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Interaction of bio-coke with different coal tar pitches

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ABSTRACT

The interactions of pyrolyzed and calcined bio-cokes with three coal tar pitches of different properties were studied using a sessile drop test at 170 °C. A model was employed to characterize and quantify the spreading and penetration of pitch into bio-coke bed. The pyrolyzed bio-cokes were produced from softwood materials by heat treatment at 426 °C. The calcined bio-cokes were produced by calcining the pyrolyzed bio-coke at 1200 °C. Optical microscope, SEM/EDS, XRD, and FTIR techniques were used to analyze the coke–pitch interface and study their interaction mechanisms. The results show that the wettability of bio-coke is related to both pitch and coke properties. It is found that the presence of small amount of uniformly distributed small size quinoline insolubles (QI) in pitch seems to help pitch spread and penetrate into the bio-coke bed. Besides, calcination changes the chemical structure of bio-coke, enriches its carbon (C%) content, increases its crystalline length (Lc), and lowers its wettability by pitch.

1. Introduction

Bio-coke is a carbon product derived from biomass materials, which have renewable, low cost, sulfur free, and abundant supply available throughout the globe [1]. Different biomass materials are used to generate bio-carbon materials for different applications according to specific demands [2,3]. The utility of bio-carbon materials in many major technologies has been studied [4,5]. Activated bio-carbon materials are mostly used as sorbents in environmental protection due to their high specific surface area, consequently, their high absorption capacity [6]. Bio-cokes made from different biomass materials are used in preparation of electrodes for energy storage [1,7–15]. It was reported that the electrodes produced with bio-coke and bio-pitch by pyrolysis of eucalyptus wood had comparable electrical and mechanical properties to those made with conventional carbonaceous materials [7]. The electrodes made from babassu coconut based bio-carbon material had similar Young's modulus and rupture strength compared to those of the electrodes produced using conventional cokes [14].

The carbon anodes consumed during the alumina electrolysis can be considered as composites, which consist of filler petroleum coke and recycled material (recycled anodes and butts) as skeleton and the binder coal tar pitch as binder [7,16,17]. The demand for petroleum coke used in aluminum industry as the main raw material is substantial; however, it is becoming harder to find good quality anode grade coke. During anode production and electrolysis, greenhouse gas (GHG) emissions take place. Aluminum industry is continuously working to decrease these emissions. It might be worthwhile to consider the utilization of bio-coke as a new, sulfur-free renewable source of coke which can contribute to further reduction of GHG emissions [1]. Thus, there might be a potential for partial replacement of petroleum coke with bio-coke, produced by biomass materials and a renewable natural resources [8]. There are very a few publications regarding the utility of bio-coke as anode raw material for aluminum industry [11,18]. It was reported that the low density of bio-cokes produced from maple and spruce affected the anode properties adversely and it did not decrease significantly the CO_2 emissions during electrolysis [11]. Huang et al. carried out structural and morphological characterization of two bio-cokes and showed that the bio-coke has a suitable structure to be used as raw material for anodes [18].

Coke/pitch interactions taking place during anode fabrication is one of important factors which influence the final anode quality. Therefore, producing a good quality carbon anodes requires a good understanding of these interactions [19]. The pitch is expected to wet the surface of coke and to penetrate through its pores while raw materials are mixed during anode fabrication. The real mixing of coke and pitch during anode manufacturing is carried out in kneader or mixer under high shear conditions. The study of penetration of pitch into coke stops at the image characterization of anode paste obtained under the real shear conditions to determine the thickness of pitch-fine coke film over the coarse coke particles [20]. To the authors' knowledge, the studies on wetting of pitch

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into coke under shear conditions are not available in the literature due to the difficulty of monitoring and characterizing of wetting under shear conditions. Strong interactions contribute to the quality of binding. Thus, both wetting and penetration (flow) should be taken into account when coke/pitch interactions are studied [21]. Penetration is a rheological or dissipative property of pitch [19]. Studies on wettability of coke by pitch are of considerable importance [22]. The wettability test can be performed under non-isothermal or isothermal conditions. A number of investigations were carried out on the wettability of petroleum coke by pitch at different temperatures [17,19,21–29]. Several methods were used for estimating the ability of a molten pitch to penetrate into a coke bed [21,22,26,28]. The temperature at which the contact angle between a pitch droplet and a bed of fine coke particles becomes 90° is defined as the wetting temperature of the pitch obtained from non-isothermal tests. Experiments carried out under isothermal conditions showed that the contact angle continuously decreases [24,29] with time. The dynamic wetting of bio-coke by pitch is not fully understood. Moreover, there is no quantitative study on the spreading and penetration properties of pitch on petroleum coke. The information on interactions of bio-coke and different pitches is very valuable to assess the possibility of using bio-coke as a potential anode raw material and to establish if a given pitch can be used to produce anodes using a specific bio-coke for the aluminum industry. However, not much information is available on the wettability of bio-cokes by different coal tar pitches. The reason is that bio-cokes usually have a low density and high porosity compared to petroleum coke, which might increase the pitch requirement, and consequently increase the cost of anode production, and decrease the anode quality [11]. Bio-coke is not ready to be used yet in anodes for aluminum smelting. It is possible that a more careful selection of feedstock and the development of new processes provide bio-cokes with suitable characteristics to be used in anode production. To the authors' knowledge, the published literature about the interaction between bio-coke and pitch during mixing is still lacking. Moreover, detailed and comprehensive studies on wetting and penetration of pitch into bio-coke and chemical analysis of bio-coke/pitch interface are not available in the literature.

