

Effect of Mg and K inorganic species on the chars properties derived from grape marc pyrolysis

M. Jeguirim, L. Limousy, K. Thabet, L. Josien, L. Michelin, C. Vaultot, S. Bennici

¹ Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

Presenting author email: simona.bennici@uha.fr

Introduction

Grape marc waste generated from agro-industries have large deposit in the world (Food and Agriculture Organisation FAO, 2006; Celma et al., 2012). To minimize environment impact and to recycle such harmful residue, several recovery methods have been proposed. In particular, grape marc waste can be used as starting material for the production of added value products (i.e. alcohol, tartar, yeast, phenol compounds, oil, pharmaceuticals and cosmetics), as decontaminant for metal rich (copper and nickel) effluents, as feedstuff and organic fertilizer for soil. However, numerous applications have been abandoned due to the difficulty of grape marc to be biologically processed (high content of lignin and tannin) and for the high C/N ratio that is not adapted for soil amendment. A promising way for grape marc recovery is the chars production using pyrolysis technique. These chars that can be applied in different applications including adsorption for gas and water pollutants removal, hybrid composites formulation,

Grape marc, as all lignocellulosic biomass, consists mainly of cellulose, hemicellulose, and lignin and contains small amounts of minerals. These latter include significant amounts of alkaline and alkaline-earth species such as potassium, sodium, magnesium and calcium, which are essential nutrients of plants. Various studies have examined the effect of the inorganic elements on the pyrolysis process and reported many contradictory results on their catalytic effect (Khelfa, 2013; Hwang, 2015; Eom, 2012).

In this context, the present investigation has been conducted with the aim to study the effect of minerals, and more specifically the role of potassium and magnesium species, on the pyrolysis process of grape marc as well as on the properties of chars which are key parameters for defining the suitable recovery process.

Methodology

The washed grape marc was impregnated with Mg- and K- chlorides and then the derived chars were elaborated in a tubular pyrolysis oven working under nitrogen flow at 300, 400, and 500 °C (CMR₃₀₀, CMR₄₀₀, and CMR₅₀₀, respectively) for the raw (B), washed (L) and impregnated samples (K, Mg).

A multi-technique characterization approach (SEM-EDX, Raman and infrared spectroscopy, XRF, CO₂-adsorption isotherms) was performed to highlight any morphological and physico-chemical changes on the chars obtained at different pyrolysis temperature and in the presence (or absence) of added inorganic salts.

In parallel, thermogravimetric analysis at various heating rates (from 1 to 15 °C/min) were used to investigate the pyrolysis behaviour of the raw (MR-B), washed (MR-L) and impregnated biomass (MR-K, MR-Mg). The role of each added inorganic element on the pyrolysis process was compared by determining the apparent activation energy of the degradation reaction by application of the Kissinger equation.

Results

Concerning the char yield production at the various pyrolysis temperatures, a decreasing in char production can be noticed for the washed biomass. Such result can be of course due to the presence of a lower amount inorganic residue at the end of the pyrolysis process, but it can also be connected to the fact that inorganics display a catalytic

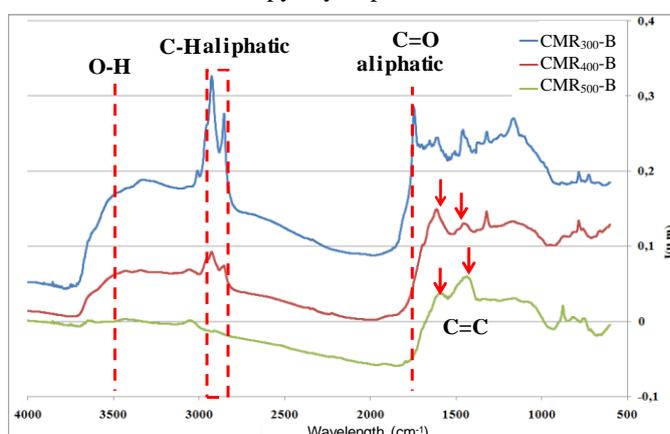


Fig.1. Infrared spectra for the chars obtained at 300, 400, 500 °C from the raw grape marc.

effect that promotes specific reactions during the char production.

This last explanation is also supported by the FTIR results. The band placed at 1743 cm⁻¹, that corresponds to the presence of aliphatic esters (C=O), is already absente at 300°C for the chars prepared from the biomasses containing the salts, thus confirming that the minerals catalyse the degradation of the oxygenated aliphatic compounds.

One of the main changes, observed on the IR spectra (Fig.1) by increasing the pyrolysis temperature, is the progressive decreasing of the band around 3500 cm⁻¹, characteristic of the hydration water. The peaks centered at 2923 and 2852 cm⁻¹ (related to the aliphatic C-H functions) are much less pronounced for the chars

obtained at 400°C than for those obtained at 300°C, and they completely disappear for those pyrolyzed at 500°C. Bands at 1450 and 1606 cm^{-1} appears for the chars obtained at 400°C, and two more supplementary peaks at 1450 and 1580 cm^{-1} for those obtained at 500°C. These bands indicate the formation of C=C bonds (formation of aromatic compounds).

