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Low temperature conversion of rice husks, eucalyptus sawdust and peach stones for the production of carbon-like adsorbent

Ayrton F. Martins *, André de L. Cardoso, João A. Stahl, Juraci Diniz

Departamento de Química da Universidade, Federal de Santa Maria, Campus Camobi, 97105-900, Santa Maria, RS, Brazil

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Abstract

In this study, the feasibility of preparing effective adsorbents from unmitigated agroforestry wastes was investigated. Three different kinds of carbon-like materials were produced by low temperature pyrolysis (LTC, <500 °C) of the raw materials rice husks, eucalyptus sawdust and peach stones. The carbon-like materials were characterized by instrumental methods (SEM, X-RDS, BET, MAS-RMN, FTIR), physico-chemical adsorption (iodine-, methylene blue- and phenazone-number; acetic acid adsorption isotherm; textile dyes- and carbohydrate adsorption), and heat value determination. The produced materials, which showed appreciable adsorption capacity, can be considered as precursors for the production of active coal or even be used directly as well.

Keywords: Carbon precursor; Pyrolysis; Adsorption

1. Introduction

Carbon-like adsorbent materials are largely employed in purification processes of water, beverage, industrial products, effluents and many others, such as for support of metallic base catalysts (Tam and Antal, 1999; Malik, 2004; Gomes et al., 2004). The production of carbon-like residues with adsorbent properties by means of thermal conversion can be highly advantageous, especially when the employed raw material is residual and the deposition becomes an environmental problem.

In Brazil, one of the largest agricultural producers (Rosillo-Calle et al., 2005) and a land with a large reforested area, the reuse of residual biomass is becoming an issue of ever growing importance, not only for economical reasons but also for environmental ones. At present, more than 2.2 Mt y^{-1} rice husks (www.valoronline.com.br/setoriais/pdfs/alimentos_02_free.pdf (10/13/2003)), 0.62 Mt y^{-1} eucalyptus sawdust (www.radiobras.gov.br/ct/1997/materia_090597_12.htm (05/04/2004)) and 0.03 Mt y^{-1} peach stones (www.IBGE.gov.br/home/estatistica/economia/pam/tabela3pam_2001.sht (02/04/2004)) are produced in the entire country. Only the Rio Grande do Sul state generated 1.1 Mt y^{-1} rice husks (www.irga.rs.gov.br/arquivos/ranking.pdf (01/02/2005)), 0.16 Mt y^{-1} eucalyptus sawdust (Pereira et al., 2000) and 0.01 Mt y^{-1} peach stones (www.emater.tche.br (01/01/2004)). Such large quantities of residues induce producers and processors to inadequate discharge or to open air incineration, causing environmental and public health problems.

The biomass conversion at the mentioned conditions is a thermochemical process characterized by emphasis on the disruption and recombination of chemical bonds in the carbon-like structure. Cellulose and lignin are the main generators of solid residue (Tam and Antal, 1999). In case of rice husks, the solid residue shows a high ash content as well (basically silica).

By means of the right choice of process parameters, such as temperature, heating rate and inert gas, the optimization of the carbon-like residue production can be performed. The process parameters serve, briefly, to prevent a high

* Corresponding author. Tel./fax: +55 55 3220 8664.
E-mail address: martins@quimica.ufsm.br (A.F. Martins).

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burning of the biomass and so to maintain its porous structure. This investigation sought to maximize the bio oil and carbon-like residue production.

Carbon-like residues are viewed today with great interest because of their varied applicability in several industrial branches, easily obtainable and appreciable economical worth. Their use as purifiers does not damage and does not contribute to the global warming process.

The action of selective collection of gases, liquids, or impurities by adsorbents can occur on the surface or into the pores of the adsorbent; for this reason, the surface area of the adsorbent is the most important factor for the determination of its quality. Adsorbent materials have micro, meso and macropores (<20; 20 to 50; >50 nm) that determine the surface area and give them the capability of clarification, deodorization and purification of liquid and gaseous samples.

The adsorption properties of the carbon-like residue from the thermal conversion of biomass, largely available at low cost, are even more favored by the positive energy balance of the pyrolysis process: the initial steps of the batch pyrolysis are endothermic, becoming exothermic in the sequence. Besides this, the pyrolysis gas of median heat value generated in the process, as well as the exceeding proper raw material, can be utilized for heating the process itself.

