

CHEMICAL AND STRUCTURAL EVOLUTION OF EUCALYPTUS TAR PITCHES UNDER CARBONIZATION

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Introduction

During wood pyrolysis in charcoal production, intense release of gases and volatiles takes place. These volatiles can be recovered by condensation to give rise to an oily mixture called wood tar. However, the costs involved and the low wood tar aggregated value has discouraged tar recovery, so that large amounts of pollutants have been released into the atmosphere. In this context, a new research line, called “Vegetal Carbochemistry”, was initiated in Brazil at the end of the 1980’s. It aims to develop new and nobler applications for eucalyptus tar fractions, therefore stimulating its recovery and aggregating revenue to the charcoal-making industry.

In this context, eucalyptus tar has been processed to separate fractions used as flavors, fragrances and source of fine chemical products [1,2]. This processing involves tar decanting to separate an aqueous phase, so-called pyroligneous acid, and posterior distillation of the insoluble tar. A heavier fraction, called *Eucalyptus* tar pitch, is generated as a distillation residue of the insoluble tar. Previous studies demonstrated that these pitches have a macromolecular structure constituted mainly of phenol, guaiacyl, and siringyl units resulting from lignin degradation. Outstanding features are their low aromaticities (60-70%) and high O/C ratios (0.20-0.27%) [3, 4]. At the moment, our research group is investigating the use of eucalyptus tar pitches as precursors of advanced carbon materials such as isotropic carbon fibers, bioelectrodes, C/C composites, and activated carbons. In this work, the chemical and structural evolution of these pitches toward a carbon material is assessed. An improved understanding about this subject is important to make it possible to plan and control the production of hard carbon better and to improve the property of the end-products.

Experimental

A precursor *Eucalyptus* tar pitch was produced as follows. Wood chips of planted *Eucalyptus* forests (Minas Gerais, Brazil) were submitted to pyrolysis (500 °C; 12–14

°C/h). The smokes were washed and condensed to produce eucalyptus tar. This tar was vacuum distilled at a cut temperature of 180 °C under a pressure of 30–38 mmHg. The distillation time was 8 h and the pitch yield was about 50% (w/w). This precursor pitch was pre-treated at different temperatures and periods of time in order to produce samples with different properties (softening point, viscosity, coke yield, etc). [3,4]

Pitch pre-treated at 250 °C for 8 h (P8250) was used as starting material in the present studies. It was heat treated at different temperatures for 1 h to generate the samples 400HTT, 600HTT, 800HTT, 1000HTT, 1300HTT, 1700HTT, 2100HTT, and 2300HTT according to the corresponding heat treatment temperature (HTT). For maximum temperatures of 1000 °C or lower, the treatments were carried out under N₂ atmosphere in a stainless steel tubular furnace, with a heating rate of 2.0 °C/min. For higher maximum temperatures, parts of the 1000 °C-coke were additionally heated at 4.0 °C/min, under Ar atmosphere in a graphite tubular furnace.

Wide-angle X-ray diffractograms of the powdered samples were obtained in a Rigaku Geigerflex diffractometer with Ni-filtered Cu-K α radiation (40 kV and 30 mA) and scanning rate of 1°/min. Silicon was used as a standard for peak position and broadening corrections. The interlayer spacing (d_{002}) of the samples constituted was determined from the Bragg's equation and the stacking size (L_c) was estimated from Sherrer's equation with $K = 0.90$. The software "Origin 5.0" was used to deconvolute the (002) profiles.

Solid-state ¹³C NMR DP/MAS (direct polarization/magic angle spinning) spectra were obtained in a Varian INOVA-300 Spectrometer at 75.4 MHz with a RT probe. The rotor (7 mm–zirconia) was spun at 5.9 kHz around the magic-angle, 54° 44'. The spectra were acquired using spectral width of 50 kHz, acquisition time of 0.05 s, pulse of 90° (6 μ s), delay time of 100 s, 400–2300 scans per spectrum, and high-power proton decoupling.

