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VACUUM PYROLYSIS OF *ASTRONIUM URUNDEUVA*

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Petroleum natural gas (PNG) reserves will last even when the oil reserves are exhausted, requiring the development of technologies for PNG storage. Activated charcoal is the best material for such a purpose. Under vacuum samples of aroeira (*Astronium Urundeuva*) underwent pyrolysis in diverse conditions. The samples were characterized by thermal analysis, scanning electronic microscopy and infrared spectroscopy. When the pyrolysis temperature increased, mechanical anisotropy resistance tended to disappear. The pyrolysis became complete only at high temperatures and using a long time of treatment.

Keywords: *adsorption, pyrolysis, wood*

Introduction

Currently, there are ecological and energy crises due to the increasing demand for industrialized products and personal comfort (thermal conditioning, alimentary needs, transport demand, etc.). The consumption of fossil energy sources (coal and oil) is significant considering depleting supplies. In underdeveloped countries, native forest territory is being lost as the original forest biomass is consumed and agricultural land borders expand. The release of pollutant carbon into the atmosphere is increasing; this carbon was previously fixed in wood, oil beds and native forest. Meanwhile, the fossil reserves will be depleted in a few decades. Due to this situation, petroleum natural gas (PNG) is beginning to be used intensely worldwide, in the past it was released into the atmosphere. The development of cheap materials for large-scale permanent fixation of carbon, while adsorbing PNG for storage and transport, is desired.

There are three options for storing PNG:

- the use of appropriate solvent; its drawback is the low solubility of the methane, requiring high pressures [1]
- the inclusion of composites [2]; its disadvantage is the low storage capacity
- the adsorption in porous materials [3–8]; that is the most promising mechanism
- A lot of research is focused on the development of microporous adsorbers with a large superficial area, high packing density and good mass and heat transfer properties [9, 10].

The best choice so far is activated charcoal acting as an adsorber. Such a system can store PNG at moderate pressures (3.5 MPa), compared with the high pressures (20 MPa) required for natural gas compression [11]. Its storage capacity is in the range of 300–700 Kg m^{-3}, with the adsorbed/adsorbent volume rate varying from 101 to 172 V/V, whereas the ideal rate is around 150 V/V [4, 5, 7, 12–17]. The pyrolysis of vegetal organics is a common process for activating carbon. The activation of carbon can occur in some environments, such as vacuum, steam, and CO_2, with different results on the microporosity lacking meso- and macroporosity. The maximization of the superficial area and adsorption capacity of the activated charcoal is still under study [18–20]. In this work, the pyrolysis of the Aroeira (*Astronium Urundeuva*), a wood of the Middle West Brazilian Biome, is presented. The samples were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TG), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

Experimental

Materials and methods

Samples with 55×20×3 mm of heartwood of aroeira were heat treated under vacuum for 60 min. Each sample was heated at 1°C min^{-1} up to a different heat treatment temperature: 230, 310, 450 and 950°C.

After heat treatment, the thermal behavior of about 10 mg of milled wood samples was characterized by DSC and TG using a Shimadzu-TA-50H, in platinum crucibles under nitrogen flow at 10°C min^{-1} heating rate. The experiments were repeated under dry air for 1 mg milled wood samples.

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The chemical compositions of the samples were determined by FTIR in a Termo Nicolet-NEXUS 670 apparatus. Chemical compositions were also determined using X-ray powder diffraction (XRD). XRD patterns were recorded using a Rigaku-Rotaflex RU200B machine connected to a multipurpose chamber using CuK$_\alpha$ radiation, an angular range of 10 to 60°, a potential difference of 50 kV and an electron current of 100 mA. The morphology was determined via scanning electron microscopy (SEM) using a JEOL- 6830-LV microscope.

Results and discussion

DSC and DTG curves of samples treated at different temperatures were initially obtained under nitrogen flow, as shown in Fig. 1.

The DSC curve for the sample treated at 230°C presents four wide and low intensity exothermic peaks near the temperatures of 290, 360, 400 and 490°C, and correlated to mass losses in the TG and DTG curves. The first peak corresponds to the hemicelluloses, the intermediate to the cellulose and lignin and the last is due to the partial decomposition of the lignin [21].

