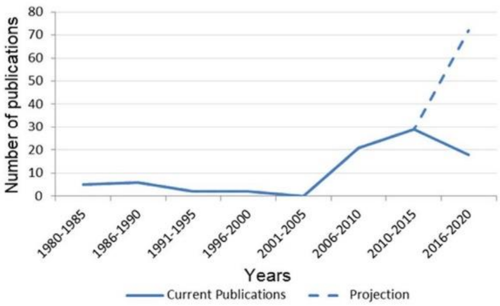

Fig. 3. Bibliometric statistics on CSP free falling receivers.

3.1. *Directly irradiated receivers*

The most innovative designs have been proposed for direct receivers; this is mainly because it is required to increase the irradiation exposure time of the HTF material to achieve the high temperatures desired. For directly irradiated receiver the importance of solid particle material absorptance is a priority [43].

3.1.1. *Free falling particle receiver*

The first approach for this design was developed during the 1980s. The design considered that the material should fall through a receiver forming a material curtain (Fig. 4) but the temperature that the material could achieve was at most of 250 °C [14]. Recent development efforts focus on achieving temperatures above 650 °C by increasing the irradiance exposure time [14].

Figs. 4 and 5 show the proposed geometry. Particles inside the receiver are heated by concentrated sunlight which enters the receiver from an aperture on the bottom.

This system uses spherical solid particles that serve as HTF as well as TES media [24]. With this approach, temperatures can theoretically go over 1000 °C without changing chemically the material; also potentially high receiver efficiency can be reached due to direct solar absorption. Using low cost solid particle materials can reduce significantly TES costs, by storing heat at higher temperatures. Free falling receiver seems to be adequate for 10–100 MWe power-tower CSP systems [20].

Several tests have been made on the more advanced prototype for evaluating outlet power and temperature for free-fall and obstructed-fall designs [27]. Also, Siegel et al. [35] performed tests to evaluate the velocity distribution and concentration of the material over the particle curtain. The prototype was tested on Sandia National Laboratories with a 61 m central receiver with one thousand suns concentration in Albuquerque, NM.

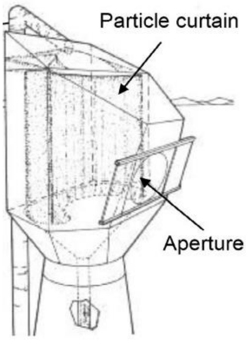

Fig. 4. Free falling particle curtain [26].

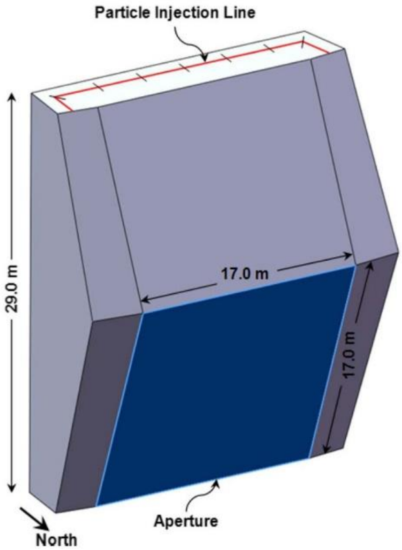

Fig. 5. Geometry of particle receiver [20].

Current research goes through the determination of the effects of the aperture size, tilt and dimension. Additional studies for developing these receivers includes different approaches to increment the residence time of the material in the receiver, and developing an air curtain for receiver aperture [26].

3.1.1.1. Particle recirculation. One way to increase residence time on the Free Falling Particle Receiver is to make the particles pass several times on the aperture for reaching the high temperatures desired [49]. Recirculation has shown, in simulations, to be effective when increasing the particle temperatures above 800 °C. In order to fully understand how the particles flow across the particle receiver, Computational Fluid Dynamics (CFD) models were developed. Several factors are included in the simulations such as solar irradiation, re-radiation and emission from the cavity walls, convection, wall conduction, and two-phase particle/air flow [35].

The strategy is to release colder particles into the locations, within de receiver, where the irradiance is lower, to preheat the particles before going into high irradiated regions [50]. Also, it has shown to reduce heat loss effect caused by external wind. Other variables had been studied, like particle size effect, in order to found their relation with the stability of the recirculation system [26] as shown in Fig. 6. In addition, heat transfer coefficient has shown to be directly related to the particle velocity, and particle volume fraction [11].

3.1.2. *Obstructed particle flow receiver*

As mentioned before, the increase of the irradiance exposure time of the solid particle material is necessary to approach the desired temperature. Another way proposed to do this is to mechanically obstruct the particle flow through the receiver using different kind of obstacles [18]. For this, different options have been proposed:

- **Ceramic porous structures.** Consists on using porous interconnected structures in which the particles go through by gravity; increasing the falling time of the particles and therefore, increasing the irradiance exposure time. Additionally, the amount of particle attrition due to wind and dispersion is considerably reduced. Small scale tests have already been performed for thousands of cycles

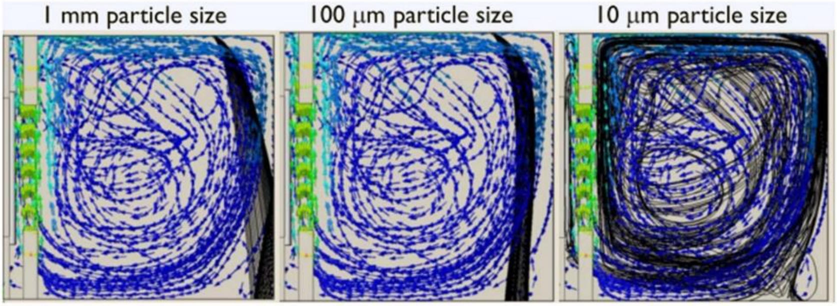

Fig. 6. Simulations of the free falling curtain stability impacted by particle size [26].

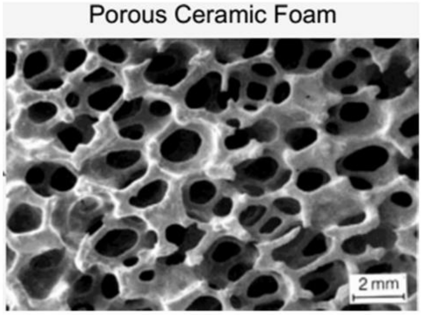

Fig. 7. Porous structure SPSR [26].

[26,50]. Fig. 7 shows the morphology of the proposed porous structure. Irradiance uniform distribution on the material flow is important for getting to the desired temperatures when material reaches the hot storage tank. Also, based on the current tests already performed, research for finding a material for the porous structure that can mitigate the deterioration due to the material flow and the high temperature is needed.

- **Porcupine structure.** This way to increase residence time is based on placing quills inside the receptor that interfere with the particle flow [26]. Fig. 8 illustrates this kind of structure. There has been some laboratory scale testing reported for this kind of structure [51] considering different mesh counts. Nevertheless, there are no considerations about the best particle material selection.

Some experimental and simulations evaluation of the different structures considering only the residence time on standard conditions are reported [52]. Also, two kinds of particles have been tested for fluency testing. Nevertheless, no clear analysis and recommendations for material selection has been made.

Finally, several aspects need to be considered about the particle material itself (heat capacity, density, thermal conductivity, etc.) to reach high temperatures on the receiver and not only the system parameters and design.

3.1.3. Rotating kiln receiver

Since the first studies of solid particle materials for solar power tower, rotating/centrifugal receiver were proposed [53]. The working principle, shown in Fig. 9 is to feed the particles into a rotating kiln which delays the particle fall by using centrifugal force against the kiln walls. These particles are irradiated from the particle outlet aperture [14]. Tests have been made in a ~10 kWth laboratory scale prototype by Wu et al. [40] at different power levels, mass flow and inclinations.

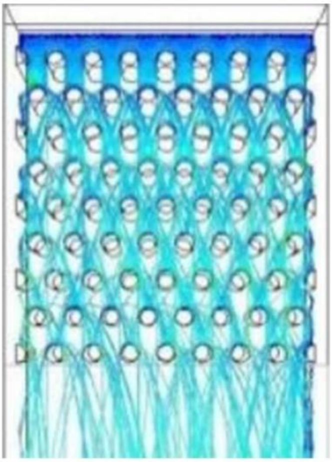

Fig. 8. Porcupine structure [26].

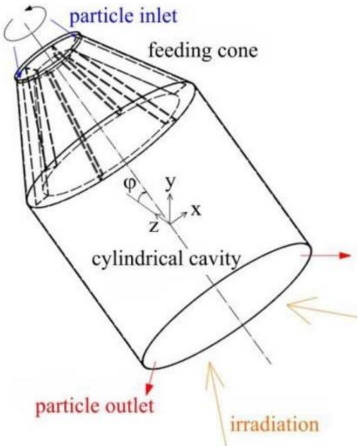

Fig. 9. Rotary kiln/centrifugal particle receiver [40].

Controllability, receiver vibration stability and thermal stability have been proved to be possible at this scale.

Current research is based on maintaining stable mass flow rate at large scale, minimizing the impact of the energy spent on moving the kiln and reliability on larger receivers [14].

3.1.4. Wind effect on open receivers

Wind effect of solar power towers using open receivers can be considerable due to the height of the tower above the ground (which can be located even at 250 m above the ground) [24]. Wind speed at those heights is considerable higher that current lab prototype or pilot plant experimental tests at lower altitudes [54].

Constant winds can enter through the radiation aperture producing air convection by the temperature difference with the air inside the receiver, and even ejecting particles from the receiver (Fig. 11). Therefore, impact on the overall efficiency of the receiver can be considerably affected. In order to prevent these problems, aerowindows have been proposed. It consists on hot-air jet curtains near the aperture of the receiver produced by a blower, which isolates the inner atmosphere from the outer [38] without having any effect on the optical performance of the receiver. It has been calculated that efficiency can be increased nearly 10% using this solution depending on wind speed [50].

Several experiments have been performed to evaluate the aerowindow effect. Increasing air speed on the curtain does not necessarily means increasing efficiency, therefore determining the best speed is complex. This effect is caused by the combination of the high speed wind and the air jet, that can produce turbulence inside the cavity [38]. Performance experiments have been carried out at different aerowindow temperatures and air jet speeds, as well as at several external wind speeds. The temperature effect has shown small influence on the overall receiver efficiency [38].

Another solution to get the way around the wind effect is to use a beam-down solar concentrator, in which solar radiation is reflected to the ground while being concentrated, replacing the tower. This concept has been studied for current molten salts systems [55,56], and has been recently tested on a pilot plant in Sicily, Italy [57]. Nevertheless, costs of the high temperature heliostats have not been proved to be lower enough to be viable for real plant implementation.

Finally, other recirculation options have been proposed, such as the suction-recirculation shown in Fig. 10. In this approach, part of the HTF material is suctioned from behind the receiver and then separated by a cyclone while the air is pumped again to the material entrance of the receiver minimizing the thermal and material loss from the outside [58]. This recirculation is proposed for managing the wind effect, and is not considered or designed for increasing the particle residence time in the receptor.

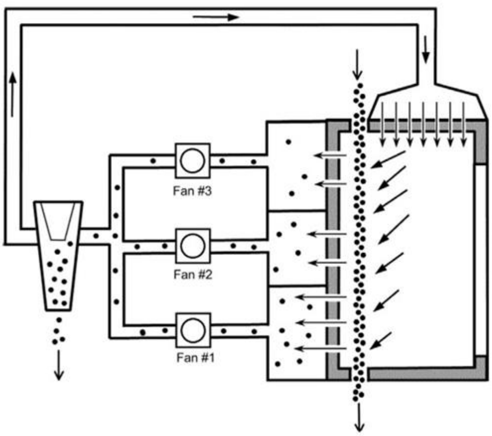

Fig. 10. Suction recirculation receiver [58].

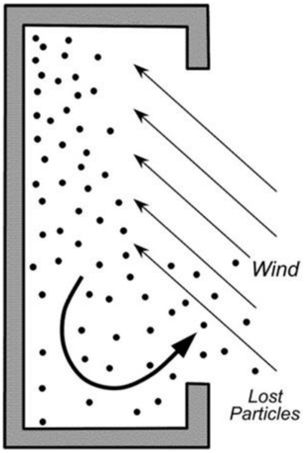

Fig. 11. Wind effect on the receiver [58].

3.1.5. Fluidized direct receiver

This receiver design consists on using fluidization to control mass flow rate and therefore increase de irradiance exposure time. Also, other benefits are that the effects of the wind at the receptor are mitigated.

Several test have been made using single or multiple tube arrays since the 1980s [11,28,53,59]. All of the reported designs and tests have been performed using a quartz tube. Nevertheless, none of them evaluate the influence of the material optical properties on the receiver's efficiency.

Different materials have been evaluated, finding some restrictions for the solid particle material [28]. It was found that a very small particle size lowers efficiency, while too large particles difficult fluidization. Optimal size was found between 0.5 and 1 mm mean size diameter for cold fluidization, but is expected to change for high temperature [28]. On single tube experiments temperatures have reached to 867 °C, while on multiple tube array has reached 624 °C [59].

Numerical simulation has been made and was found that heat transfer between air and particles is good, showing differences under 25 °C [60]. Efficiency calculations showed that when the air flow was higher, the outlet temperature was lower but the efficiency was higher. Also, increasing the input temperature (which will correspond with increasing the solar irradiance) increases the outlet temperature but lowers the efficiency [60]. This behavior contradicts the objective of the whole solid particle CSP concept, which relies on reaching high temperatures to increase the electricity generation cycle efficiency. Therefore, a correct balance between the two efficiencies should be reached in order to make this design viable.

On other experimental tests it was found that a good air flow distribution on the tube reflects on a good overall performance, and that the fluidized states depends also on the temperature difference between the particles and the air [59].

Future work for this receiver design should include ways to reduce the thermal loss on the external walls of the tube [60], getting more accurate optical concentrating ratio, improving the design of the air inlet, define the optimal particle parameters on high temperature fluidization and optimize the design of the receiver according to the irradiation area [28].

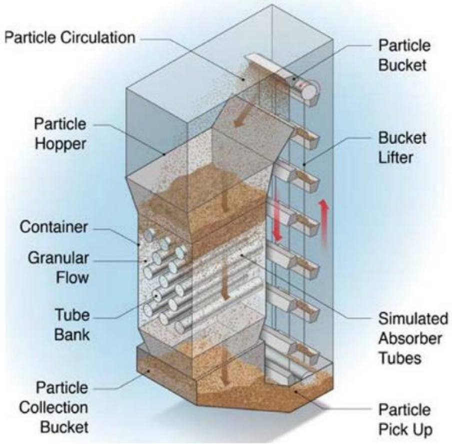

Fig. 12. Particle flow with HEX receiver [36].

3.2. *Indirectly irradiated receivers*

Indirect receiver concept relies on using solid particle materials as HTF but use another surface to receive the solar irradiation. This can be convenient for using solid particle materials without a high solar absorptance. Nevertheless, exergy on heat exchange between the surface and the particles must be considered [19].

Two main designs have been proposed for indirect receiver according to their particular principle of work.

3.2.1. *Particle flow integrated with heat exchanger (HEX) receiver*

SunShot CSP program [61] includes the design of another approach for particle receiver. The main objective of this program is to design a high-temperature particle receiver and heat-exchanger system, and also build a prototype receiver that can reach a thermal efficiency over 90%, reaching a fluid temperature greater than 650 °C, and particles outlet temperature of 800 °C [36]. The general concept for the particle receiver is shown in Fig. 12.

The work principle of this design is to exchange heat between an array of staggered tubes that receive concentrated sunlight on their interior surface, and the solid particles that flow downward the main receiver enclosure having contact with the exterior surface of the tubes [14].

Also, the SunShot initiative considers a simulation program called Bridge project [62]. This tool brings the fundamentals of heat transfer and material-fluid flow modeling for designing the particle receiver, making the system behavior easy to analyze. Another tool of particular importance for predicting the operation temperature is the Multiphase Flow with Interface eXchanges (MFIX) [62], with which transfer models for solid and fluid phases can be built.

Another related approach under development uses a two-phase flow as HTF, and solid particles as TES medium. It uses a near-blackbody receiver which transfer the heat to the HTF by an integrated fluidized-bed heat exchanger [37]. The main goal of these initiatives is to get up to 30 years of service life, with an overall cost estimated at less than $100/kW$_{th}$ and with heat storage costs under $6/kWh$_{th}$ [36].

As occurs on directly radiated designs, solid particle material selection plays a minimal role on this approach. Thus, material properties needed to ensure correct heat exchange and good flow thru the system should be taken into the account for future research.

3.2.2. *Fluidized indirect receiver*

This design is very similar to the fluidized direct receiver on work principle. However, the absorptance variable is limited to the material of the tube, extending the possible solid particle candidate materials. The solid particles are forced upward through the irradiated tubes by airflow increasing the heat transfer between the tube walls and the solid particles [14]. Both, single a multiple tube experiments have been reported and compared with fluidized direct receiver [11,41,53].

Using ceramic tubes is possible for this design, and can extend the operating temperature around 1000 °C with a good efficiency [11]. Also, ceramic tubes can allow a better thermal isolation than quartz improving the efficiency of the receiver. Nevertheless, heat loss can still be considerable and should be reduced. No efficiency has been reported on the experimental or theoretical analysis.

4. Particle conveyance through the system

One of the main concerns of particle conveyance is the system used to lift the particles up to the solar collector. Other elements that will carry the material have not been directly reported. Nevertheless, fluidized bed manufacturers and other suppliers have experience on studying erosion and corrosion protections. Tube-bend design, weld overlay and plasma spray coatings have been developed based on ceramic materials [19].

For particle lifting, several technologies are considered such as mine hoists, bucket elevators, pocket elevators, screw conveyors, Olds elevators, pneumatic conveyors, conveyor belts, cleated conveyor belts, metallic belted conveyors, En-masse's elevators, bucket wheels, linear induction motor powered elevators, and electromagnetic field conveyors. Notwithstanding that these technologies are commonly used on mining industry, some of these equipment have been evaluated for temperatures over 800 °C (Olds elevator, conventional bucket lift, and pocket elevator), to determine their efficiency and performance on the solid particle approach [50].

Mine hoist using insulated containers is considered due to its efficiency in relation to the weight of the material hoisted, and to the possibility to take advantage of the potential energy of the material on the way down from the receiver. Other capable concept is the pocket elevator, in which particles are transported to the receiver by pockets that discharge the material when getting inverted at the top [50].

A possible way to avoid energy expenses and investment on lifting the material up to the tower, as well as the difficulty of placing the receiver at the top of the tower, is to use a the beam-down solar concentrator concept described previously. Another advantage of this technology is to avoid heat losses when the heat transfers from the receiver to the energy converter [56].

Finally, there is lack of compatibility analysis between the solid particle materials and the material of which the conveyance system will be made. Therefore, more extensive research an analysis must be made for the long term.

Regarding to sensible heat storage, the solid particle concept needs to be experienced out from lab-scale. The transportation of large masses cause critical parasitic loads which have to be minimized, as well as the mechanical loads of heat exchanger for solids at high temperatures [17]. Also, Investigation of particle elevators that satisfy requirements for flow rate, temperature, and particle retention is needed [26]. In addition, the materials selected will withstand these high temperatures while yielding a receiver cost of less than $150/ kWh$_{th}$ [36].

5. Solid particle storage

Two different containers are required for storing solid particles: the first one will contain hot material (at around 800 °C) that have just been heated up, while the second one will contain only "warm sand" (at around 350 °C) that has been already cooled down by the heat exchanger that powers up the generation cycle [63,64].

Mainly cost aspects motivate the application of solids as heat storage media. The material costs for concrete, per stored energy unit, for example, are in the range of 10–20% of the corresponding costs for molten salts, and maintenance costs are also expected to be lower for solid media storage systems [12]. The goal of these options is to reduce the path for heat transfer from the bulk of the storage material to the transfer medium [17].

The construction of a well-insulated TES system becomes important in such a high-temperature application because the thermal losses are anticipated to be higher, resulting in more substantial thermal cycling issues. However, the cost of such TES system should be minimized so that operating at higher temperatures can still be economically justified. High-temperature TES systems can be constructed with readily available materials that yet meet the heat-loss requirements for a falling particle receiver system, thereby contributing to reducing the overall cost of concentrating solar power systems [50].

The tower design bin has several key aspects that require experimental development. The TES bin proposed by Abdelrahman El-Leathy [64] had a rectangular shape; this shape would not be suitable for large-scale TES bins due to its structural issues, especially at the corners. It was determined that a round-shaped TES bin would be a suitable option to pursue and build for continued testing. The prototype, in Fig. 13, exhibited superior performance and no degradation of the materials. This design can also be suitable for high-temperature applications other than the falling particle receiver, and further tests will explore the effectiveness of the materials as insulators, particularly at high temperatures, as well as further examining their structural soundness at these elevated conditions [64].

A high temperature lining material is required so that it will be capable of storing the heated material with minimal heat losses while remaining structurally stable. In this regard, a series of high-temperature insulating concretes are being tested. The first was aerated autoclaved concrete (AAC), and the second was perlite concrete (PC). Perlite concrete has been tested in lab-scale furnaces up to 1000 °C cycles, without cracking or crumbling for approximately 50 h' worth of exposure. Portland cement-based concretes typically begin to lose strength at temperatures above 300 °C. Despite the durability and low cost of firebrick, its thermal performance was not suitable, due to its high thermal conductivity; AAC is not suitable for use in future designs, due to the issue of cracking caused by high temperatures. Consequently, the investigation with regard to these materials was incorporated in one multiple material wall. Moreover, to ensure proper insulation of the hot bin, it is important to have materials with minimal thermal conductivities and insulating firebrick (IFB) and expansion joint (EJ) are thus considered [64].

On the other hand, TES system using solid graphite modular blocks for CSP plants stores energy at temperatures higher than 800 °C, and is robust enough to withstand the thermal cycles foreseen in a lifespan of 30 years, with no parasitic energy consumption [65]. The graphite material proposed appears to be superior to concrete for use as a TES storage medium. This technology can upgrade the operating range of thermal storage to significantly beyond that of molten salt (1650 °C vs. 565 °C), which could also have direct application to solar power towers.

The usable TES storage capacity is derived from multiplying the design point power-cycle thermal load by the required hours of thermal storage, and it is rated with power-cycle efficiency, η_p, considering the TES exergy loss, η_{TES}. To use the TES capacity rating to size of the physical dimensions of the storage system, one must calculate the heat capacity, density, and distribution of all active storage materials [19].

As occurred on other parts of the solid particle CSP system proposed, there must be more research of the particle material itself. The effect of density stratification, sintering and agglomeration resistance and particle size stratification must be considered for future work. Also, possible solid-solid phase changes could occur to some materials changing the density and heat properties between the two different storage tanks or even at one same tank if there is considerable temperature gradient stratification.

Cost-effective solid storage materials show low thermal conductivities representing the main challenge for the implementation of an effective storage concept [12].

Storage systems are being investigated at two different levels: on the one hand, the interaction of storage units with the other components of a CSP plant; on the other hand, storage concepts aims at cost reduction by more efficient material usage based on an improved understanding of the heat transfer processes in the storage system [17]. Also storage systems must be planned specifically for CSP SPT application, inasmuch as the systems commonly proposed were made for other industries.

Further development of existing storage concepts deal with capital costs in the range of 35–50 €/kWh$_{th}$, or even more because of the increase of efficiency due to high temperature generation cycles considered for solid particles approach. Two-tank molten salt systems provide a benchmark for acceptable investment costs for sensible heat storage concepts. Various aspects should be considered here: costs should only be compared for systems with the same temperature range,

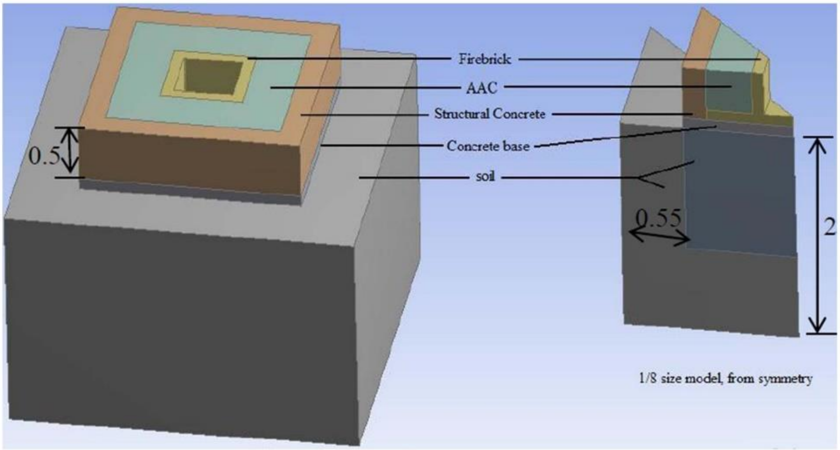

Fig. 13. Solid particle TES bin prototype [64].

Table 1
System challenges and current research.