Infrared analyses (KBr pellets) were carried out in a Perkin-Elmer FTIR SPECTRUM 1000 spectrometer. The samples were prepared as. The porous structure of the carbonized samples was characterized from 77 K N₂ isotherms obtained in a Quantachrome Nova-1200 High Speed Gas Sorption Analyzer. Surface area and porous volume were calculated by the BET and BJH method, respectively. The apparent density of the powdered samples was measured using a Quantachrome Multipycnometer with helium as the displacement fluid.

Results and Discussion

Treatment up to 600 °C

Figure 1 demonstrates that the X-ray diffraction patterns of the P8250 pitch and cokes generated from its carbonization at 400 and 600 °C presents a wide band around $2\theta = 21\text{--}23^\circ$. This band results from a short range ordering of adjacent aromatic rings and demonstrates that the samples have an amorphous polymer-like structure.

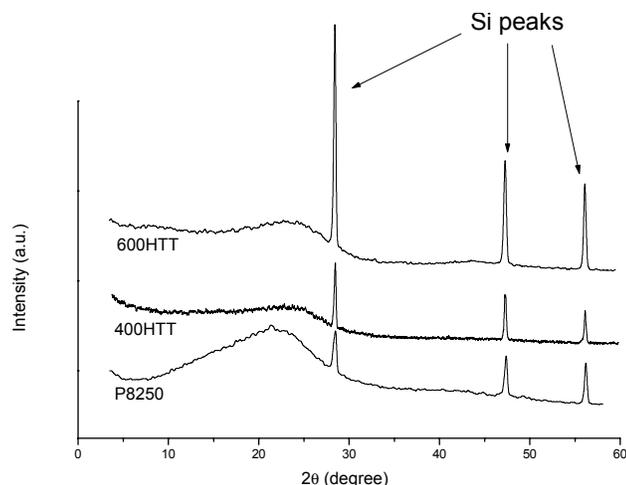


Figure 1. X-ray diffractograms

Despite the similarities among X-ray diffractograms, the sample underwent pronounced chemical changes during treatment from room temperature to 600 °C. Treatment up to 400 °C involved pyrolytic homolytic cleavage of C—O bonds. While side chains are released, the heavier fragments rich in aromatic rings can recombine to form larger and larger molecules. Decarboxylation and condensation of phenols are others reactions taking place in this temperature range, the later mainly when temperature nears 400 °C. As a consequence of the mentioned reactions, the material reached a thermosetting structure, at the same time that the content of aliphatic carbons was strongly reduced and carboxyl carbons were completely eliminated from NMR ^{13}C spectrum of the 400HTT coke (Table 1).

Table 1. ^{13}C NMR signal intensities

sample	carbon signal intensity (%)		
	carboxyl	aromatic	aliphatic
P8250	2	70	28
400	-	90	10
600	-	97	3

In turn, temperatures over 400 °C provided sufficient energy to directly degrade alkyl groups. Therefore, only a small amount of aliphatic carbons is present in the 600HTT coke (Table 1). FTIR spectrum (Figure 2) provides important information about this sample. Besides the bands near 1600 cm^{-1} and below 900 cm^{-1} (C=C stretching and C—H out-of-plane bending in aromatic rings, respectively), the spectrum has a sharp band at 1380 cm^{-1} , which is attributed to symmetrical bending of CH_3 groups directly linked to aromatic rings, and a large absorption band around $1300\text{--}1200\text{ cm}^{-1}$, which is attributed to the formation of xanthene and diphenylene oxide structures (Figure 3).

The removal of aliphatic side chains permitted a more closed packing of the aromatic rings, so that helium density increased for treatments up to 600 °C (Figure 4).