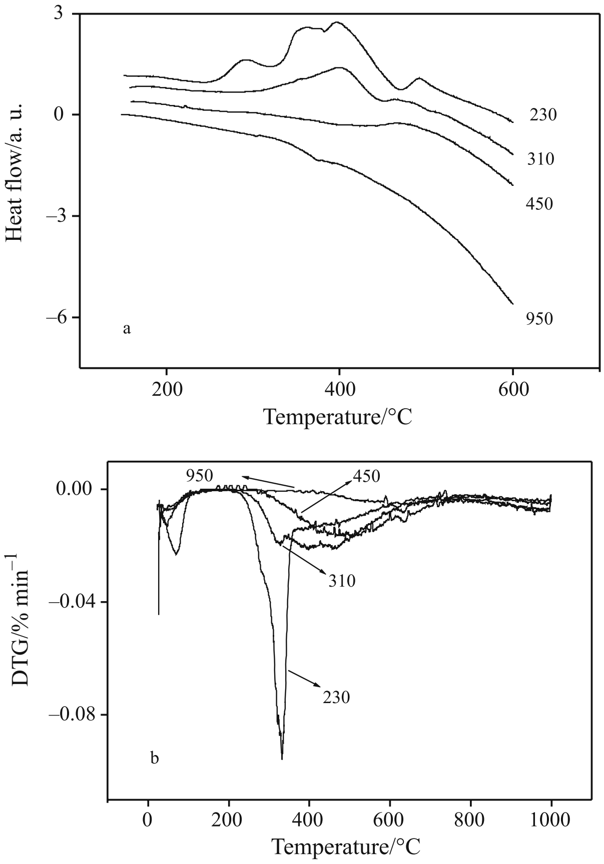

Fig. 1 a – DSC and b – DTG curves of samples previously treated at different temperatures in nitrogen

Thermal degradation is usually the result of a thermal response of three main wood components: hemicelluloses, cellulose and lignin. However, since the samples were previously heat treated, there were some chemical transformations before thermoanalytical experiments. Although thermal degradation of the three components starts at 200°C, the degradation rates differ for each one, so there are three peaks in the DSC curve. This fact explains the different behavior observed in DSC and DTG curves: for samples treated at lower temperatures, the transformation rates are higher.

The thermal behavior of the samples is in accordance with other authors' reports on wood degradation under nitrogen and oxygen atmospheres [21]. The peaks at 225–325 and 370°C in the DTG curve have been attributed to hemicelluloses and cellulose polymers, respectively. According to the DTG graphs, the beginning of lignin degradation occurred at 200°C but lignin presented high thermal stability remaining in the samples after most carbohydrate polymer degradation (in the range of 300 to 375°C).

Figure 1 reveals that while the carbonization of hemicelluloses and cellulose is a fast process, the lignin carbonizes slowly. The shift of lignin peaks to higher temperatures in the DTG curve is due to the partial carbonization of the lignin in the treated samples.

For temperatures above 450°C the charcoal looses oxygen and hydrogen beginning to tend to graphite structure [19]. Even the sample treated at 950°C shows some mass loss in the TG and DTG curves. A peak maximum at 600°C indicates that the pyrolysis and graphitization processes require longer time or higher temperature to be complete.

Figure 2 shows DSC and DTG curves obtained under air flow. The samples treated at temperatures lower than 950°C present two exothermic peaks: the first and wider peak is attributed mainly to the hemicelluloses and cellulose; and the second peak to the lignin as a major contributor. Hemicellulose and cellulose are the main components of the primary wall of the cells. When hemicellulose combusts, the cellulose content will combust as well, due to the close physical proximity of these components and to the exothermic nature of the reaction. Even if the hemicelluloses and cellulose have been partially carbonized they are still more reactive with the oxygen than the lignin and the oxidation occurs at lower temperatures. The sample treated at 950°C presents only one narrow peak with a maximum around 450°C due to nearly complete carbonization of the sample before thermal analysis. The peak corresponds to the combustion of charcoal.

