

REGULAR ARTICLES

CARBONIZATION OF "ALGARROBO NEGRO" (*Prosopis nigra*): A STUDY OF ITS MICROSTRUCTURE AND MAIN VOLATILE COMPONENTS

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Abstract—Modifications in the micro-structure of wood from Algarrobo negro (*Prosopis nigra*) in function of the temperature were studied by scanning electronic microscopy (SEM). Some non condensable gases obtained by isothermal pyrolysis were investigated employing gas chromatography (GC). The results showed that the basic anatomic structure of wood remains almost unchanged in the working temperature range. It was also found that in the gas phase and with increasing temperature, the concentrations relative to carbon monoxide and water decrease whereas there is a pronounced increase in the concentration of methane from 300°C.

Keyword— wood, carbonization, micro-structure, gas analysis

I. INTRODUCTION

We have previously studied the thermal degradation process of wood sawdust of six hardwood species from the Chaco-Santiagoño region in Argentina under isothermal conditions. "Algarrobo Negro" (*Prosopis nigra*) was one of the wood species analyzed there (Herrera *et al.*, 1986), and is the species studied in this work. We have also reported on the pyrolysis of its lignins (López Pasquali and Herrera, 1997). The thermal behavior of each of the main components of wood (lignin, α -cellulose and hemicelluloses A and B) gives information about the different processes that take place in each of them and that affect the overall thermal degradation of wood (Herrera *et al.*, (1989) and Wottitz *et al.* (2001)). In 1988, Bourgois and Guyonnet demonstrated that the hemicelluloses in pine wood are the most sensitive thermal components. Therefore, they are the first components to degrade and go into the gas phase. They also, start the decomposition of lignin that has a more stable structure.

As the size and distribution of the particles influence the reactions occurring during the wood degradation processes (Lahiri, 1980), we employed here wood cubes having a side of 2 mm and analyzed the degradation process under these new working conditions. The experimental information gathered was compared with the behavior predicted by the Avrami Erofeev and Arrhenius equations. Agreement was observed between the experimental results and the Avrami Erofeev equation. In contrast, no agreement was found with the Arrhenius equation in the whole temperature range studied but the model was found suitable when separate and

definite temperature ranges were taken into account (López Pasquali and Suarez, 2000).

Scanning electron microscopy (SEM) has been employed by several authors to explain the changes that occur in wood as a result of temperature effects. Thus, Kollmann and Sach (1967) employed SEM to get an insight into the high temperature effects on certain wood cells from *Fagus sylvatica*. Zicherman and William-son (1981, 1982) used SEM to observe the changes in wood microstructure as a result of fire effects and in 1982 and 1992 several authors have reported on the effect of different chemical substances applied to wood as fire retardants.

Connor and Daria (1993) found in wood from *Eucaliptus delegatensis* that visual observation studies give quantitative information on the changes that occur in wood when it is carbonized. Rivera *et al.* (1994) used SEM to identify vegetal charcoal whereas the use of this technique allowed Donaldson (1995), to determine the fractures of the cells on the tangential surface of air dried woods.

Gas chromatography analysis of the gases generated during thermal degradation of woods has been used by Bourgois and Guyonnet (1988) in pine wood and Faix *et al.* (1991) in *Picea abies* and *Fagus sylvatica*. This technique allows identification of the gases as well as understanding the pyrolysis evolution during carbonization.

It is possibly that during this process the reactions are strongly influenced by the resistances to mass and heat transfer in wood particles. This resistance is dependent upon the inner structure of the wood and the physical and chemical changes that are produced during carbonization. As no information is available in the literature on wood from "Algarrobo negro", we investigated the modifications of the microstructure in function of the temperature and of the analysis of some non condensable gases obtained from isothermal pyrolysis. Our aim was to obtain further information on the physical and chemical changes that take place during the isothermal pyrolysis of wood.