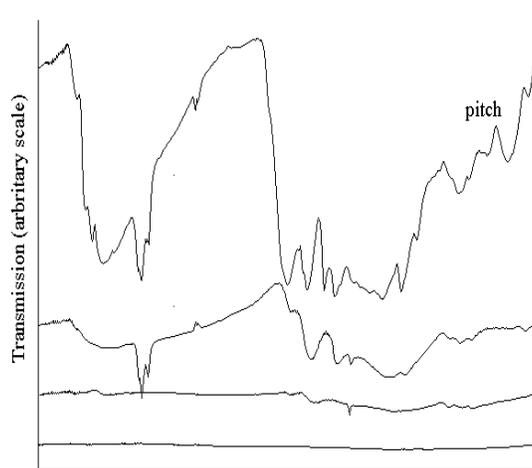


Figure 2. FTIR spectra for the P8250 pitch and cokes resulting from its carbonization.

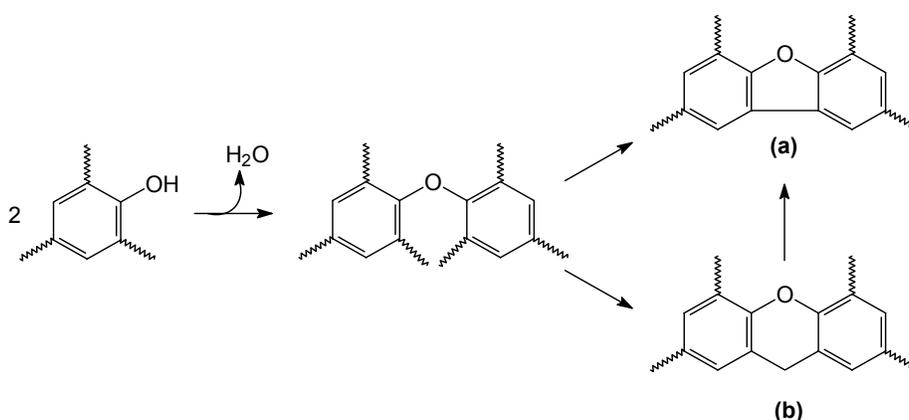


Figure 3. Xanthene (a) and diphenylene oxide (b) structures.

Treatment from 600 °C to 800 °C

After treatment up to 800 °C a prominent band centered at $2\theta = 43.2$ aroused in the X-ray diffractogram (Figure 5). It shows that dehydrogenation of aromatic rings took place at this temperature range, giving rise to extensive condensation among the rings. In addition, a peak emerged at $2\theta = 25.81^\circ$ ((002) peak), although the (002) band remains as a shoulder at lower scattering angles. These results show that 800HTT coke is constituted by two phases: a crystalline one, composed by carbon atoms arranged in planar hexagonal networks, and another corresponding to reminiscent highly disordered carbon. However, the absence of (hkl) reflections characteristic of three-dimensional crystals allow us to say that, even for the more ordered carbon, there is not any measurable crystallographic order correlating the position of atoms belonging to different carbon planes.

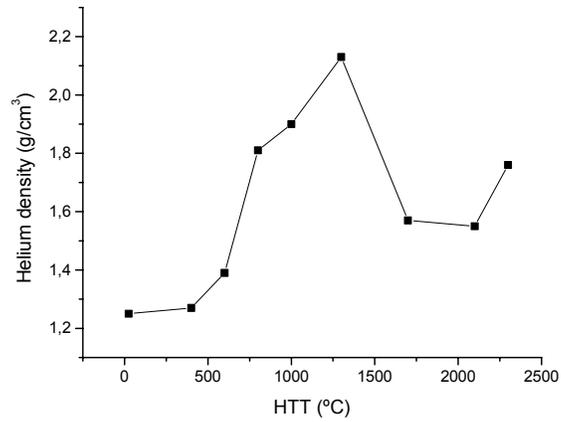


Figure 4. Helium density as a function of HTT for biopitch-based carbons.

