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Biomass and Bioenergy 28 (2005) 53–61
BIOMASS & BIOENERGY
www.elsevier.com/locate/biombioe

Structural evolution of *Eucalyptus* tar pitch-based carbons during carbonization

Marcos J. Prauchner[a,*], Vânya M.D. Pasa[b], Nelcy D.S. Molhallem[b], Choyu Otani[c], Satika Otani[c], Luiz C. Pardini[d]

[a]*Instituto de Química, Universidade de Brasília, C.P. 4478, Brasília, CEP: 70910 970, Brazil*
[b]*Departamento de Química, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, Belo Horizonte, CEP: 31270 901, Brazil*
[c]*Departamento de Física, Instituto Tecnológico de Aeronáutica, Centro Técnico Aeroespacial, São José dos Campos CEP: 12228 901, Brazil*
[d]*Divisão de Materiais, Instituto de Aeronáutica e Espaço, Centro Técnico Aeroespacial, São José dos Campos CEP: 12228 904, Brazil*

Received 20 January 2004; received in revised form 4 May 2004; accepted 5 May 2004
Available online 6 July 2004

Abstract

Wood tar pitches are generated as by-products by the charcoal manufacturing industry. They have a macromolecular structure constituted mainly by phenolic, guaiacylic, and siringylic units common to lignin. Due to their characteristics, biopitches are been investigated as precursors of carbon materials such as carbon fibers, bioelectrodes and activated carbons. In the present work the structural evolution of *Eucalyptus* tar pitches under carbonization is investigated, which is important for the improvement of planning and control of pitch processing and end-product properties during carbon material production. The studies involve X-ray diffraction and infrared analyses, besides helium density, BET surface area and BJH pore volume measurements. The results showed that the conversion of pitch into carbon basically involves three steps: (1) Up to around 600 °C the material has an highly disordered structure, being the release of aliphatic side chains and volatiles the main events taking place. (2) Between 600 °C and 800 °C, condensation of aromatic rings occurs to form bi-dimensional hexagonal networks so that micro- and mesoporosity are developed. The 800 °C-coke is constituted by two phases: one highly disordered and another more crystalline. (3) Over 800 °C, both phases are gradually ordered. As defects are gradually removed, surface area and porosity decrease, approaching zero for the 2100 °C-coke.

Keywords: Pitch; Wood by-products; Biomass; Carbon; Charcoal; Pyrolysis; Carbonization; X-ray; Porosity; Surface area

1. Introduction

Brazil is one of the few countries where forest biomass has always played an important role as an

*Corresponding author. Tel: +55-61-307-2167; fax: +55-61-273-4149.
E-mail address: marcosjp@unb.br (M.J. Prauchner).

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doi:10.1016/j.biombioe.2004.05.004

energy source because the tropical climate favors forest growth. In 2000, about 6.5×10^6 tons of charcoal was consumed in Brazil, 88% of which were destined to the siderurgical industry. [1] Charcoal is produced by pyrolysis of wood at final temperatures on the order of about 400–500 °C. This treatment is followed by intense release of gases and volatiles generated by wood decomposition. Volatiles can be recovered by condensation, giving rise to a liquid called wood tar. This tar can be separated by decanting to give rise to an aqueous fraction (so-called pyroligneous acid) and an organic fraction (insoluble tar), which corresponds to around 35% and 7% of the initial mass of wood, respectively.

For 2000, 72% of the Brazilian charcoal production used planted *Eucalyptus* forests [1]. The use of charcoal produced from planted forests presents advantages when compared to the use of metallurgical coke: biomass is a renewable energy source; charcoal minimizes the environmental impact arising from the siderurgical activity because it does not affect the natural carbon cycle and gives rise to a comparatively low level of emission of toxic gases such as SO_2, NO_2 and NO [2].

However, the use of charcoal has faced some serious drawbacks. Due to the low price for charcoal and the relatively high costs for forestation, charcoal from planted forests may have an incompatible cost. In addition, the low wood tar aggregated value has discouraged its recovery, so that large amounts of volatiles have been released into the atmosphere. The way envisaged to overcome these problems is to develop nobler applications for wood tar, in order to increase its aggregated value and develop it as a revenue source for the charcoal manufacturing industry. In this way, it is possible to stimulate tar recovery at industry chimneys and balance forestation expenses and charcoal price.

Therefore, a new research line called "Vegetal Carbochemistry" was initiated in Brazil during the early 1990s. In this respect, *Eucalyptus* tar has been distilled aiming to separate fractions used as flavors, fragrances and source of fine chemical products [3,4]. A heavier fraction, *Eucalyptus* tar pitch, is generated as a tar distillation residue (about 50% mass). Taking into account the high Brazilian potential for producing this kind of pitch and its lack of applications, our research group is developing works aiming to make possible the use of biopitches as precursors of advanced carbon materials such as isotropic carbon fibers, bioelectrodes and activated carbons.

Previous studies demonstrated that *Eucalyptus* tar pitches have a macromolecular structure constituted mainly of phenolic, guaiacylic, and siringylic units resulting from lignin degradation during wood pyrolysis. Remarkable features are their low aromaticities (60–70%) and high O/C ratios (0.20–0.27%), which lead them a high reactivity. In addition, they present large molar mass distribution, purely viscous and Newtonian behaviors, low ash contents (about 1%), and isotropic character [5–7].

In this work, structural changes occurring during carbonization of *Eucalyptus* tar pitch up to 2300 °C are investigated step-by-step. 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. The results presented are based mainly on X-rays diffraction and infrared analyses, besides weight loss, helium density, BET surface area, and BJH pore volume measurements.

2. Experimental section

2.1. Materials

A precursor *Eucalyptus* tar pitch was produced as follows. Wood chips of planted *Eucalyptus* forests (Minas Gerais, Brazil) were submitted to slow pyrolysis in industrial masonry ovens with a maximum pyrolysis temperature of about 500 °C (12–14 °C/h). The smokes were washed and condensed to produce *Eucalyptus* tar. This tar was vacuum distillated in a 3000-L boiler coupled to a fractionation column of four drilled plates. The cut temperature was 180 °C at 30–38 mmHg. The distillation time was 8 h and the pitch yield was about 50% (w/w). This precursor pitch was pretreated for different periods of time and at