II. MATERIALS AND EQUIPMENT

A hardwood from the "chaqueña" region in the Argentine Republic, "Algarrobo Negro" (*Prosopis nigra*) was selected. The samples preparation for their later analysis required close attention due to the hardness and other particular features of this wood. On this account,

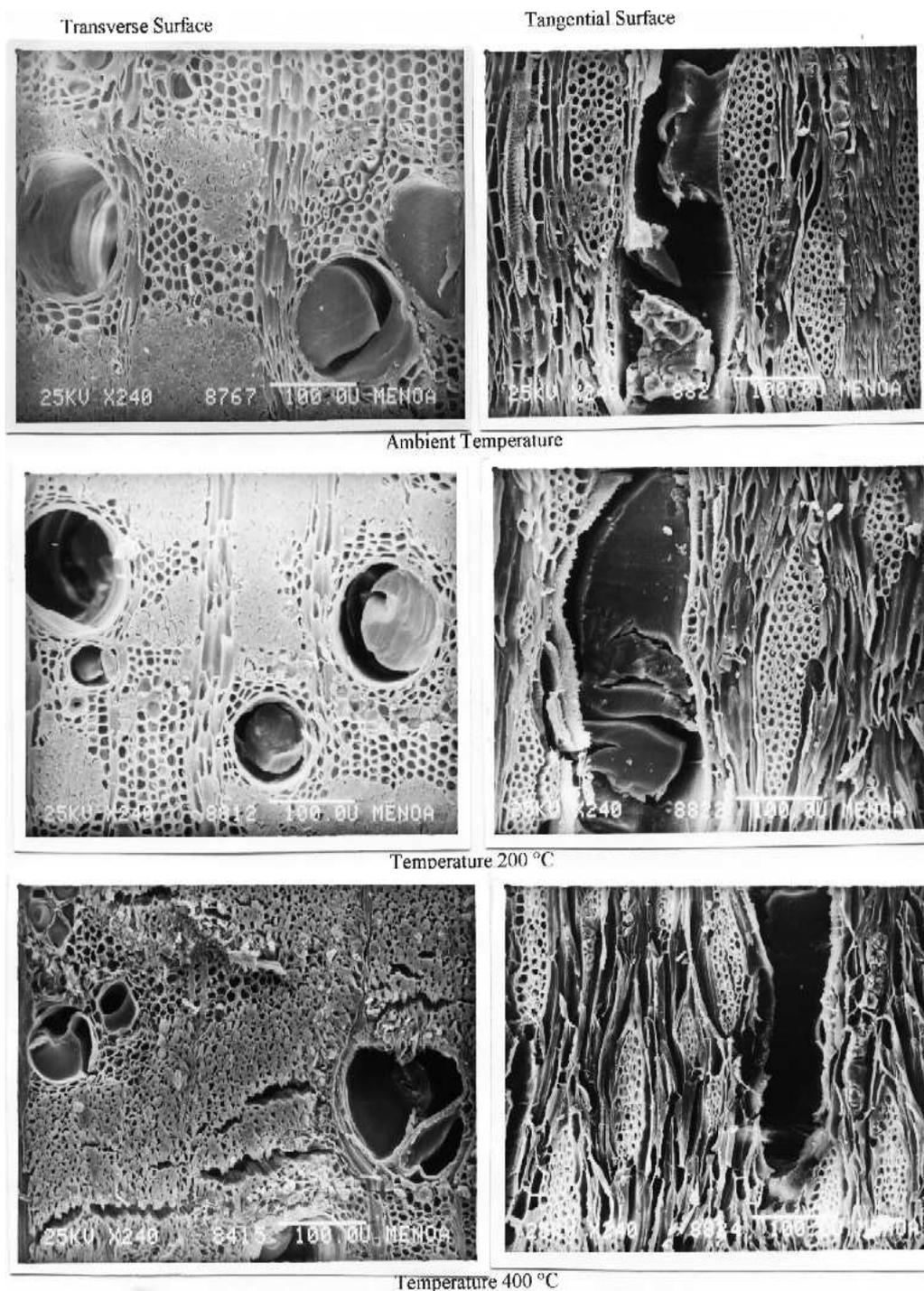


Fig. 1: Microphotographs of the SR according to the transversal and tangential planes.

we considered the following steps: a) sectioning, b) softening and c) smoothening of the surface

- a) Sectioning: thick discs (1-1.5 cm) were cut with a saw from a trunk chosen at random. Then blocks with a side of approximately 1.5 cm were cut, taking into account that they should be displayed in one of the radial, tangential or transversal planes. A magnifying lens (10 x) was employed for observation of the plane.
- b) Softening: the blocks were placed in a container with water which was connected to a refrigerant tube to avoid evaporation losses. The water boiled for around 140 hours until the blocks became soft enough to facilitate sectioning. The softening time was established by trials and error tests, considering that the wood sample was soft enough when it was possible to cut 10-15 microns layers without fractures using a xylotom.