The different samples showed the same carbon structure, as noticed by comparing the Raman spectra that in each case display two well defined D and G peaks. By increasing the temperature, the G band moves towards higher wavelengths, due to the formation of more complex aromatic systems in the char structure. The increasing of the temperature from 400 to 500°C does not impact the I_D/I_G ratio. This ratio is indeed expected to vary only at higher pyrolysis temperature. The addition of inorganic salt would theoretically increase the disorder in the carbon matrix, but such an augmentation of the I_D/I_G ratio was not observed. The amount of deposited salt was probably too low to provoke the structural modification.

In the same way, no dramatic differences were found in the morphology of the chars prepared in presence of K and Mg species, but the stronger interaction of Mg-species was clearly evidenced by SEM microscopy (Figure 1) and EDX: Mg-species are homogeneously distributed into the chars' pores, while K-species forms crystallites dispersed on the external surface (Figure 2 and 3).

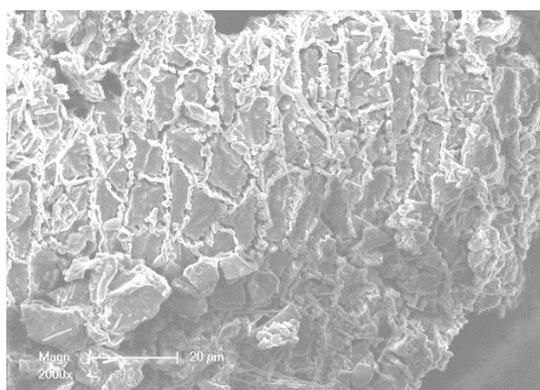


Fig.2. Photo SEM of the chars obtained at 400°C from the Mg-impregnated biomass

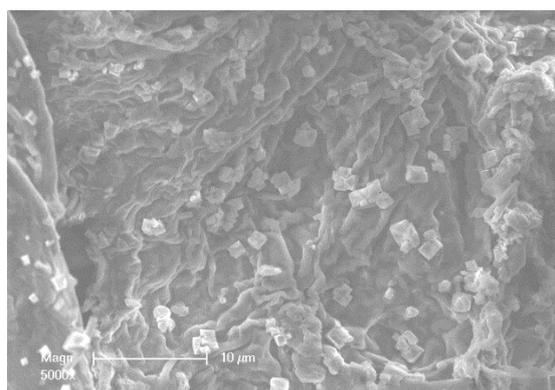


Fig.3. Photo SEM of the chars obtained at 400°C from the K-impregnated biomass.

Table 1. Composition and morphological properties of chars obtained by pyrolysis at 500 °C

Char Sample	XRF analysis (%)		S_{CO_2} (m^2/g)	V_{P,CO_2} (<1nm) (cm^3/g)
	K	Mg		
CMR ₅₀₀ -B	1.97	0.35	189	0.054
CMR ₅₀₀ -L	0.13	0.23	213	0.059
CMR ₅₀₀ -K	2.73	0.07	225	0.065
CMR ₅₀₀ -Mg	0.04	2.29	220	0.061

The potassium and magnesium content for the different chars is reported in Table 1. It is worth to notice that the char derived from the raw biomass (CMR₅₀₀-B) already present a quite high amount of potassium. As expected, the specific surface and porous volume values (measured by CO₂ adsorption at 0°C) are higher for the samples derived from the washed biomass; the accessibility to the ultramicro- and micro- pores increases by eliminating the impurities blocking the access to the pores. The higher pore volume of the CMR₅₀₀-K and MR₅₀₀-Mg samples is probably due to the further washing performed during the salt impregnation procedure.

In conclusion, the low amount of deposited salt presents only a slight impact the physico-chemical properties the char produced, but modification in the mechanism and kinetics of pyrolysis can be expected. A deep analysis of the TG analysis realized for the different biomass will clarify this point by comparison of the thermogravimetric curves and activation energies of the different biomass samples.

Acknowledgements

The authors would like to thank the Carnot Institute MICA for supporting a part of this study in the frame of the Carbovit project. All physico-chemical analyses were performed on the technical platforms of IS2M.

References

- Khelfa A, Bensakhria A, Weber JVJ Anal Appl Pyrolysis 2013;101:111e21.
- Hwang H, Young S, In-Gyu O, Joon C, Choi W. J Anal Appl Pyrolysis 2015;113:27e34.
- Eom I, Kim J, Kim T, Lee S, Choi D, Choi I, et al.. Bioresour Technol 2012;104:687e94.
- Celma, A.R., Cuadros, F., López-Rodríguez, F. Food Bioprod Process 2012; 90:224–234.