In this article, solid materials resulting from a low temperature pyrolysis process from agroforestry residues – rice husks, eucalyptus sawdust and peach stones – were characterized and investigated relatively to the adsorption capacity.

2. Experimental

The thermal conversion at low temperature was conducted in a fixed bed reactor [Tubular oven Maitec FT-1200/BI (www.maitec.com.br (01/01/2005))], under a minimal flow of inert gas (nitrogen) using agroforestry residues rice husks (*Oryza sativa*, local producer), sawdust (*Eucalyptus grandis*, local lumber), and peach stones (*Prunnus persica*, regional compote industry), following a temperature program developed to maximize the bio oil and solid residue production.

The biomass samples were ground in a Marconi TE 048 mill (Piracicaba, SP, Brazil, www.tecnallab.com.br (01/01/2005)), sieved and dried (105 °C, 60 min), and weighed. The particle fraction of 0.24 mm (0.18–0.30 mm) was used in this study.

Thirty-gram (30.0 g) rice husks and peach stones and ten-gram (10.0 g) eucalyptus sawdust samples were prepared, as described before, disposed in a glass boat ($d = 15$ mm; $l = 250$ mm), and inserted into a home-made boronsilicate glass tube reactor ($d = 30$ mm; $l = 500$ mm). This assembly was then positioned into the tubular electrical oven provided with a digital system for the temperature program. A cooling system was adapted at the end of the reactor for quenching and collection of the products. A scheme of the utilized system for thermal conversion can be seen on Fig. 1.

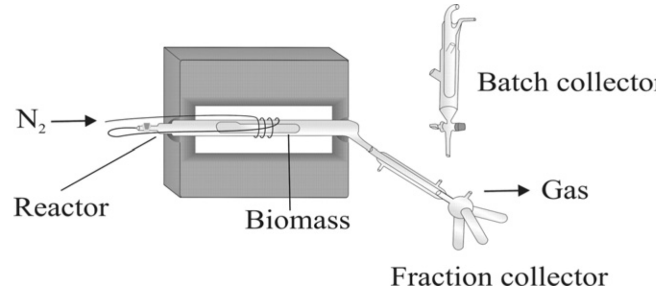

Fig. 1. Biomass thermal conversion system at low temperature.

2.1. Conversion process

The biomass was heated in an inert atmosphere (N_2, 0.5 L min^{-1}) for 90 min starting from room temperature until reaching almost 500 °C, using five temperature intervals – 25–100; 100–200; 200–300; 300–400 and 400–500 °C – at the heating rate of 15 °C min^{-1} and standby times of 10 min at each interval maximal temperature (Table 1).

The surface area of the carbon-like materials was determined by the BET method of N_2 adsorption using volumetric apparatus and Turbomolecular Edward vacuum pump (Milwaukee, OR, USA, www.edwardsmfg.com (01/01/2005)).

The iodine-, methylene blue-, and phenazone numbers and the acetic acid and carbohydrate adsorption capacity of the carbon-like residues were determined according to the literature (AWWW B604-74, 1974; Barton, 1987; ANVISA, 1997; Silva et al., 2003; Aygün et al., 2003). The adsorption of dyes (Malik, 2003) was studied with the aid of Acid Red 1 (C.I. 18050) and Erionyl yellow 2G (C.I. 18950). For this, a Sigma 3K30 centrifuge (Osterod am Harz, Germany, www.sigma-zentrifugen.de (01/01/2005)) and a Shimadzu MultiSpec-1501 spectrophotometer (São Paulo, SP, Brazil, www.shimadzu.com.br (01/01/2005)) were employed.

The scanning electron microscopy of the carbon-like materials was done with a Thermo Noran Jeol JSM-6360 Microscope (Peabody, MA, USA, www.jeolusa.com (01/01/2005)). For the high heating value of the materials a VEB Vereinigte Babelsberger calorimeter (Potsdam-Babelsberg, Germany) was used. A Varian INOVA 400 Spectrometer (Palo Alto, CA, USA, www.varianinc.com (01/01/2005)) was used for the determination of the magic angle solid nuclear magnetic resonance (MAS-NMR) of the carbon-like residues. The infra-red spectra were obtained with a

Table 1
Mean temperature ranges and obtained fractions by the thermal conversion process of the different biomasses

Fractions →	Gaseous	Aqueous	Oily	Solid
Temperature range (°C)	25–500	100–300	300–500	25–500
Heating rate (°C min^{-1})	15	15	15	15