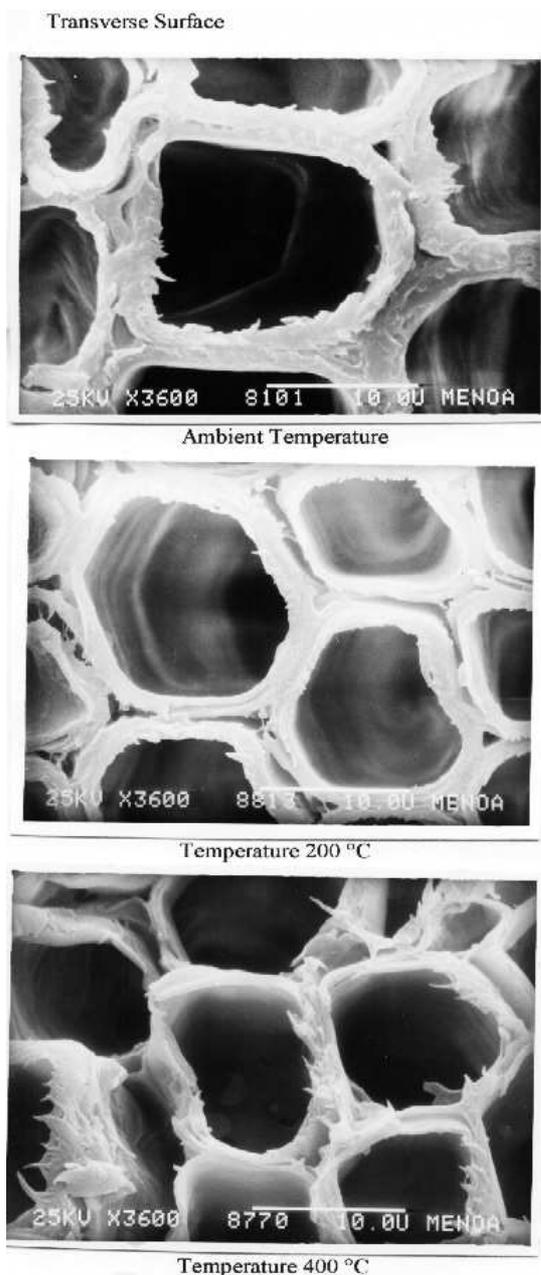


Fig. 2: Microphotographs of the axial parenchyma.

- c) Smoothing: the thickness of the blocks was reduced down to 2 mm with a xylotom by smoothing the surface corresponding to the cross, tangential or radial sections. They were air dried and cubes of side 2 mm were cut. They were stored in sealed containers.

A thermobalance Stanton Redcrof 750 TG was employed for thermal pyrolysis in a nitrogen atmosphere (50 cm³/min) in the temperature range between 200 and 400 °C (when the pyrolysis process takes place, Herrera *et al.*, 1986), using samples of around 20 mg of mass. The samples were placed in the oven, which was previously set to the working temperature and placed in the crucible of the thermobalance, with the smooth surface up. A different wood sample was used for each determi-

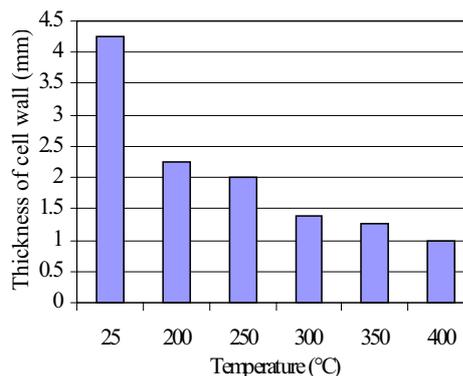


Fig. 3: The thickness of the parenchyma cell wall in function of the temperature.

nation. Temperature was kept constant for 60 minutes, the solid residue (SR) obtained was removed and attached to the plate of the electronic microscope so as to keep the smooth surface up. The residues thus obtained were analyzed by scanning electron microscopy (SEM) using a Scanning Electron Microscope JEOL 35 CF.

The non condensable gases were simultaneously collected for chromatographic analysis using a solid-gas chromatograph Konik 3000 with a thermal conductivity detector, a 6" long column and 1/8" internal diameter, packed with Porapak Q 80/100 and nitrogen as gas carrier. The working conditions were: oven temperature 40°C, detector 125 °C, injector 110 °C, filament current 135 mA, injection volume 5 ml, nitrogen flow 20 ml/min. The peaks corresponding to methane, carbon monoxide and dioxide and water were determined under these conditions using pure gases.

