Summary

Currently, power generation from waste or landed biomass already provides relevant benefits for the environment, as well as for rural areas, and regional economies. The upgrading of biomass to liquid or gaseous biofuels, instead of its direct conversion to energy, would allow and easier way to integrate the biomass utilization to the primary energy network. Within this scope, the most promising conversion routes are gasification and pyrolysis. However, both technologies have not yet reached maturity and are still —to a certain extent— in a developing stage (chapter 1, "General Introduction").

The development of thermochemical processes for biomass upgrading or treatment requires, among other considerations, a better knowledge of the kinetics concerning the thermal decomposition of the lignocel·lulosic materials. This kinetic investigation is of wide interest for both, future scientific research and practical applications (i.e., coupling chemical kinetics with conservation equations for reactor simulation, design, and/or operation).

Numerous researchers have intensively investigated cellulose and biomass kinetics in the past two decades. The current state of the art on "micro-particle" pyrolysis is presented in chapter 2. The char and product yield variations during the primary pyrolysis of the cellulose can be described using "competitive" reaction schemes (Broido-Shafizadeh models). However, these mechanisms have the inconvenience that they cannot be validated by thermogravimetric analysis because this technique cannot differentiate between tar and gas phases. For this reason, the kinetic parameters directly obtained from the adoption of these models, as well as their experimental validation, have been questioned. In this sense, the heat and mass transfer limitations (for the experiments carried out using micro-reactor systems) can dramatically influence the experimental results reliability. Alternatively, a single step, nth-order model can

accurately describe the global weight loss of small samples of cellulose at low-to-moderate heating rates.

In order to describe the pyrolysis of lignocel·lulosic materials, previous investigations provide evidence that the overall biomass pyrolysis behaves as a superposition of the independent kinetics of the primary components or pseudo-components (summative models).

Nevertheless, a major revision of the current advances on this subject reflects that it is yet necessary to deeply investigate the influence of the biomass composition on the pyrolysis process. In this sense, the knowledge of the biomass contents on cellulose, hemicellulose, and lignin is not sufficient to predict the biomass thermal decomposition behavior. Additionally, amounts of mineral matter naturally present in whole biomass samples, which can strongly catalyze the thermal decomposition, should be also taken into account from both, qualitative and quantitative points of view.

Experimental measurement of the pyrolytic behavior of biomass at high heating rates is an issue of extraordinary interest in the research community due to its application to fast pyrolysis processes. Practical problems associated with this subject due to heat transfer limitations have often been overlooked and, consequently, discussed by several authors.

This thesis focuses on the experimental study of the kinetics of primary pyrolysis. Sugarcane bagasse and waste-wood matter have been chosen as two widely different types of lignocellulosic materials. The objectives of this thesis (chapter 3) are to obtain experimental data and to propose kinetic models useful for the prediction of the biomass global weight loss at two different heating conditions: slow heating rates (slow/conventional pyrolysis) and fast heating rates (pseudo-isothermal conditions).

An experimental study using thermogravimetric analysis has been carried out in order to characterize the kinetics of the slow pyrolysis. Experiments have been carried out at three linear heating rates: 5, 10, and 20 K/min (chapter 4).

The weight loss associated to the pyrolysis process is simulated assuming the addition of three independent parallel decomposition reactions, each one corresponding to a single pseudo-component (linked to hemicellulose, cellulose, and lignin). Firstly, an irreversible first-order reaction model is assumed for each pseudo-component. The kinetic parameters have been obtained from DTG curves by adjusting non-linear least-squares algorithms. Results show that the simulated curves do not fit well to the experimental data. Consequently, a further kinetic study is carried out for pure lignin, which demonstrates that the pyrolysis of lignin is better described by a third-order reaction rate law. The reformulation of the lignin kinetic model, and its subsequent implementation in the global decomposition summative model (for the third pseudo-component), has allowed to reach a good agreement between simulated and experimental data.

Both types of raw materials were washed with water at 80ºC during two hours. This pretreatment and the comparison of results with untreated samples have allowed to identify the catalytic effect of the mineral matter, which has been more relevant for the sugarcane bagasse samples.

Also in this chapter, an additional study on the influence of the operating pressure has been carried out. Thermogravimetric experiments were performed at 0.5, 1.0, and 2.0 MPa. Results show that at 1.0 MPa the volatile matter production increases, while for 2.0 MPa the char production significantly increases.

In order to evaluate the global weight loss measured for fast heating rates, an additional experimental study has been carried out using a micro-reactor system (chapter 5). Although the initial sample mass (100–200 mg) could be considered excessive, a qualitative analysis has shown that the insidious effects of heat and mass transfer limitations have not been critical.

The experimental weight loss evolution as a function of temperature as well as of the residence time, has been acceptably described using the global summative model previously developed in this thesis (equation 5.12). Main model kinetic parameters have been obtained by fine-tuning their initial values to better fit experimental isothermal results. In this way, the adjusted model has been able to reproduce the isothermal experiments more accurately than a model based on competitive reactions (Miller-Bellan kinetic model).

One possible explanation for a better prediction from the proposed model is that the kinetic parameters were obtained separately for each sample. This allowed to take into account the effect of inorganic mater on the model parameters.

Main results from this thesis can be summarized as an improved modeling for the description of the thermal decomposition of two types of biomass at two different heating regimes, and a proposed methodology for the characterization of lignocellulosic materials (chapter 6, "Conclusions").