Production and characterization of microporous activated carbons and metallurgical bio-coke from waste shell biomass

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ABSTRACT

To produce activated carbon and bio-coke, palm kernel shells (PKS), walnut shells (WNS) and cashew nut shells (CNS) were carbonized and (or) activated. The activation was conducted using CO_2 in a fixed bed reactor. In the activation of PKS, the influence of CO_2 flow rate on the surface area development was also examined. Meanwhile, to evaluate the suitability of chars obtained from CNS as metallurgical bio-coke, carbonization was carried out in N_2 at temperatures of 700–800 °C. The maximum surface areas of the resultant activated carbons derived from each biomass were about 700–810 m^2/g, and all the activated carbons had a microporous nature. At a CO_2 flow rate of 1 NL/min, the activated carbon obtained from PKS showed the highest surface area of 912 m^2/g. The char produced from CNS, with its low ash and volatile matter contents and its sufficient compressive strength, demonstrated promising potential as metallurgical bio-coke.

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1. Introduction

Activated carbon is used in many industrial applications as pollutant-gas adsorbent, water purification media, and catalyst support because of its pores with high surface area and high mechanical strength [1]. Due to its multipurpose applications, the demand of activated carbons is growing in many countries [2]. The precursors of commercial activated carbons are lignite, coal, peat, and coconut shells. The conventional manufacturing process of activated carbon consists of a two-step process, carbonization and activation, which takes place separately in two reactors. In the carbonization step, precursors are converted into carbon-rich material (char) in the absence of oxygen at a moderate temperature. In the activation step, the resultant chars from the carbonization are mainly activated by oxidizing gases such as carbon dioxide and steam at a higher temperature (physical activation) to produce activated carbon with a high surface area.

Recently, many researchers have tried extensively to produce activated carbons from various waste biomasses [3–7]. It was revealed in a study on physical activation that the activation process using carbon dioxide promoted the development of microporosity, whereas the use of steam enhanced the mesoporosity [8]. In addition to the physical activation, the chemical method, which

applies chemicals such as zinc chloride, potassium hydroxide and phosphoric acid, has attracted much attention, because it produces activated carbon with higher surface area at a lower activation temperature, compared to physical activation. Haimour et al. [9] carried out chemical activation with phosphoric acid and reported that the physicochemical properties of the precursors and the activation conditions (final activation temperature and final activation time) strongly influenced the pore size distribution and adsorption properties of activated carbon. The precursors with high lignin content, for example, resulted in the development of a macroporous structure, whereas those with high cellulose content yielded a more microporous structure [10]. Fan et al. [11] conducted steam activation of agricultural residues (oat hulls and corn stover) and found that the maximum surface area of oat hulls was 625 m^2/g with a final activation temperature of 800 °C and a final activation time of 120 min. Yun et al. [12] carried out carbon dioxide activation of rice straw and reported that the surface area of the resultant activated carbon was optimized (790 m^2/g) with a final activation temperature of 800 °C and a final activation time of 180 min. They also reported that the pore structure and adsorption properties of activated carbons were strongly affected by the nature of the precursors and the heat treatment profile of the process. Meanwhile, attempts have been made to produce chars by carbonization of biomass, which can be used as a reducing agent in metallurgical industries instead of coke. In that sense, the char is referred to as bio-coke. The use of coke in metallurgical industries causes high CO_2 emissions, which would be decreased by the use of

Table 1
Main characteristics of the samples.

Proximate analysis[a] (wt%)	PKS	WNS	CNS	Ultimate analysis[c] (wt%)	PKS	WNS	CNS
Moisture	6.6 ± 0.25	11.2 ± 0.24	1.4 ± 0.07	C	52.1 ± 0.8	45.9 ± 0.19	51.3 ± 3.57
Volatile matter	68.2 ± 1.90	79.1 ± 0.70	85.2 ± 1.06	H	5.9 ± 0.10	5.7 ± 0.05	6.2 ± 0.68
Fixed carbon[b]	13.5 ± 1.00	8.7 ± 0.04	9 ± 0.11	N	1.0 ± 0.07	0.4 ± 0.03	1.0 ± 0.08
Ash	11.7 ± 3.15	1 ± 0.86	4.4 ± 0.91	O[d]	41	48	41.5

[a] Wet basis.
[b] By difference.
[c] Ash free.
[d] By difference.

bio-coke obtained from biomass, because biomass is CO_2 neutral. As an example, blast furnaces in Brazil were operated using char obtained from Eucalyptus wood [13].