As on-line determinations could not be made, a glass ampule was fabricated for this purpose. It was (200 ml) had a teflon inlet and outlet and a device with an exchangeable silicon septa that allowed extraction of different volumes of gas. Other syringes with different volumes were also employed to injected gas into the chromatograph. used to carry the pyrolysis gases along a nitrogen current coming from the thermobalance. The ampule (200 ml) had a teflon inlet and outlet and a device with an exchangeable silicon septa that allowed extraction of different volumes of gas. Other syringes with different volumes were also employed to injected gas into the chromatograph

III. RESULTS AND DISCUSSION

We began analyzing the SR obtained by treating the samples at 200°C and 15°C intervals beginning at 200°C. As no substantial differences were observed in samples treated in such a short temperature gap, the temperature increase from one sample to the next was set to 50°C. Therefore, the samples obtained at 200, 250, 300, 350 and 400°C were analyzed in detail and according to the different cutting.

Examination of the microphotographs revealed structural similarities and differences between wood and the carbonization product. The Fig. 1 show the microphotographs of the SR according to the transversal and

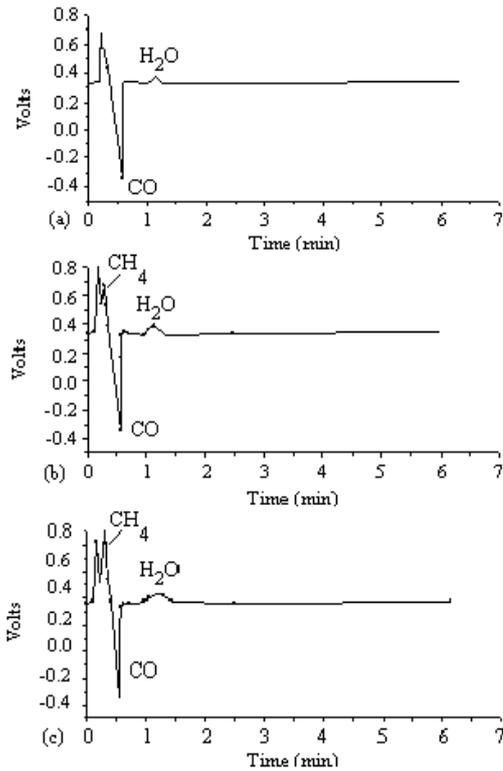


Fig. 4: Chromatograms performed at 3 minutes: (a) 200 °C, (b) 300 °C and (c) 400 °C.

tangential planes. It see that the wood structure of “Algarrobo negro” does not suffer significant qualitative changes because of the temperature effect, that is, the carbonized wood keeps its basic structure almost unaltered.

However, the mechanical tissue that strengthens the wood showed increasing changes with temperature rise until small fractures are noticed in the sample treated at 400°C. This alteration could be due to the effect of different contractions that are produced in its secondary and primary walls.

The Fig. 2 shows the axial parenchyma from the cross surface cells from the axial parenchyma. It see although the keep their shape and structure, the thickness of its walls decreases with increasing temperature. Thus and in order to look into the way in which such modification was produced, the thickness of the cell wall was determined from these photographs as the average of thirty measurements obtained at each temperature.

The Fig. 3 shows the decreases of the thickness of the wall cell of the parenchyma in function of temperature. An important diminution of the wall thickness was observed in the samples heated at 200 °C, when compared with non-carbonized wood. The cell wall thickness keeps going down until the sample reaches 400 °C. From 200° C to 300 °C, the thickness decrease is more important than the decrease observed from there to 400°C. These result coincide with the dehydration process (Herrera *et al.*, 1986) which runs up to 200 °C and

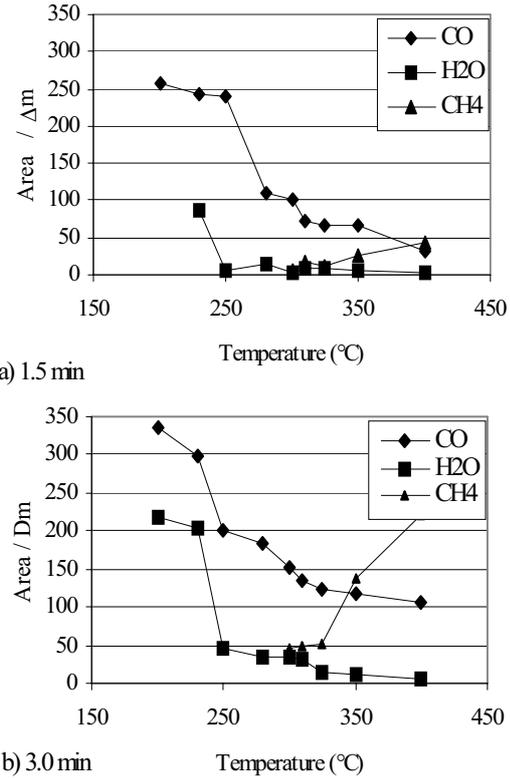


Fig. 5: Area / Δm in function of temperature: (a) for 1.5 min and (b) for 3 min.

the following stages that run consecutively, from 200 °C to 300 °C, and from 300 °C to 400 °C.