In the IR absorption curves (Fig. 3) the sample treated at 230°C presents bands corresponding to the

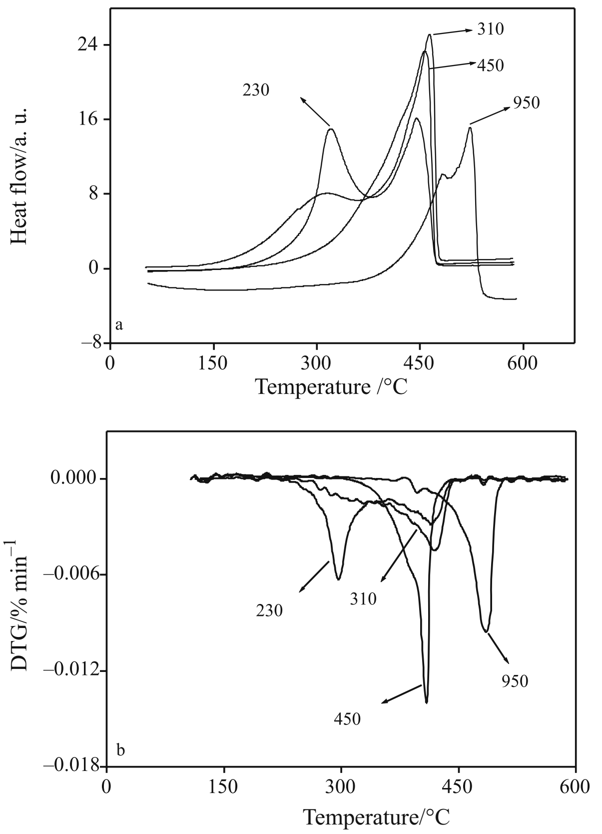

Fig. 2 a – DSC and b – DTG curves of samples in air

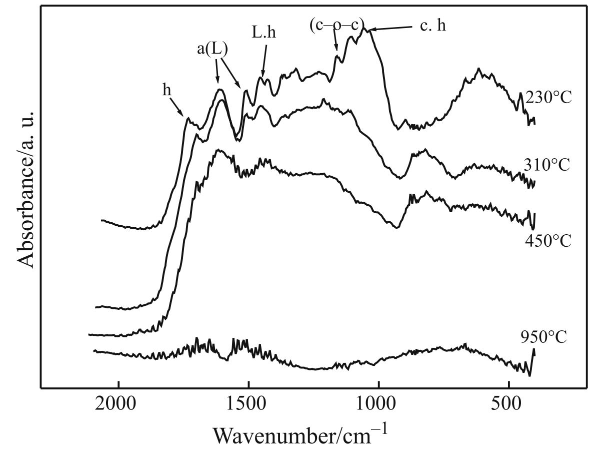

Fig. 3 FTIR spectra of samples treated at different temperatures

hemicelluloses (h), celluloses (c), lignin (L) and aromatic rings of lignin (a).

In the characteristic bands of hemicelluloses, the peaks of C=O from the acetyl group occurred at 1740, 1450 and 1032 cm^{-1}. There is a cellulose band at 1052 cm^{-1}. The bands at 1458 and 1611 cm^{-1} are assigned to lignin and to its aromatic ring. There is a characteristic band at 1160 cm^{-1} attributed to C–O–C bonds, which are very common in treated wood.

The corresponding peaks from hemicelluloses and cellulose vanish as the treatment temperature increases, remaining only the bands belonging to the lignin aromatic rings. The absorption peaks corresponding to hemicellulose and cellulose do not appear in the sample treated at 310°C remaining only the bands of lignin. At 450°C the single absorption band corresponds to the aromatic rings of the lignin, which disappears completely for the samples treated at 950°C. This evidence confirms the pyrolysis kinetics determined by DTG and the attribution of degradation peak to different elements.

