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Thermal decomposition of the different particles size fractions of almond shells and olive stones. Thermal behaviour changes due to the milling processes

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ABSTRACT

The aim of this study is to investigate the effect of particle size on the non-isothermal pyrolysis of almond shells (AS) and olive stones (OS) and to show possible differences in the composition of the different fractions obtained after milling and sieving. The results obtained from the study of different particle size of AS and OS samples show significant differences in the solid residue obtained and in the shape and overlapping degree of the peaks, especially with the smaller particle size. These differences can be due to different factors: (a) the amount of inorganic matter, which increases as particle size decreases, (b) heat and mass transfer processes, (c) different sample composition as a consequence of the milling process which may provoke changes in the structure and the segregation of the components (in addition to the ashes) increasingly changes the composition of the sample as the particle size decreases.

1. Introduction

Thermogravimetric analysis is one of the pyrolytic techniques more frequently used to study primary reactions of solid decomposition and is widely used to study the thermal degradation of biomass. The measurements in TGA can be performed under dynamic or in static conditions. The interpretation of experiments, in our case dynamic, provides information about the composition (cellulose, hemicellulose and lignin) of the materials studied (AS and OS in this paper) and the number of different processes that take place during decomposition, that is, the sample characterization. Moreover, TGA is frequently employed in the kinetic modelling of the thermal degradation of biomass materials, both pyrolysis and combustion processes.

The thermal decomposition of lignocellulosic materials takes place through a complex series of chemical reactions coupled with heat and mass transfer processes. Several mechanisms have been published in the literature to explain such processes mainly for the thermal decomposition of cellulose and lignin [1]. Nevertheless, the mechanisms become more complex when a sample of biomass or waste wood is pyrolysed. The differences observed between the results reported by different authors can be due to several factors related to the experimental methods, operating conditions, such as temperature, data analysis, and also to the chemical composition of the raw materials used in each study [2].

Forest biomass, energy crops and agricultural wastes are some of the main renewable energy resources more often studied in this kind of analysis. Numerous investigations of thermogravimetric analysis have been carried out with this type of samples and with different aims. Therefore, several studies have been focused on the thermal degradation of cellulose, hemicellulose and lignin, as well as many lignocellulosic materials, since the 60 s. From then until today, it is possible to find out numerous publications about thermal decomposition of almond shells and olive stone, the biomass used in this paper, which cover many different aspects.

Some of these papers are focused on analyzing the influence of several parameters, such as temperature, heating rate or particle size, on the yields obtained from pyrolysis of biomass in different reactors. Manyà et al. [3] studied the pyrolytic behaviour of olive stones and almond shells using a bench scale system based on a packed bed reactor. Font et al. [4] carried out the flash pyrolysis of almond shells in a sand fluidized bed reactor within the 745–950 °C temperature range and in a Pyroprobe 100. In this last case, the results indicate that the particle size of the sample (in the range 0.21–0.84 mm) shows significant effects on the hydrocarbons yields generated. Both papers analyse the evolution of the mass product yields and gas composition as a function of temperature, heating rate and particle size. Di Blasi et al. [5] carried out experiments in a small packed bed reactor at 257 °C with several biomasses, including almond shells and olive husks, with particular

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emphasis on the yields of furfural. Finally, an example of pyrolysis in a grey-king type furnace is that presented by Blanco Lopez et al. [6] which studied the variation of the composition of gases released during olive stones pyrolysis as a function of the temperature.

Most of the thermogravimetric studies are focused on the proposals of kinetic models for the decomposition processes. Thus, for example, Caballero et al. [7] carried out thermogravimetric analysis of olive stones with sulphuric acid treatment. A kinetic model was suggested and tested to study the relationship between the kinetic parameters and the intensities of the acidic treatments. They found that this relationship could be considered as a measure of the alterations of the structure of cellulose, hemicellulose and lignin and of the breakdown of the interactions between them. This group also studied different kinetic models for thermal decomposition of almond shells and olive stones and the possibility of correlating the data considering the kinetics for the isolated thermal decomposition of lignin, cellulose and hemicellulose [8]. They found that the addition of the kinetics of isolated compounds could not reproduce the kinetic behaviour of the raw material. This study of the kinetics of lignocellulosic and their fractions could reveal the correlations between their behaviour when isolated and when forming part of the raw material.

However, in most of these works, the effect of particle size of samples was neglected or not considered. Some other papers studying the thermal behaviour of biomass in which the influence of particle size was taken into account are shown next.

