EFFECT OF CATALYSTS ON THERMOGRAVIMETRIC ANALYSIS OF OLIVE STONE

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Abstract

Thermogravimetric analysis of two olive stone (OS) samples of different particle size were carried out with the aim to study possible differences due, not only to heat transfer but also to a possible variation of the composition and segregation of the fractions during sieving. Furthermore, $ZnCl_2$, $CoCl_2$ and $MnCl_2$ were used in order to study the effect of these catalysts on their thermal degradation. The results obtained show a displacement of the decomposition process to lower temperatures when different catalysts were used as well as changes on the sharpness of the decomposition peaks. $ZnCl_2$ seems to be the most active catalyst followed by $CoCl_2$. Their behavior on the thermal decomposition was more remarkable that the results obtained with $MnCl_2$.

Keywords: *thermogravimetric analysis, olive stone, effect of $ZnCl_2$, $CoCl_2$ and $MnCl_2$, particle size*

1. Introduction

Nowadays, Spain is the first country in the ranking of global production of olive oil with an average annual production of 700000-800000 tons [1]. Olive stone represents about a quarter of the total fruit and it is rich in polysaccharides (cellulose and hemicellulose). So, the possibility of using olive stone, which would otherwise be discarded, in the production of biofuels becomes important.

The study of the different fractions of lignocellulosic materials (hemicellulose, cellulose and lignin) may give information about the behavior of the raw material in accordance with the different proportions of its components [2].

Thermogravimetric analysis of lignocellulosic material reveals different decomposition regimes. The first peak in the decomposition rate at lower temperatures can be associated with pyrolysis of hemicellulose and the peak at higher temperatures is associated with cellulose decomposition. However, the wide range of temperatures, where lignin decomposes, hinders the appearance of a peak attributable to its component. So, this fraction usually overlaps with hemicellulose and cellulose peaks.

The aim of this work is to study the effect of three different catalysts ($ZnCl_2$, $CoCl_2$ and $MnCl_2$) at different impregnation degrees on the thermal degradation of two different particle sizes of olive stone.

2. Materials and Methods

The material employed in this study was olive stone which was supplied by region manufacturers. The sample was milled, sieved and dried. Experiments were carried out with two different particle sizes ($1.5 < d_p < 1.25$ mm and $d_p < 0.21$ mm) to observe possible differences between them.

The samples were impregnated with a solution of a known concentration of three different catalysts ($ZnCl_2$, $CoCl_2$ and $MnCl_2$) commercially available. The facility of impregnation of biomass with small particle size was higher than that of the large sizes. The impregnation percentages were in the range 2-15%.

A Perkin Elmer TGA7 apparatus was employed for the dynamic pyrolysis experiments. The heating rate used was 10 ºC/min from 30 ºC to a final temperature of 700 ºC in an inert atmosphere of N_2 with a flow rate of 20 ml/min.

3. Results and Discussion

Figure 1 shows TG and DTG curves for both particle sizes studied without catalysts. As can been seen, large differences were found out between them. DTG curve of small particle size presented differences in size and shape of the characteristic peaks respect to the DTG curve of large particle size. Furthermore, TG curves showed a difference in the residue obtained between each particle size about 10%. The studies carried out showed that these differences obtained were due, not only to the heat transfer because of the particle size, but also to the different composition of each size due to a possible composition differences in the particles

depending on the size achieved during the milling and sieving process.

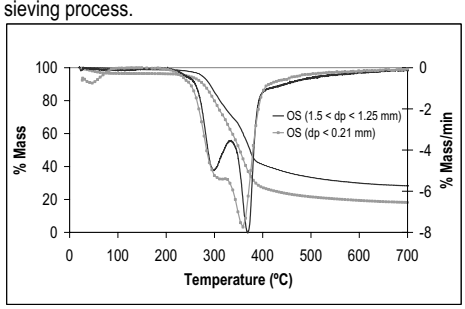

Fig. 1. TG/DTG curves of both particle size of OS

The catalyst which appeared to be more active was $ZnCl_2$ as Figures 2 and 3 show, which represent both particle size and concentrations studied (about 15 and 6% for small and large particle size respectively). As can be seen in these Figures, the catalyst produced a displacement of the decomposition process to lower temperatures and changes in the size and shape of characteristic peaks. DTG curves showed less pronounced peaks which were advanced about 100 ºC respect to the sample without catalyst .

