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Materials Today: Proceedings 4 (2017) 11617–11623

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ANM2016
Structural behavior of coal obtained from Kraft lignin at different carbonizing rates

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Abstract

Biomass is a renewable resource which importance has attracted much attention face to the concerns involving the environmental and the oil crisis. The aim of this work is to convert lignin into coal by carbonization heat treatment of this biomass up to 1000 ^{o}C, under inert atmosphere, at different heating rates. The resulted coal samples were characterized by X-Ray diffraction, Raman spectroscopy and surface area analyzes. Raman spectroscopy and X-ray diffraction results show that longer heat treatment resulted in coals more ordered structurally. On the order hand, longer heat treatments favored the coal production with smaller surface area.

Selection and Peer-review under responsibility of 7th International Conference on Advanced Nanomaterials.

Keywords: lignin; coal; conversion

1. Introduction

The current concern about the environment has been responsible for the growing interest in the use of biomass and optimization of the processes for obtaining and using it [1-5]. Lignin is a macromolecule present in cell walls of plant. In companies that produce pulp and paper, the lignin is available in large quantities, as residue of pulp production. Until now, the residue of lignin is used, almost exclusively, to produce energy by the direct burning of this biomass. However, recent studies show its potential as precursor to produce activated coal. Lignin is rich in carbon and its molecular structure is similar to the bituminous coal [6-16].

Carbon materials can be natural or synthetic. They are formed by layers constituted of carbon atoms with sp^2 hybridization, arranged in hexagons. These materials have different degrees of organization and their structures are, in smaller or larger in proportion, similar to the graphite [17-19]. Coals belong to this class of materials and have important roles in the generation of energy and adsorption of contaminants (activated coal). Generally, the coal has origin from natural residues, like biomass. The coal structure can be described as a set of functional groups,

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structured by aromatic rings connected [11, 20-23]. Thus, the coal surface chemistry has been extensively studied, since it has promising applications, i.e. obtaining activated charcoal [24-25].

Carbonization process consists in submit the material under a thermal treatment, where the temperature can reach approximately 1000 ^{o}C and the process is realized under inert atmosphere. During the process, crosslinks between carbon chains are broken and light gases, volatile molecules and small organic molecules are liberated. As a result, a porous structure is formed, containing a large quantity of carbon and porous that can be filled or partially blocked with tar resulted from the carbonization or disorderly carbon chains [3,4, 26-29]. Depending on the used parameters in this process the crystalline ordering of the resulted carbon material is affected.

The crystalline structure of coal is characterized by the presence of a few numbers of graphitic regions, surrounded by large amorphous regions. This kind of organization is named as turbostratic structure. The turbostratic structure is an intermediary condition between graphitic and amorphous phases. In this context, the heating rate of the carbonization process can influence the structure ordering of coals. Aiming to contribute to this area, the purpose of this study is assessing the influence of carbonization time of Kraft lignin on structural ordering and surface area of coal produced.

2. Experimental Procedure

2.1 Sample preparation

The samples of coal studied in this work were obtained from Kraft lignin. This sample was kindly provided by FIBRIA, a Brazilian company world leader in cellulose processing from *Eucalyptus*. This company produces approximately 5.3 million ton of cellulose per year. The lignin was carbonized up to 1000 ^{o}C, under inert atmosphere of N_2. Heating treatment times (HTT) varied in 90, 180 and 420 min, which correspond to heating rates of approximately of 11, 5.6 and 2.4 ^{o}C.min^{-1}.

2.2 Characterization

X-ray diffraction (XRD) technique was used to characterize the crystallographic structure of produced coals. The experiments were performed in a Rigaku Ultima IV automatic diffractometer. This equipment has a source of X-ray radiation of Cu Kα and a filter Kβ radiation. It uses a tension of 50 kV and electric current of 40 mA. The measurements were performed in flat-plate geometry and the region of 2Θ between 10 ^{o} e 50^{o}. The relation between X-ray radiation wavelength (λ), angles of diffraction (Θ) and the interplanar distance (d_{hkl}) was obtained based on Bragg equation. The average height of coal crystallites (Lc) was calculated from Scherrer equation [18,21].

The structures of coals were also evaluated by Raman spectroscopy analyzes, using a Horiba equipment, Olympus model. This equipment has a laser with wavelength of 514 nm and spectrum range between 800 and 1900 cm^{-1}. The spectral parameters were obtained according to the method proposed by Sadesky et al., 2015. The curves were adjusted using the software OriginLab. This quantification uses two different factors: the intensity of the peak (I_D, intensity of D-peak (disorder); I_G, intensity of G-peak (order)) and the areas under the peaks (A_D, area under D-peak; A_G, area under G-peak; A_{D2}, area under D2-peak) [30].

Coal surface areas were determined according to Brunauer, Emmett and Teller theory (BET). The porous distribution was calculated according to the theory of Barret, Joyner and Halenda (BJH) [31]. For this, it was used an equipment from Quantachrome, model NovaWin. The samples were heated until 300 ^{o}C and held at this temperature for 4 h. This process guarantees the humidity removing. A volume of 17.84 mL of sample was used. The specific mass was determined using a picnometer of helium (Quantachrome, model Ultrapyc 1220e). The experiments were performed under 20 psi-pressure.

3. Results and discussion

Figure 1 shows the diffraction patterns of the three coal samples produced in this study. The three patterns exhibit two peaks, large and diffuse, centered around 23^{o} and 43^{o}. These peaks correspond to planes (002) and (100), respectively. These two planes characterize the carbon materials and refer to the contribution of graphitic microcrystallites which are present in the turbostratic structure [21, 32].