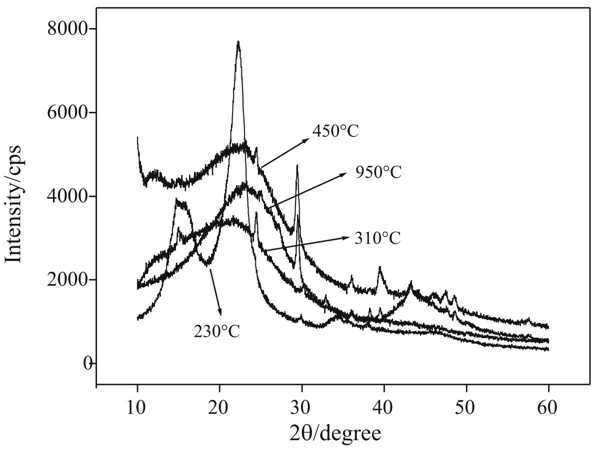

Fig. 4 XRD curves of samples treated at different temperatures

The X-ray diffraction patterns in Fig. 4 show that the carbonization at 450°C enhances the amorphous character of charcoal by destroying crystalline cellulose. Pyrolysis at higher temperature increases the ordering of aromatic rings beginning to form some structures similar to graphite from the charcoal, changing the local structure.

The main cellulose crystalline planes [22] correspond to Bragg angles (2θ) near 23° (plane 002), 20° (020), 21° (021), 17° (101), 15° (101) and 35° (040). The peak intensity is similar for the lines corresponding to 23° (plane 002) and 20° (plane 020). The diffraction line near 2θ=15° is difficult to identify due to the diffusive diffraction of the amorphous components of the samples. Some authors observed slightly different reflections due to different cellulose hosts. A wide reflection was observed near 2θ=22° [23], probably associated to an overlapping of the peaks at 23 and 21°. This reflection changed as a function of heat treatment temperature demonstrating the change in the structure of cellulose. At temperatures above 800°C the crystallization reflections are due to aromatic ring ordering leading to graphite structure above 1800°C.

These results are in accordance with the IR spectroscopy findings where the absorption lines of cellulose vanished at higher temperatures leaving only the broad bands in the lignin carbon ring positions. These results also agree with thermal analysis,

Table 1 XRD phase observed for samples with different thermal treatments

Heating temp./°C	Chemical compound	Formula	File (ICDD)	Figure of merit/%
230	Native cellulose	$(C_6H_{12}O_6)_x$	000-03-0289	84
310	Hydrate calcium oxalate	$CaC_2O_4 \cdot H_2O$	000-01-0157	74
450	Calcite	$CaCO_3$	000-01-0837	89
950	Calcite	$CaCO_3$	000-01-0837	88

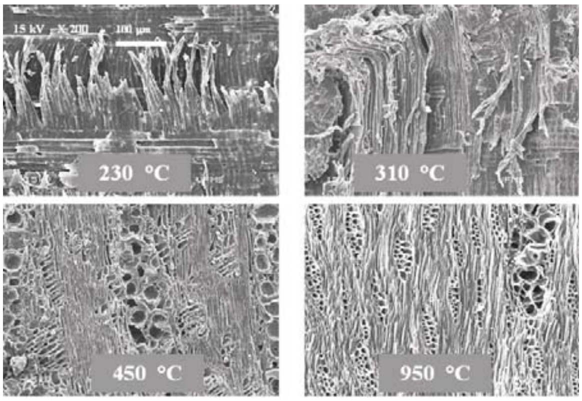

Fig. 5 SEM (200×, 15 kV) of samples treated at different temperatures

which explains why dramatic changes only occur in the samples treated at higher temperatures. The narrow peaks superposed over the large ones in all samples are related to inorganics such as Ca, Mg and K present in wood as pectins that form oxalates and carbonates when decompose. The lines at 24.5 and 38.3° for the samples treated at 310°C are attributed to calcium oxalate, and the lines at 24.5, 29.5 and 36.1° for the samples treated at higher temperature relate to calcium carbonate or calcite (Table 1).

The surface fracture morphology of the samples determined using the SEM images in Fig. 5 demonstrated intense physical-chemical changes. The samples treated at 230 and 310°C show fibrous structures that are frayed due to the presence of lignin and cellulose not totally reacted. So, the heterogeneous mechanical characteristics of wood are sustained. Although cellulose underwent almost complete carbonization the heterogeneous structure remained due to poorly reacted lignin. At 450°C the lignin was completely carbonized and the structure became mechanically homogeneous: the fractures were planar. Also, the samples treated at 950°C were very flat.