Functional part	Challenges	Current Research
Open direct receivers	• Increase residence time. • Improve materials used for slowing flow structures. • Research for optimal solid particle materials for improving absorptance efficiency. • Study material compatibility of solid particles and material of the system itself. • Convective and radiant heat losses problems must be solved.	• Increase residence time and the effect on the receiver efficiency. • Prototype testing is under way looking for best geometries. • Energy balance and CFD for air curtain and particle recirculation are being enhanced.
Closed direct receivers	• Increase residence time. • Study possible thermal losses on the tube due to the optical properties. • Study parasitic energy requirements due to the fluidization. • Make pilot plant scale testing. • Work on enhancing the thermal isolation of the tube. • Poor heat transfer. Low conductivity in the particle side.	• Define desired properties of particles for fluidization on high temperature. • Optimize the design of the receiver according to the irradiated area. • Improve air intake according to particle size distribution.
Indirect receivers	• Increase residence time. • Define desired properties of particles for fluidization. • Study parasitic energy requirements due to the fluidization. • Work on enhancing the thermal isolation of the tube. • Maintain a uniform particle concentration and temperature. • Improve thermal isolation to decrease potential thermal loss.	• Exergy analysis on the heat exchange to the solid particles and according to the design used. • Define desired properties of particles for fluidization on high temperature. • Optimize the design of the receiver according to the irradiated area. • Improve air intake according to particle size distribution.
Conveyance system	• Material compatibility needed for assuring long term durability, especially on the particle lifting systems. • Research for using potential energy lost when particles go down from the receiver.	• Use technologies already developed for particle materials and adapt them to the current needs. • Study of the parasitic charges related to the large masses of material that are expected to be moved.
Storage tanks	• Reach investment costs lower than 35 €/kW_{th}. • Consider and evaluate changes on the solid particle material, such as variations on mean size and size distribution through the plant lifetime. • Study designs for avoiding particle agglomeration and sintering. • Evaluate the impact of density and/or temperature stratification inside de tanks.	• Tank built materials durability on the long term. • Adequate thermal isolation to minimize energy loses. • Interaction of the storage elements with the rest of the CSP plant. • Study of efficiency and durability of different tank geometries.
Heat exchanger	• Enhance heat transfer coefficients. • Evaluate particle changes during plant lifetime and due to temperature change over the exchanger (like possible allotropic changes). • Integrate parasitic loads on the energy balance.	• Improve fluidization stability. • Study of particle requirements.

identical discharge duration and the same storage time [17]. Other research efforts need to be made related to testing of prototype thermal storage bins using new geometries [26].

6. Heat exchanger between solid particles and the electricity generation cycle

For using solid particles as HTF, the most deeply investigated heat exchanger is the fluidized bed-CSP system (FB-CSP) [19,21,66]. FB-CSP uses two phases gas-solid flow to replace liquid salt or oil as HTF, and allows using the solid phase as storage. The thermal system implemented in FB uses sensible heat of solid particles for thermal energy storage, besides it has the ability to integrate latent and thermochemical storage [21].

FB-CSP operation is composed of a hot storage tank connected to the solar receiver output. In this configuration, solid particles are introduced to the heat exchanger in order to transfer energy following conventional configuration. The cooled particles that exit the heat exchanger are sent to the cold storage tank pumped by mechanical force, pneumatic force or gravity force [11].

In order to ensure a desired efficiency in the FB-CSP, some parameters must be controlled: maximize the heat transfer between the solids and the heating surface, guarantee a stable fluidization by means of operating as close to the minimum fluidization conditions, and the particles selected have to accomplish certain requirements such as performance of fluidization and flowability. Schwaiger et al. [66] modeled and analyzed costs and challenges for an active FB (called by the authors SandTES).

The efficiencies to be considered in the heat exchanger fluidized bed in terms of TES performance metrics are: storage effectiveness and first law and second law efficiencies [21]. The storage effectiveness accounts for usable storage out of the gross TES media load, and can also be denominated as the discharge efficiency or the storage fraction [67]. The implementation of solid particles-TES in the FB-CSP can lead to a 100% storage effectiveness [19]. The first law and the second law of efficiency describe the losses in terms of heat and energy conservation (exergy), respectively, during charging and discharging process. Zhiwen et al. [19] and Ma et al. [21] established the equations for the corresponding efficiencies defined above.

A major cause of exergy losses in CSP systems is any place in a system where heat transfer from one fluid to another occurs, usually in a heat exchanger. Major areas of heat exchange in CSP systems can include:

- From HTF to storage medium.
- From HTF to power cycle working fluid.
- From storage medium to power cycle working fluid.
- From power cycle working fluid to ambient air (condenser or cooling tower).

Fig. 1 shows the main scheme of a particle TES with FB (Fluidized Bed) heat exchanger integrated in a CSP plant with a tower solar field. The integrated FB-CSP system can drive different power generation cycles, including a Rankine power cycle, or a high-efficiency supercritical carbon dioxide ($s\text{-}CO_2$)-Brayton power cycle [21,31,68].

Heat exchangers suitable for coupling particulate media to process fluids such as pressurized air and steam have been developed in the past [34]. However, many of these systems have not been evaluated and optimized for the temperatures, particle materials, and flow rates being considered for high-temperature falling particle receivers. Other aspect that must be evaluated is the possible variation of the shape and mean size of the material over time and caused by the thousands of thermal cycles expected.

7. Challenges

The development of the solid particle technologies for sensible heat storage at high temperatures for using con solar power tower CSP has three main challenges. The first one related to the complete integration of all concepts. Several studies and developments are under way but not all the functional units are equally developed; for example, lack of studies on particle conveyance are not clearly reported even that it could affect critically the complete energy balance of the plant. Only on complete pilot plant some integration studies have been made, but are mainly focused on the receiver concept. With a complete plant integration analysis, possible conflicting working requirements can be detected and avoided. The second type of challenge requires that each functional part of the concept should be proven enough to achieve commercial viability. The main aspects to develop the technology are summarized in Table 1. This summary can help not only new researchers in the area to fulfil the main gaps of the current technology, but also people working in other areas with similar challenges to implement them in that technology. Finally, it is the current picture with the know-how updated details.

Finally, the third challenge is about selecting the optimal materials for using as solid particles and for building the system itself. Some materials have been suggested and compared but no proper search, selection and evaluation has been made. This is important because there are few materials that can be used on these conditions and the absence of optimal materials could seriously jeopardize the current developments. In relation to suitable particles, the desirable properties reported are associated with [26]:

- Complete optical characterization of particles.
- Development of new formulation for increased solar absorptivity.
- Identify methods to mitigate abrasion and attrition.

8. Current research

Nowadays, the new concept of dense suspension of particles receiver (DSPR) purposed by Flamant and Hemati (2010), is expected to reach suspension temperatures up to 750 °C for metallic tubes. The particle velocity and the particle volume fraction are the main parameters influencing the heat transfer coefficient. The higher the particle velocity, the higher the heat transfer coefficient, because the particle agitation increases, thus improving the particle movement and the exchange between the wall and the tube center [11].

Another line of research lies in the particle receiver modeling [69] in order to optimize the optical particle properties for a high temperature solar particle receiver. It consists of a non-homogeneous slab of particle dispersion composed of two-layers at high temperature, submitted to a concentrated and collimated solar radiation flux with a reflective receiver back wall as shown in Fig. 14.

The research on a particle receiver composed of two layers with the same thicknesses has been optimized according to the volume fraction. The optimization is conducted for both constant and linear temperature profiles. There is no benefit in using different particle sizes in each layer because the receiver temperature is uniform. The optical thickness of this first layer is so large that it has no effect on the second layer efficiency [69].

Falling particle receiver development is focused on enhancing the receiver by means of [26]:

- Conduct optimization of receiver efficiency using CFD models.
- Perform tests with prototype receiver to investigate proposed enhancements.
- Continue evaluation of flow through porous media for increased residence time and particle heating.

Additional improvements are being sought, and features that are being evaluated and optimized include aperture size, nod angle, alternative geometries, particle flow rate per unit length (opacity), particle size, release location, and inclusion of an air curtain [50].

Parameters such as particle-drop position, particle size, particle mass flow rate, and solar input power are under evaluation. Other interactions should be investigated to determine an optimized design [35].

Computational fluid dynamics models of the falling particle receiver have been developed to assist in predicting the performance of these systems. Recent studies are aimed at advancing solid particle receiver technology that will improve the performance and efficiency through the development of novel features and components (e.g., recirculation, increased residence time, solid/fluid heat exchangers, storage, fluidized bed, particles) [18].

The solid particle receiver is now being investigated in multiple configurations, as a technology that could enable lower cost, dispatchable solar power production including ~15 h of thermal energy storage. Combining a mature SPR with an advanced power cycle has several possible benefits including higher efficiency operation and inexpensive, non-corrosive storage media [43].

Indirect particle receivers are planned to take the novel approach of using stable, inexpensive materials for the high-temperature receiver, energy storage, structure, and containment. Successful development of the proposed near black body (NBB) receiver and fluidized-bed heat exchanger would achieve high thermal efficiency and higher operating temperatures, and could significantly reduce CSP thermal system capital and operation costs. When integrated with SunShot initiative, solar collectors and power cycles, the combined system is expected to achieve a levelized cost of energy of $0.06/kWh$_{th}$ [61].

There is also a modeling tool that is being used for design of particle receiver to understand and predict the heat transfer in solid flows, including radiation, which is called Discrete Element Model [62].

Table 1 summarizes and compares all the information available for the whole plant concept. Notice that receivers are the main plant part

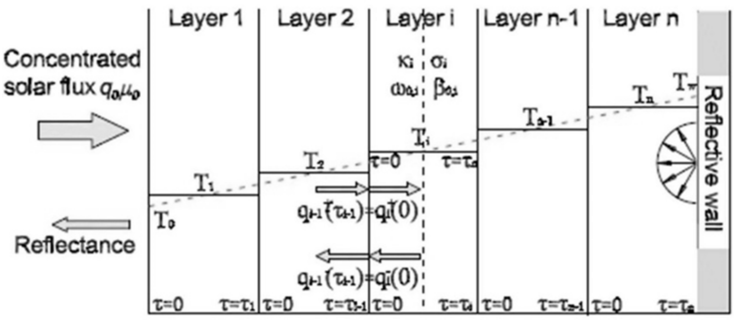

Fig. 14. Schematic of a multi-layer solar particle receiver [69].

developed at this time.

9. Conclusions

A resurgence of solid-particle receivers is occurring as corrosion and material interaction appears favorable for this approach. However, particle conveyance, attrition, and transport remain a challenging prospect.

For now, solid particle CSP TES systems are not commercially available. Several issues must be developed in order to make it a reality. Nevertheless, after about 20 years of standstill, there have been big breakthroughs on the last years. The operating conditions and parameters make this technology especially attractive for today's world energetic context.

The present review condenses all the available information and classifies them considering the main functional parts and remarking the current research in that part as well as the future challenging issues (see Table 1).

Solar receivers are the driver on the development of the technology, compared with the rest of the elements of the plant sections. The following years real tests must be performed in order to reach the next step out of lab-scale. Also, there are concerns that need to be more profoundly developed, such as storage bin materials and particle conveyance systems.

Important issues include increasing the heating of the particles in the receiver while mitigating heat losses. In addition, the design of balance-of-plant components specific to particle heating, exchange, and storage is necessary to enable a working particle receiver system. These include: (1) advances in receiver design with consideration of particle recirculation, air recirculation, and interconnected porous structures; (2) advances in particle materials to increase the solar absorptivity and durability; and (3) advances in the balance-of-plant for falling particle receiver systems including thermal storage, heat exchange, and particle conveyance.

Many properties have been evaluated on previous studies for choosing the optimum material to be used as solid particles for TES. Nevertheless, there is lack of studies that consider most of all the relevant properties in a single evaluation. For this, we must consider environment conditions and a specific kind of system, defined by the particle receiver, heat exchanger, conveyance system and storage bins. Finally, there are different forms for measuring one single property and methodologies and accuracy of results should be considered prior comparing results. Hence we must define which method is more suitable according to the ranges and conditions of the samples.

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REVIEW

ENERGY STORAGE WILEY

Review of solid particle materials for heat transfer fluid and thermal energy storage in solar thermal power plants

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Abstract

Current concentrated solar power (CSP) plants that operate at the highest temperature use molten salts as both heat transfer fluid (HTF) and thermal energy storage (TES) medium. Molten salts can reach up to 565°C before becoming chemically unstable and highly corrosive. This is one of the higher weaknesses of the technology. Solid particles have been proposed to overcome current working temperature limits, since the particle media can be stable for temperatures close to 1000°C. This work presents a review of solid particles candidates to be used as HTF and TES in CSP plants in open receivers. In addition, the interactions between solid particles with major system components are described in this review, for example, with TES system or heat exchanger. The parameters and properties of solid particles are identified from the material science point of view explaining their nature and the relation to the power plant efficiency and lifetime durability. Finally, future development is proposed; such as material selection according to each specific design, materials characterization, or durability test.

KEYWORDS

concentrated solar power, granular materials, sensible heat, solar tower, solid particles, thermal energy storage, thermal storage

1 | INTRODUCTION

It has been well established that renewable energy have a major role in energy systems development, energy security and climate change fight.[1] In the last years, electricity capacity additions have grown for renewable technologies such as photovoltaic and wind, reaching greater development than coal or gas utilities.[2] Therefore, the total electricity generation from renewables reached 25% in 2018 and is expected to grow up to 40% in 2040.[3] This can be understood by the current downfall of renewable prices, which is expected to continue with the new International Energy Agency (IEA) expected policies scenario[4] in contrast with the increase of oil prices up to 80 USD/barrel in 2018.

Nevertheless, the variable renewable energies growth has some limitations due to lack of flexibility. Solar and wind production (which are the ones that are being more developed) do not match the electricity daily demand. Other dispatchable renewables such as geothermal, hydropower or bioenergy, have resource limitations either because of geographical resource availability or because of conflict with other human activities (such as agriculture and human consumption).[5-7] Several strategies have been considered for solving this lack of flexibility, being energy storage one of the most promising. Nowadays, one of the most commercially viable energy storage solutions with high capacity is thermal energy storage (TES) system integrated with concentrated solar power (CSP) thermal plants. CSP central tower can achieve high power, high efficiency in the electric generation cycle due to the high operation temperatures, high land efficiency, and enough heat storage to overcome solar energy resource variability.[8,9] Power output in CSP thermal plants is important, which is in part influenced by the operating temperature. Achieving high temperature reflects in an increase of heat to electricity conversion efficiency; therefore, increasing temperature is desirable. Central receiver tower concentrator using molten salts reaches temperatures up to 565°C—this limit is determined by the molten salt material itself. For higher temperatures molten nitrates salt becomes chemically unstable, becoming highly corrosive and decomposing.[10]

Solid particle CSP technology can overcome the molten salts temperature and stability drawbacks, since solid particles are used as TES and heat transfer fluid (HTF) material.[11] The solid particles TES system is expected to have high performance due to the high service temperature, and to the relatively low cost of the material itself.[12] Direct solar absorption receivers, in which particles fall through a beam of concentrated radiation, have the potential to increase temperature of HTF/TES media over 1000°C.[13] Therefore, a complete CSP solar tower system that operates over 600°C and up to 1000°C is feasible, since stable materials are available and thermal self-insulation can minimize thermal losses in the heat storage medium.[14] Finally, media storage system is projected to have cheap maintenance and low material costs.[10]

Thus, the main advantages relative to the storage media compared with current commercial molten salts solution can be summarized[13]:

1. Proposed solid particles materials are chemically inert and stable beyond 1100°C.
2. Particles are capable of storing energy over a greater temperature span compared with other media currently in use; thus, increasing the energy storage density.
3. Materials cost is expected to be relatively low.

Proposed power plant configuration can be appreciated in Figure 1. The sunlight is reflected and concentrated by the solar field heliostats into a central tower. Particles are flowing through the receiver at the top of the tower, capturing the concentrated sunlight. After reaching the desired temperature, the solid particles are moved by the conveyance system to a hot storage tank, in which the material is collected until it is moved into a heat exchanger (HEX) to transfer the high temperature heat to the power generation cycle.[15]

Exhausted heat particles are then moved to a (relatively) low temperature storage tank to be stored until they can be moved back to the solar receiver on the top of the tower to harvest solar heat again.[12] This plant distribution is similar to the current commercial molten salts CSP tower system[16]; however, almost all the components of the plant should be specially redesigned for working with solid particles at high temperature.

The main facets involved in solid particle CSP development that have been identified are:

- The receiver design in which particles receive concentrated solar flux and get to the desired high temperature is of great importance. Several designs had been proposed, although some of them are still under development. The most important goal for the receiver is to retain the particles so that they can reach the desired temperature with a high solar absorptance efficiency (either directly or indirectly).[17]

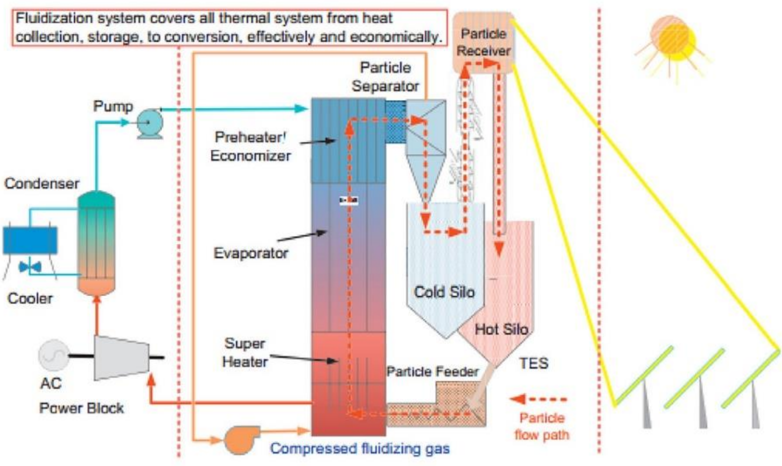


FIGURE 1 CSP solid particle system with TES and fluidized bed[14]

- The solid particle TES will allow the power plant to operate at any time and in the most convenient moment (according to the electricity production needs). Reduce heat losses and guarantee silo durability are the main objectives of current research efforts.
- The HEX must provide heat to the power block as quickly as possible and in the shortest possible length. The HEX is expected to be one of the most expensive parts of the system, so making it smaller is highly desirable.
- Particle conveyance considers how to move the solid particles between the receiver, the particle silos, and the heat exchanger.
- A solid particle material selection of the must be made to the best meet requirements of each part of the system. In addition, the material compatibility between the particles and the materials of which system parts are built of, must be taken into account.

CSP solid particle technology progress has several challenges. The main concerns that are subject to more study and development are[18]:

1. The complete integration of all concepts. Some functional units are at early stages of study, in contrast to other parts that are much more developed such as solar receiver or heat exchanger. An example of underdeveloped functional unit is the particle conveyance system; even that the energy employed in moving the solid particles through the power plant can seriously affect the energy balance of the plant, and therefore its viability. There is only one reported solar tower developing some integration studies (the National Thermal Test Facility in New Mexico[19,20]); nevertheless, reported studies show that their focus is centered in the receiver concept and HEX design. A full integration study can detect possible conflicts with the working requirements so that they can be properly solved.
2. Prove the commercial feasibility for each functional part of the plant, including but not limited to the solar receiver, heat storage, heat exchanger, conveyance system, and the particle medium.
3. Selecting the optimal materials for solid particles and the system is of big relevance and they must be chosen together, since the interactions between the particles and the components' materials can affect in a great manner the plant and particle medium lifetime and system maintenance cost. Particle media have been suggested and compared in bibliography, but an exhaustive search, selection and evaluation has not been performed. Since there are only a limited number of particle materials that can be used under these high temperature conditions, it is difficult to perform an appropriate materials selection. Selecting materials that are not available reduce the projected viability of the technology. The main desirable characteristics under research for particulate media reported in the literature can be grouped by:
   - Complete optical characterization.
   - Research for new formulations to increase solar absorptance efficiency and absorptance durability over time.
   - Finding ways to reduce abrasion and attrition caused by/to the particles.

This work presents a review of solid particle CSP technology, its importance, its impact compared with current CSP solutions and their interactions with major components of the plant design not only focused on the receivers or other components because this revisions are available in the literature. Thereby, the key overview is motivated on the particle media point of view, interacting with all the components of the system design.

2 | CSP COMPONENTS: CONCEPTUAL DESIGN

2.1 | Solid particles receiver

The most studied functional part of solid particle power plants is the particle receiver, since there are several proposed designs.[14,17,18,21-30] Only some of them have been deeply studied, and the most remarkable designs are presented in Figure 2. Solar receivers can be classified according to the way they capture solar heat[15]:

a. Direct receivers, in which the particle media (acting as HTF) directly absorb the solar irradiance. These receiver designs make high solar absorptance to be included among particle media desirable properties.
b. Indirect receivers that use another material to absorb the solar heat and then exchange it to the particle media.

Once classified in direct or indirect receivers, they are divided according to their working principle. On one hand, the most noticeable direct receivers are the free-falling particle, the obstructed flow, the rotating kiln, and the fluidized receivers. On the other hand, the most outstanding indirect receivers are the particle flow with HEX and the fluidized indirect receivers.[19,31]

It is noticeable that there are no material compatibility studies, for any of the reported receiver designs, between the HTF-TES particle material and the material of which the receivers are going to be built with. Future design studies should include the interactions of plant component with the

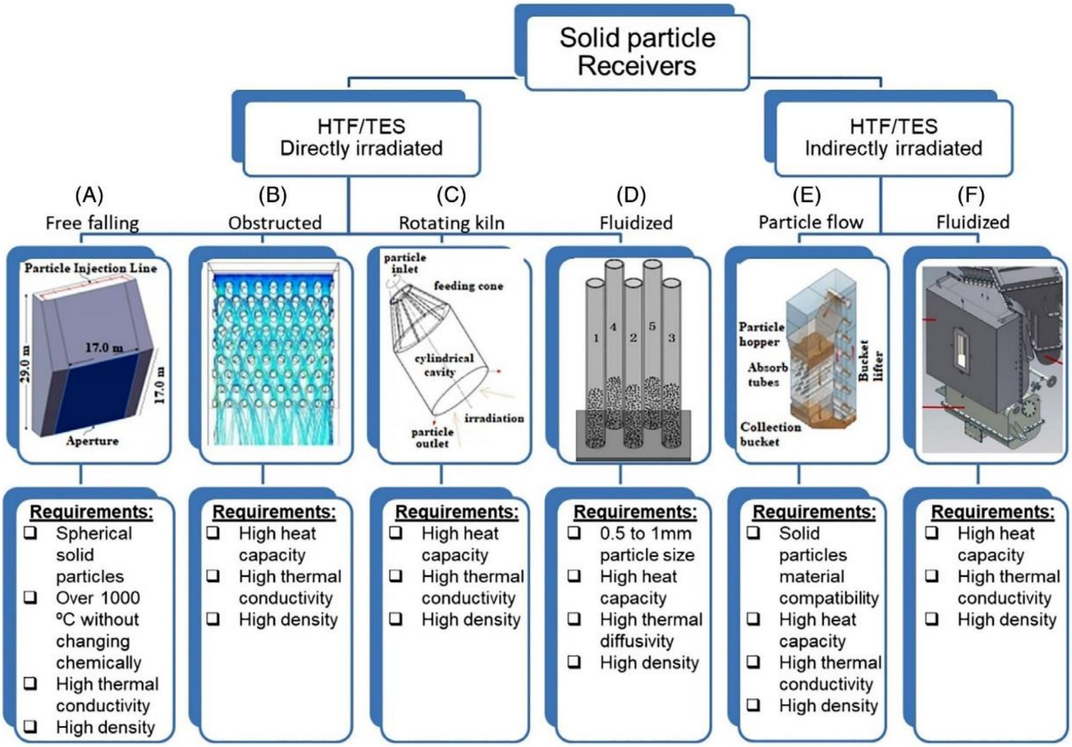


FIGURE 2 Main parameters and properties for different solid particle solar receivers

particle media and their stability in the long term. These interactions have been already observed during the receiver prototype development,[32] but even then, has been reported no material selection based on them.

The most groundbreaking designs are for direct receivers' design, in which there is an important need to increase the solar irradiation exposure time to reach the desired high temperatures. To decrease radiative losses and reduce exposure time, the solar absorptance becomes and important property, and a high priority for directly irradiated receiver development.[33]

The most relevant receiver designs that are under progress or being designed can be appreciated in Figure 2. Their working principles are explained below:

1. **Free falling particle receiver.** In this design, the particle media falls through the receiver in a curtain shape, while an aperture allows concentrated solar flux entering the receiver and thereby heat the particles. Current efforts are centered in researching ways to increase particle exposure to concentrated sunlight.[21] As mentioned before, it is expected that temperature goes over 1000°C without changing the chemical properties or composition of the material, while additionally achieves high solar absorptance efficiency due to direct solar absorption. It is projected that this design will be feasible for 10 MW-100 MW systems.[13] Current studies are centered in[18]:

   - Effects of the receiver aperture size tilt and dimension.
   - Different ways to increase the particles residence time.
   - Develop an air curtain for protecting the receiver aperture.

One option to control residence time is the particle recirculation by making the particles to pass several times through the aperture until they reach the desired temperature.[15] This approach has been modeled and simulations have shown it is effective enough to reach 800°C; nevertheless, possible particle losses in the aperture must be reduced either by using an air curtain or by any other solution.

2. **Obstructed particle flow receiver.** Another option to increase particle exposure is by mechanically obstructing the particle media flow. Despite of shortage of material

properties considerations (heat capacity, density or thermal conductivity), several options have been proposed[17]:

- **Ceramic porous structures.** In this option, particle media flow by gravity across porous interconnected structures; thus reducing flow speed and allowing more irradiance exposure. Some tests have already been performed on these structures; results show that there should be a previous material selection that can deal with the deterioration over the porous structure at high temperature.
- **Porcupine structure.** Theoretically by placing quills inside the solar receiver, particle media flow can be reduced[18]; however, several testing and material selection must be performed to experimentally assure it.