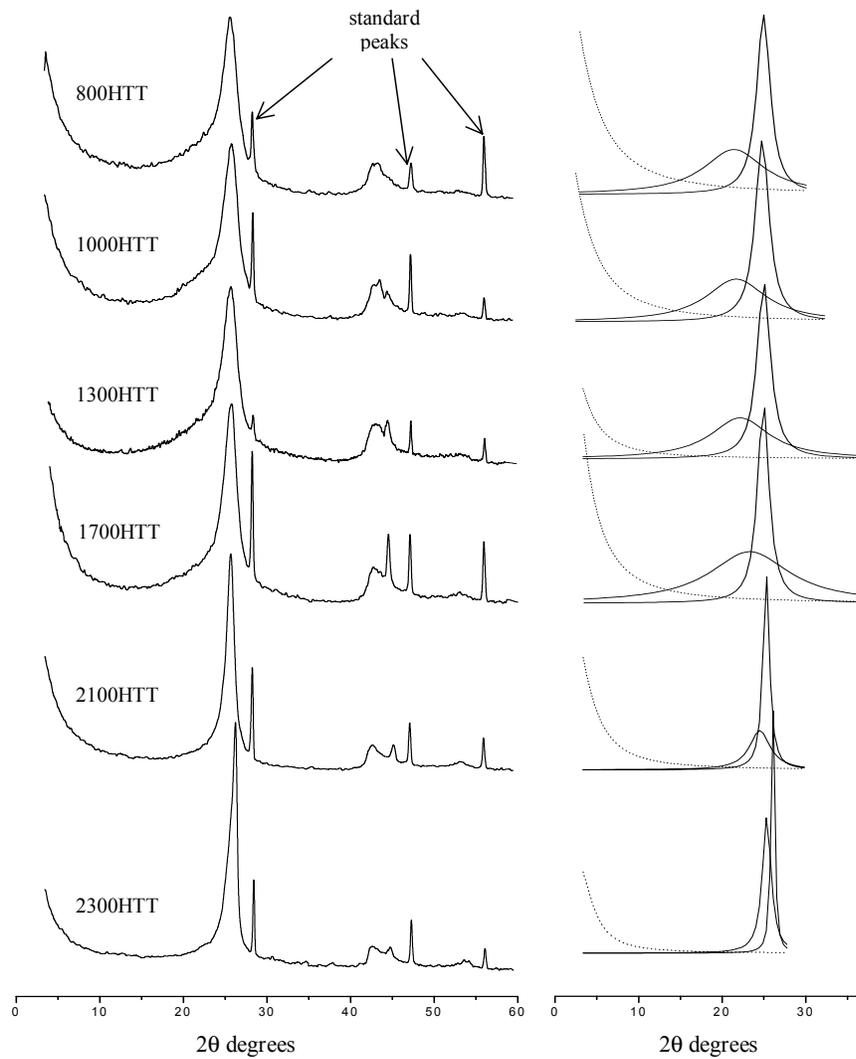


Figure 5. X-ray diffractograms of biopitch-based carbons obtained. (a) experimental spectra; (b) resolved components of the (002) profile.

Treatment between 600 and 800 °C led to pronounced helium density increase. It occurred mainly due to the formation of carbon crystallites, which are denser than disordered carbons. In addition, 800HTT coke presents relatively high pore volume and surface area (Figure 6). This behavior can be understood taking into account that large density variations of carbon atoms occur during the condensation of the aromatic rings to form bi-dimensional hexagonal networks. Therefore, sparse regions are created, which gives rise to cracks, and consequently forms micro and mesopores.

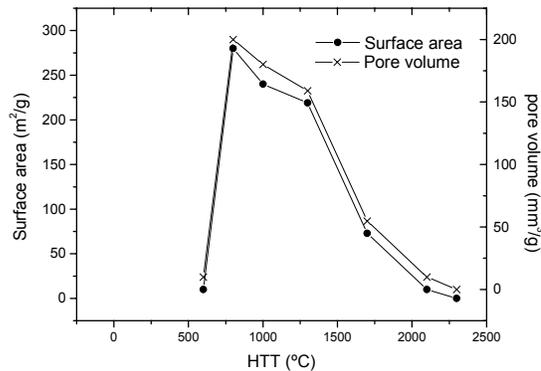


Figure 6. BET surface area and pore volume of biopitch-based carbons.

