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Wettability of bio-coke by coal tar pitch for its use in carbon anodes

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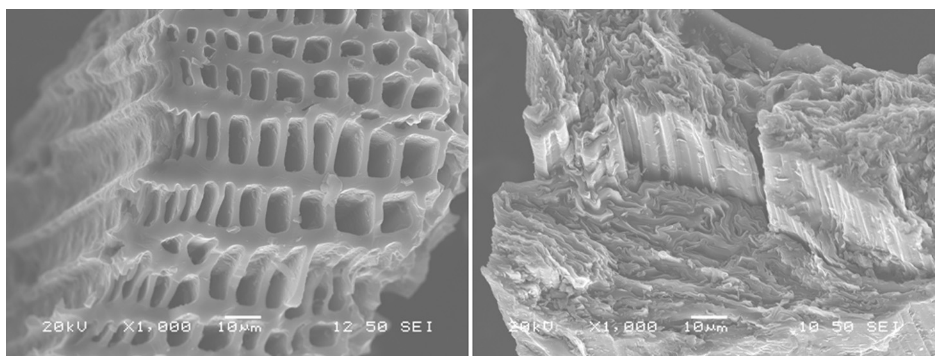
HIGHLIGHTS

- Comparative study on the microstructures and the chemical compositions of the bio-cokes.
- Quantitative study on the spreading and penetration ability (wetting capacity) of the pitch on all bio-coke beds.
- The relationship between the characteristics of the bio-cokes and its wettability by coal tar pitch was established.

GRAPHICAL ABSTRACT



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ABSTRACT

Information on the wettability of a bio-coke substrate is of great value in assessing its possible use as a potential raw material for carbon anode production. In this study, the interaction mechanisms of a coal tar pitch with six bio-coke substrates were studied at a temperature of 170 °C, a typical industrial value for coke-pitch mixing, using a sessile-drop test. Three bio-cokes were produced from different bio-materials by pyrolyzing them to 426 °C, and the other three by further calcining them to 1200 °C. Different techniques were used to analyze the structural and chemical characteristics of the six bio-cokes. The results show that the heat treatment temperature has a significant influence on the chemical properties of bio-cokes and the wettability of pitch/bio-coke systems. The possibility of partial replacement of petroleum coke by bio-coke is discussed from the point view of the suitability of its structure and its wettability.

1. Introduction

Carbon anodes are consumed during the electrolytic production of primary aluminum. Dry aggregate which is composed of calcined petroleum coke and recycled materials (rejected anodes and butts) is mixed with coal tar pitch used as the binder. Then, this paste is compacted and baked to produce anodes [1,2]. Calcined petroleum coke is one of the main raw materials used in producing carbon anodes, and its properties are important because they directly affect the quality of anodes, the cost, and the environmental emissions. New sources of carbon materials with desired properties are being sought to reduce emissions. Bio-cokes, carbon materials derived from biomass, are low in cost, considered renewable, abundant in supply, and readily available around the globe. The

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partial replacement of petroleum coke by bio-coke, produced from a lignocellulosic material and a renewable natural resource, would potentially reduce the cost and the emissions during the carbon anode fabrication for aluminum production [3].

Considering the relevant properties and the requirements for various applications, different biomass materials have been studied to produce bio-carbon materials [4,5]. Researchers have used biomass materials to generate activated bio-carbon materials and have studied their utility in many major technologies such as environmental protection (sorbent of dyes and heavy metals [6,7]) and energy storage (electrode material for super capacitors [8]). However, due to their high specific surface area and consequently high absorption capacity [8], bio-activated carbon materials are mostly used as sorbents in environmental protection. A few studies are reported in the literature on some of the properties of electrode grade carbons prepared with bio-cokes made from different biomass materials [1,3,9–16]. Bio-coke and bio-pitch, produced by pyrolyzing Eucalyptus wood, were used as renewable sources to make small experimental electrodes [1]. It was reported that the electrodes produced by bio-coke and bio-pitch had comparable electrical and mechanical properties to those made with conventional carbonaceous materials [1]. Emmerich et al. [15] have employed babassu coconuts to generate carbon material, and they found that it had similar Young's modulus and rupture strength to those observed in electrodes produced using conventional cokes. As the carbon anodes in aluminum industry are consumed during the electrolytic process, anodes made with petroleum coke contribute to carbon and sulfur oxide emissions. However, the bio-coke which is a sulfur-free renewable raw material does not contribute to environmental emissions [9]. Thus, the current emissions could be reduced through the partial replacement of petroleum coke with bio-coke [3]. Nevertheless, the published literature on the use of bio-coke in anodes used for aluminum production is rare [12,17]. Monsen et al. [12] has studied the possibility of replacing petroleum coke with bio-cokes produced from maple and spruce to make pilot scale anodes and then to produce aluminum. They reported that the low density of bio-coke affected the anode properties adversely, and it did not decrease significantly the CO_2 emissions during anode consumption. In a previous study by the authors of the current article, the structural and morphological characterization of two bio-cokes was carried out in order to compare them with those of two calcined petroleum cokes. It was found that the bio-coke seems to have a suitable structure to be used as raw material for anodes utilized in aluminum industry [17].

