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Research paper

Study of the kinetic parameters of thermal and oxidative degradation of various residual materials

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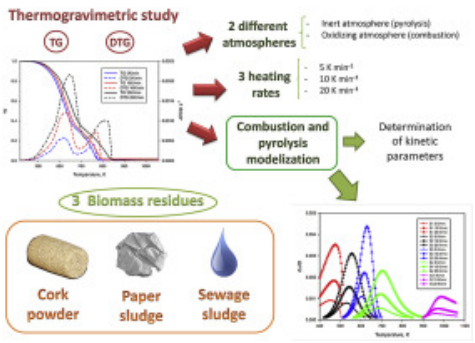
Abstract

The thermal decomposition of three biomass residues was studied in this work: cork powder, paper sludge and sewage sludge. Firstly, characterization of the materials was carried out by elemental and proximate analysis and FT-IR spectroscopy. Experiments were carried out in a thermobalance to obtain thermogravimetric curves (TG) and differential thermogravimetric curves (DTG). Two different types of atmosphere were investigated: pyrolysis (100% N_2) and combustion (80% N_2 20% O_2). The effect of the heating rate (5 K min^{-1}, 10 K min^{-1} and 20 K min^{-1}) was also investigated. Moreover, important combustion parameters were calculated, namely ignition and burnout temperatures and calorific value. A model was proposed for each of the materials and atmospheres in order to calculate the kinetic parameters. The proposed model fitted adequately to the obtained experimental data in all cases, giving and R^2 higher than 0.995 and 0.9858 in TG and DTG curves respectively.

Graphical abstract



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Introduction

In the last few decades, energy demand is continuously increasing due to the rising global population and industry development. As a consequence, greenhouse emissions and pollution are increasing and the traditional energy sources (fossil fuels) are depleting. For that reason, it is crucial to find new ways of generate power [1]. The use of renewable sources is limited due to high cost, the low reliability on supply and because these technologies are still developing. One promising alternative energy source is biomass [2,3]. It reduces greenhouse gases emissions and it is renewable and globally available resource [4]. Biomass has several advantages: it is clean, it has a low cost, has a high compound diversity and it is widely available in nature [5].

The biomass can be used either directly or it can be subjected to different conversion processes such as pyrolysis, combustion and gasification. Further investigations are required in order to optimize the conversion processes and widespread the use of this energy source [6].

Pyrolysis is a process which is carried out in inert atmosphere (absence of oxygen). It converts the feedstock into three fractions: gases, liquid (tars or oils) and solid (char). Either energy or chemical compounds can be obtained from each of the fractions. One advantage of this technology is that it is possible to maximize one of the fractions by changing the process conditions. The process conditions that affect the process are residence time, temperature, heating rate, kind of pre-treatment of the samples, particle size, geometrical configuration of the reactor and solid heat carrier [7].

On the other hand, combustion is an exothermical oxidation reaction where carbon is turned into carbon dioxide and hydrogen is converted to water producing energy [8]. It consists of burning the biomass material using air atmosphere. The material must be subjected to a temperature up to 1000 °C. As a result, hot gases and ash are generated and the chemical energy of the biomass is converted into heat, kinetic or electrical energy. The direct combustion is the simplest process for energy generation [9].

A kinetic thermogravimetric study was carried out in this work. Other authors [10] have carried out kinetic studies by iso-conversional models. However, other type of modelization was used. This technique is based on the measurement of the mass loss as the temperature of the sample increase. Different kinds of atmosphere can be used (for example inert atmosphere or oxidizing atmosphere). Pyrolysis and combustion

processes of biomass have been extensively investigated using TG curves. It allows the study of the mechanism of decomposition and it enables the calculation of kinetic parameters of the reactions which occurred [11]. The main advantage of knowing the mechanism and kinetic parameters is that it permits the simulation of the behavior of a specific material when it is subjected to a particular atmosphere and temperature. Additionally, it is fundamental for the design of reactors and for and efficient process operation, which should be fully adapted to the specific biomass of the region [12]. Selecting a kinetic model which reasonably reproduces the behavior without mathematical complexities is crucial in kinetic simulation [13].

Five basic categories of biomass materials are used for energy generation including crops, virgin wood, agricultural residues, food wastes and industrial wastes and coproducts. The use of crops is the most frequent, which are materials with a high content in lignocellulose [9]. The thermal decomposition in oxidizing and inert atmosphere has been extensively studied in bibliography. For example, Morais et al. [14] studied the pyrolytic behavior of sugarcane bagasse. Moreover, Romero Millán et al. [15] investigated oil palm shells, coconut shells and bamboo guadua. On the other hand [16], the pyrolysis of microalgae.

This work focuses in the study of industrial by-products such as sewage sludge and paper sludge. Thermal behavior of sludge is very different from traditional feedstock such as coal. For that reason, the investigation of thermochemical conversion of these materials is needed for a more efficient management of them [17]. The cork powder, which is a residue from the agroforest industry, was investigated in this paper too.

A very simple kinetic model was developed in this paper for complex materials, which have a high amount of impurities. The main novelty of this work is the possibility of describing complex systems using a very simple model.

Additionally, the energy behavior of the materials selected has not been previously studied in detail. Pyrolysis and combustion kinetics were studied in order to quantify the potential of each material to generate bioenergy. The models were based on the experimental TG and DTG curves. This study enhances the knowledge about the energetic valorization of biomass waste and proposes an interesting model that could be applied to other similar materials.

Section snippets

Materials

Three different materials were used in this work: cork powder (CP), paper sludge (PS) and sewage sludge (SS):

- Cork powder: this material was provided by the company EUROTAPON NÚÑEZ located in Badajoz (Spain). The moisture content was lower than 1.9% so a previous step of drying was not required. The material had a particle size lower than 0.5 mm.…
- Sludge: paper sludge and sewage sludge are very heterogeneous materials. For that reason, previous steps of milling and sieving were performed. The…

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Physical-chemical characterization of the materials

Table 1 shows elemental analysis for the three materials.

The values for the cork powder (CP) are practically the same values than the ones found in Ref. [19]. It was observed that the amount of carbon in this material is greater than in other lignocellulosic wastes such as pine cone shell and olive tree pruning [20,21].

With respect to the elemental composition of the paper sludge, the carbon content obtained was poor compared to other lignocellulosic materials such as cork, which was previously …

Conclusions

Thermal behavior in two kinds of atmospheres (inert and oxidizing) of three different materials was studied in this work. A model was proposed to predict the experimental data obtained. It could be concluded that the model reproduced very well the behavior of the three materials. The model showed to be able to predict the thermal decomposition of complex biomass materials. The most positive aspects of the model proposed are the simplicity and the goodness of fitting obtained (higher than 0.995…

Acknowledgements

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The author Irene Iáñez-Rodríguez acknowledges the financial support provided by the Ministry of Education…

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