Treatment over 800 °C

From 1000 to 2100 °C the material underwent pronounced structural ordering. (002) band and (002) peak narrowed and intensified, and the (004) peak became clearly perceptible around $2\theta = 54^\circ$ (Figure 5), which reflects the thermally activated coalescence of different groups of carbon planes and/or the removal of crystallite defects. In addition, (002) reflections shifted to higher scattering angles, which resulted from decreases in d_{002} . These changes became specially pronounced in the 2100-2300 °C temperature range. Outstandingly, the d_{002} of the less ordered phase reached 3.50 Å, a value characteristic of turbostratic structures, with $L_c = 64$ Å. In turn, d_{002} of the more ordered phase decreased abruptly to 3.39 Å, approaching the value corresponding to a perfect graphite crystal (3.354 Å), with L_c reaching 167 Å.

Treatments over 800 °C gradually reduced the measured porosity and surface area. They approached zero for 2100HTT coke. This reduction occurred partially because defects (pores) are removed during the material ordering, and partially because some pores become closed. The latter is evidenced by the pronounced reduction verified for helium density between 1300 and 1700 °C, in spite of the material ordering. Kercher and Nagle reported similar behavior during carbonization of charcoal [5]. They proposed that small pores eventually become choked off by the carbon crystallites becoming drawn together and also by vapor deposition processes. However, we believe that the more disordered phase, which acts as a matrix containing the carbon crystallites, also plays an important role in the formation of closed porosity. Over 1000 °C, defects are continuously removed from this less ordered phase and, as a consequence, it becomes more and more impermeable to work gases (Figure 7), therefore making density measurements underestimated.

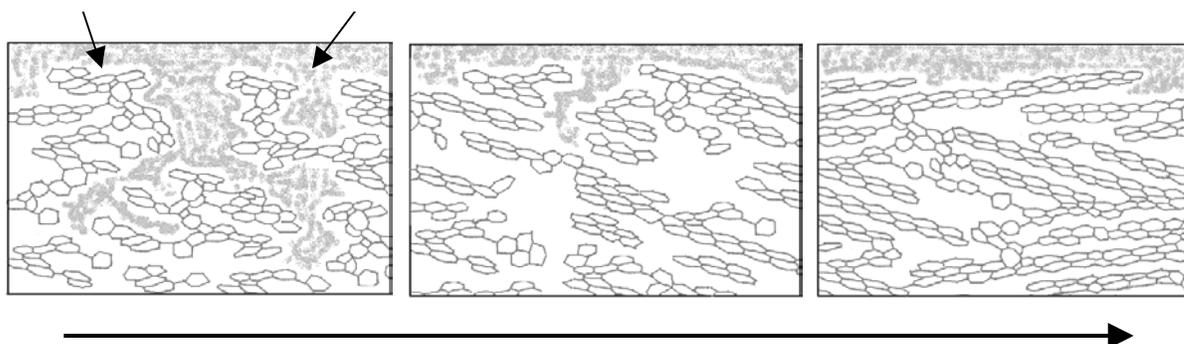


Figure 7. Scheme illustrating the structural evolution of the less ordered phase during eucalyptus tar pitch carbonization: (a) highly disordered and permeable carbon; (b) the structure becomes impermeable to gases and forms closed pores; (c) a turbostratic structure is formed and the volume of closed pores is reduced.

Conclusions

Although carbonization is an immensely complex process, the present work permitted to elucidate important features about the conversion of eucalyptus tar pitches toward a carbon material and correlate some chemical and structural changes with the properties of the resultant material. We hope that these results will help guide planning and controlling the processing of biomass precursors toward hard carbons and the properties of the end-products.

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