3. **Rotating kiln receiver.** In this receiver, centrifugal forces are used to slow particle media fall by making them to impact with the kiln walls. Research is focused in maintaining mass flow stability at a large scale and minimizing the energy spent for moving the kiln.[21] Other considerations are related to the particle attrition effect, since the main force that is delaying media flow is due to friction between the kiln walls and the particles.
4. **Fluidized direct receiver.** Fluidization in the receiver is only possible by controlling the particle flow atmosphere; therefore, to continue working as a direct receiver at high temperature, quartz receivers have been proposed.[34] By controlling particle media flow by fluidization, the solar irradiance over the particles can be increased. A possible drawback that must be studied is the effect of the quartz tube on the solar absorptance of the particle flow. Further studies on different candidate materials show that the particle flow is influenced by particle size, since very small particles decrease the receiver efficiency and very big particles are more difficult to fluidize. Optimal size has been found between 500 μm and 1000 μm at ambient temperature,[34] but it is expected to change at higher temperatures. One improvement compared with other designs is that outside wind has no influence on particle flow.
5. **Particle flow integrated with HEX receiver.** This indirect receiver considers using an special designed HEX (Figure 2), in which an array of tubes receive the solar irradiance in their interior surface, heating the particles that flow outside the tubes.[21] It is expected that with this design outlet temperature of the particles can reach up to 900°C. Current studies do not report any material design consideration, not even that they have a central impact on receiver's durability, and on a correct heat exchange and good particle media flow through the receiver.
6. **Fluidized indirect receiver.** This receiver design considers absorbing the solar heat by a mostly black surface (defined by its weighted solar absorptance in the whole solar spectrum length wave). Then, the heat is exchanged to the particle media flow, controlled by a fluidized bed and forcing the particles upward, increasing heat transfer by convection with the tube walls.[21]

2.2 | Storage

The original proposed design considers two containers for storing the particle media: a hot and a cold storage. The hot container will hold the particles coming from the solar receiver at high temperature (~800°C), and will held them until the electricity production is convenient. The cold container will hold the solid particles after they exit the heat exchanger, storing them at low temperature (~350°C) before sending them back to the solar receiver to be heated up again.[35,36] The cold tank will store the particle media until the solar resource is available for solar heat harvesting.

Current research is focused on two main approaches[10]:

1. Interaction between storage elements and other plant components.
2. Cost reduction of storage containers based on understanding heat transfer processes.

The study of possible thermal losses has been found remarkable, and should be studied for several charge/discharge cycling. Efficient insulation TES systems are important due to the high temperature of the stored particle media.[19]

2.3 | Heat exchanger

There are several options available for discharging heat from the particle media into the power generation block, such as using fluidized bed or packed bed heat exchangers. The most studied is the fluidized bed, which uses two-phase gas-solid HTF flow.[12,14,20] The solid phase corresponds to the particle media while the gas phase corresponds to pressurized air. This design has also been studied for latent and thermochemical storage heat discharge, besides the sensible heat used in particle media.[14] In the past, HEXs have been proven to be useful for integration of solid particles with fluids such as compressed air and steam; nevertheless, no studies on their implementation at high temperatures are found, or on the optimization of working conditions, fitting flow rates such as those used in solid particles CSP, or considering shape and size variations of particles during plant lifetime.[25]

Other studies can be found related to gravity driven packed bed heat exchangers that evaluate the heat transfer coefficient under different flows and temperatures. They state that when increasing the flow rate the heat transfer increases as well[37]; but also, when temperature is over 600°C heat transfer changes from a linear heat transfer coefficient to a faster one.[38] Another proposed HEX solution has been made by Albrecht et al[31] by using a particle sCO_2 heat exchanger. Predictive numerical models have been performed for moving packed-bed exchangers, finding performance relations with particle size, operating temperature, and flow speed. These models are expected to allow heat exchange simulations after being it experimentally validated.

2.4 | Conveyance

Particle transport is considered to be of special importance due to the energy spent in moving the solids. By now, only the particle media lift to the solar receiver has been reported; while other conveyance elements for the rest of media transportation have not been described. For fluidized bed, there are some testing on erosion and corrosion protections, such as weld overlay and plasma spray coatings which have been useful for ceramic materials.[12] A formal material selection must be performed, since the used particle media determines the interaction and durability of the possible materials used for the conveyance system caused by their interaction.

Energy spent in particle lifting is a main concern when considering the whole system viability. Almost all the proposal-lifting technologies come from mining industry, such as mine hoists, bucket elevators, pocket elevators, screw conveyors, olds elevators, pneumatic conveyors, conveyor belts, cleated conveyor belts, metallic belted conveyors, En-masse's elevators, bucket wheels, linear induction motor powered elevators, and electromagnetic field conveyors. Nevertheless, only olds elevators, conventional bucket lifts, and pocket elevators have been tested at temperatures above 800°C and had been considered for efficiency calculations.[19]

3 | PLANT COMPONENTS INTERACTION WITH PARTICLE MEDIA

The overall concept in solid particles as HTF and TES for CSP tower was explained in previous sections. The suitable selection of the particle media is one of the most important considerations to evaluate the viability of the overall plant. In order to reach an optimal performance several aspects must be considered, which must be congruent with the desired particle media properties and other design parameters such as low price and high temperature stability.[35] Natural materials or byproducts should be considered due to their low price, while composite materials that can enhance some desired behaviors, must be with caution considered due to their possible high price.

A material selection must be performed to choose the best material available for particulate media.[39] Thus, the main properties and funciontal parameters must be identified before starting any material selection process. Some efforts for indentifying these parameters have been made before[40]; specific heat, thermal shock, thermal conductivity, particle size and shape, and attrition effect have been considered. Nevertheless, further efforts to identify all properties and their interaction on the different parts of the solid particle solar plant have been not found on literature. There are specific requirements for the solid particle material according to functional parts of the plant or to desirable behavior of the solids. In Table 1, suggested properties and funciontal parameters are presented according to the mentioned criteria.

Different approaches for determining the most important functional parameters have been made; sometimes there are focused on a general view of the plant, while in other cases they are analyzed from the perspective of a single functional unit or constraint (HEX, receiver, storage, durability, etc.). In the following sections, different perspectives have been grouped according to the functional unit or constraint, without differentiating the plant design, in order to consider all parameters and properties. Future work should consider these elements for specific material selection according to each type of plant design.

3.1 | Receiver thermal efficiency

Some traditional high temperature ceramic materials available in the particle sizes of interest for falling particle receiver development have been considered for evaluation studies. Some of these materials are: alumina, silica, silicon carbide, zirconia, as well as sintered materials such as those used as proppants.[17]

For direct receivers, the particle media serve as solar absorber, HTF, and TES material. Therefore, optical radiative properties of the particles have a critical role in the receiver overall efficiency. Thermal losses can increase if solar absorptance of the particle media is too low and/or if the emissivity is too high because within this scenario, the time of residence of the particles to achieve the desired temperature must be increased, and this fact will increment the energy losses.

Solar absorptance has shown to be a more important parameter to maximize compared to getting down emissivity; meaning that a high emissivity material can be considered as good if solar absorptance is high, while a low solar absorptance material cannot be considered even if its emissivity is low.[19]

TABLE 1 Desired properties and functional parameters for solid particles for CSP

	Range	Desired value	Unit	Reference
Receiver thermal efficiency				
Absorptivity	0.55-0.93	High	%	19
Emissivity	0.72-0.88	Low	%	19
Particle size	200-1000	ATD[a]	μm	29
Sphericity	0.9	High	Parts per unit	26,29,41
Roundness	0.9	Low	Parts per unit	42
HEX efficiency				
Particle size	160-504	Low	μm	43
Thermal conductivity	0.5-2	High	W/m K	14
Thermal energy storage capacity				
Density	2.56-5.37	High	g/cm^3	44
Specific heat	621.75-923.36	High	J/kg K	44
Agglomeration				
Sphericity		High		45
Size uniformity		High		43
Melting point	1135	High	°C	46
Particle size	150-200	High	μm	46
Absorptance		Low		18
Sintering				
Melting point	>1000	High	°C	47
Sphericity	0.9	High	Parts per unit	26,29,41
Roundness	0.9	High	Parts per unit	42
Size uniformity (mass median diameter)	As much as 0.26	High	Parts per unit	47
Particle size	200-1000	High	μm	29
Agglomeration		Low		45
Sintering heat[a]	>1000	High	°C	33
Durability				
Sand erosion	0.0001-0.1	Low	%	35
Thermal shock degradation		Low		19
Mechanical shock degradation	0.004-0.01	Low	%	19
Economic factors				
Price	0.01-17	Low	USD/kg	18,48
Sand erosion		Low		
Durability		High		

[a]Abbreviation: ATD, according to the design.

The fraction of radiation absorbed on material surface is called the absorptance or absorptivity.[49] Absorptance is determined by the amount of light absorbed by a material surface compared with a black body,[50] and it depends on the source from which the surface absorbs radiation.[51] Solar absorptance is weighted according to the amount of light received from sunlight into the Earth. Figure 3 shows the variation of solar irradiance according to each wavelength starting in the ultraviolet, including the visible spectra and finishing in the infrareds.

The ratio of the total radiating power of a real surface to that of a black surface at the same temperature is called the emittance of the surface (for a perfectly plane surface, the emissivity).[42] Emittance is determined by physical properties and temperature of the surface[53]; therefore, the higher the temperature, the higher the emittance. In CSP, TES, and

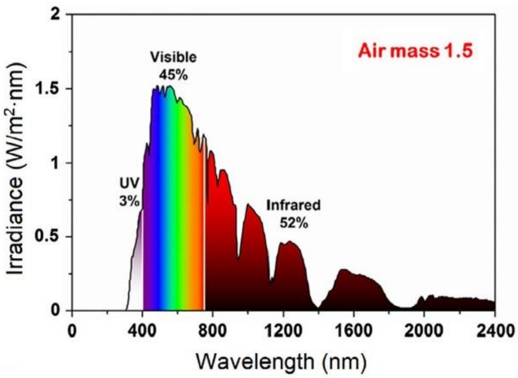


FIGURE 3 AM 1.5 solar irradiance on Earth[52]

HTF materials, emittance is undesired through the whole plant, except for the HEX (even that it is not de main heat transfer mechanism).[54]

Thermal heat transfer by thermal radiation is almost immediate, and it depends mainly on the concentrating factor, absorptance, emittance, temperature distribution, and scattering medium.[55]

Concentrated solar radiation harvesting study is not a new subject, since it has been exploited for solar thermal power (thermal energy), solar thermochemistry (chemical energy), and concentrated solar photovoltaics (electric energy).[56]

Solar concentration ratio is the very first parameter to consider in CSP systems. Desired concentrating ratio defines the configuration and dimension of the solar field. Solar field constitutes one of the main expenses of any kind of CSP technology. Ideal solar irradiance is about 1 kW/m^2 without any concentration. For reaching high temperature, the concentrating ratio must be increased in order to limit the radiation losses in the solar receiver.[56]

Thermal radiation heat transfer is determined by electromagnetic waves emitted by matter, which changes the molecular energy levels of the receptor material[55]; this is significantly different when compared with thermal conduction or convection, which require a material medium to transfer the heat (which is ruled by Fourier's law). Solar thermal radiation used for obtaining solar absorptance include wavelengths between 10^{-7} m and 10^{-3} m (ultraviolet, visible, and infrared), since they are determined by solar irradiance spectrum. In contrast, emissivity relies only in the infrared wavelengths.[55] Since the heat transfer net balance goes from the hotter material to the colder (because of the temperature dependence), the heat transfer relative to the absorptance comes from the Sun, while the heat transferred relative to the emittance is transferred from the particle media to its surroundings.

Heat transfer by conduction and convection has a linear relation to temperature, but in radiation heat transfer, there is a proportional relation to at least the fourth power with the temperature. As a consequence, radiative heat transfer becomes much more important when increasing temperature, overriding the conduction and convection heat transfer.[55] Therefore, there are high potential losses due to radiation rejection and radiation emitted by particle media compared to those from the insulation of the solar receiver.

When dealing with small particles, such as solid particles for CSP, the interaction between the electromagnetic waves and the particles can change when compared to a continuous solid. When dealing with a particle cloud, radiation may be transmitted, reflected or absorbed (as well as in homogeneous solids); but the directions in which the particles scatter the electromagnetic waves depend of particle's shape, size, material, and space between the particles.[55] For ideal particles, the shape is assumed spherical or cylindrical when making analysis. Therefore, the solar irradiance electromagnetic waves (or photons) will be absorbed or scattered by diffraction, reflection, or refraction.[57] Theoretically, the properties that can be measured on solid materials are extinction coefficient, absorption coefficient, and scattered intensity. For some authors, the easiest property to measure is the extinction coefficient.

In Table 2 several candidate materials for particle media are presented with their solar absorptance at ambient temperatures and thermal emissivity calculated to 700°C. These materials include sintered bauxite proppants (CarboHSP, Accucast, and CabroProp), fracking sand, and Pyromark paint (used as reference). The reported measurements were made with a Surface Optics Corporation 410 Solar reflectometer. Absorptance for some of the proppants is relatively high; nevertheless, these results are for particles without any exposure to high temperatures. In Table 2, selective absorber efficiency, η, is defined as:

$$\eta = \left(\alpha Q - \varepsilon\sigma T^4\right)/Q \tag{1}$$

where α is the solar absortance, Q is the irradiance in the receiver (W/m^2), ε is the thermal emissivity, σ is the Stefan-Boltzmann constant (5.67×10^{-8} W/m^2 K^4), and T is the surface temperature (K). For current suggested particle materials, Q is assumed to be 6×10^5 W/m^2 and T is assumed to be 700°C (973 K) on the reported analysis.

As mentioned above, solar energy received on an individual particle within a particle curtain is absorbed or scattered. Therefore, if the curtain density is high enough, it is expected that a big part of the scattered energy will be absorbed by surrounding particles. This phenomenon allows current solar absorptance and thermal emissivity measurements to use particle media packed bed model, since the incident wavelengths can be absorbed as well as the scattered reflections. Previously commented ceramic proppants have shown high sphericity and roundness; they are ideal for its use in the solid particle receiver (SPR) since scattered radiation can be easily absorbed with current particles shape.

The main design purpose of proppants is hardness, since it is expected to hold hydraulic cracks open in order to allow oil flow out the impermeable rocks. Proposed proppants are made from sintered bauxite, which is non-corrosive, resistant to sintering by pressure, and cheap due to the large production economic scale. Several different proppant formulations have been evaluated in terms of their absorptance with a mean solar absorptance over 90%. Nevertheless, as-received proppants are not designed for high temperatures and are not stable under oxidation conditions.[33] Oxidation changes color of the proppants when reaching temperatures over 700°C; this will be discussed in Section 3.5, which is focused on particle durability.

Manufacture process, as well as raw materials used for proppants, are the cause of high absorptance. The fabrication steps are not usually published. One example is that the humidity in the air at during the particle sinterization affects the color of propanant (due to the change in oxygen partial pressure). Raw feedstock is processed into powder, which is pelletized producing green particles. These particles are sintered at temperatures over 1400°C in a rotary kiln in a non-oxidizing controlled atmosphere.[33] The main proppants considered by different research groups are the ones from CARBO Ceramics, including CARBO HSP, CARBO Accucast, and CARBO Prop formulas. In Table 3 CARBO HSP main properties are presented, while in Table 4 chemical composition, size, specific heat capacity, and measured solar absorptance are presented for other CARBO Ceramics products, as well as Norton Masterbeads, which is no longer produced but was earlier studied.

These proposed particles are engineered materials for high-pressure applications; nevertheless, they exhibit high absorptance and durability while remaining useful for temperatures over 1000°C.[36]

For falling particle receiver, different particle size media have been tested between 200 μm and 1000 μm. It has been found that smaller particles result on a bigger receiver solar aperture if the same operation conditions remain. The study suggests that particle media selection must consider manufacturing issues, since too small particles can lead to mass flow loose through the concentrated sunlight aperture.[29]

For direct fluidized bed receivers a two-phase suspension with small particles is considered, which flows vertically through the absorbing tubes to harvest solar thermal energy. For previous reported testing, the particle media used was silicon carbide. This material was chosen due to its high sintering temperature, high specific heat capacity, availability, and intermediate cost (depending on the literature reference).[11,12] Silicon carbide media average diameter also allowed good fluidization quality with low velocities, which yield to parasitic electric charges reduction.

3.2 | TES capacity

For thermal storage, the thermal capacity of the storage media should be as large as possible (Equation 2); Table 5

TABLE 3 CARBO HSP particle properties[26]

Property	Value
Density (kg/m^3)	3560
Median diameter (μm)	697
Estimated thermal conductivity (W/m K)	2.0
Estimated specific heat (J/kg K)	$-.12e{-}3T^2 + 2.07T + 264$
Estimated emissivity	0.8
Sphericity	0.9

TABLE 2 Measured solar absorptance and thermal emissivity of candidate particles and Piromark 2500 paint used as reference 19

Material name	Type	Solar weighted absorptivity (parts per unit)	Thermal emissivity (parts per unit)	Selective absorber efficiency (parts per unit)
Carbo HSP	Sintered Bauxite	0.934	0.843	0.864
CarboProp40/70	Sintered Bauxite	0.929	0.803	0.862
CarboProp30/60	Sintered Bauxite	0.894	0.752	0.831
AccucastID50	Sintered Bauxite	0.906	0.754	0.843
AccucastID70	Sintered Bauxite	0.909	0.789	0.843
Fracking Sand	Silica	0.55	0.715	0.490
Pyromark2500	High-Temperature Paint	0.97	0.88	0.897

show values for iron ores and some slags. However, a high real density will penalize the fluidization, since materials with high density require more energy to get to the minimum fluidization speed, u_{mf}. This minimum speed can be compensated with a smaller particle size in order to keep the design velocity constant no matter the material used. On the other hand, as has been commented on Section 2.1, too small particles can be negative for fluidization as well. Finally, smaller size will have a negative effect on sintering, as will be explained on Section 3.5.

TABLE 4 Summary of physical properties of commercially available proppants[33]

Composition/Physical property	CARBOHSP	CARBOCCUCAST	CARBOPROP	Norton Masterbeads
AlO_3 (wt%)	83	75	72	86
SiO_2 (wt%)	5	11	13	3
TiO_2 (wt%)	3.5	3	4	4
Fe_2O_3 (wt%)	7	9	10	7
Others (wt%)	1.5	2	1	-
Mean diameter [μm]	697	300	443	~600
Heat capacity [J/kg^3 K]	1275 (700°C)	1175 (700°C)	1175 (700°C)	-
Bulk density [g cm^3]	2.0	2.0	1.88	1.76
Weighted solar absorptance (%)	93	91	89	94

TABLE 5 Potential storage media[20]

	C_{pm} [J/kg K]	ρ [t/m^3]	$\varepsilon = \rho Cp$ [J/cm^3 K]	U_{mf} [mm/s] 50 μm	U_{mf} [mm/s] 100 μm	U_{mf} [mm/s] 150 μm
Quartz SiO_2	742.13	2.65	1.97	2.5	8.5	17.2
Feldspar						
Albite $NaAlSi_3O_8$	782.16	2.62	2.05	2.4	8.5	17.0
Microcline $KAlSi_3O_8$	727.19	2.56	1.86	2.4	8.3	16.6
Anorthite $CaAl_2Si_2O_8$	759.85	2.76	2.10	2.6	8.9	17.9
Mica						
Muscovite $KAl_2(AlSi_3O_{18})(F,OH)_2$	818.71	2.83	2.32	2.6	9.1	18.4
Fluorphlogopite $KMg,AlSi_3O_{10}F_2$	812.83	2.88	2.34	2.7	9.2	18.7
Pyroxene						
Jadeite $NaAl(SiO_3)_2$	791.29	3.35	2.65	3.1	10.6	21.8
Diopside $CaMg(SiO_3)_2$	768.96	3.28	2.52	3.0	10.4	21.3
α-Spodumene α-$LiAlSi_2O_6$	853.89	3.19	2.72	2.9	10.2	20.7
β-Spodumene β-$LiAlSi_2O_6$	874.85	2.38	2.08	2.2	7.7	15.5
Iron Ores						
Hematite Fe_2O_3	650.31	5.28	3.43	4.7	16.3	34.2
Magnetite Fe_3O_4	651.25	5.20	3.39	4.6	16.0	33.8
Slags						
Aluminium oxide, Al_2O_3	761.05	3.97	3.02	3.6	12.5	25.8
Magnesium oxide, MgO	923.36	3.58	3.31	3.3	11.3	23.3
Manganese oxide, MnO	621.75	5.37	3.34	4.7	16.5	34.8
Titanium dioxide, TiO_2	687.73	4.23	2.91	3.8	13.2	27.5

$$\varepsilon = \rho c_p \quad (2)$$

Specific heat capacity is the quantity of heat needed to raise the temperature one degree Celsius per gram of sample at constant pressure.[58] This property is inherent to each material, and is different according to the physic state of the material and for each temperature.

Specific heat is of great matter due to its relation to the storage energy density. When combining it with bulk density, it has a major role in determining the size of the heat storage container and to the charge/discharge time. For ceramic materials (which are the most commonly suggested materials for solid particle CSP) the specific heat is between 0.75 J/g K and 1 J/g K.[45] For example, specific heat for granite is 0.79 J/g K at 25°C.

Real density of particles is the mass of the material related to its volume, excluding porosity and empty space between particles. On the other hand, bulk density (also known as apparent density) includes the space between particles and the pores (open or isolated) of the material itself. Because of this, bulk density for packed solid particles is closely related to the pack arrangement of the particles.[59] Density variation can be appreciated in Figure 4, depending on the way the particles are packed.

It can be expected that in particle storage a bulk density gradient can be formed, having tightly packed particles in the bottom of the storage, since material pressure from above help to pack the particles below them.[49] This phenomenon must be considered for avoiding sintering since area contact and pressure increase can enhance sintering. Density values are highly important to be taken into account that will define the energy density of the material and the final total heat storage capacity of the system.

The first suggested particle media is silica sand, since it is a natural product, abundant, available all over the earth crust, it is an inert material, and with a good TES capacity. It is mostly made of SiO_2 and has been used as TES material for other applications.[35,60] Also, silica sand can be easily presented in a large variety of size distribution and, since it is used for fluidization technology, the correlations used in fluidization engineering are valid.[20] Thereby, Diago et al[61] suggested silica sand as storage medium although the calcium content of the sand must be controlled since the highest the calcium content, the highest the sand agglomeration in the receiver. An alternate option to overcome agglomeration is to use two type of sand, a commercial silica and a foundry sand made from olivine.[35] The originality of this system is that it uses a combined sand conveyor and a HEX called Sand Shifter. Test results of this system are shown in Table 6. From these results, the Sand Shifter system costs are estimated in Table 7.

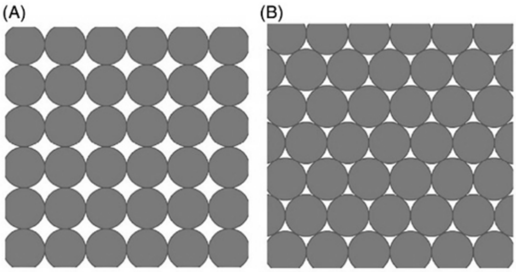


FIGURE 4 Loosely packed (A) and tightly packed (B) particles

3.3 | HEX efficiency

From the HEX point of view, the parameters to consider include their thermal and mechanical stability, material properties, performance of fluidization and flowability (either for fluidized or packed bed), understanding of the heat transfer and heat exchange design, and material handling knowledge. Also, other factors that should be considered are grouped to be included into the selection process[14]:

1. Factors that influence in the fluidized bed system performance, stability, and energy density. Some of the properties reported that affect these factors are composition, softening temperature, density, specific heat capacity, mean particle size, particle size distribution (PSD), and void fraction.
2. For packed bed solutions, a high packing density with a high heat capacity is desirable. In addition, high

TABLE 6 Preliminary heat transfer results[35]

Material	Heat transfer (W/m^2 K)
Silica sand over flat plate	310-400
Silica sand over finned plate	212-405
Olivine sand over flat plate	550-925
Olivine sand over finned plate	376-635

TABLE 7 Sand shifter TES system costs[35]

	Storage (hours)				
	System costs ($/kWh$_{th}$)				
Kind of storage	2	4	6	8	10
Shifter, silica	165	91	68	57	51
Shifter, olivine	128	75	59	51	47
Alternatives (high)	100	100	100	100	100
Alternatives (low)	70	70	70	70	70

resistance to agglomeration and sintering is important for durability considerations. Resistance to mechanical and thermal shock is important due to the high mechanical and thermal stresses that the particles receive in the HEX.[17]

3. Factors related to particle size. Although the particle size has little influence in the storage, it has a big influence in the heat transfer, either for indirect receivers or for the HEX performance. It is expected that smaller particle sizes have a better heat exchange performance for most of the cases; however, there is a limit for fluidized bed heat exchange in order to get the higher heat transfer coefficient.
4. Another factor is related to the fluidized bed boiler, which separates gas/solid phases. This element is influenced by the particle size and density relation in order to get the best possible performance.