In this work, the interaction mechanism of three different types of coal tar pitches with bio-cokes before and after calcination are studied by means of a sessile drop test, optical microscopy (OPM) and scanning electron spectroscopy with X-ray microanalysis (SEM/EDS), Fourier transform infrared spectroscopy (FTIR) and X-ray Diffraction (XRD). The wetting and penetration behavior was characterized by initial contact angle, total wetting time, dynamic contact angle, and penetration and spreading rate constant (K-value) obtained from a dynamic wetting model for porous materials [30,31]. The effect of the structure and chemical properties of the pitches and bio-cokes on their interaction was also studied. The relationships of pitch penetration and spreading capacity with the characteristics of pitches and bio-cokes are discussed with the aim of identifying suitable bio-coke/pitch pairs.

2. Experimental

2.1. Materials

Three commercially available coal tar pitches, presently used in aluminum industry, with different properties have been selected as the binder. The main physical and chemical characteristics of the pitches are given in Table 1. The values were provided by the supplier. Differences in their quinoline insoluble (QI) contents are found to be significant. The pitch viscosities are also different. However, β-resins and toluene insoluble (TI) contents of all three pitches are similar. The differences most probably affect the wettability of coke by these pitches. Besides, inorganic impurities, such as Na and Ca, also might influence the pitch/bio-coke interactions [23].

Table 1
Properties of pitches used in the study.

Properties	Coal tar pitch		
	Pitch-1	Pitch-2	Pitch-3
Quinolineinsolubles (%m/m)	6.9	7.5	10.8
Toluene insolubles (%m/m)	29.1	29.6	33.0
β Resin (%m/m)	22.2	22.1	22.2
Density at 20 °C (g/ml)	1.320	1.312	1.326
Ash at 900 °C (%m/m)	0.12	0.17	0.16
Coking value (Alcan/ISO) (%m/m)	59.1	59.9	61.2
Softening point (°C)	119.6	121.5	118.0
Dynamic viscosity 170 °C (MPa s)	1390	2070	Not available
Ca (ppm m/m)	34	27	96
Fe (ppm m/m)	192	101	153
Na (ppm m/m)	111	130	100
Pb (ppm m/m)	144	176	147
S (%m/m)	0.47	0.17	0.58
Si (ppm m/m)	132	94	250
Zn (ppm m/m)	241	202	197

The biomass materials used in this study and the conditions used during the bio-coke manufacturing process (pyrolysis and calcinations) are summarized in Table 3. One pyrolyzed bio-coke samples received from Boisaco Inc. was studied (No. 1as shown in Table 3). The pyrolyzed (uncalcined) bio-coke was obtained from softwood trees at the maximum temperature of 426 °C; other information on heat treatment is not available. The calcined bio-coke samples (No. 2 in Table 3) were obtained by calcining the pyrolyzed bio-coke at University of Quebec at Chicoutimi (UQAC) laboratory using an induction furnace. Details of calcination are presented in Section 2.2. Specimens for the experimental study were arbitrarily selected for a complete statistical randomization. They were stored in a room at 20 °C and 40% relative humidity. The characterization tests are described below.

2.2. Calcination of bio-coke

The bio-coke samples received from Boisaco Inc. were heat treated (calcined) in a Thermogravimetric Analyzer (TGA) using induction heating at UQAC, Quebec, Canada. Treatment temperatures and heating rates, which are typically used for petroleum coke calcination, were used during the bio-coke calcination tests. The uncalcined bio-coke samples were put in a graphite crucible which was suspended from a balance to follow the weight loss of the sample during calcination. The nitrogen, used as the protection gas, enters the induction furnace from the bottom. The maximum calcination temperature of 1200 °C, the heating rate of 40 °C/min and 15 min of holding time at maximum temperature were used.

2.3. Sample characterization

2.3.1. Wetting tests

The contact angles between pitch and bio-coke were determined using a sessile-drop experimental system (see Fig. 1a)

Table 2
Types of QI present in coal tar pitch.

	Source	Size	Shape
Primary QI	Coke oven	~1 μm	Sphere
Carry over QI	Coke oven	5–500 μm	Sharp contours
Mesophase	Thermal treatment	4 + μm	Sphere