On the other hand from the thermograms obtained under isothermal conditions, the experimental values of m_i = initial mass of the wood sample to heat, and m_t = mass corresponding to time t of the SR were determined for each temperature.

The mass loss was determined from these parameters and is defined as follows:

$$\Delta m = m_i - m_t \tag{1}$$

The gas analysis was done simultaneously with the SR obtained. As the relative concentrations of each gas for a certain temperature varies according to the heating time (Oren *et al.*, 1987), the samples were taken at 1.5 and 3 min. after placing the sample in the oven.

Fig. 4 (a, b, b and c) shows the chromatograms performed at 3 minutes at 200, 300 and 400 °C. The carbon monoxide and water peaks are observed in all these temperatures, except for the carbon dioxide whereas the methane peak appears only after 300 °C.

The area for the peaks of carbon monoxide, water and methane was calculated from the chromatographed gases obtained at 1.5 and 3 min after placing the sample in the oven. The relative concentration (X) of each gas is represented by the equation.

$$X = \text{area} / \Delta m \tag{2}$$

The Fig. 5 shows these values in function of the temperature. It can be clearly seen in this figure the variations of the relative concentration for each gas accord-

ing to time and temperature. Both plots show that the temperature increase occurs with a diminution in the relative concentrations for carbon monoxide and water, an increase in methane relative concentration takes place after 300°C, more evident in samples taken at 3 minutes.

The kinetic study of wood from "Algarrobo Negro" under isothermal conditions (López Pasquali and Suarez, 2000) indicated the presence of two well defined kinetic processes, one between 200 and 300°C and the other between 300 and 400°C, with activation energy values of 6.55 and 69.45 KJ mol⁻¹ respectively, for reactions in the order of n = 0.5.

In a previous study we showed the effect of the degradation processes of the main components of wood from "Algarrobo Negro" on the overall degradation process (Herrera *et al.*, (1989), Wottitz *et al.*, (2001)). It was observed that the components do not degrade simultaneously but follow a certain sequence. It was also found that almost complete degradation of hemicellulose A and B takes place at 300°C whereas between this temperature and 400°C, the degradation of α -cellulose and lignin occurs.

On account of the foregoing results it can be suggested that the degradation process of "Algarrobo Negro" takes proceeds in two steps, the first between 200°C and 300°C, with a pronounced diminution of the cell wall thickness, an important contraction of the tissues, the appearance of the maximum peaks of carbon monoxide and water tissues, the appearance of the maximum peaks of carbon monoxide and water.

This evidence agree with the first kinetic process whose activation energy is 6.55 KJ mol⁻¹ for n = 0.5 and coincide with the temperature range where the degradation of hemicelluloses A and B is produced. The second step occurs between 300 and 400°C in accordance with the second kinetic process and whose activation energy is 69.45 KJ mol⁻¹ for n = 0.5. This step shows a lesser variation of the cell wall thickness, a larger structural alteration, appearance of cracks and larger alteration of the mechanical tissue along with appearance of the methane peak. This step also coincides with the temperature range where the degradation of α -cellulose and lignin is produced.

These data allows us to suggest that wood from "Algarrobo Negro" behaves in a similar way to the species studies by Connor and Daria (1993), when we analyze the influence of particle size in the carbonization process, and the resistance to mass and heat transfer.

IV. CONCLUSIONS

The results obtained suggest that the basic anatomic structure of wood remains almost unchanged during the pyrolysis. This in turn would indicate that mass and energy transfer in bigger particles would be the critical step of the carbonization process.

Even though the temperature does not substantially modify the basic structure, there is a general contraction of tissues which is seen in the diminution of the cell wall thickness of the axial parenchyma and the contrac-

tion of the mechanical tissue. The fact that the original basic structure is kept in the solid residues can be attributed mainly to residual lignin, which is the structural component of wood that degrades more slowly.

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