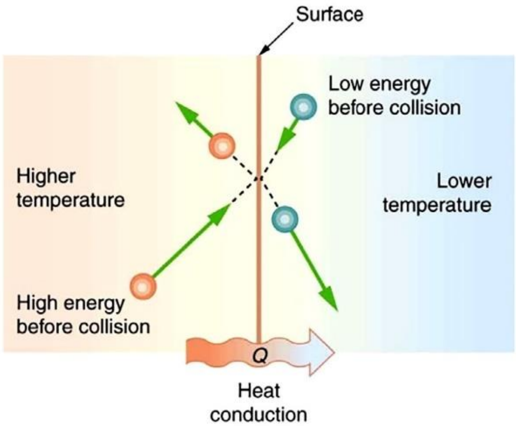


FIGURE 5 Molecule kinetic energies interaction during thermal conductivity[63]

Thermal conductivity and specific surface area are related to the HEX size and therefore, to its building cost. The thermal conductivity represents the relation between heat transferred and the temperature difference given a certain material thickness. This can be appreciated in the one-dimensional equation:

$$Q = k \cdot \frac{\Delta T}{L} \tag{3}$$

where L is the thickness, Q is the thermal energy, k is the thermal conductivity value, and ΔT is the temperature difference between the beginning and end of the conducting material.[62]

As shown in Figure 5, the molecules in two bodies at different temperatures have different average kinetic energies. Collisions occurring at the contact surface tend to transfer energy from high-temperature regions to low-temperature regions. Thermal conductivity is related to the heat exchange rate for charging (at solar receiver) and discharging (at heat exchanger), and it is considered one of the main properties that are not related directly to the particle durability.[14]

The relation between the surface area of a solid and the mass contained in it is defined as the specific surface (surface area divided by the mass), including the exposed pores in the material.[64] Particles with high specific surface can favor a quick discharge in a convective heat transfer (such as in fluidized bed heat exchangers). Specific surface for some concrete particle materials are presented in Figure 6.

In practice, it is not common to find particle materials that are monodisperse, even that it is desirable for solid particle CSP. The reality is that knowing the mean size is not

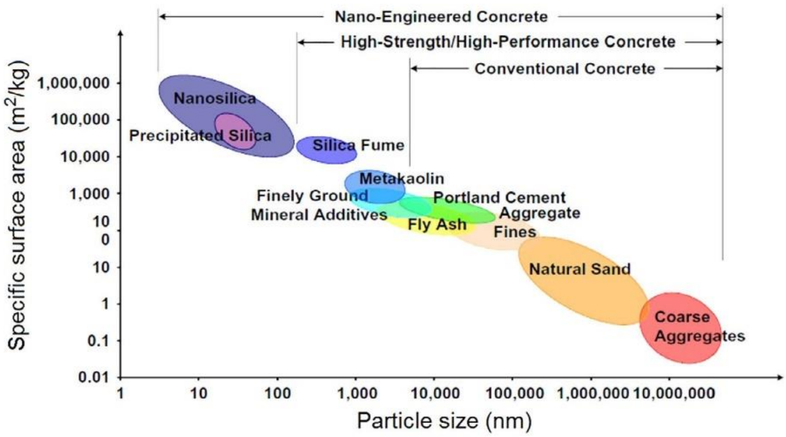


FIGURE 6 Specific surface area for different concrete materials[65]

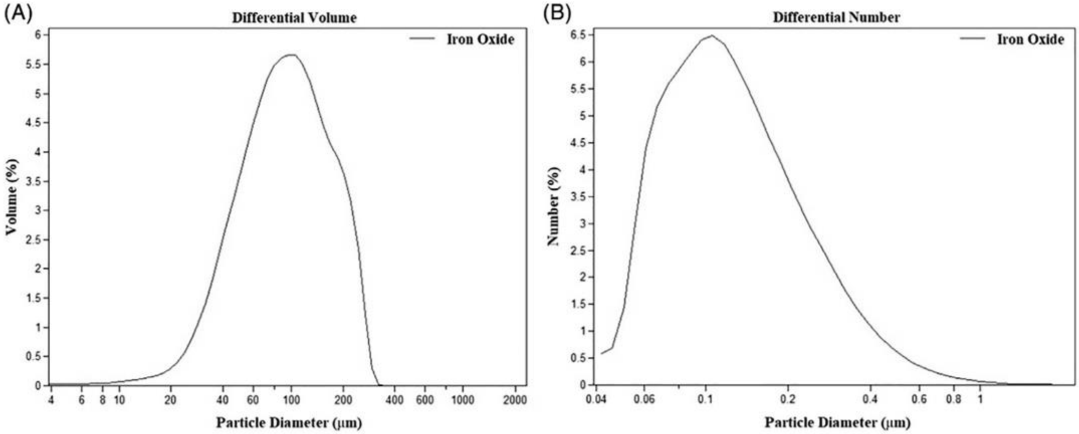


FIGURE 7 Example of PSD by volume (A) and by number (B) for the same sample

TABLE 8 Solid-particle materials considered to be used on the heat exchanger[12]

Material	Composition	Cost	Benefits	Concern
Silica sand	SiO_2	Low	Stable	Low thermal conductivity
Quartz sand	SiO_2	Medium	Purity	Quartz inversion
Alumina powder	Al_2O_3	High	Stable	High cost
Fly ash	$SiO_2 + Al_2O_3$	No/low	Experienced	Containing Corrosive minerals
Silicon carbide	SiC	High	High thermal conductivity	Hard surfaces
Graphite pebble	C	High	High specific heat	Oxidization, easy attrition

enough to make an enhanced analysis of the material; therefore, a complete distribution analysis is desirable. PSD can be analyzed by volume or by number; each one of both interpretations has its advantages.[66] For example, determining PSD by number can easily detect smaller particles, which cannot be seen in a PSD by volume. An example of both ways to analyze PSD results is shown on Figure 7 for the same sample.

Knowing the size distribution in the particle material is a very useful way to measure and predict solid particle material stability. PSD is an important indicator of quality and performance, and values like mean, median, and mode are used to determine the kind of distribution being measured.[67] An increase in bigger particles and a decrease in the smaller ones can indicate sintering, while a decrease in bigger particles and increase in smaller ones can indicate particle rupture. Also, removing particles can help to avoid possible sintering, since smaller particles increase packing and contact area between the particles.[45]

Some materials have been proposed considering them from the HEX point of view, such as silica sand and fly ash. Since fly ash has Al_2O_3 in its composition, it has a high thermal conductivity and stability when compared to silica sand even that both are low cost and have good thermochemical stability.[12] Some of the proposed materials properties can be appreciated in Table 8.

Other material challenges for particle media from HEX perspective suggested by Zhiwei Ge et al[68] include: high energy density, great durability, large temperature range, improved thermal properties, and low cost. Also, Geldart et al[44] suggested a classification founded on material's performance based on particle mean diameter and on material's real density. They concluded that if the particles are too small they cannot be easily fluidized. A diagram was created to classify the particles in A-aeratabel, B-sand like, C-cohesive, and D-spoutable; as consequence, optimal materials to be fluidized should be type A and type B granular materials. Other observation was made by Schwaiger et al who concluded that a higher heat capacity has more benefits than higher real density.[20]

Some artificial or sintered materials have been considered, such as crushed firebricks or powder made of heat resistant coatings. These materials are easy to fluidize, have high specific heat capacity and high density. Main composition for both of them includes aluminum oxide (Al_2O_3) (~2/3) and magnesium oxide (MgO) (~1/3). Actually, it has been proposed to try to minimize particle density so that air

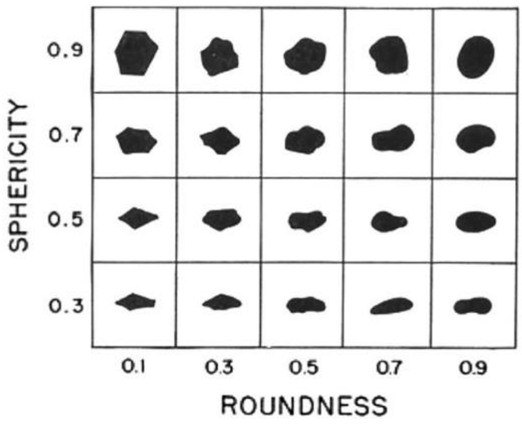


FIGURE 8 Sphericity and roundness classification[71]

needed for fluidization can be reduced as well as the parasitic energy consumption. The main disadvantage for artificial or sintered materials is that the price is expected to be higher compared to natural o byproduct materials.

3.4 | Erosion evaluation

When moving particle media there are two phenomena that create particle attrition, the first is the inter-particle collision, and the second is the interaction between the particle media and the walls (either of the conveyance, HEX, or SPR systems).[69] The greater attrition effect is expected on the HEX fins and tubing, but can be important on fluidized bed receivers and some of the particle elevators previously considered.

Roundness and sphericity define the factor shape of particles, and it is an important factor (together with material hardness) that determines the erosion damage to the system. Roundness define how smooth are the edges of the particle, while sphericity defines the relation to its three orthogonal axes.[70] Mathematically, the sphericity can be defined as:

$$\text{Sphericity} = \sqrt[3]{\frac{\text{Particle volume}}{\text{volume of a sphere that completely surrounds the particle}}} \tag{4}$$

While roundness can be calculated by:

$$\text{Roundness} = \frac{\text{Average radius of corners and edges}}{\text{Radius of maximum inscribed circle}} \tag{5}$$

A table guide was proposed by Krumbein et al in 1956,[71] and showed in Figure 8, makes more easy to identify the sphericity and the roundness based on the particle appearance.

Some studies have made analysis by mass measurement at periodic attrition intervals using silica sand as particle media. The results indicate that copper tubes with aluminum fins experience wear in short time, while copper tubes with steel fins took more than 10 times longer to experience the same wear. Early results showed that, by using silica sand, a steel HEX tube can lose only 1% of its mass. When using olivine for evaluating the erosion on the previous described scenarios, no significant wear was found.[55] This suggests that there is a dependence on the combination of materials used for the system and the particle media; hardness (that has a variation with temperature) and shape can have critical influence when evaluating wear.

Erosion effect on the falling particle receiver has been evaluated within the collection hopper and other structures. Loss of less than 0.004% mass was reached by particles velocities below 7 m/s. For velocities of more than 10 m/s loss exceeded 0.01%. The attrition was expected to be high for the first cycles, as the surface of the particles may not be too smooth. The particle media used for the evaluation of the erosion on the falling SPR was proppants, which have high roundness and sphericity, but high hardness.[54]

A suggested alternative for reducing wear on falling receiver is to buffer the particle impact by using some of the previously studied porous structures. Nevertheless, it has been appointed that for these structures the attrition effect must be mitigated when considering the ceramic material to be used. Also, curved structures made of resistant ceramics have been suggested for slowly decelerate the particles fall.[54] From the particle media point of view, the fracture resistance tests show that there is a critical impact velocity related to the compressive stress and fracture toughness of the particles. This impact fracture is more relevant for particles with reduced sphericity and roundness.[42]

3.5 | Particle durability

When evaluating particle media durability for CSP, we must consider that the high temperature conditions will remain years while residing on the TES tanks. Some studies suggest that there should be a regenerating process for the particle media; nevertheless, the complexity and energy required has not been evaluated as far.[33] Another effect on durability is the one caused by the stress generated by quick temperature variation and continuous heat charge/discharge cycles. This effect must be further studied since there are no reported works on this matter.

Since proppant materials proposed are primarily composed by sintered bauxite, the variation between them from the chemical composition point of view depends on the ratio of alumina to silica and to the minor oxides present. It is expected that a material used for direct solar irradiance

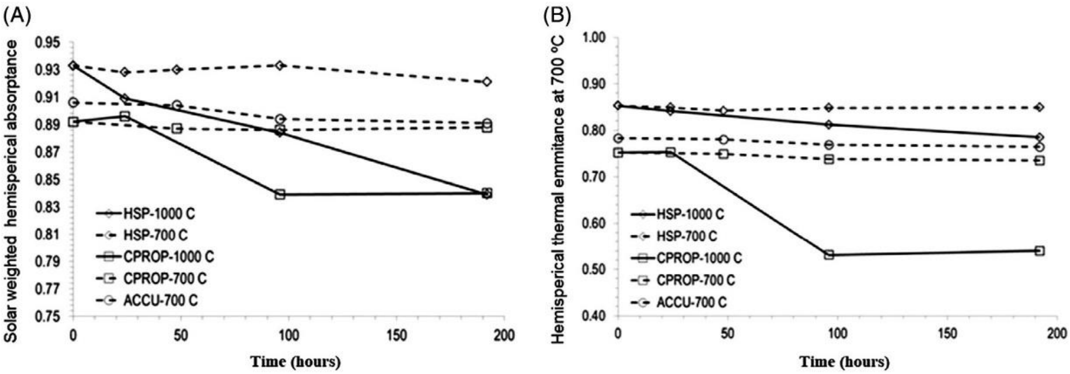
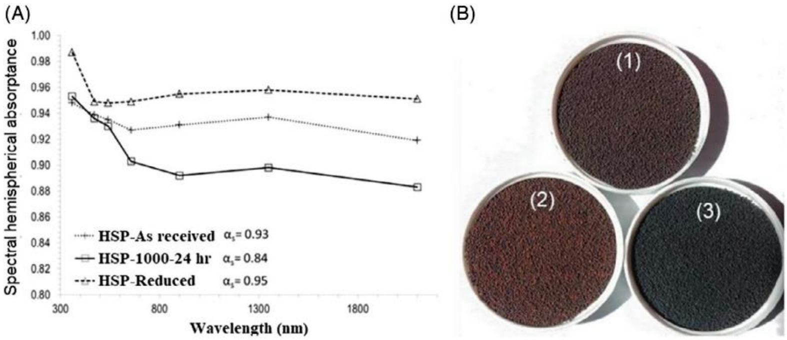


FIGURE 9 A, Solar weighted hemispherical absorptivity for three proppant candidates as a function of heating duration. B, Hemispherical thermal emissivity as a function of heating duration[33]

FIGURE 10 A, The spectral hemispherical absorptivity of chemically reduced CARBOHSP (700°C for 20 hours) compared to as received and heat treated samples. B, Images of CARBOHSP in the (1) as received condition, (2) after heating in air at 1000°C for 24 hours, and (3) after chemical reduction[33]



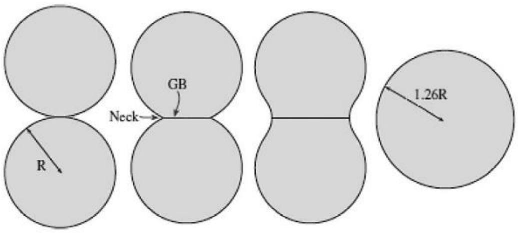


FIGURE 11 Two-dimensional 4 step sintering model[45]

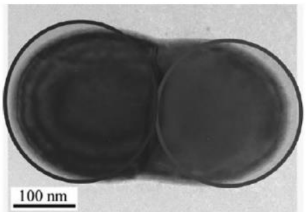


FIGURE 12 Si particles partially sintered[45]

harvest, should have at least 85% of solar absorptance. When considering particle media durability, long-term heat effect must be considered, since a minor variation in composition can lead to considerable solar absorptance variation. Solar absorptance characterization has been performed to the previously mentioned proppants after up to 200 hours heat treatment at 700°C and 1000°C. Absorptance and emissivity variation can be appreciated on Figure 9 for several proppants. At 1000°C, CARBO HSP changes considerably after only 24 hours, dropping from 93% to 91%, while emissivity decays from 85% to 84%. In contrast, at 700°C the change takes place considerably slower.[48]

At long term, the absorptance can be reduced below 85% critical point at 1000°C, while for 700°C remains above 92%. Composition analysis by X-ray diffraction (XRD) showed evidence of small chemical transformations in the bauxite crystalline

TABLE 9 Summary of solid particle optical properties, cost and density to be used for CSP; where, α—absorptance, ε—emissivity, ρ—bulk density

Material	Composition	α	ε	Cost (eur/kg)	ρ (g/cm^3)	Reference
Silica Sand	92%—SiO_2 06%—Al_2O_3 <1%—Fe_2O_3 <1%—K_2O <1%—TiO_2	0.44-0.66	0.59-0.9	0.35-0.52	2.1-2.65	20,50,51,69,72-74
Hematite	98%—Fe_2O_3 01%—FeO <1%—Mn_2O_3	0.85	0.56	N/A	5.28	20,75,76
Silicon Carbide	SiC	N/A	0.83-0.96	12.3-17.5	3-3.2	51,72
AccucastID	75%—Al_2O_3 11%—SiO_2 03%—TiO_2 09%—Fe_2O_3	0.906	0.754	N/A	N/A	19,33,73
CarboHSP	83%—Al_2O_3 05%—SiO_2 04%—TiO_2 07%—Fe_2O_3	0.934	0.843	N/A	3.56	19,26,33
Alumina	Al_2O_3	0.1-0.25	0.3-0.5	28.1-35.1	3.94-3.96	20,51,77
Zirconia	95%—ZrO_2 04%—MgO	N/A	0.42-0.62	15.8-22.8	6.03-6.16	51,78
CarboProp	72%—Al_2O_3 13%—SiO_2 04%—TiO_2 10%—Fe_2O_3	0.89-0.93	0.75-0.80	N/A	1.56	19,33,79
Titanium Dioxide	99%—TiO_2	0.4-0.7	0.5-0.8	21-31.6	3.97-4.05	51,77
Magnesium oxide	MgO	N/A	0.2-0.5	29.8-43.8	3.54-3.58	20,51,64,77
Manganosite	98%—MnO 1.7%—MgO <1%—Fe_2O_3 + FeO	N/A	N/A	N/A	5.43	76,80-82
Olivine	42%—MgO 39%—SiO_2 19%—FeO	N/A	N/A	35-43	2.8-3.37	51,83
Fly ash	88%—SiO_2 05%—CaO 02%—Al_2O_3 <1%—Fe_2O_3	N/A	N/A	0.03-0.14	1.83-2.2	51
Graphite	C	0.84	0.98	9.47-14.4	1.61-1.67	51,69,75
Basalt	48-59%—SiO_2 15-18%—Al_2O_3 07-12%—Fe_2O_3 06-09%—CaO 04-05%—Na_2O 03-05%—MgO 01-02%—TiO_2	N/A	0.72	2.01-2.22	2.5-2.89	51,72,84

phases, containing oxides of aluminum, silicon, titanium, and iron. These results suggest that there are changes on the oxidation state without a related phase change.[54]

When making the thermal treatments under a chemically reducing atmosphere (5% H_2 in either N_2 or Ar) the solar absorptance increased for either as-received particles or previously degraded particles.[33] Absorptance variation can be appreciated in Figure 10A and color change on the particles in Figure 10B.

Sintering happens when material small particles (or powder) transform into a solid body without melting the original material,

TABLE 10 Summary of solid particle thermal properties to be used for CSP; where, k—thermal conductivity, C_p—specific heat capacity

Material	Melt point (°C)	Service temp (°C)	k (W/m°C)	C_p (J/kg°C)	Reference
Silica sand	1200-1400	400-600	1.14	742-1175	20,50,51,69,72-74
Hematite	1565-1597	N/A	N/A	650	20,75,76
Silicon carbide	2150-2250	1470-1540	90-110	663-677	51,72
AccucastID	N/A	N/A	0.7	1175	19,33,73
Carbo HSP	N/A	N/A	2	1275	19,26,33
Alumina	2050	977-1030	20-25.6	790-800	20,51,77
Zirconia	2550-2700	2150–2250	1.7-2	418-436	51,78
CarboProp	N/A	N/A	N/A	1175	19,33,79
Titanium dioxide	1830-1850	1570-1640	4.8-9.2	683-697	51,77
Magnesium oxide	2810-2860	1980-2130	30–60	880-1030	20,51,64,77
Manganosite	1945	N/A	N/A	621-788	76,80-82
Olivine	1870-1950	778-821	8–10	700-900	51,83
Fly ash	1270-1470	873-973	1.11-1.25	813-867	51
Graphite	3530-3680	2580-2690	44.2-48.3	852-941	51,69,75
Basalt	1410-1490	500-850	0,03-0,04	840	51,72,84

no matter if it is composed of crystalline o amorphous structures. This phenomenon can seriously affect particle shape and size distribution; therefore, it affects the particle media durability. Sintering is enhanced by high temperatures, high pressure, and high contact surface between the particles and the amount of time these conditions are applied over the particle media.[65]

Agglomeration happens when there is a radical rearrangement of particles; it is more noticeable in metals and solid ceramics. Agglomeration is considered an early stage of sintering, since it is one of the conditions that favor sintering. Several experiments and simulations have shown that strength, shape, mean size, and size distribution affect the evolution of the microstructure on agglomeration process and then on sintering process.[63] A PSD with a big SD causes the smaller particles increase the contact areas, as well as they are more vulnerable to get sintered into a bigger particle. For solid particle CSP the main objective is avoiding agglomeration and sintering, and the most vulnerable moment for particles to agglomerate or sintering is at the lower part of the hot tank storage.

For characterizing the degree of agglomeration of one sub-section of particle media there is a parameter called "variance," for which the effects of PSD and inter-particle viscosity are analyzed.[63]

Agglomeration research has found that alumina, silica, and zircon have the best behavior when being used between 1000°C and 1200°C. There has also been found that there is a relationship with solar absorptance, since low solar absorptance indicates that the particle media can behave better on agglomeration issues. Therefore, further studies on material selection and research has to be performed to find a good balance for these contradictory conditions.

Determining agglomeration by experimental or theoretical research has been found difficult since agglomeration occurs with smaller particles, broader PSD, higher temperature, smaller tangential viscosity, or smaller initial volume fraction[42]; therefore, even having different initial PSD it can still lead to different agglomerations.

Melting point of a solid is the phase change from solid to liquid. For solid particle materials for CSP it is very important because this change should be avoided during materials lifetime.

For ceramic materials, low melting points (even if it is over the service temperature) can indicate possible agglomeration and sintering problems. Sintering is enhanced with pressure, temperature, and/or surface area increase. For ceramic materials, sintering temperature is close to 70% of the melting point temperature.[45] Sintering process can be appreciated in Figure 11 (concept model) and Figure 12 (TEM image).

Other solid-solid phase change must be considered and studied for the service temperature range, since they can result in a density change that can modify the particles physically, causing rupture, or increasing the specific surface (increasing the possibility for chemical reactivity).

4 | SUMMARY OF PROPERTIES OF SOLID PARTICLE MATERIALS

Tables 9 and 10 summarize the solid particles properties which are available in the literature. Therefore, absorptance, thermal conductivity, specific heat, density, and price are listed in this table in order to compare the proper candidates available to be used as solid particles for CSP plants.

5 | CONCLUSIONS AND FUTURE WORK

The use of solid particle materials has big potential for developing a new generation of solar power towers. This new technology can enhance CSP thermal power plants to reduce electricity cost production as well as adding flexibility to the electric network, allowing a bigger renewable energies implementation. This technology will benefit highly irradiated regions, which happens to be the most expected regions to be developed during the following years increasing their energy needs over the world's average.

Incrementing current CSP service temperature has shown to have performance benefits when converting heat into electricity in the power block, by being able to use more efficient thermodynamic cycles or even use combined cycles using exhausted heat from topping cycle as input for one or more bottom cycles.

Current solid particle technology development has proven to be viable in the specific functional units balance (solar particle receiver, HEX, thermal storage). Nevertheless, further studies must be performed for conveyance and storage systems, since the most advanced research has been made on solar particle receivers and heat exchangers. Also, material considerations must be taken into the account, since the different parts of the power plant design expect different properties and parameters to be met by the particle media.

Future work should include:

1. Material selection according to each specific design (direct/indirect receiver, free falling or fluidized receiver, fluidized or packed bed heat exchanger, etc.), and needs to be optimized considering tradeoffs of particle properties in the major components. Therefore, there are properties that are in contradiction with others. For example, the mean size of the particles must be high to avoid sintering and agglomeration but must be low to facilitate heat transfer within the heat exchanger. Hence, the selected materials must present a compromise that fit all the requirements from the different parts of the system.
2. Thermal stress tests due to the high temperature itself in the long term and to the high number of charge/discharge thermal cycles expected during power plant lifetime (up to 11 000 is expected, that is one cycle per day during 30 year standard power plant lifetime). This behavior will influence particle media durability.
3. Mechanical stress tests due to possible attrition and erosion caused by/to the particle media and the plant built in materials.
4. Complete characterization of the best materials obtained from material selection, since most of the properties and parameters are expected to change because of the high temperature exposure, to the thermal cycles, and to the interaction with the plant functional units.

Finally, once best candidate materials have been completely studied, material combinations or material enhancement can be considered to level up the possible drawbacks of the best material selected.

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LIST OF ACRONYMS

CSP	concentrated solar power
HEX	heat exchanger
HTF	Heat transfer fluid
IEA	International Energy Agency
PSD	particle size distribution
SPR	solid particle receiver
TEM	transmission electron microscopy
TES	thermal energy storage
XRD	X-ray diffraction

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Material Based Design for solar tower applications using solid particle materials

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Abstract

Renewable energies have risen, all over the world, with the objective to reduce greenhouse gas emissions and the dependency in fossil fuels. Actual CSP renewable energy has a limitation of operation temperature due to solar salt operation temperature limit. Solid particle materials had been proposed for sensible heat storage in solar towers for temperatures over 600ºC. Some materials have been previously suggested, some of their properties and parameters have been identified and measured. Nevertheless, no standardized materials selection has been performed. The aim of this study establish the base for finding a proper material for a specific design, taking into the account the properties and key parameters interactions between the different parts of the system. This methodology consists on re-designing according to the material selection, which is named as the *Materials-Based Design* (MBD) process. During this work key properties and parameters of materials were obtained and a MBD was performed, obtaining as a result the different material indices, for all the operation stages, that must be complied in order to make a formal material selection process. Recognizing the design objectives, and not only the properties, has allowed building one or more material indexes which allows to make a first screening and selection task.