Wettability of coke by pitch is influenced by the surface properties; and the degree of wetting is of considerable practical and economic significance for understanding the interactions between the dry aggregate and the binder that occur during mixing. Mixing is one of the important steps which determine the final properties of a carbon anode [18]. Information on wettability also gives an idea of the different pitch and coke characteristics required in order to improve the quality of final material. This is one of the important criteria for the selection of a particular coke or pitch for a given application. A number of investigations were carried out on the wettability of petroleum coke by pitch during mixing at different temperatures. The results showed that the wettability depends on the physicochemical properties of pitch, the nature and surface properties of coke [18–28]. The effects of the properties and the process temperature of petroleum coke on its interaction with pitch at the mixing stage were studied by many researchers [18,26,28]. Wettability is normally assessed based on the pitch behavior during the initial stages of a penetration test [22]. The contact angle between a pitch droplet and a bed of fine coke particles or the change in the height of the pitch droplet with time is recorded as the temperature is increased during the test [18,21,24,27]. The temperature at which the contact angle becomes 90° is determined as the wetting temperature of the pitch. However, this kind of test does not provide enough information on the true wettability of a coke by a pitch. It was reported from the isothermal penetration experiments that the contact angle continuously changes from an angle greater than 90° to an angle less than 90°, even to 0°, at constant temperature [22,28]. The quantitative characterization of the true spreading and penetration capacity of a pitch is important. Studies which quantify the dynamic wetting process for a pitch on a coke bed are rare. Sarkar et al. [28] studied the dynamic wettability and interaction of different cokes by pitch. However, there is no quantitative study on the spreading and penetration properties of pitch on either petroleum coke or bio-coke. The dynamic wetting behavior of bio-coke by pitch is not fully understood.

It was reported that bio-coke usually exhibits low density and high porosity compared to petroleum coke [12], which might contribute to the wettability if the open pores of bio-coke can be successfully filled with pitch during mixing. However, high porosity might also decrease the density of a coke and increase the pitch requirement, which may, in turn, decrease the anode density and increase the cost for anode production. As explained previously, various studies were carried out on the utility of bio-carbon as sorbent and the wettability of petroleum coke by pitch. To the authors' knowledge, the published literature about the wettability of bio-coke by pitch at the mixing stage is still lacking. Moreover, a detailed and comprehensive analysis of the wettability of bio-coke by pitch and the chemical analysis of bio-coke are not available in the literature. In addition, the difference between the wettability of bio-coke or petroleum coke by pitch is not completely clear. The current study aims to fill this void and to evaluate quantitatively the dynamic wettability of different bio-cokes prepared using different raw materials and temperatures by coal tar pitch.

In this paper, pitch wettability on a bio-coke substrate at 170 °C (a typical coke/pitch mixing temperature used in the aluminum industry) is studied by using a sessile-drop experimental system to understand their interactions. A typical coal tar pitch and six bio-cokes were used. Three bio-cokes were produced via heat treatment to 426 °C of biomass from different sources and the other three by further calcining them to 1200 °C.

During the wetting test, due to the non-homogeneity of coke samples, it is often observed that the initial contact angle may vary. This, in turn, may affect the value of the contact angle at a certain time. To reduce the influence of variation in the initial contact angles, a dynamic wetting model was used to describe and quantify the spreading and penetration ability (wetting capacity) of the pitch on all bio-coke beds.

The model can be expressed as [29,30]:

$$\theta = \frac{\theta_i \theta_e}{\theta_i + (\theta_e - \theta_i)\exp(K(\frac{\theta_e}{\theta_e - \theta_i})t)} \quad (1)$$

where θ is the contact angle measured at time t, θ_i is the initial contact angle, θ_e is the apparent equilibrium contact angle and K is the penetration and spreading rate constant. Spreading and penetration for a given pitch-coke system can be quantified if the K -value is known. The K value represents how fast a liquid can spread and penetrate into a solid. A higher K -value indicates that the pitch penetrates and spreads faster (increased wetting).

The effects of the structure and the chemical composition of bio-cokes on the wettability were also studied. Optical microscopy (OPM), scanning electron spectroscopy (SEM), Fourier transforms infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were used to establish the relationship between the characteristics of the bio-cokes and its wettability by coal tar pitch.