Some papers focused on studying the influence of particle size on the pyrolytic products evaluated from different reactors are found. For example, Putun et al. [9] carried out experiments of pyrolysis and hydropyrolysis with sunflower pressed bagasse. They reported that in contrast to coal and oil shales, char and oil yields from these biomass samples were found to be largely independent of particle size. Demirbas [10] investigated the pyrolysis of olive husk in a cylindrical reactor where the bio-char yielded at 677 °C decreased in mass from 35.6 to 19.4% when the particle size was reduced from 2.2 mm to 0.5 mm. Finally, flash pyrolysis of cellulose in the temperature range of 313–700 °C in a microfluidized bed was investigated by Funazukuri et al. [11]. Residence times were of the order of 1 s, while heating rates were estimated at higher than 100,000 °C/s for cellulose particles of 0.06 mm diameter and about 1000 °C/s for cellulose particles having about 0.6 mm particle diameter. No pronounced effects of particle size were observed.

Numerous pyrolysis processes have been conducted with thermogravimetric analysis, as have been studied in this work. Luangkiattikhun et al. [12] studied the effect of the sample particle size (0.36–1.4 mm) on the behaviour of thermogram of oil-palm solid wastes at the heating rate of 20 °C/min. There was no significant effect on the thermogram at the initial stage of pyrolysis but the residual mass of sample and the final yield of char increased by increasing the particle size at the same pyrolysis temperature. Moreover, the first and second peak of DTG curve occurs approximately at the same temperature, independently of the particle size. On the other hand, the aim of Haykiri-Acma [13] was to study the role of particle size (0.15–1.4 mm) in the non-isothermal pyrolysis of hazelnut shell up to 900 °C at a heating rate of 20 °C/min. They found out that the particle size of the sample influenced on the yields of the chars, which were lower for the smaller particle sizes that show enough surface area to interact with the pyrolysis medium to form volatile products. In case of bigger sizes, narrower surface areas required higher apparent activation energies to complete the pyrolysis process. As the particle size was decreased, the peaks on the DTG curves could not be separated because of the reactions of the constituents take place at near temperatures.

These and other authors [3,4,14] attribute any difference observed on the thermal study of biomass with different particle size to the heat transfer as an increase in particle size can establish temperature gradients, causing an increase heat transfer resistance inside the pyrolyzing particles.

Nevertheless, the different mechanical properties of the constituens of the different biomasses, as well as their structure may lead to distinct behaviours under the milling and sieving processes. Thus, some authors have studied the influence of mineral matter on different particle sizes of biomass pyrolysis. Bridgeman et al. [15] demonstrated that the inorganic content of the smaller sized particles was approximately twice that of the larger particles (>90 μm). They indicated that the process of size reduction does not randomly reduce all different mineral components of biomass material in a uniform manner; instead it causes partial separation of the inorganic and organic material into different size particles. Consequently the different particle sizes exhibit different combustion and pyrolysis behaviour in terms of the magnitude of the mass loss peak. Raveendran et al. [16] found out that the yield of volatiles, the devolatilization rate and the initial decomposition temperature increase the demineralization for most of the kinds of biomass they tested. Moreover, researches about how to reduce the amount of this mineral matter have been performed by other authors. Vàrhegyi et al. [17] reduced the amount of inorganic elements in the samples by simple water or dilute acid washing procedures resulting in sharper peaks with a better separation, as initially the peaks associated with the components of an untreated plant material are relatively wide and strongly overlap each other. In the case of wheat straw, pine and cotton wood samples, all of the pretreatments resulted in a better separation of the cellulose peak and the removal of the catalytic ions increases the peak temperature of the cellulose decomposition (around 30–50 °C in the case of wheat straw depending on the pretreatment carried out).

Thus, the aim of the present work is to study the thermal decomposition behaviour of samples of almond shells and olive stones of different sizes, prepared in a selected way, in order to establish and separate the influence of heat transfer, mineral matter and the possible variations of the composition of the different sizes during the milling process of both biomasses. To our knowledge, this last possibility has not been considered up to now in the literature.

2. Experimental methods

2.1. Samples preparation

The raw materials employed in this study were almond shells (AS) and olive stones (OS) which were supplied by the South Eastern Spain region producers. These materials were milled in a roller mill (Herzog HG) with a milling time of 15 s and 2 min for AS and OS respectively. The different milling times used were selected to obtain adequate amounts of each selected size and due to the different hardness of the samples. After milling process, no particles larger than 3.5 mm were found being the smallest particle sizes close to 0 mm (powder). The mesh size of sieves used was 1.5, 1.25, 1.0, 0.72, 0.42 and 0.21 mm. The samples were named as AS1 to AS7 and OS1 to OS7 (the figure indicating the decreasing size). Table 1 shows the particle size range of each fraction obtained from AS and OS and also the mass percentage of each one of them. Both materials show a bimodal distribution but in the case of AS, it is shifted to lower particle sizes with a significant peak at the lowest value. In the case of OS, even with a longer milling time, there is a great percentage of the largest size fraction, which shows its greater hardness.

Furthermore, another two more samples were obtained by milling, the samples of larger size, AS1 and OS1, for 15 s and 2 min, respectively, to obtain samples $AS1_{milled}$ and $OS1_{milled}$ which completely passed through the mesh of the smallest size, in this way assuring the same overall composition as the sample they respectively come from. This procedure provides two identical samples