Keywords: materials based design, solid particle, material index, concentrated solar power, thermal energy storage

1. Introduction

With the creation of the Intergovernmental Panel on Climate Change (IPCC) in 1988 [1], it has been clearly established that the climate change is related and accelerated by human activity, mostly from fossil fuels used for energy purposes. Within this context, renewable energies have risen, all over the world, with the objective to reduce greenhouse gas emissions and the dependency in fossil fuels. Similarly, energy efficiency improvement is one of the most promoted subjects by the European commission [2] through their energy efficiency directives. Energy technologies interactions must be developed and deployed together between energy policies and the market. Integrated and connected electricity systems are key to the transformation of the energy sector. In addition, energy systems integration and enhanced demand response will bring new opportunities for optimization and increased efficiency in delivering services. In this scenario, thermal energy storage has been proposed as one of the promising side technologies to reduce energy consumption, splice energy supply with energy demand, improve the energy efficiency of renewable energies and improve energetic efficiency by applying it to waste heat systems, all consequently reducing CO_2 emissions [3,4].

Between 2004 and 2014, solar thermal electricity capacity has increased from about 0.4 MW to more than 3.7 GW worldwide. Although it is true that these numbers are still far from the targets set for the future, the main trend is to continue to increase these percentages [5].

Thermosolar energy has been studied for more than a hundred years, and the first concentrating solar power (CSP) plant built was in 1968 in Italy. This plant, built by Professor Giovanni Francia, could produce 1 MW of energy using superheated steam [6]. Since then, the CSP plants have evolved and have been implemented in different countries. This work is focused on the high temperature concentrating solar towers, because they offer high conversion efficiency from thermal energy to electric energy and are highly scalable.

Nowadays, most of the concentrating solar towers work with molten salts as the main Thermal Energy Storage (TES) and Heat Transfer Fluid (HTF) material due. However, this material presents several drawbacks because of the corrosion and low reliability when reaching temperatures over 565 ºC [7–9]. Therefore, innovation on selecting and developing new materials for CSP tower plants is one of the main goals to improve the actual commercial technology.

Research groups and enterprises are commonly focused on system design and afterwards they search for the materials that best fit the specified boundary conditions of the designed system. Nonetheless, there are several instances in which the number of the available materials is limited and the system design must be performed according to the available materials. Even that the available materials can be enhanced there are a limited number of them. This happens in high temperature systems, where the highest temperature the less stable materials are available to operate on such conditions.

Our case of study is the use of solid particle materials for sensible heat storage in solar towers for temperatures over 600ºC [10,11]. Solid particle materials have been proposed for enhancing concentrating solar power plants, but these materials can be potentially used for waste heat exploitation and solar heat industrial applications [12,13]. Some materials have been previously considered, such as silica sand, alumina powder, fly ash, silicon graphite, among others; nevertheless, non-standardized materials selection [14] has been performed [11,15]. Even though, properties and parameters have been previously identified and measured for some of the considered materials; such as particle size distribution, thermal conductivity, specific heat, thermal shock, attrition and even rheological properties [11,16].

During the conventional design procedure, the market need is translated as a concept which is the promising principle. Afterwards, the embodiment part of the design process defines the layout and assemblies the proof of concept. Then, this concept is optimized and it is evaluated. However, materials behavior is not taken into account until stages far away from the concept design stage. Following the conventional design procedure, the boundary conditions are defined and these are the ones used to find the best material available.

The *design-led* approach [17] starts from the requirements that the materials must meet to achieve an acceptable performance of the main design concept. For finding a proper material for a specific design, properties and key parameters interactions, manufacturing processes and energy and environmental impacts must be evaluated to determine the relevance of each of them. Moreover, it could be necessary to go back to the design process several times adapting the layout, scale, or even the work principle according to the best materials available. This process of re-designing according to the material selection can be considered as a whole *Materials-Based Design* (MBD) process as shown in *Figure 1*.

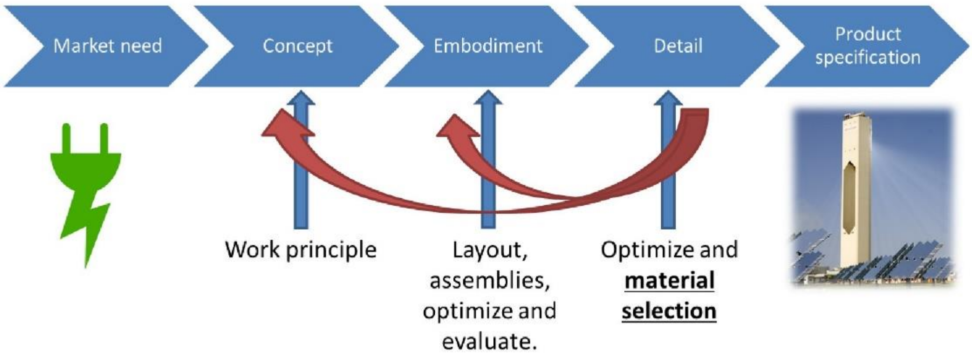

Figure 1. Materials selection within system design process [18].

This is the scenario of solid particle CSP technology development, since there are a limited number of materials that could handle the proposed service temperatures of almost 1000 °C. Parameters and properties can have big impact in the material performance and its durability. Several materials have been previously proposed for this application but all of them have showed some backward or have lack of information of their properties and parameters at the operation conditions [11].

Properties and parameters of a specific material can then determine changes in the CSP plant design. An example could be the particles storage capacity that could change according to thermal properties such as heat capacity and to morphological conditions such as particle size distribution or particle shape. Other example could be the receiver particle holding time design that is related with optical, thermal and morphological properties and parameters.

In this way, the material selection have more relevant impact in the contept, working principle and design. To perform the MBD, it is important to identify the parameters and properties of materials the marked needs in order to perform the material selection in a proper way.

Therefore, this study is focused on identifying key properties and parameters of materials in order to develop a MBD based on the main requirements for high temperatures solid particle to be used as TES medium in CSP tower systems. Therefore, key parameters and properties should be identified, finding their relation with the different plant design stages (solar receiver, TES and HEX). In addition, thermo-mechanical stability and material compatibility transversal objectives are considered.

2. Key parameters and properties

Based on a former literature search in handbooks and scientific publications, the most significant parameters in the evaluation of the materials to be used as solid particles for direct CSP systems are listed in Table 1. This table provides technical and scientific basis in order to perform the formal selection of the most appropriate candidate materials. In some cases, desired values are proposed by researchers.

In this table, parameters of particles and properties of the materials are differentiated, being these later those related to the bulk material intrinsic properties, while parameters refer to particle physical conditions (which in some cases can be modified).

Table 1. Key properties and parameters of solid particle materials for CSP [11].

	Properties and parameters	Relevance	Desired value
Optical	Solar Absorptance	Determines the ability of the material to capture heat from solar energy.	$\alpha > 0.85$
	Emissivity	Reflect the potential energy losses by heat radiaton of the material.	$\varepsilon < 0.88$
Physical	Sphericity	Affects on the particle material flowl thru all the system.	0.9
	Roundness	Affects on the particle material flowl thru all the system.	0.9
	Solid density	Determines the energy density and have influence the heat exchange process (fluidized or not)	High
	Particle size distribution	Determine the volume or number of particles of a certain diameter. Important to prevent the sintering and agglomeration of the material.	100-300 nm
Mechanical	Hardness	Determine the wear and mechanical degradation of the solid particle under stress conditions.	High
	Yield strength		High
	Fracture toughness		High
Thermal	Specific heat capacity	Determines de energy density of the material.	High
	Thermal conductivity	The ability of the particles to absorb heat and to transfer it to the heat exchanger.	High
	Melting point	Melting point have a close relationship with sinterizing, which must be avoided.	Higher than 1500°C
	Elongation	Ability to withstand of a material when temperature has big and fast changes. Thermal shock can cause dynamic crack propagation producing fatigue in the material structure. Also, material physical degradation can make the material more reactive.	High
	Thermal expansion coefficient		High
Chemical	Chemical composition	Determines chemical stability influence on the durability	Stable with temperature

There are several stage objectives that should be identified in order to choose the most appropriate material; each of these most significant objectives dictates the optimal behavior of one or more material properties and/or parameters. Nevertheless, these properties and parameters can influence more than one stage objective each, and even the desired value can be significantly different between stage objectives. The authors proposed the following objectives and properties/parameters that must be evaluated on solid particle CSP technology with directly irradiates media, and is presented on *Table 2*:

Table 2. Material Stage Objectives and properties/parameters relation.

	Stage	Main objectives	Properties and parameters involved
System	Solar receiver	Improve solar field exploitation	Absorptivity, emissivity, specific heat, thermal conductivity, specific surface
	Thermal energy storage	Increase thermal storage, decrease thermal losses, avoid sintering and reduce material cost.	Specific heat, bulk and solid density, melting point
	Heat exchanger	Release thermal energy in short time	Particle size distribution, solid density, specific heat, thermal conductivity, specific surface, sphericity, roundness
Transversal	Thermo-mechanical stability	Improve durability of the particles and system materials	Chemical composition, sphericity, roundness, melting point, particle size distribution, hardness, yield strength, fracture toughness, elongation, thermal expansion coefficient
	Material compatibility	Avoid corrosion and wear	Corrosion enhancement of system components

3. Materials Based Design approach

During a design process and further material selection is primordial to evaluate the performance of the material on the final task or application. This performance depends on different properties and parameters that can be grouped according to the objectives based in the specific needs of each application stage.

When combining different material objectives (and therefore, properties and parameters) the performance of the material for an specific application is determined by the material index [19]. Typically this material index or indexes are performed after an initial screening and evaluates the performance of the candidates materials under the defined boundary conditions [20].

The materials based design approach is based on obtaining a material index based on the existent methodology for material selection [14]. In the case under study (*Figure 2*), the TES medium selection is based in three main parts of the CSP tower system: Receiver, heat exchanger and TES system.

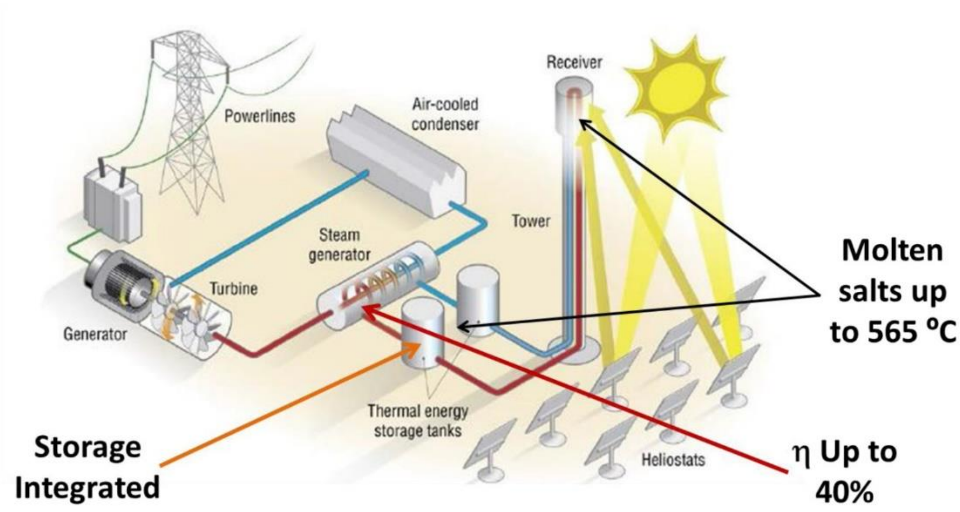

Figure 2. Main parts of CSP Tower system configuration

3.1 Solar absorptance

The receiver which is designed to allow the HTF to absorb directly the solar irradiance is called Direct Receiver. The most studied direct receiver are the Free-falling particle receiver [10]. To evaluate the heat transfer capacity once the solid particle is located into the direct solar absorption receiver, certain properties need to be considered. The optical properties have been considered critical for optimizing solar field. Solar absorptance efficiency has been used to evaluate the efficiency of this sunlight heat harvesting [21,22]. This efficiency must be the higher as possible in the whole solar spectrum, especially in the most energy intensive wavelength ranges. In a flow of particle media solar absorptance efficiency is affected fundamentally by absorptivity and emissivity particle materials properties. However, absorptivity should be interpreted in terms of solar absorptance, taking into the account the sunlight spectrum [22]. Emissivity is only influenced by the temperature of the particles and the environment. Since in heat to electricity efficiency increase with high temperatures, low emittance and high absorptance is required [23].

The absorption efficiency η is determined by *Eq. 1* where η is the absorptance efficiency, α is the material solar absorptance, $\dot{q}_i$ is the incoming irradiation into the receiver in $W\,m^{-2}$, Ɛ is the material emittance, σ is the Stefan-Boltzmann constant with a value of $5.61x10^{-8}\ W\,m^{-2}\,K^{-4}$ [24], Ta is the ambient temperature, and Tr is the temperature in the receiver.

$$\eta = \frac{\alpha \dot{q}_i - \varepsilon\sigma(Tr^4 - Ta^4)}{\dot{q}_i} \qquad \text{Eq. 1}$$

When considering real conditions, solar absorptance has a stronger influence in the efficiency. However, when increasing temperatures emissivity becomes more and more relevant. *Figure 3* shows solar absorptance efficiency of four materials usually referenced by research groups. A relation of concentration 600 to 1 in order to reach 6x10^5 W· m^{-2} in the incoming radiation $\dot{q}_i$ with an ambient temperature of 25 °C is assumed. *Table 3* shows the reported solar absorptance and emissivity values considered in *Figure 3*.

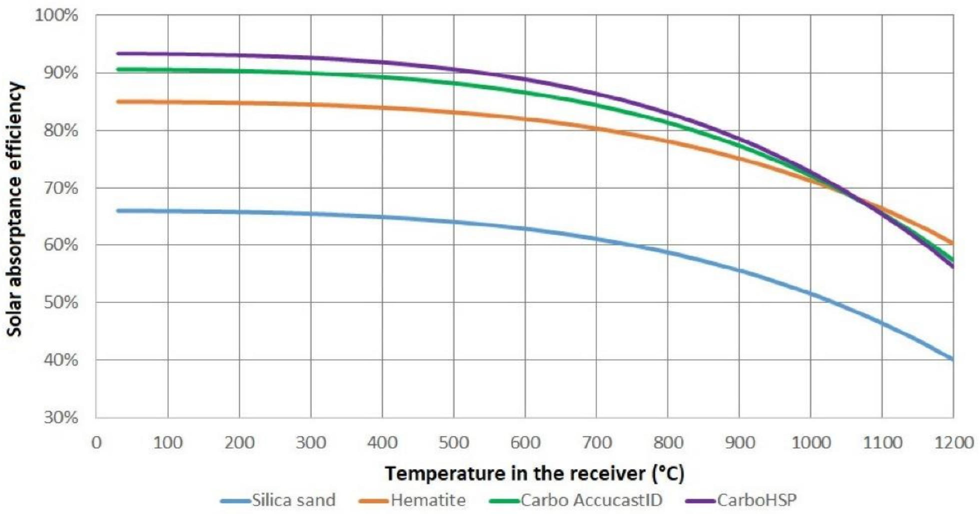

Figure 3. Effect of temperature in the solar absorptance efficiency according to the use of Silica sand, hematite, Carbo AccucastID or CarboHSP.

Service temperature for solid particle CSP are expected to be over molten salts limit of 565 °C [7–9] and below 1000 °C [10]. At this temperatures, *Figure 1* denotes that solar absorptance is more relevant. Therefore, it will be preferable a material with high emissivity than another with low solar absorptance. Maximizing solar absorptance in the material selection will be more critical than reducing emissivity.

Table 3. Solar absorptance and emissivity for solid particle CSP materials [11].

Material	Solar absorptance	Emissivity
Silica sand	0.66	0.59
Hematite	0.85	0.56
Carbo AccucastID	0.90	0.75
Carbo HSP	0.93	0.84

For obtaining the material index, function, constraints, objective and free variables should be identified. *Table 4* summarizes this information for directly irradiated solar particle receivers.

Table 4. Material index definition of solar receiver.

SOLAR RECEIVER	Function	To absorb concentrated solar heat into the solid particle material
	Constrains	Mechanical properties
		Working service temperature
	Objective	To maximize the heat absorbed per m^2 of receiver apperture
	Free variables	Material choice
		Dimensions

The main function is to absorb the maximum amount of direct solar radiation by each particle. The main o**bjective** is to maximize the absorbed per square meter based on the *Equation 2*.

- **Constrains:** the boundary conditions are the mechanical properties that must be higher enough to not fracture the material under operating conditions; the service temperature of the material must be higher than the operation temperature.
- **Free variables:** the material is one free variable in this material index due to the objective is proceeding to a materials selection. As the dimensions and shape of the particles don't have influence in the receiver heat flux it is also defined as a free variable.

Taking into account the material index definition, and based on the mathematical equation and geometrical constrains, the objective equation can be obtained for the solar receiver efficiency (*Equation 1)*, and is described in *Equation 2* where $\dot{q_a}$ is the heat flux being absorbed by the solid particles in the receiver.

$$\dot{q_a} = \alpha\dot{q}_i - \varepsilon\sigma({T_r}^4 - {T_a}^4) \quad \text{Eq. 2}$$

In order to comply with the objective, $\dot{q_a}$ must be maximized. Therefore, two material indexes are obtained (*Equation 3* and *Equation 4*). M_1 and M_2 index should be maximized while the inverse should be minimized. *Figure 4* shows the selection criteria for some of the materials reported in literature [11].

$$M_1 = \alpha \quad \text{Eq. 3}$$

$$M_2 = 1/\varepsilon \quad \text{Eq. 4}$$

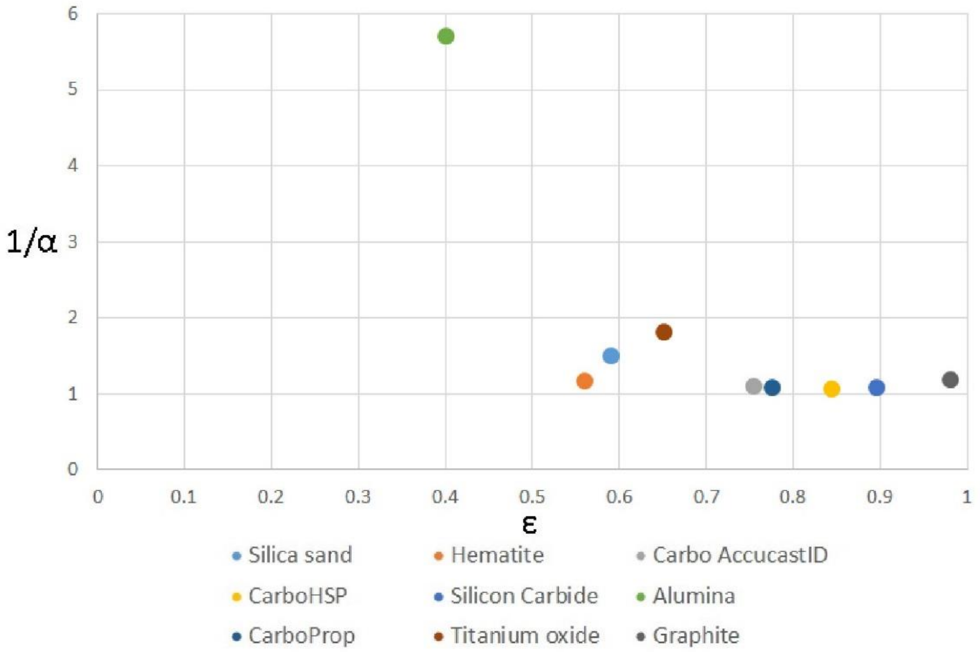

Figure 4. Materials to be used for storing solar thermal energy maximizing solar absorptance and minimizing emissivity.

3.2 Thermal energy storage capacity

TES objectives have been presented in *Table 2*. Sintering is related to melting point property, shape parameters and storage design layouts (due to the packing and pressure applied during the storage). Thermal losses have geometrical relations between are and volume of the storage design and the amount of energy that can be stored in a specific volume. Therefore, from the material perspective energy density should be maximized. Energy density has already discussed to be related to bulk density and specific heat from the materials perspective and to the temperature increase, which is a design parameter [14,18]. This can be observed in the *Equation 5*:

$$\frac{Q}{V} = \rho\, C_p\, \Delta T \qquad \text{Eq. 5}$$

where Q is the amount of heat energy stored (Joules), V is the volume (m^3), ρ is the materials bulk density (kg/m^3), C_p is the heat capacity (Joules/kg K), and ΔT is the temperature increase between lower and higher operation temperatures.

Cost of the material is relevant for TES system, since determine the amount of total energy that can be stored by the system. From the particle media perspective, the amount of heat per unit cost can be defined as shown in *Equation 6*, where C_m is cost of the material per mass unit.

$$\frac{Q}{C} = \frac{C_p}{C_m} \Delta T \qquad \text{Eq. 6}$$

Thermal conductivity and thermal diffusivity are not considered in TES material selection, since releasing the heat easily is important as well in other stage. Insulation of TES should be of concern of material selection and design of the storage tanks which are not related to this stage but to the materials compatibility evaluation.

Table 5 summarizes the function, constrains, objective and free variables for this kind of TES system.

Table 5. Material index definition of TES material

STORAGE	Function	To store the solid particles in order to store the energy for later electricity production
	Constrains	High maximum service temperature
		Good thermal conductivity (above 1W/m K).
	Objective	Maximize the energy storage per volume (for reducing thermal loss rate) and per unit of material cost.
	Free variables	Material choice
		Dimensions

The main function is to store the maximum quantity of heat as TES material in CSP systems. The main o**bjective** is to maximize the heat absorbed per material cost unit a per volume unit in order to reduce thermal losses as shown in *Equation 5* and *Equation 6*. In order to comply with the objectives, both equations must be maximized.

- **Constrains:** is the high service temperature for avoiding sintering and a good thermal conductivity.
- **Free variables:** the material is the free variable in this material index due to the objective is proceeding to a materials selection and the dimension and shape of the particles.

Therefore, two material indexes are obtained (*Equation 7* and *Equation 8*). M_3 index should be maximized as well as M_4 index. *Figure 5* shows the selection criteria for some of the materials reported in literature [11].

$$M_3 = \rho\, \mathrm{C_p} \qquad \text{Eq. 7}$$

$$M_4 = \frac{C_p}{C_m} \qquad \text{Eq. 8}$$

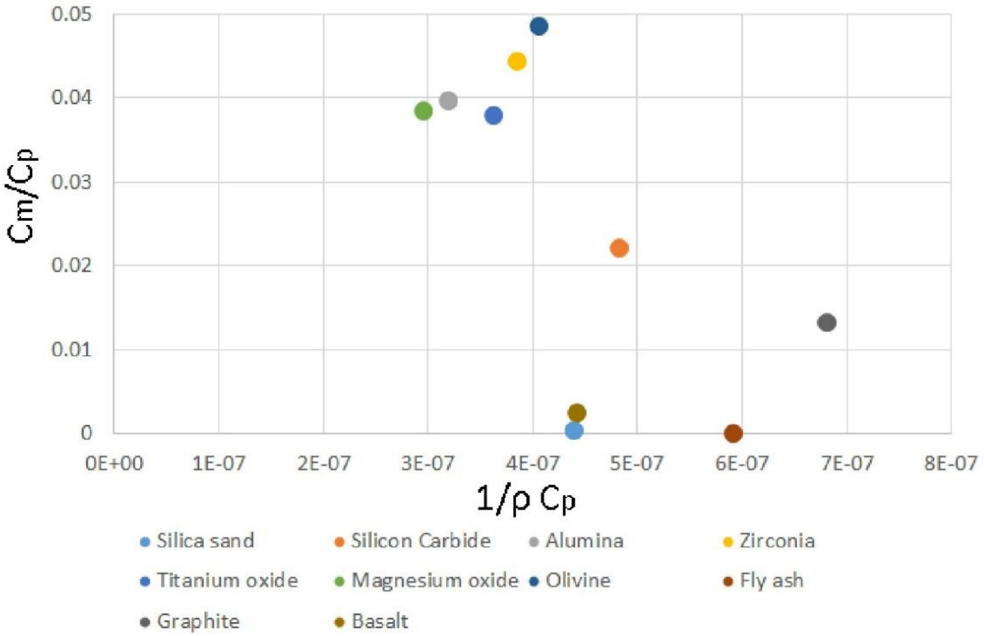

Figure 5. Materials to be used for storing solar thermal energy maximizing amount of heat per volume and per unit cost.

3.3 Heat transfer capacity

The heat transfer capacity is a main objective in terms of transmitting the heat that was stored previously in the solar receiver from the sun in the material and transferring the heat stored in the solid particle to a heat exchanger for power production. This is also relevant for indirect receivers that doesn`t directly irradiate the particles.

In a heat exchanger the thermal conductivity depends on several properties and parameters related to the material of the HEX, the flow of particles (depending if is a fixed bed or a fluidized bed) and into the specific heat capacity and thermal conductivity of the particle media. However, specific heat capacity is more related design parameters, since it will influence mostly flow speed of the particles. In order to efficiently transfer heat from the solid particle surface, only the thermal conductivity has a direct influence from the solid particles perspective [16].