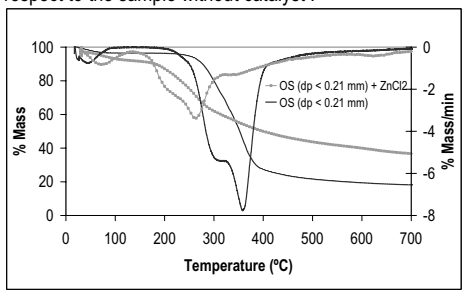

Fig. 2. TG/DTG curves OS (dp < 0.21 mm) with $ZnCl_2$ (15%)

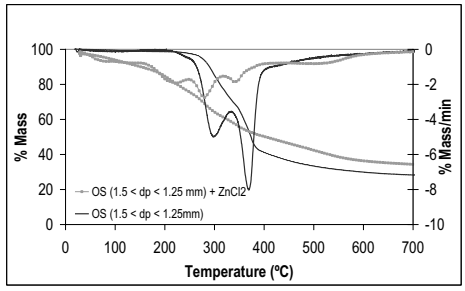

Fig. 3. TG/DTG curves OS (1.5 < dp < 1.25 mm) with $ZnCl_2$ (6%)

The behaviour of $CoCl_2$ is similar to $ZnCl_2$ although in this case, the advancement of the process is somewhat lower (between 60 and 90 ºC). These results are presented in Figure 4 corresponding to the small particle size.

The catalyst $MnCl_2$ appeared to be the less active as shows Figure 5 where the first peak of decomposition only changes from 310 to 274 ºC being more acute and marked, while the second one moves from 360 to 351 ºC losing sharpness. Besides, it is important to note the two peaks appearing at temperatures between 100-200 ºC.

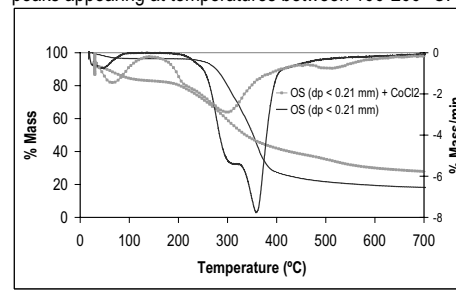

Fig. 4. TG/DTG curves OS (dp < 0.21 mm) with $CoCl_2$ (10%)

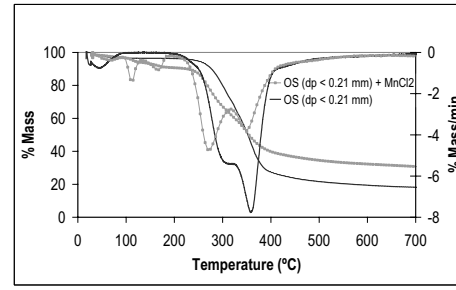

Fig. 5. TG/DTG curves OS (dp < 0.21 mm) with $MnCl_2$(12%)

4. Conclusions

The results reached indicate that the processes of milling and sieving of the biomass can produce a segregation of its components leading to thermogravimetrical curves that depend on the particle size of biomass.

Thermogravimetric analysis carried out after impregnating olive stones with $ZnCl_2$, $CoCl_2$ and $MnCl_2$ show that $ZnCl_2$ presents a high activity reducing the decomposition temperature significantly. Although $MnCl_2$ produces a low reduction of degradation temperature, comparing with the other catalysts, it can modify the process by acting on the different components in a different way.

Acknowledgements

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