The pyrolysis temperature dramatically affects the physical-chemical properties of activated charcoal.

Conclusions

The complete vacuum pyrolysis of aroeira takes place at temperatures over approximately 800°C and requires long treatment times. The lignin pyrolysis is slower than that of cellulose and hemicellulose. Between 600 and 700°C, the aromatic rings start tending to the graphite structure, although the samples are still largely amorphous. Between 700 and 950°C large peaks arise in XRD as the samples approach a graphite structure.

Acknowledgements

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References

1 L. Wang, H. Gardeler and J. Gmehling, Sep. Purif. Technol., 12 (1997) 35.
2 G. Y. Yevi and R. E. Rogers, J. Energy Res. Tech., 118 (1996) 209.
3 J. A. F. MacDonald and D. F. Quinn, Carbon, 34 (1996) 1103.
4 J. A. F. MacDonald and D. F. Quinn, Fuel, 77 (1998) 61.
5 J. Alcaniz-Monge, M. A. De La Casa Lillo, D. Cazorla-Amóros and A. Linares-Solano, Carbon, 35 (1997) 291.
6 F. S. Baker, Highly Microporous Carbon, 1998, US Patent 5710092.
7 S. Manzi, D. Valladares, J. Marchese and G. Zgrablich, Adsorpt. Sci. Technol., 15 (1997) 301.
8 J. A. Schwarz, K. Putyera, T. J. Bandosz, J. Jagiello and K. A. G. Amankwah, Composite Microporous Carbons for Fuel Gas Storage, 1998, US Patent 5837741.
9 E. A. Dawson, G. M. B. Parkes, P. A. Barnes, M. J. Chinn and P. R. Norman, J. Therm. Anal. Cal., 56 (1999) 267.
10 F. Suárez-García, J. Nauroy, A. Martinez-Alonso and J. M. D. Tascón, J. Therm. Anal. Cal., 79 (2005) 525.
11 D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares Solano and D. F. Quinn, Activated Carbon and Carbon Monoliths for Methane Storage at Relatively Low Pressure, 1st World Conference on Carbon, Berlin 2000, pp. 131–2.
12 J. Wegrzyn and M. Gurevich, Appl. Energy, 55 (1996) 71.
13 T. A. Brady, M. Rostam-Abadi and M. J. Riid, Gas Sep. Purif., 10 (1996) 97.
14 F. S. Baker, S. C. Wando, R. B. Beckler, J. R. Miller and Z. Q. Yan, Highly Microporous Carbon and Process of Manufacture, US Patent 5965483, 1999.

15 T. D. Burchell and M. R. Rogers, Natural Gas Storage Monoliths Based on Activated Carbon Fibers, 1st World Conference on Carbon, Berlin, 2000. pp. 133–4.
16 A. M. Rubel and J. M. Stencel, Fuel, 79 (2000) 1095.
17 T. K. Bose, R. Chahine and J. M. St-Arnaud, High-Density Adsorbent and Method of Producing Same, US patent 4999330, 1991.
18 A. Amaya, J. Píriz, N. Tancredi and T. Cordero, J. Therm. Anal. Cal., 89 (2007) 987.
19 R. W. Soares, V. J. Menezes, M. V. A. Fonseca and J. Dweck, J. Thermal Anal., 49 (1997) 657.
20 M. Gao, C. Y. Sun and C. X. Wang. J. Therm. Anal. Cal., 85 (2006) 765.
21 R. M. Rowell and S. L. Levan-Green, Thermal Properties, NETHERCOT, D. Handbook of Wood Chemistry and Wood Composites. Taylor & Francis, 2005, Cap. 6.
22 K. Nishimiya, T. Hata, Y. Imamura and S. Ishihara, J. Wood Sci., 44 (1998) 55.
23 M. Ota and H. M. Mozammel, J. Wood Sci., 49 (2003) 248.

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