In a fluidized heat exchanger the solid particles have to meet certain requirements in order to satisfy the solid fruitification and circulation, high sintering temperature, high heat capacity, high thermal conductivity, a mean diameter, solid density and shape that permits a good fluidization quality [25]. Nevertheless, these parameters are related to functional and geometric functions. Considering a fixed bed HEX, and from the solid particle material perspective, the heat transfer flux can be defined in relation to the thermal conductivity k, the width of the particle bed w and the temperature difference in both sides of the HEX T_1 and T_2 as shown in *Equation 9*.

$$\dot{q}_h = \frac{k}{w}(T_1 - T_2) \qquad \text{Eq. 9}$$

Table 6 summarizes the function, constrains, objective and free variables for the heat transfer fluid used in the HEX.

Table 6. Material index definition for solid particle HEX

HEAT EXCHANGER	Stage function	Transfer the heat from the particles to the power block
	Constrains	Particle size distribution and shape
	objective	Maximize the energy flow per area of HEX
	free variables	Density
		Specific heat
		Material choice

The main function is to transfer the heat from particle media to the HEX. The main **objective** is to maximize the heat transferred per unit of HEX. Taking into account the material index definition, we can consider that *Equation* 9 is the objective equation that should be maximized.

- **Constraints:** the dimensions of the particles are defined by the supplier, we will consider them as a constraint (including shape and/or particle size).
- **Free variables:** the material, the density and the specific heat are free variables for this material index.

Therefore, the material indexes are obtained as shown in *Equation 10*. M_5 index should be maximized to comply with the objective. There has been reported several materials conductivity in the literature [11]. However, only bulk thermal conductivity should be considered for the selection

$$M_5 = k \qquad \text{Eq. 10}$$

3.4 Thermo-mechanical stability

The effect of the temperature over the material related to fracture resistance includes the chemical composition, agglomeration and sintering (sphericity, roundness), melting point, particle size distribution.

Temperature variation over time can cause changes on the initial chemical composition and structure of the materials. These changes can be permanent or can appear once and again form each thermal cycle. This effect is related with thermal stress, or thermal stability.

On solid particle materials, fracture is the result of three phenomena. The first one is due to the collision between the particles themselves, the second one related to the rate of temperature change and the third one is because of the compression.

Thermal shock and thermal fatigue occurs when there is a sudden change on temperature on the surrounding of the particles, exceeding the strength of the material. Thermal shock or fatigue is related to thermal conductivity; materials with low conductivity, like ceramics, will be more susceptible to suffer greater degradation [26]. Also, crack study and propagation increase on each thermal charge/discharge cycle, and therefore must be studied for more than one simple cycle [27] and for several mean sizes of the same material.

The main effect of thermal shock is the variation of the particle size distribution of the material, affecting different properties and parameters such as specific surface, bulk thermal conductivity, fluidization, bulk density and even shape parameters (roundness and sphericity). Some characterization has been made for small number of thermal cycles [16], but there is no clear tendency enough to extrapolate for larger number of cycles.

Decrease of mean particle size and the increase of the number of very fine particles can decrease the temperature and pressure where sintering can occur. This happens because of the increase of the diffusion paths between different particles favored by fine particles [28].

3.5 Materials compatibility

The solid particles are subjected to thermal shocks, mechanical efforts and thermal degradation during the thermal cycles accounted in CSP system. The study of the corrosion/erosion between solid particles, solid particle/medium, and solid particle/ construction materials as well as, material degradation, is crucial in order to endure many cycles.

Erosion strongly depends on hardness and attrition constant. Evaluating this property helps to compare the attrition between different solid particles and possible system materials to be used in CSP. The fact that solid particles are ceramic materials and less reactive, bring to fewer problems of compatibility and corrosion between the heat transfer materials and construction materials than hydrated salts [29]. The use of solid particles as HTF eliminates liquid phase corrosion problems [30]. Nevertheless, depending on the solid particle selected, some oxidation or degradation processes can appear due to the highest working temperatures. Further studies of materials compatibility has to be conducted to assess the material selection.

4. Conclusions

Material based-design has shown useful for solid particles due to lack of materials that meet the desired behavior for high temperature thermal storage applications. Recognizing the design objectives, and not only the properties, has allowed building one or more material indexes (according to the application), which allows to make a first screening and selection task.

However, in order to perform an optimal selection, the material performing the best should maximize all material indices together. This analysis can only be performed through a multi-variable optimization study.

Finally, durability of the materials should be added to the material selection. However, these criteria are related to each plant particular design. In addition, other known factors of each material in particular should be considered (such as allotropic changes or effects of material impurities), since they can change material behavior.

Next step after selecting the best available material will be to identify the properties that can be enhanced in order to improve one or several stages. Either enhancing properties or not, final step on design will be system design in order to make the most accurate viability evaluation.

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Study on solar absorptance and thermal stability of solid particles materials used as TES at high temperature on different aging stages for CSP applications

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ABSTRACT

The use of solid particles as heat transfer fluid (HTF) presents a great potential to overcome drawbacks addressed in commercial Concentrated Solar Power (CSP) plants. The solid particles thermal energy storage (TES) system allows achieving both high thermal performance at high temperature and low cost from the material perspective. The conversion efficiency of CSP solid particles-based systems at high temperatures strongly depends on the optical properties and thermophysical properties of materials used both as HTF and as storage medium. The present study is aimed to provide more experimental data and evidences of the potential in using particulate solids for CSP application. The solar absorptance and the specific heat capacity of silicon carbide (SiC), silica sand (SiO_2), and hematite (Fe_2O_3) are studied after different aging times at 750 °C and 900 °C. The solar absorptance slightly increases over the aging process except for the silica sand, which decreases its absorptance in the first 100 h, reaching a plateau. After the aging treatment, the specific heat capacity is increased for both SiC and silica sand. However, for the iron oxide the specific heat capacity is lower after aging. The black silicon carbide SiC is proven to be the best option to be used up to 900 °C as it shows the highest solar absorptance (96%) and the highest heat storage capacity.

1. Introduction

Lately, renewable energy sources have gained attention due to the depletion of fossil fuels, the increase of greenhouse gas concentration, the climate change and the energetic security for countries with small fossil energies reserves. For these reasons, the European Commission has set up targets to increase the renewable energy supply share in Europe in order to reduce greenhouse gas emissions and mitigate the climate change effects [1]. The highest power density of all renewables by land surface area is offered by direct solar conversion into heat or electricity [2]. Solar energy is one of the most environmentally friendly energy sources [2], and the milestones for solar energy exploit are energy capture, energy conversion, and energy storage. Solar energy can be harnessed generally in two different ways [3]: photovoltaic cells and thermal conversion systems.

In few words, concentrating solar collectors use mirrors and lenses to concentrate and focus sunlight onto a thermal receiver, similar to a boiler tube. The receiver absorbs and converts sunlight into heat. The heat is then transported to a steam generator or engine, where it is converted into electricity or this heat is stored as sensible heat, which can be used once it is required. Concentrated solar power (CSP) using sensible heat system [4] consists on a storage medium (liquid or solid) commonly contained inside a tank.

The CSP technology that has better commercial deployment is the one that uses molten salts as heat transfer fluid (HTF), since it has the advantage of being a relevant energy storage medium [5]. The major drawback of molten salt systems is the allowable operating temperature range, which is limited by the phase change temperature at the low end and the thermal decomposition onset as upper limitation [6]. Therefore, conventional central receiver technologies are limited to temperatures between 220 and 600 °C.

The use of solid particles as HTF is an option to overcome these drawbacks [7]. The solid particle thermal energy storage (TES) system can achieve both high thermal performance at high temperature and

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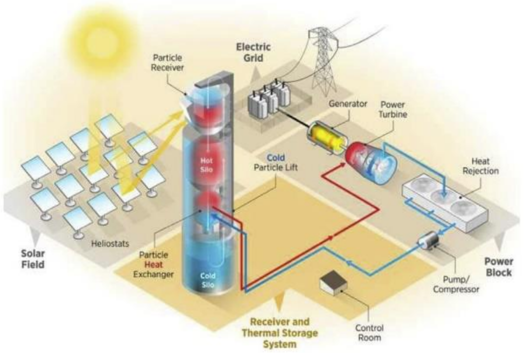

Fig. 1. Solid Particle CSP plant layout [17].

lower cost from the material perspective [8]. Thereby, solid particles fall through a beam of concentrated solar radiation for direct heat absorption and storage. For that reason, direct absorption receivers using solid particles have the potential to increase the maximum temperature of the heat transfer media to more than 1000 °C [9]. Considering this configuration, CSP systems, from the HTF and TES material viewpoints, are able to operate from 600 °C to more than 1000 °C. The application of solid particles as storage media is motivated mainly by cost-efficiency aspects. On the other hand, the material and maintenance costs are expected to be lower for solid particles storage systems [6] as was stated by Calderon et al. [10]. Fig. 1 illustrates solid particle CSP plant layout, which includes a solar receiver, high and low temperature storage tanks, a heat exchanger, a conveyance system. In addition, solar field and power block integration with the solid particle system is showed.

Many development efforts are carried out for achieving direct solar solid particle open systems at commercial level. Since efficiency increases with working temperature in CSP systems, finding the optimum properties of solid particle medium at high temperatures is one of the main R&D challenges in this field. A first attempt to characterize materials for particle receiver applications was conducted by Sandia National Laboratories in the 1980s [11]. Besides, Falcon et al. [12] in 1982 identified silicon carbide, alumina and quartz sand as suitable materials for CSP systems. In the latest years, this topic has kept the researcher's community attention. N. Siegel et al. [13] studied the radiative properties, solar weighted absorptance and thermal emittance for several commercially available proppants. The authors concluded that the solar weighted absorptance and thermal emittance of the particles are stable at 700 °C, but not at 1000 °C. From the materials perspective, Baumann et al. [14] studied the grain size, the specific heat capacity, the thermal shock properties, and attrition of different solid particles: silicon carbide, silica sand, alumina, and basalt. This study concluded that none of the materials considered as candidates perfectly fulfills all the requirements. Therefore, compromises and some concessions have to be assigned. In addition, Zhang et al. [15] evaluate some materials to be used in solar tower power plants with the falling particle curtain receiver configuration, concentrating mainly on the fluidized bed recirculation. The materials considered were silica sand, silicon carbide and calcium carbonate. The published studies are focused on the system and solid particles properties in the recirculation and heat exchanger parts of plant [4,11,16]. Nevertheless, there is lack of studies including optical properties characterization of the solid particles.

The efficiency of CSP system conversion at high temperatures strongly depends on the optical properties and thermophysical properties of materials used as heat transfer fluid and as storage medium. Therefore, the present study is focused on the study and comparison of the solar absorptance and specific heat capacity of solid particle materials as these properties are stated as the most important for a proper material selection for this application [14]. Natural and synthetic materials have been studied and treated with different thermal aging times to simulate material changes due to the high temperature exposure. After the ageing treatment, the materials were characterized to test the optical absorptance, the specific heat, the structural changes and the thermal stability at high temperatures.

2. Materials

Since efficiency increases with working temperature in concentrated solar power (CSP) systems, 900 °C can be easily reached by the CSP receiver and the storage medium. Therefore, the materials used for CSP must fulfill certain requirements restricted by the maximum operation temperature of the application: to withstand high temperatures, thermal shock resistance, high melting temperature, thermal stability and with non-polymorphic changes. The materials source, composition and main advantages and disadvantages to be used as HTF and TES material in CSP systems are listed in Table 1. Notice that silica sand as curtain receiver configuration TES material has been studied for comparison purposes due to the relevance this material has in the reported literature even though it presents polymorphic changes [12–15].

Notice that two working temperatures were defined in this study. The lower one is 750 °C since this temperature allows the use of commercially available materials for components, pumps, etc. The upper temperature, 900 °C, has been chosen as the optimal for increasing the efficiency of heat to electricity conversion.

3. Experimental methodology

3.1. Aging

An isothermal aging treatment was performed to simulate the thermal stress that materials must deal with under the operating conditions in a CSP system. The expertise of the Abengoa researchers and co-authors suggested the two temperatures that were selected for the aging treatment.

- The first one is 900 °C, to simulate the upper limit working temperature of the system, since the open direct receptor can reach this temperature.
- The second isotherm used to age the samples was 750 °C in order to cover the operational temperature range in the receiver and inside the heat exchanger.

The isothermal aging treatment was performed inside a furnace under air atmosphere.

Samples were gathered at six aging stages and were evaluated after 24, 72, 168, 312, 405, and 500 h of aging. Hence, the initial stage under study is the material samples as received, and the final stage is the 500 h aged samples at 900 °C and at 750 °C, respectively.

3.2. Thermal stability and specific heat capacity

The thermal degradation and stability upon the thermal treatments were evaluated by thermogravimetric analysis (TGA) of the solid particles under study, for the initial stage and the final stage at 900 °C as the worst scenario. The measurements were conducted between 300 °C and 900 °C under N_2 atmosphere, with a flow of 80 ml/min, at a heating rate of 10 K/min, with around 30 mg mass, in a TA Instruments SDT Q600.

The specific heat capacity (*Cp*) is a key property to be considered and measured for thermal energy storage materials and must be maximized [14] to achieve higher heat storage capacity. The *Cp* was

Table 1
Materials characterized in this study.

Material name	Source	Composition	Particle size (mm)	Advantages	Disadvantages	Previously studied
Black silicon carbide	Synthetic material (Panadyne F150)	Silicon Carbide SiC_{min} 99.2%	0.02–0.2	High wear resistance with good mechanical properties, including high strength at elevate temperature and thermal shock resistance. High thermal conductivity. Naturally black color.	Cost (synthetic material).	[12,14,15]
Silica sand	Mineral (Sílice de Segovia SL)	Silicon oxide SiO_2 95.3% Al_2O_3 2.3% K_2O 1.5%	0.2–0.5	Very durable mineral, resistant to heat and chemical attack, high melting point, and non-corrosive.	White color and polymorphic changes.	[12–15]
Iron oxide	Mineral (Óxidos férricos S.A)	Hematite (Fe_2O_3) 95.5% Dolomite 1.5% Epidote 1.4%	< 0.15	Paramagnetic iron oxide. Naturally black color.	No notable disadvantages.	[13]

analyzed by using a Differential Scanning Calorimeter (DSC). Different methods [18,19] have been proposed to measure the *Cp*: dynamic method, iso-step method and areas method. The method selected in the present study was areas method given its highest precision. This method consists on increasing 1 °C the material temperature inside the DSC and the area is integrated and related to the heat flow response. This area is compared with the one obtained by an internal standard (in this case sapphire). The full-methodology has been previously described by Ferrer et al. [19]. The analyses were performed under 10 K/min heating rate. The amount of sample used was around 15 mg and the sample was located into 40 μL aluminum crucible in a DSC 822e device from Mettler Toledo. The experiment was performed under 50 ml/min N_2 flow. Notice that the equipment precision is ± 0.3 °C for temperature and ± 0.1 kJ/kg·K for *Cp* results.

3.3. Optical properties

The solar absorptance was measured using a PerkinElmer spectrophotometer Lambda 950 with a 150 mm integrating sphere. This equipment allows to measure transmittance and reflectivity in the whole solar spectrum within 200 nm–2500 nm wavelength (λ) range. Two different lamps depending on the wavelength provide the illumination: a deuterium lamp is used for the ultraviolet region (UV), and a halogen lamp is used for the visible and infrared (IR) region. For study purposes, the reflectivity measurements were conducted from 300 nm to 2500 nm, in the UV–Vis–NIR.

A home-made sample holder was designed to enable the measurements of granulated materials (see Fig. 2). The window, made of sapphire crystal, acts as a protector preventing the solid particles from entering the spectrophotometer equipment. The sample holder was filled with solid particles and it was enclosed with polymeric cover foam to slightly press the particles towards the sapphire crystal.

Given that there is a sapphire crystal between the material and the incident light, it interacts with the light and the solid particles. The crystal reflects a percentage of the incident light, the surface material reflects another percentage, and other minimum fraction is diffusely reflected between the surface and crystal. Therefore, the calibration of the equipment has to be run according to these parameters. To that end, the equipment was calibrated using the sapphire, and the light reflected was considered in the base line.

The methodology used to calculate the solar absorptance has been:

1 **Calibration** using the sapphire crystal with a white color material for 100% reflected light to compensate crystal effect.
2 Once the spectrophotometer is calibrated, the **reflectivity** (*R*) can be measured in the desired wavelength.

The transmittance (*T*) is assumed as 0% when calculating the absorptance (*A*). Then, *A* is calculated following Equation (2).

$$R_\lambda + T_\lambda + A_2 = 1 \quad (1)$$

$$R_\lambda + T_\lambda + A_2 = 1 \quad (2)$$

where λ indicates the wavelength at which the measure has been performed.

3 Absorptance values are **weighted** with respect to the values of the solar spectrum AM1.5 (Equation (3)) following the standard test conditions defined for solar systems [20].

$$A_{weighted} = \mathrm{AM1.5} = (W/m^2nm)\cdot A_{measured}$$

4 Subsequently, a **trapezoidal integration** [21–23] is performed under the curve to calculate the absolute absorptance of the material as shown in Equation (4).

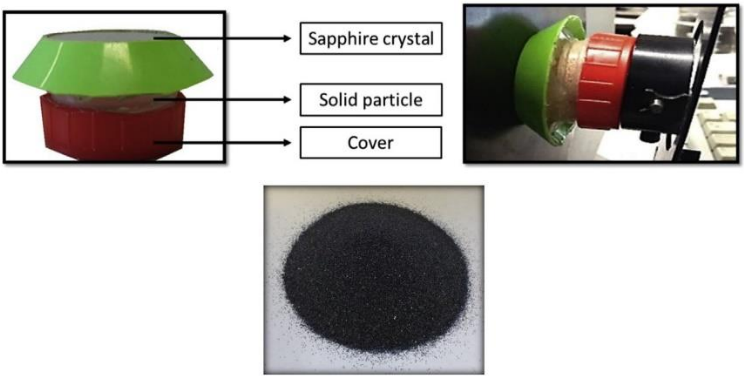

Fig. 2. Sample holder and SiC sample.

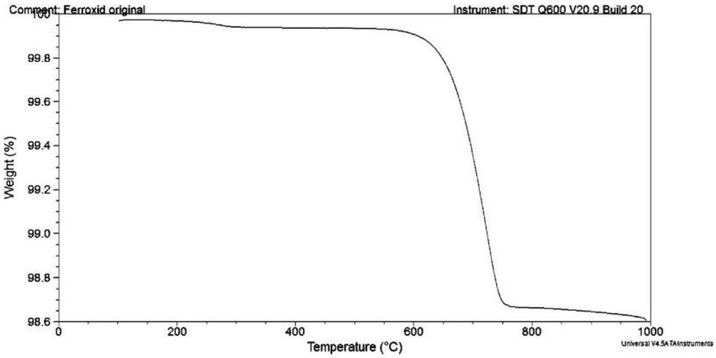

Fig. 3. TGA result for initial sample Fe_2O_3.

Table 2
Cp results for the studied samples as received and after aging at 750 °C and 900 °C. Values measured at 100 °C and 400 °C by DSC.

Material	*Cp* initial (J/g·°C)		Aging temperature (°C)	*Cp* after 500 h of aging (J/g·°C)	
T. Sample	100 °C	400 °C		100 °C	400 °C
Black silicon carbide	1.3 ± 0.1	1.5 ± 0.1	900	1.6 ± 0.1	1.8 ± 0.1
			750	1.3 ± 0.1	1.4 ± 0.1
Silica sand	0.9 ± 0.1	0.8 ± 0.1	900	1.2 ± 0.1	1.2 ± 0.1
			750	–	–
Iron oxide	1.2 ± 0.1	1.2 ± 0.1	900	1.2 ± 0.1	1.0 ± 0.1
			750	0.9 ± 0.1	0.7 ± 0.1

Overall, black silicon carbide shows the highest *Cp* value while the aged iron oxide reports the lowest values, even lower than the iron oxide without aging treatment.

$$\sum_{i=1}^{N} \frac{\frac{A_i + A_{i+1}}{2}}{N-1} \tag{4}$$

Where A_i is the first low range value, A_{i+1} is the higher range value, and N is the number of values.

Notice that since the absorptance measurements were calibrated with two standards and the noise within the measurement was reduced below 1% due to the sensor exposure time on each wave length analyzed.

3.4. Particle color change

The results from X-Ray diffraction and thermal characterization were analysed to explain the particles colour change after the aging, which could be related to a phase transformation mechanism or a change in oxidation state of the metal ions either accomplished or not by a phase change [13]. X-Ray diffraction was used to determine changes in the crystalline phases; the equipment used was a PANalytical X'Pert PRO MPD θ/θ Bragg-Brentano powder diffractometer of 240 mm of radius. The experiments were performed at room temperature and the samples were prepared by manual pressing some of the received powder material, in rectangular standard sample holders of 20 mm of length, 15 mm of width and 1 mm of height.

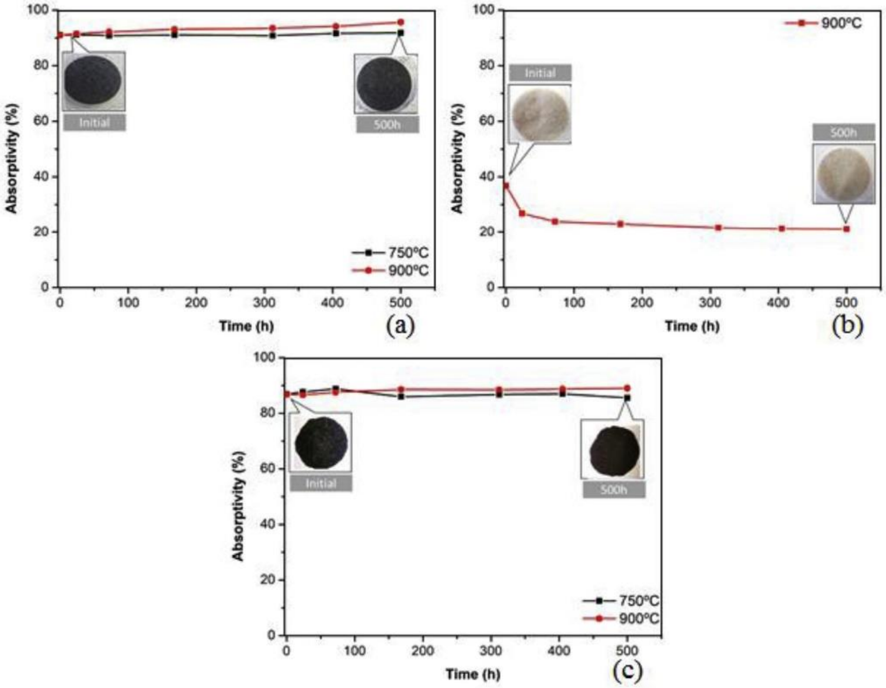

Fig. 4. Absorptance for samples aged at 900 °C (red) and 750 °C (black): (a) black silicon carbide, (b) silica sand, and (c) iron oxide. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

4. Results and discussion

4.1. Thermal stability and specific heat capacity

The thermal degradation test of initial and aged materials at 750 °C and 900 °C shows that, after the aging treatment, materials are thermally stable, and TGA results show no mass change with temperature for the three solids. Despite the TGA results for the initial SiC and silica sand samples show no thermal degradation, the result for the iron oxide is different. As it can be seen in Fig. 3 a slight mass loss (1.36%) is observed when heating the initial Fe_2O_3 sample, within the temperature range from 600 to 800 °C. This mass loss is attributed to the thermal decomposition of the impurity dolomite ($MgCO_3 \cdot CaCO_3$) to form the corresponding MgO and CaO and releasing CO_2. Notice that this mass loss is only measured in the initial Fe_2O_3 sample.

The heat capacity of the solid particles under study was measured at different isotherms using a DSC. The measurements were performed at 100 °C and 400 °C, according to the technical specifications of the DSC with a ± 0.1 error.

The results are summarised in Table 2 for initial and aged samples. For the initial materials (as received), the specific heat capacities of silicon carbide and iron oxide are higher than for silica sand. After the aging treatment at 750 °C, black silicon carbide maintains its *Cp* value, while in iron oxide remains the same. Silica sand aging treatment at 750 °C was excluded, since solar absorptance initial measure was too low. Instead, a complete characterization of iron oxide was carried out. In the case of 900 °C treatments, black silicon carbide and iron oxide *Cp* is increased while in iron oxide remain the same at 100 °C and decreases at 400 °C.

The highest *Cp* values are achieved by silicon carbide aged at 750 °C and 900 °C when the *Cp* is measured at 400 °C. The obtained values are 1.4 J/g·°C and 1.8 J/g·°C, at 750 °C and 900 °C, respectively. Regarding silica sand, the measured values are higher when aged at 900 °C in comparison with initial *Cp* measured, which is consistent with other values reported in the literature due to its differences in composition (impurities) [14,24].

4.2. Optical properties

The absorptance values at different aging stages are shown in Fig. 4. A first analysis shows that iron oxide and black silicon carbide are the solid particles that present the highest absorptance over time and temperature.

