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## INTRODUCTION

The olive oil industry produces more than 250 000 tons of olive-pomaces (O-P) a year in Morocco and the production of the Meknès-Tafilalet country represents 25 to 30 %. The O-P are lignocellulosic solid residues resulting of the oil extraction process (pulp and stones for example). This organic matter can be valued especially for heat generation but also for activated carbon (AC) synthesis. The aim of this work is to study the combustion and the carbonization of these lignocellulosic residues. The study of the experimental parameters is not sufficient to control pyrolysis and combustion gases as well as the final solid material obtained after the thermal treatments. A kinetic model, based on the decomposition kinetics of the three fractions which composed the materials (hemicellulose, cellulose and lignin), has also to be realized and validated [1,2].
In a first step, the residues, raw and pressed O-P, were dried using thermal solar energy at various temperatures (40°C, 60°C, 80°C), a quantification of the residual oil in the samples was performed and their elemental composition and chemical composition (FTIR data) were analyzed. In a second step, for each sample, the composition of hemicellulose, cellulose, and lignin was determined. The TGA/DTA experiments were carried out on all the O-P residues and their three components (H., C., L.) in order to estimate the respective contribution of their solid and gaseous phases in the final mass during combustion and carbonization treatments.

## METHODOLOGY

Isolated lignocellulosic fractions supplied by Sigma Aldrich Co were used in this study, namely xylan (ref:36-355-3) corresponding to hemicellulose (H.), cellulose (ref:9004-34-6) (C.) and lignin (ref:8072-93-3) (L.). Prior to any pyrolysis and combustion treatments, elemental analysis (in a THERMO SCIENTIFIC – FLASH 2000 apparatus) were carried out to quantify the percentage of carbon, hydrogen, oxygen, nitrogen and sulfur in the raw, pressed and dried materials. The FTIR spectra of the different raw materials before and after thermal solar drying were obtained on a THERMO SCIENTIFIC - Nicolet 6700 spectrometer.
Thermogravimetric experiments were carried out to determine the rate and temperature range of decomposition of pure hemicellulose, cellulose, lignin and of the raw materials during the

carbonization step. This has been achieved using a thermobalance (TGA 92, Setaram) and samples were analyzed in platinum crucibles under an argon flow at 1.6 L $h^{-1}$. A mass of approximately 0.070 g of sample was heated from room temperature to 1100 °C at a rate of 10°C $min^{-1}$. The samples were then cool down to room temperature at the same rate (10 °C $min^{-1}$). The equipment was calibrated using three standards under the same conditions as those used for measurement of the samples.

## RESULTS AND DISCUSSION

The elemental analyses show that the raw lignin presents the highest carbon content (47.8% in w.) compared to cellulose (42.3% in w.) and hemicellulose (41.3% in w.) and the lowest oxygen content (33.3% in w. against 50% in w. for the C. and the H.). Hydrogen contents of the three basic components are similar and close to 6%wt. Moreover, both hemicellulose and lignin present important ash content (respectively 2.9%wt and 9.9%wt) compared to cellulose (<0.3%wt). The elemental analyses of the raw and pressed olive-pomaces are very close because no chemical modification occurred during oil extraction. These samples present a carbon content close to 45-50% in w., a hydrogen content close to 5-6% in w., a nitrogen content close to 2-3% in w. and an oxygen content close to 30%. The water content decreases as a function of the solar drying temperature confirming the efficiency of the drying. The FTIR data show that the spectra of the olive-pomaces are close to the hemicellulose one. These results are in agreement with the chemical analyses (carried out by INRA Ardon) and quantification of the hemicellulose, cellulose and lignin contents in the raw materials. Indeed, the olive-pomaces content 38% in w. of H., 33.3% in w. of C. and 28.7% in w. of L. The TGA/DTA data show that the thermal decomposition of the three components (H., C. and L.) occurs at different rates and within distinct temperature ranges. For each component, the mass loss observed at 150°C is high, representing approximately 10% of the initial mass. It corresponds to the water which is initially physisorbed. The hemicellulose fraction decomposes in a narrow temperature range, 250°C - 325°C, with a high conversion rate at 306°C. The cellulose fraction decomposes in a narrow temperature range, 300°C - 400°C, with a high conversion rate at 364°C, while the lignin fraction decomposes over a wide temperature range, from 200 to 800°, with a lower conversion rate at 388°C. In the raw materials, there is a natural deconvolution of the H. and C. peaks with a high conversion rate at 280°C for H. and at 330°C for C. A peak is observed at 380°C-405°C which corresponds to the residual oil still present in the olive-pomaces. The presence of oil is confirmed by the FTIR spectra with a band at 2900 $cm^{-1}$ which corresponds to aliphatic carbons. When the oil is extracted from the sample, the ATG peak and the FTIR band at 2900 $cm^{-1}$ disappeared confirming the occurrence of residual oil in the raw olive-pomaces.

## CONCLUSION

This study allowed to highlight the importance of the knowledge of the raw materials in terms of chemical composition and thermal behavior during the heat treatment. These results will be used to establish a kinetic model of thermal decomposition during the carbonization and the combustion of these olive-pomaces.

## ACKNOWLEDGMENT

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