This study reports the effects of activation parameters (final activation temperature and final activation time) on the textural properties of activated carbons from three kinds of waste shells (palm kernel shells (PKS), walnut shells (WNS) and cashew nut shells (CNS)). PKS, a residue of oil palm processing, is produced in large quantity especially in Indonesia and Malaysia. Estimated volume of PKS from palm oil industry in the two countries is over 7 million tons per year [14]. The global production of walnut amounts to 1.5 million tones, and the USA and China are the two major producers. CNS, a product of cashew tree which is widely grown in tropical regions such as Vietnam and Nigeria, is also an important renewable energy source. In contrast to the conventional preparation of activated carbon, where carbonization and physical activation process take place separately using two reaction systems, this study conducted the carbonization of the biomass in N_2, followed by CO_2 activation in a fixed bed reactor. In addition, this study reports the influence of CO_2 flow rate on the development of surface areas of activated carbons from PKS. Finally, the suitability of chars obtained from the carbonization of CNS as metallurgical bio-coke was investigated.

2. Experimental

2.1. Precursors

The three kinds of waste shells (PKS, WNS and CNS) were used as precursors of activated carbon. WNS and CNS were purchased in a store, and PKS was imported from Malaysia. Prior to the carbonization/activation experiments, the samples were crushed and then sieved to reduce their particle size to within the range of 1–2 mm. The main characteristics of the samples are shown in Table 1.

Proximate analysis was done according to the American Society for Testing and Materials (ASTM D3172). The analytical results showed that all samples were mainly comprised of volatile matter. In particular, PKS had a high ash content of about 12 wt%, which was much higher than that of the other samples (about 1–4 wt%). These results were attributed to the prior food processing, such as washing, of WNS and CNS, whereas PKS was obtained as a raw material without any pretreatment. The elemental analysis revealed a high carbon content for all the samples, which could make these materials suitable as precursors for activated carbon. Nitrogen contents of the three biomass were very low (0.4–1 wt%), and sulphur could not be found in the analysis (detection limit (~0.1 wt%)).

2.2. Preparation of activated carbons and bio-coke

The carbonization/activation experiments were conducted in a fixed bed reactor made of 310 stainless steel with an inner diameter of 83 mm and a height of 410 mm. During the carbonization process, char and vapor generated in the reactor were collected by a cyclone and quenching system, respectively. The quenching system

was composed of a water-cooled (10 °C) condenser, impact separator and electrostatic precipitator. Finally, the non-condensable gas was burned using a Bunsen burner. A diagram of the carbonization/activation process is given in Fig. 1.

In each of experiment, 50 g of a precursor was put on the metal mesh distributor in the reactor. Before the experiment, the process was purged with N_2 gas for 30 min to render the atmosphere inert. During the carbonization stage, nitrogen gas was constantly introduced into the bottom of the reactor at a flow rate of 10 NL/min through the pre-heater, and then the temperature increased up to 500 °C at a heating rate of 10 °C/min and the final temperature was maintained for 20 min. Thereafter, the activation stage started with CO_2 gas up to the desired final temperatures in the same manner as the carbonization stage. The activation was conducted at final temperatures of 850, 900 and 950 °C and with a final activation time of 60, 120 and 180 min. After the recovery of activated carbon, the burn-off (%) was calculated according to Eq. (1).

Burn-off(%)

$$= \frac{\text{weight of reference char} - \text{weight after activation}}{\text{weight of reference char}} \times 100\% \quad (1)$$

In Eq. (1), the reference char was obtained only with carbonization carried out under the same conditions for the carbonization for the production of activated carbon.

The experiments to determine the influence of CO_2 flow rate on the surface area properties at the activation stage were conducted using PKS at CO_2 flow rates of 5, 1, 0.5 and 0.1 NL/min, and the results compared to those obtained with 10 NL/min. The experiments on bio-coke were carried out with CNS, carbonizing it at final temperatures of 700 and 800 °C at a heating rate of 10 °C/min and N_2 flow rate of 10 NL/min.

2.3. Characterizations

To investigate the effects of activation conditions (final activation temperatures and time), the reference chars and activated carbons were analyzed by nitrogen adsorption at 77 K (BEL-Belsorp-mini Π), which gave information on the surface area, pore volume and pore size distribution. In each analysis, the amount of sample used was about 0.1 g. Before the adsorption experiment, the sample was degassed at 300 °C for 6 h under vacuum for the removal of surface contaminants. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method within a relative pressure range of 0–0.5; the volumes of micro- and mesopores were determined by micropore analysis (MP-method) and the Barrett–Joyner–Halenda (BJH) model, respectively. Consequently, the total pore volume was calculated as the micropore volume plus the mesopore volume. The entire pore size distribution, including the micro- and mesopores, was determined using the MP-method and BJH-model. Field emission scanning electron microscope (FE-SEM, Hitachi S-4700) analysis was conducted to observe the surface morphology of the activated carbons. Elemental analysis of the reference chars and activated carbons were performed using an