A deep analysis of the observed differences within the materials studied can be explained as follows:

- Black silicon carbide. Silicon carbide presents the highest absorptance, around 91% in initial stage, and 96% fter aging at 900 °C. XRD patterns for SiC before and after the thermal aging during 5 h at 900 °C are compared in Fig. 5a. There are not significant changes in XRD patterns. Most of the peaks coincide and are assigned to some of the patterns included in the database for SiC. These patterns slightly differ among them because of different stacking sequences. Slight differences may be also attributed to the sample preparation, as by milling the sample a wide particle size distribution is achieved, thus originating preferential orientation of some crystals.
- Iron oxide. The absorptance is slightly enhanced from the initial state to the aging one (500 h at 900 °C). No substantial changes can be seen in the XRD diffractogram of samples heated at 900 °C (*Figure* 5b), despite a low intensity new peak at a position 42.8°. This peak

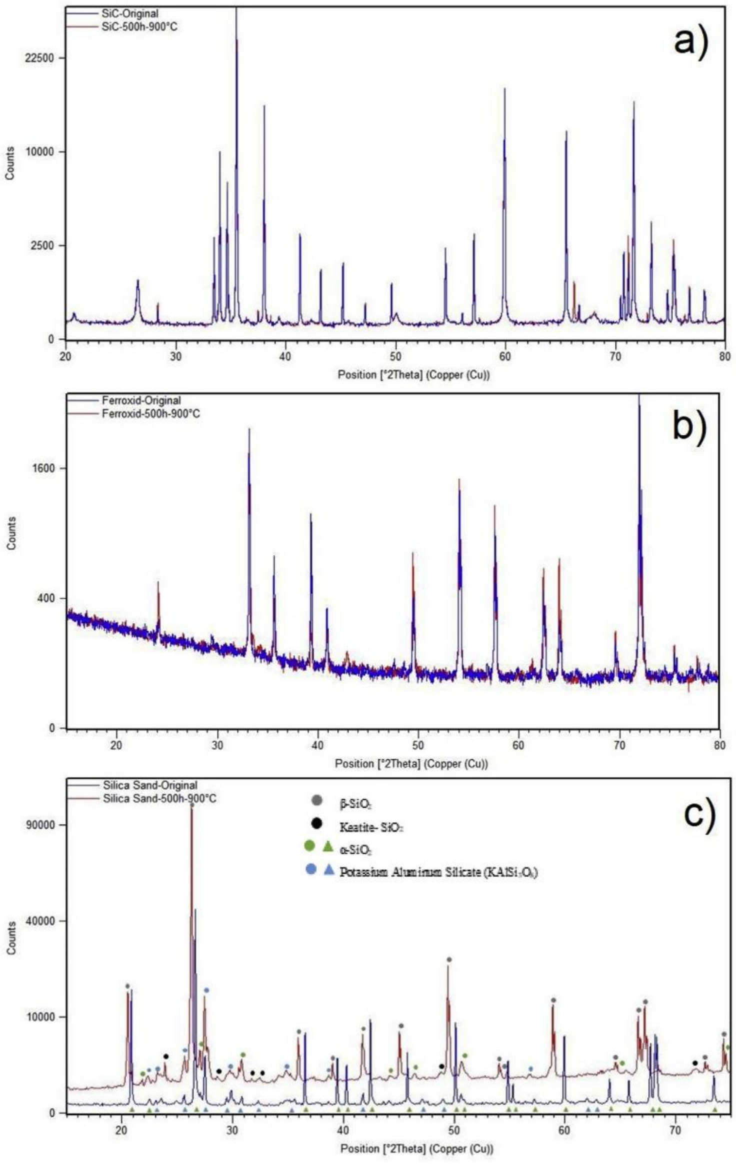

Fig. 5. XRD for initial stage, and after aging at 900 °C for a) black silicon carbide, b) iron oxide, and C) silica sand. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

was checked with the different patterns taking into account the possible presence of impurities (Ca and Mg from dolomite and Ca and Al from epidote), and it can be assigned to $CaFe_3O_5$. Decomposition of dolomite observed by TGA (Fig. 3) could favour the formation of this oxide.

- Silica sand. The opposite tendency is followed in this case. The solar absorptance is decreased down to 14% over the aging time. As reported in literature [25], SiO_2 has polymorphic changes with temperature and pressure towards stable and metastable phases. In particular, at 573 °C α-quartz (rhombohedral) changes to β − quartz (hexagonal). XRD diffractograms for the initial sample and the sample aged at 900 °C are shown in Fig. 5c. It is clear that structural changes took place when thermal aging treatment was applied. While in the original sample peaks are assigned to α-quartz as major phase and potassium aluminium silicate as minor phase, the aged sample shows β − quartz as major phase, but also keatite, α-quartz and potassium aluminium silicate as minor phases.

Overall, black silicon carbide and iron oxide are the solid particles that present better results and almost constant absorptance values over time after extreme conditions (900 °C and 750 °C).

5. Conclusions

The absorptance and thermal stability of three solid particles materials were studied after aging for 500 h at 750 °C and 900 °C to evaluate their possible use as both TES materials and HTF for solar tower with falling down curtain receiver configuration.

The absorptance was observed to increase over the aging stages for black silicon carbide and iron oxide samples. However, for silica sand it decreases with time. The highest absorptance value (95.6%), within all the materials under study, is shown by black silicon carbide after aging at 900 °C for 500 h, and this value fits with the one desired for such application. The black silicon carbide also shows the highest specific heat capacity value (1.67 J/g °C), after aging at 900 °C for 500 h, measured at 400 °C.

For the reasons previously stated, black silicon carbide stands out as the most appropriate material candidate from the absorptance perspective. It can also be considered thermally stable as no significant changes are expected due to long-termhigh temperature effect.

In summary, this work is focused on the study of some of the most important key properties of materials to ensure a proper heat transfer and thermal stability. The characterization carried out is an approach to the selection and development of solid particle systems for solar power tower plants. Given the different nature of the materials selected (natural and synthetic materials), manufacturing costs should be considered in future analyses. Further thermal, chemical and mechanical characterization is required to validate the material selection procedure.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solmat.2019.110088.

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Abstract: Material durability and reliability of solid particles to be used in concentrating solar power tower plants is critical for all project viability. This study is focused on thermal aging and thermal cycling stability evaluation of solid particles at high temperatures. A new device has been developed to perform accelerated-durability tests, that allows to emulate thermal cycling stress from years to days, and even evaluate the 11,000 cycles expected to be reached during 20 years' plant's lifetime in less than four months. A description and explanation of the operation of this device is included in this paper. In addition, current solar absorptance, chemical composition, physical properties, thermal characteristics and morphologic analysis of the samples before and after thermal treatments and cycling have been performed. The materials under the scope of this study are the most reliable solid particles reported in CSP field: silicon carbide and CarboHSP® 30/60. Characterization results show that SiC is more affected on its durability by thermal cycling than by constant temperature aging, while CarboHSP® is affected by temperature aging rather than thermal cycling. SiC reacts with oxygen in the air to form SiO2 on the surface, with a positive effect in its solar absorptance. Nevertheless, with thermal cycles, SiC particle surface becomes damaged and the reaction continues with more new exposed surface. Meanwhile, CarboHSP® reduces its solar absorptance with high temperature only due to changes in its surface chemical composition. However, thermal cycling shows no negative effect in CarboHSP® properties.

Thermal cycling test of solid particles to be used in concentrating solar power plants

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ABSTRACT

Material durability and reliability of solid particles to be used in concentrating solar power tower plants is critical for all project viability. This study is focused on thermal aging and thermal cycling stability evaluation of solid particles at high temperatures. A new device has been developed to perform accelerated-durability tests, that allows to emulate thermal cycling stress from years to days, and even evaluate the 11,000 cycles expected to be reached during 20 years' plant's lifetime in less than four months. A description and explanation of the operation of this device is included in this paper. In addition, current solar absorptance, chemical composition, physical properties, thermal characteristics and morphologic analysis of the samples before and after thermal treatments and cycling have been performed. The materials under the scope of this study are the most reliable solid particles reported in CSP field: silicon carbide and CarboHSP® 30/60. Characterization results show that SiC is more affected on its durability by thermal cycling than by constant temperature aging, while CarboHSP® is affected by temperature aging rather than thermal cycling. SiC reacts with oxygen in the air to form SiO2 on the surface, with a positive effect in its solar absorptance. Nevertheless, with thermal cycles, SiC particle surface becomes damaged and the reaction continues with more new exposed surface. Meanwhile, CarboHSP® reduces its solar absorptance with high temperature only due to changes in its surface chemical composition. However, thermal cycling shows no negative effect in CarboHSP® properties.

Keywords: solid particles; thermal energy storage; concentrated solar power; solar tower; heat transfer fluid; accelerated thermal cycling

1. INTRODUCTION

It is expected that, with the appropriate support, Concentrating Solar Power (CSP) technology can reach over 11% of global electricity generation by 2050 [1,2]. Just in 2017, 11 TWh were produced by CSP compared to 1 TWh in 2000. This capacity is estimated to reach 68,000 MW of power in 2040, reflecting a big increase compared to the 4,650 MW registered in 2015, and the 1,250 MW power capacity installed in 2010 [3,4].

CSP with central tower configuration is a promising option for harvesting solar power due to the high power that can be reached, with a high thermal-to-electric conversion efficiency (due to the high working temperature), high land efficiency, and large scale thermal energy storage [1,5].

CSP plants offer, within its design, energy storage with high efficiency. This fact gives to CSP an advantage over other clean energies like photovoltaic or wind, since it can produce electricity at any time after sunset and for at least 8 hours [6,7].

For the International Energy Agency (IEA), CSP is considered favorable for those regions with high direct normal irradiance (DNI) such as North Africa, southern Africa, the Middle East, northwestern India, the southwestern of the United States, Mexico, Peru, Chile, the western part of China and Australia. However, other regions with less favorable DNI like the south of Europe, Turkey, southern United States, central Asian countries, places in Brazil and Argentina, and some other parts of China, are also viable for CSP implementation [1].

The current state-of-the-art of the technology shows that the best commercial configuration for CSP towers is the one that uses molten salts as both thermal energy storage (TES) and heat transfer fluid (HTF) [8]. Molten salts working on CSP plants can reach over 500ºC, and they had shown technological and financial viability. The known as solar salt (60% $NaNO_3$ + 40% KNO_3) is the main system used as TES material in commercial CSP plants [8]. On this kind of power plants, thermal-to-electric conversion is achieved with efficiency up to 40% [9,10]. Nevertheless, efficiency can be improved up to 50-60% by increasing the operation temperature. This is achieved by using more efficient thermodynamic cycles in which, theoretically, 80% conversion efficiency can be achieved by using cogeneration. However, molten salts become chemically unstable and highly corrosive at temperatures over 565 ºC [11–13]. To overcome this temperature limitation, solid particles have been proposed as TES since they can reach temperatures up to 1000 ºC without becoming chemically unstable or corrosive. Also, solid particles can easily fluidize and therefore can be used as HTF [14].

Current proposed solid particle CSP plant configuration is shown in Figure 1. This figure represents the configuration proposed by Sandia National Laboratories research team, with an open falling particle receiver, thermal energy storage in the tower and with fixed bed heat exchanger (HEX) at the bottom. Different configurations for solid particle CSP have been previously reported [15,16]. Despite it is similar to current molten salts tower configuration, transport, heat exchange, storage silos and receiver should be designed or adapted for handling granular materials around 1mm or smaller [15]. There are very active research topics for the overall plant design, especially for the solar receiver [17]. However, optimal solid particle materials must be screened and properly evaluated to decide the final material selection.

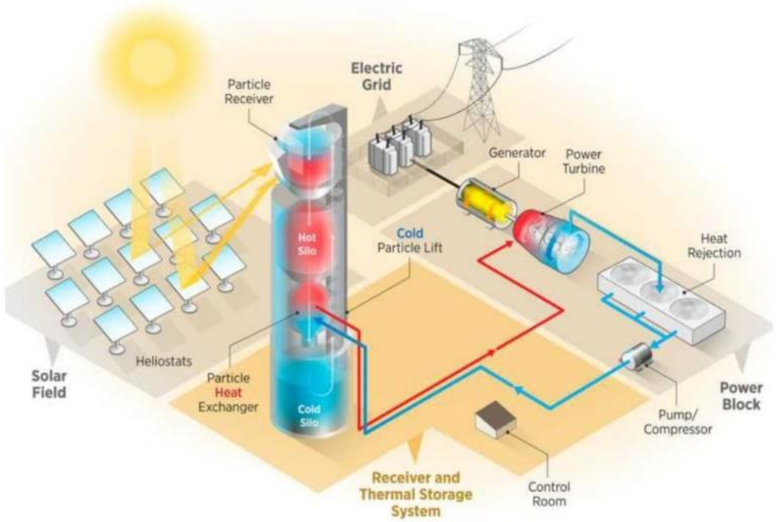


Figure 1. CSP solid particle system with TES and fluidized bed [16].

Particle media durability is essential for a proper material selection. This is affected by thermal and mechanical combined stresses. Wear (mechanical interaction between the solid particles and the system materials) and attrition (mechanical interaction between the solid particles themselves) are the interactions that determine the mechanical stresses [18]. Thermal stability is related to the high temperature exposure for long periods when particles are stored. Moreover, it is related to thousands of thermal heating-cooling cycles between low and high temperatures performed during power plant lifetime [19]. In the present study, thermal aging and accelerated thermal cycling analysis have been carried out in order to perform accelerated-durability test to solid particles (SiC and Carbo HSP®) and relate the main results with the reliability of these solid particles in CSP tower plants.

2. MATERIALS and METHODOLOGY

2.1. Materials

Two materials were selected based on the materials reported in the existing bibliography, considering the properties listed in Table 1.

These selected materials were thermally aged and thermally cycled, and evaluated by different characterization techniques for studying their durability and reliability. The materials under study are Carbo HSP® [20] from CARBO Ceramics Inc., and black silicon carbide (SiC) [21] from Panadyne Inc., which have been suggested by several authors as excellent candidate materials for solid particle CSP [11,20–25].

Carbo HSP® is a synthetic proppant originally designed for hydraulic fracture industry, while SiC is a highly thermal shock and corrosion resistance material commonly used for seal faces, bearings, turbine rotors, pistons, hydraulic plungers, cylinder liners, aircraft armor, as reinforcements in ceramic and metal matrix composites, etc. [26].

Table 1. Reported properties of SiC and Carbo HSP ®

Material	Silicon Carbide			Carbo HSP®	
Melting point (°C)	2150 - 2250			2000 – 2100	
Service temperature (°C)	1470 - 1540			1500	
Thermal conductivity (λ) (W/m·K)	90 – 110 *			2 **	
Specific heat (C_p) (J/kg·K)	663 - 677			1275	
Composition	Min 99.3% SiC	Max 0.4% SiO_2	Max 0.02% Magnetic Iron	83% - Al_2O_3	5% - SiO_2
	Max 0.4% C	Max 0.2% Si		4% - TiO_2	7% - Fe_2O_3
Absorptance (α)	N/A			0.934	
Emissivity (ε)	0.83 - 0.96			0.843	
Cost (€/kg)	12.3 - 17.5			0.60	
ρ (kg/m^3)	3000 - 3200			3560	
References	[26–28]			[20,23,24,26]	

* Thermal conductivity for bulk material, ** Thermal conductivity of particle bed.

2.2. Thermal treatments

The temperature effect produced on the studied solid particles has been evaluated in this study by applying two different tests. Samples have been characterized before, after each thermal treatment, and at intermediate states.

Test 1: thermal aging test

Thermal aging test is defined as the degradation of a material over time, due to its exposure to temperature. This test was performed by placing the studied samples in a sintered alumina crucible into a laboratory furnace. Temperature has been set at 900ºC and samples were kept at this temperature for 500 hours. Even though the most significant changes were expected during the first hours, the long-term stability of the material was primarily evaluated with this test.

Test 2: thermal cycling test

To evaluate the thermal aging due to thermal cycles a novel automatic cycling device was designed for this specific purpose. No device like this has been found either commercially or at the research level. Each thermal cycle was performed between 300°C and 900°C. During the process, the materials were in contact with air and without any pressure control, since these are the boundary conditions at the CSP power plant. Air contact was assured since one end of the tube was open during the tests, and an airflow test was performed through the packed particle media before starting the thermal cycling. The evaluated materials were thermally aged during 500 hours at constant 900 ºC before thermal cycling. This developed device is described in the next section.

2.3. Experimental set-up: Thermal cycler device

To test the thermal cycling durability of solid particles a device has been developed by University of Barcelona researchers. This setup can perform, in three months, a test equivalent to a daily cycle for 30 years between the established temperature limits. Each thermal cycle takes between 11 (for black silicon carbide) and 14 minutes (for Carbo HSP®) for the temperature range between 300 ºC and 900 ºC, depending on the material being cycled. Each thermal cycle includes both thermal charging and discharging, meaning that a cycle starts at 300 °C and ends when the particles get 300 °C again. No reference has been found about the time needed for the particles to remain in the receiver (charging) or in the heat exchanger (discharging), as theoretical time calculations have shown to differ significantly from those of the pilot scale (when the design has been tested) [23,29–31]. For that reason, cycling tests have been designed to be as short as possible, although the time for each cycle is finally defined by the tested material.

The temperature range was determined according to the ideal conditions of the CO_2 super critical Brayton thermal-to-electric cycle, in which conversion efficiency can reach up to 60% under these conditions [32]. This conversion cycle has been proposed by Sandia National Laboratories for fixed-bed heat exchanger [31].

The device (see Figure 2) consists of two furnaces vertically faced: one at the highest temperature (below) and the other at room temperature (above). Both furnaces have holes on top, and the one at room temperature has also a hole below so the alumina tube can move across one to the other (Figures 2b and 2c).

The granular material sample is placed inside the sintered alumina tube and this tube is automatically moved between the two furnaces. The temperatures inside the furnaces are controlled: the hot furnace at 1050 °C and the cold furnace at room temperature (~23 °C). The upper part of the tube is painted in black and a color sensor helps to identify the position of the tube in the device.

To move the tube automatically for 24 hours a day and unattended, several system components were added as shown in Figure 3. A motion unit is responsible of moving the tube between the two furnaces. The sample remains at the heating position (Figure 2c) until reaching 900°C. Afterwards, the tube is automatically moved to the cooling position (Figure 2b) until the sample reaches 300°C, at which time it moves back down to the heating position, thus completing one thermal cycle, and starts again.

Temperature is monitored and controlled by four Type K thermocouples: one inside the tube for monitoring the temperature of the sample, one in each furnace, and the fourth in the motion unit for its thermal monitoring. The temperature sensor inside the tube, which was in contact with the sample, was carefully placed in the center of the volume occupied by the particles. This guarantees that the lowest and highest temperatures are reached by all the material. In addition, the inner diameter of the tube was 14.5 mm, which resulted in less than 7.25 mm in width of material between the thermocouple and the alumina tube (whose thickness was 2.75 mm).

To quickly cool the sample, an air fan was placed in the low temperature furnace, causing forced air convection on the outside of the tube when the sample is at the cooling position. In addition, another air fan helps to prevent temperature increase at the motion unit due to natural convection of heat. For the same reason, a thermal gap has been left between the low temperature furnace and the motion unit.

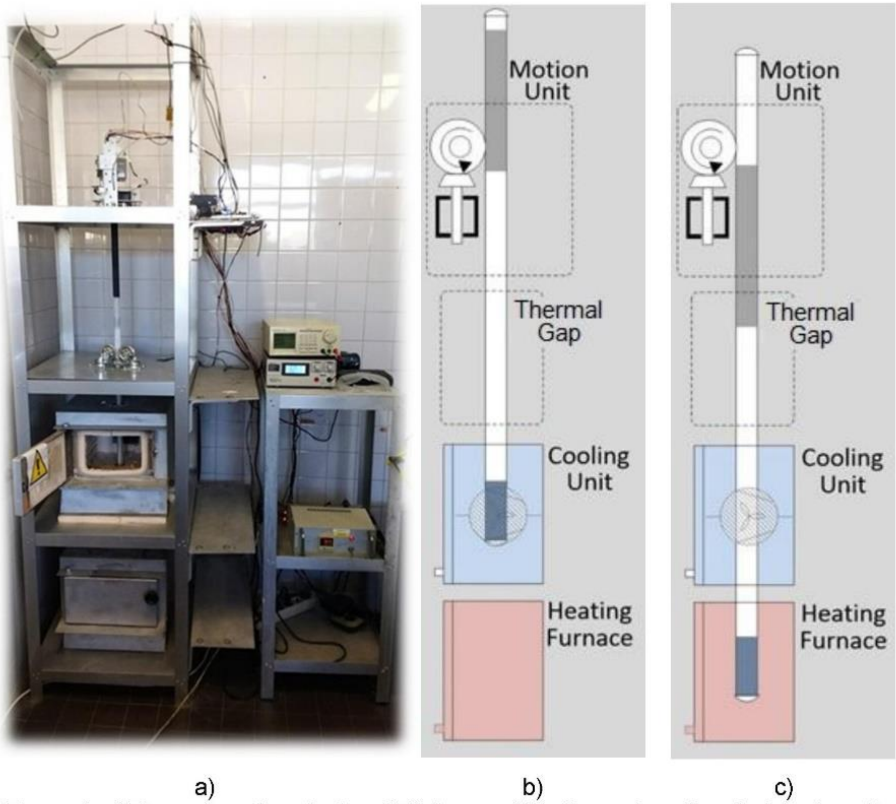


Figure 2. a) Thermal cycling device; b) Scheme of the thermal cycling device at cooling position; c) Scheme of the thermal cycling device at heating position.

Since the device works unattended 24 hours a day, the controller monitors several safety conditions: it can interrupt the cycling process by turning off the power supply of both the heating furnace and the motion unit in case of alarm, while emits an audible alarm sound.

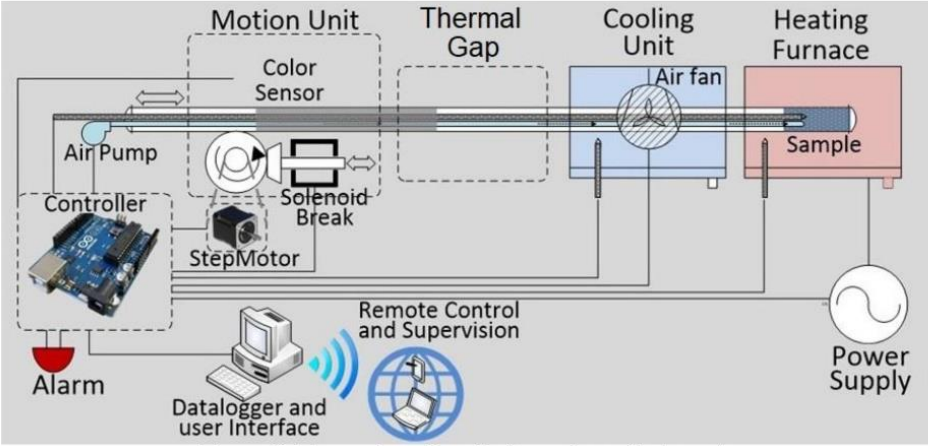


Figure 3. Thermal cycling device schematic layout.

The controller unit was built using an Arduino Mega 2560® card and an electronic board for all the electronic interfaces. This controller was programmed to handle the thermal cycles and the security triggers, as well as to communicate with the computer interface. For data collection and user control, a computer interface was developed as shown in Figure 4. This program receives all the data from the thermocouple, displays the recorded temperatures for the last hour on a graph, and stores all the data on a database for further analysis (if needed). Also, the basic functions and parameters of the device can be managed, such as starting/stopping the thermal cycles, defining the number of cycles to be performed, the set point for low and high temperatures, the alarm tolerance temperature, activating the alarm, etc.

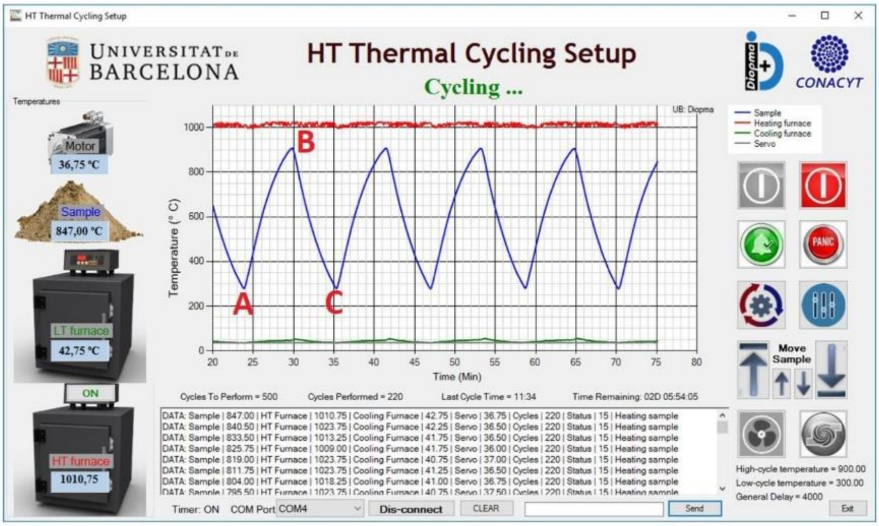


Figure 4. Thermal cycling device computer interface

Figure 4 shows a typical temperature profile obtained for a sample under thermal cycling. On the left you can see the temperature of the motor, the sample and the two furnaces. Point A corresponds to the sample in the cooling position, point B when it has reached the maximum temperature, and point C when it returns to 300 °C. The time elapsed between A and B, and between B and C depends on the thermal diffusivity of the sample tested. Thus, the greater the energy density (that is the product of density by the heat capacity) of the material, and the lower the thermal conductivity, the more time it will take to reach point B and further re-cool (reaching point C).

2.4. Characterization

Both selected materials were thermally treated (with thermal aging and thermal cycling tests) and characterized by Scanning Electron Microscope (SEM), Particle Size Distribution (PSD), Energy Dispersive X-ray Spectroscopy (EDS), X-ray diffraction (XRD), density by Helium pycnometer, Thermo-Gravimetrical Analysis (TGA), Differential Scanning Calorimetry, and by solar absorptance spectrophotometer analysis. Analyses were performed to the samples progressively, beginning with the materials as received, then after thermal aging, and finally after thermal cycling; this allowed to analyze the effect of each of the thermal stress applied to sample durability.

Physical and morphological characterization.

- Helium pycnometer measures the real density of the samples. The real density measurements were carried out in a Micrometrics Pycnometer Accu-Pyc 1330. The differences between samples before and after thermal tests can be due to sinterization of materials or particle breakage. These morphological changes can result in significant real density changes.
- Particle size distribution of the samples was measured with a Beckman Coulter LSTM 13 320 laser diffraction particle size analyzer with Universal Liquid Module using Electrical Sensing Zone Method for Particle size distribution (PSD) analyses. Data used for analysis was the average of three measures made for each sample. Particles were scattered using water for avoiding particle agglomeration. Results were analyzed using Fraunhofer mathematical model, which is used for opaque materials and bigger than 30 µm. The differences between samples before and after thermal treatments can be attributed to sinterization or particle breakage.

- Scanning electron microscopy (SEM) was performed in a FEI Quanta 200 SEM. The images can show changes in the morphology of the samples before and after the thermal treatments, as well as cracks on the solid particles surface.

Chemical characterization.

- Energy Dispersive Spectroscopy (EDS) was performed in a FEI Quanta 200 SEM integrated with EDS detector, obtaining semi-quantitative results between 0 and 11 keV, performed on single spots with an exposition time of 100 seconds. All samples were coated with graphite for electric conductivity requirement.
- X-ray diffraction (XRD) analysis was performed in an XRD from Philips MRD to identify the crystalline phases in the solid particles. Any significant changes in the chemical composition leading to a structural modification after thermal treatments may be detected.

Optical properties characterization.

- In order to analyze the capacity of the SiC and Carbo HSP® particles to absorb solar radiation, a Perkin Elmer Lambda 950 spectrophotometer with a 150 mm integrating sphere was used. Absorptance was measured each 20nm within a 300nm to 2500nm wavelength range using 1-inch diameter circular sample. Once absorptance was obtained for each wavelength, a trapezoidal integration was performed and weighted with respect to solar spectrum AM 1.5 in order to obtain the solar absorptance value for the whole 300nm to 2500nm wavelength range. For absorptance measuring of granular materials a previous developed technique was used employing a special crucible [33].

Thermal characterization.

- The thermal energy storage capacity of both solid particle materials was studied by differential scanning calorimetry (DSC) technique. The method used was the areas method reported by Ferrer et al. [34] to characterize TES materials. The analyses were run in a DSC 822 from Mettler Toledo. Around 7 mg samples were studied and 50 mL/min N_2 flow was applied.
- Material evaluation with thermogravimetrical analysis (TGA) was made for the material as received, after aging at 900ºC, and after thermal cycling as the worst scenario. The measurements were conducted between 300ºC and 900ºC under N_2

atmosphere, with a flow of 80 mL/min, at a heating rate of 10 K/min, with around 30 mg mass, in a TA Instruments SDT Q600.

3. Results

3.1. Physical and morphological characterization.

Real density

Real density changes measured by Helium pycnometer for each material (Carbo HSP® and SiC) after thermal treatments are presented in Table 2. Carbo HSP® shows no significant variation, while SiC shows a slight decrease of around one percent after the thermal cycling test. This change reflects that a change in SiC particles took place and are in concordance with EDS results.

Table 2: Real density (kg/m^3) for SiC and Carbo HSP® as received and after thermal treatments.

Material	As received	After 500 hours aging	After 1500 cycles
Carbo HSP®	3645.1 ± 0.5	3635.5 ±0.2	3637.4 ±0.2
SiC	3206.4 ±0.5	3202.4 ±0.5	3176.5 ±0.1

Particle Size distribution

Evolution of PSD with thermal treatments for Carbo HSP® and SiC are shown in Figure 10 and Figure 11, respectively. Carbo HSP® shows a very similar profile and mean values for volume and number distributions showing that the Carbo HSP particles have a very homogeneous size. A slight displacement is observed related to a small increase in mean particle size due to thermal treatments. Meanwhile, SiC PSD seems to be more affected by thermal shock than by aging. Although the volumetric distribution slightly changes for the thermally cycled sample, the number distribution shows an increase in the fraction corresponding to smaller particles, between 90 µm and 150 µm, thus reflecting that there has been an increase of fines probably originated by the fracture of the bigger particles due to thermal cycles.

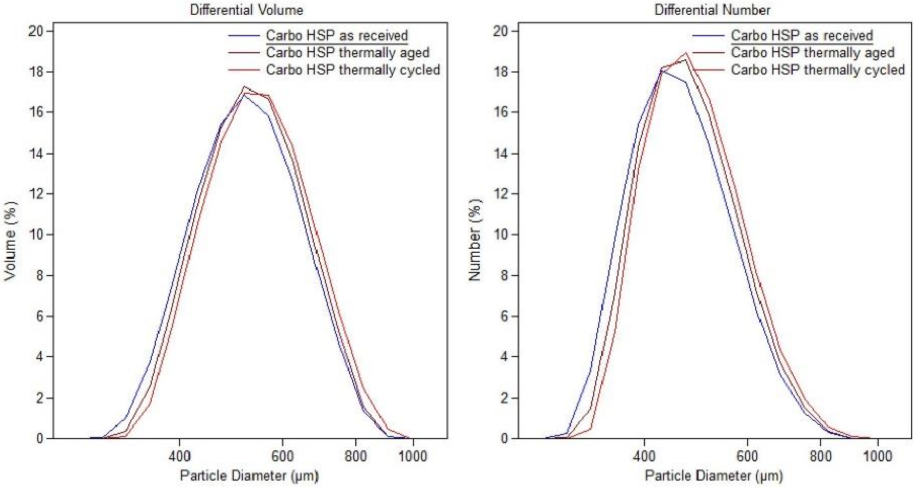


Figure 10. PSD for Carbo HSP® samples.

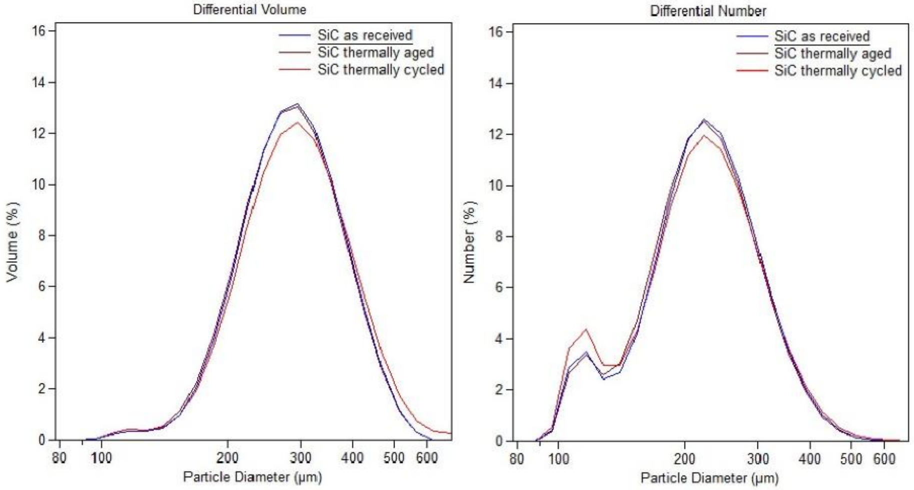


Figure 11. PSD for SiC samples.

SEM analysis

SEM images of Carbo HSP® show that, apparently, particles were not affected by the thermal stress tests. This material is one of the most promising candidates to be used as solid particle materials for CSP since no changes can be observed on its surface as shown in Figures 5.a), 5.b) and 5.c). In the case of SiC, SEM images (Figure 6) show some changes on the surface of the particles, mainly after 1500 cycles between 300°C and 900°C. These changes can be clearly observed in Figure 6.c) where several cracks and fissures on the material surface appeared. Magnification of most significant material irregularities have been added for the three SiC samples.

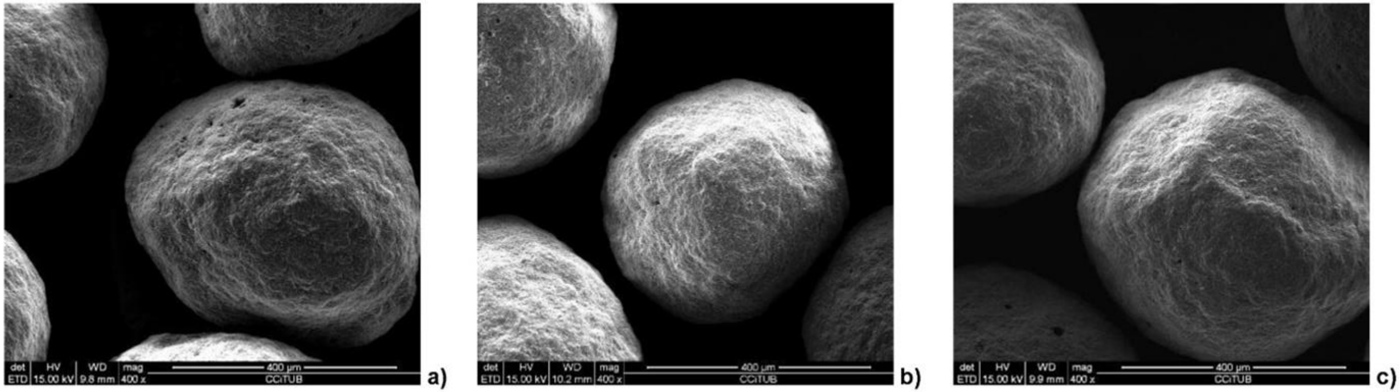


Figure 5. SEM images of Carbo HSP® sample a) as received; b) after 500 hours at 900 ºC; c) after 1500 thermal cycles between 300 ºC and 900 ºC.

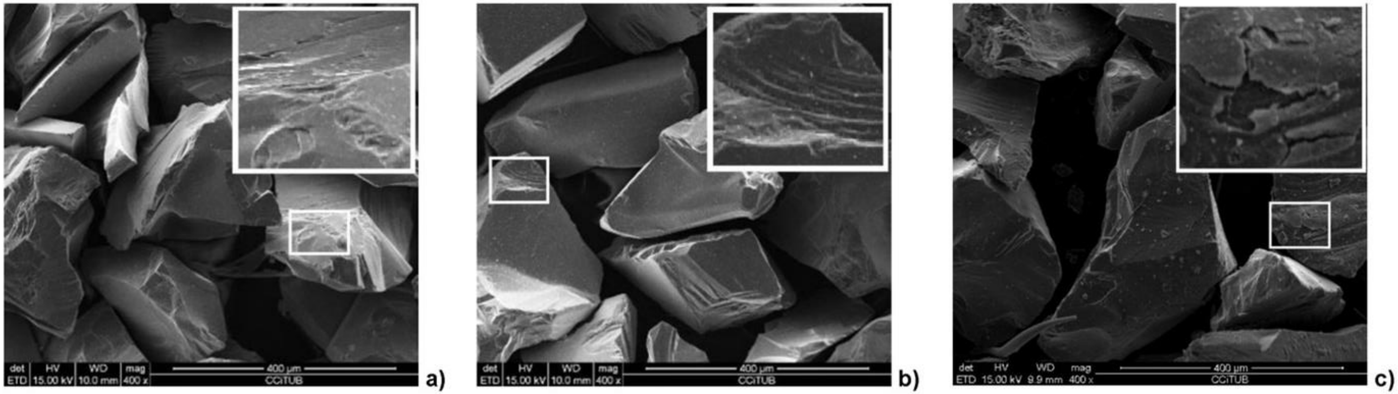
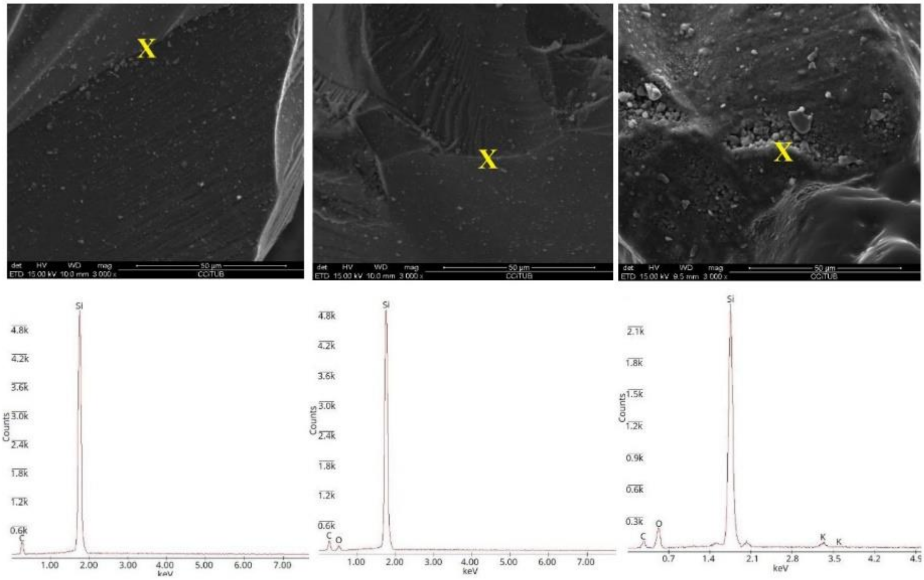


Figure 6. SEM images of SiC with inserted magnification a) as received; b) after 500 hours at 900 ºC; c) after 1500 thermal cycles between 300 ºC and 900 ºC.

EDS analysis

EDS semi-quantitative elemental analysis showed that there is non-detectable change in the surface composition of Carbo HSP® due to thermal treatments. EDS analysis for Carbo HSP® were performed in some areas free of defects or in small particles. For SiC, EDS shows a slight change since oxygen appears in thermally aged sample and in the thermally cycled sample (Figure 9). This suggests that SiC surface reacted with oxygen in the air during the test and formed SiO_2 while releasing CO_2. Carbon presence cannot be evaluated, since all Carbo HSP® and SiC samples were graphite-coated to increase electrical conductivity for SEM analysis. EDS analysis were performed on the most pronounced edges of the particles, since authors assume that the increase of exposed surface will result on elevated reactivity compared to the flat surface of the particles.



a) b) c)

Figure 9. SEM images and corresponding EDS analysis of SiC a) as received; b) thermally aged; c) thermally cycled.

X-Ray diffraction analysis

XRD diffraction analysis of Carbo HSP® (Figure 7) shows that the main crystalline phases are Al_2O_3, SiO_2 and Fe_2O_3 with no visible composition changes after aging treatment and thermal cycling tests. Figure 7 represents the three Carbo HSP® samples, which present identical XRD spectra.

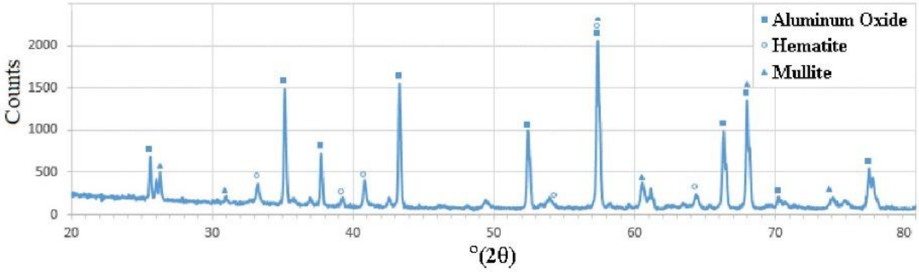


Figure 7. XRD spectra for Carbo HSP® for all studied conditions (as received, aged at 900 °C for 500 hours, and after 1500 cycles between 300 °C and 900 °C).

For SiC, the presence of oxygen during thermal treatments could favor a reaction with SiC, releasing CO_2 and leaving SiO_2 on the particle surface. For original and aged samples only SiC was detected, since only fractions with more than 4% w/w can be securely identified. The change on SiC particles composition can be appreciated by XRD analysis. Figure 8a shows XRD analysis for a SiC sample after 1500 thermal cycles, which differs only in one peak (marked with a triangle) from the corresponding XRD for as received and thermally aged samples. In Figure 8b analysis for the three samples are presented between 20° and 30° position in a logarithmic scale to appreciate the phase of SiO_2 that was detected in the cycled sample at about 22° position. Pure SiC sample should not react with oxygen at temperatures under 1200ºC. Nevertheless, there has been reported that the SiC develops a protective surface layer of SiO_2 which prevents SiC decomposition [35]. It is important to remember that the XRD analysis detects only crystalline structures of the material, whereas changes on amorphous fraction are not detectable. In this case, SiC base line indicates that it is almost in pure crystalline form.

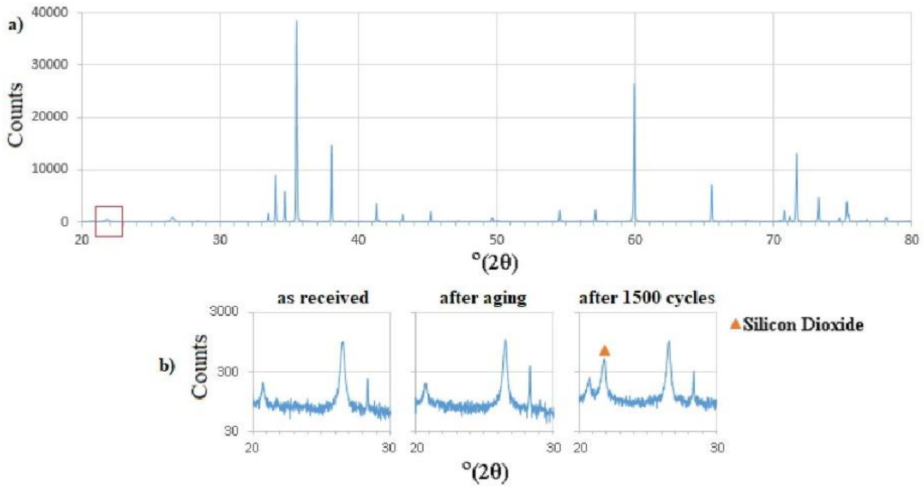


Figure 8. XRD spectra for SiC a) after 1500 cycles between 300 ºC and 900 ºC, b) expansion of the spectrum between 20 and 30º angle for as received, after aging at 900 ºC for 500 hours, and after 1500 cycles between 300 ºC and 900 ºC.

3.2. Optical properties characterization: Solar absorptance

Solar absorptance results of Carbo HSP® can be observed in Figure 12, where solar absorptance decay is observed after thermal aging (Figure 12a), while thermal cycling (Figure 12b) does not affect the sample on its solar absorptance capacity. Results show that for an early thermal aging stage the absorptance decreases constantly, but it is not severe enough compared to other proposed materials like silica sand, olivine, slate, alumina, etc. [33,36]. Therefore, it is advised to perform long thermal aging and thermal cycling tests to guarantee the material stability during the expected lifetime. For SiC, both thermal treatments had a positive effect on its solar absorptance: even during thermal cycling, solar absorptance increase continued. Results for SiC are shown in Figure 12c) and Figure 12d). It appears that thermal aging and thermal cycling benefits the solar absorptance of the silicon carbide particles.

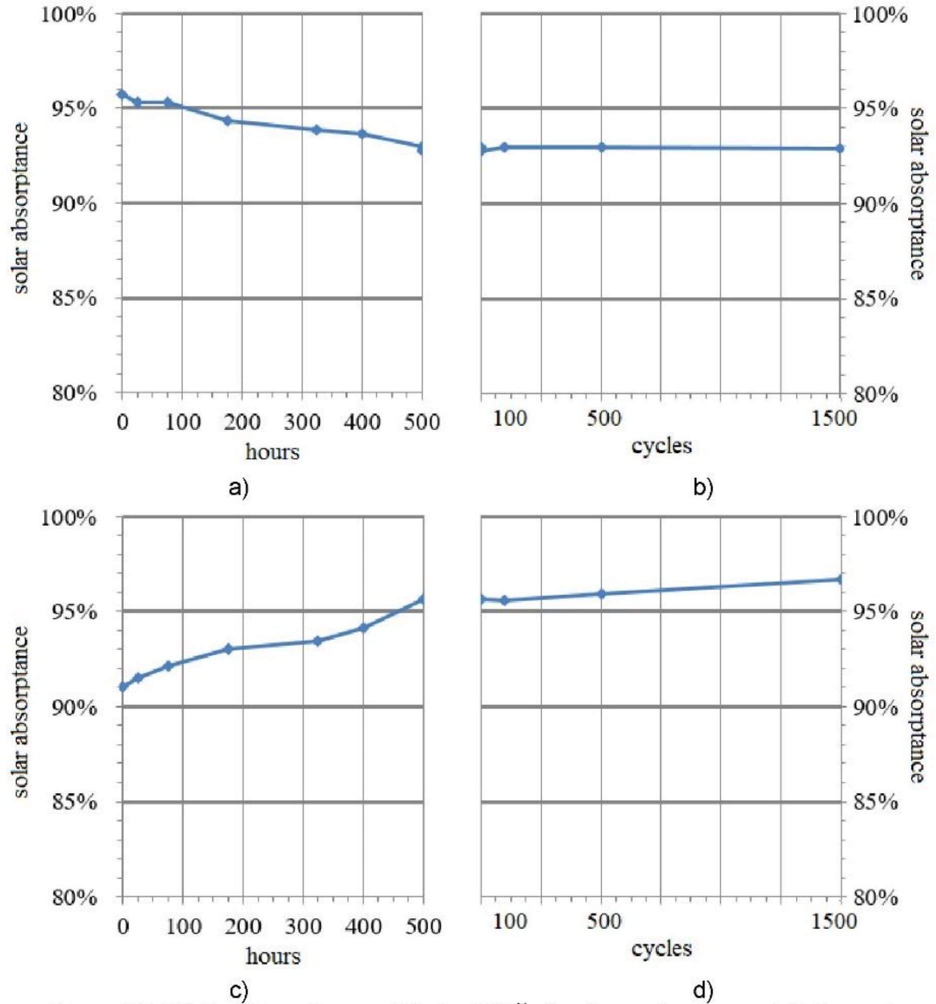


Figure 12.a) Solar absorptance of Carbo HSP® after thermal aging, and b) thermal cycling; c) solar absorptance of SiC after thermal aging, and d) thermal cycling.

3.3. Thermal properties characterization: thermal storage performance

The thermal properties analyzed with the DSC in terms of heat capacity (C_p) are listed in Table 3.

Table 3. Heat capacity results (J/kg·K) for SiC and Carbo HSP® as received and after thermal treatments.

Material	As received	After 500 hours aging	After 1500 cycles
Carbo HSP®	1.19 ± 0.01	1.14 ± 0.01	1.10 ± 0.01
SiC	1.31 ± 0.01	1.05 ± 0.01	1.00 ± 0.01

A reduction of the heat capacity after thermal treatments is observed, being more significant in the case of SiC than for the Carbo HSP®, which is in accordance with the optical and chemical characterization. In the case of Carbo HSP® the C_p reduction is around 7.5%.

However, the thermal treatments modified the SiC composition by oxidizing the SiC surface exposed to the environmental atmosphere as shown in EDS results. The thermal energy storage capacity reduction measured in this study is significant, being around 20%.

TGA tests were performed up to 1250°C. Results for Carbo HSP® and SiC as received, thermal aged and thermal cycled showed that there was non-significant mass variation with temperature, within equipment measure limit of 1% of weight.

4. Conclusions and future work

In summary, the thermal aging tests reveal that this thermal treatment affects the material under study being more noticeable in the SiC case according to the C_p and XRD results. However, these chemical changes seem to benefit SiC solar absorptance. Moreover, the thermal cycling test performed in our own-developed equipment changes the chemical structure of SiC as shown in EDS results, being even more noticeable the SiC oxidation. This fact is confirmed by the C_p analyses, the XRD results, and can be appreciated in the SEM images obtained. Instruments uncertainties are well known so only changes significantly above the instrument uncertainties have been considered.

Carbo HSP® after thermal aging and thermal cycling tests remains almost equal, thus being the material with highest reliability. Slight changes in its chemical structure causes a C_p slight decrement but this is neither appreciated in the XRD obtained results nor in the SEM images.

Results analysis has shown that black silicon carbide had mayor problems when dealing with long-term thermal cycling. Evidences have shown that the mean particle size lowers, and that the particle increases its reactivity with air. Particles damage can be observed by SEM, EDS and changes in the measured particle size. Previously reported SiO_2 surface layer protects the rest of SiC particle from reacting with oxygen present in air, but experimental evidence in this study has shown that thermal cycling causes thermal stress that breaks the SiO_2 coating, exposing new surface of SiC particle to oxygen. Carbo HSP® has higher resistance to thermal cycling and it is stable enough for longer thermal cycling evaluation, thus becoming a good candidate for CSP plants.

Thermal cycling evaluation has shown its relevance when selecting the best material available for this new type of CSP plants. Then, the novel thermal cycling device has shown to be effective to evaluate the thermal stress durability. Ensuring a proper and cheap material that can be used for all the power plant lifetime is essential for reaching a commercially viable system.

Future studies should include combined thermal and mechanical stress for a more accurate durability prediction studies. In addition, mechanical and thermal conditions should be similar to the ones in the solid particle CSP plant design.

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