Development of activated carbon products by the utilization of locally bioresource coconut shell

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1. Introduction

Activated carbon is an amorphously porous material, which exhibit a high adsorption capacity due to its large specific surface area and pore volume. These unique pore structures play a very important role in many different liquid- and gas-phase applications for removal of organic pollutants. Although most types of industrial activated carbons are produced from naturally occurring carbonaceous materials like coal by activation process, some agro-industrial wastes or by-products have been found recently to be suitable precursors for the preparation of activated carbons owing to their characteristics of high carbon and low ash contents.

In Southern Taiwan, coconut shell is the most primary agro-industrial waste or by-product. The yearly generation of the waste has exceeded ten thousands metric tons. The current treatment approaches for this biomass waste are the combustion-heat recovery and farmland dumping. However, these methods will generate serious environmental problems, such as air pollution and greenhouse gas (e.g. CO_2) emission. The objective of this research was to investigate the feasibility of reusing this local biomass coconut shell as a precursor for activated carbon, and producing high-performance cylindrical activated carbon product.

2.Materials and Experiments

2.1. Materials

The coconut shell samples studied in this work was obtained from the local markets in Kaohsiung and Pingtung districts (Taiwan). The hard and fibrous fractions were first extracted and then dried at about 100 °C for at least 24 h. Its characterization, including elemental analysis, heating value and thermogravimetric analysis (TGA), was carried out by Elementar Co. (Germany) Model vario EL III, Parr Co. (USA) Model CALORIMETER ASSY 6200 and Shimadzu Co. (Japan) Model TGA-51, respectively. The proximate analysis was based on the ASTM Standard method.

2.2. Activation experiments

Using a fixed-bed furnace, a series of activation experiments of preparing activated carbon products from the coconut shell were conducted under different activation temperatures of 750-1000°C at various holding times of 0-180 minutes. A heating rate of about 10°C/min was applied under dynamic atmosphere of flowing nitrogen (500 cm3/min, up to 500°C) and carbon dioxide (50-250 cm3/min, heated to prescribed activation temperatures). This process involves the carbonization of a carbonaceous precursor (i.e., coconut shell) followed by activation of the resulting char in the presence of carbon dioxide at 750-1000°C to further develop micropores and/or porosity by selective gasification, thus obtaining a well-developed carbon structure.

2.3. Analytical measurements

The pore characterization of the resulting activated carbons was carried out by measuring nitrogen (N2) adsorption-desorption isotherms at –196°C on an automatic apparatus (ASAP 2020; Micromeritics Co., USA) and displacing helium gas on a pycnometer (AccuPyc 1340; Micromeritics Co., USA). From the data of total pore volume and true density, the particle density and porosity of resulting activated carbons can be thus obtained. In order to observe the variations on the surface morphologies of coconut shell-derived CO_2-activated carbons with different activation conditions, these samples were examined using a scanning electron microscopy (S-3000N; Hitachi Co., Japan), which was operated at a 15 kV accelerating potential. Prior to the work, the surface of the sample was coated with a thin, conductive gold film. On the other hand, the iodine number values of the resulting activated carbons, which can be used to determine their approximate extents of specific surface area, were measured according to ASTM Standard Method D-4607 (Standard Test Method for Determination of Iodine Number of Activated Carbon).

3. Results and Discussion

The data in Table 1 shows the results of proximate analysis, elemental analysis and heating values of the dried coconut shell residues (hard and fibrous fractions) from Kaohsiung and Pingtung districts. It is obvious that the biomass comprises a large percentage of the organic constituents because the dried biomass is rich in carbon, hydrogen and oxygen contents. Regarding the hard fraction, its proximate analysis reveals the low ash content, thus making it a potential precursor of activated carbon.

Table 1. Properties of coconut shells obtained from markets in Kaohsiung and Pingtung

Property values [a]	Pingtung -hard fraction	Pingtung -fibrous fraction	Kaohsiung -hard fraction	Kaohsiung -fibrous fraction
Elemental analysis				
Carbon (wt%)	46.63	47.52	50.97	50.80
Hydrogen (wt%)	4.75	5.34	6.11	4.87
Nitrogen (wt%)	0.08	0.16	0.25	0.15
Sulfur (wt%)	0.00	0.00	0.00	0.00
Oxygen (wt%)	37.76	26.41	38.70	28.03
Ash (wt%)	0.78	4.90	0.59	3.68
Heating value (kcal/kg)	4,902	4,530	5,003	4,946

[a] On a dry basis; two or three measurements.

The TGA curve of the as-received coconut shell samples at a constant heating rate of 10°C/min is shown in Fig. 1, revealing the residual weight loss with increasing temperature. It is clearly seen on the figure that there are three distinct stages during the thermal decomposition of the biomass. In the first stage (up to 250°C), weight loss increased smoothly, reducing the sample mass by about 5-12 wt%. This was attributed to the releases of water and light fractions absorbed on the surface of the hydrophilic lignocellulosic structure. After the first stage, a sharp decrease in weight occurred until approximately 400°C under N2 gas flow. This significant decrease could be associated with the lignocellulosic structure devolatilization. In the third stage (400 to 900℃), weight loss began to die down due to the decomposition of organic residues such as lignin and low melting point ashes. Due to its aromatic content, lignin component thermally degrades slowly and gradually, making a major contribution to the char yield. The data on the TGA curve will be applied in the carbonization-activation experiments; hence, confirming that a carbonization temperature of about 500°C under N2 gas and an activation temperature of above 500°C under CO_2 gas are suitable to produce a highly porous carbon product.

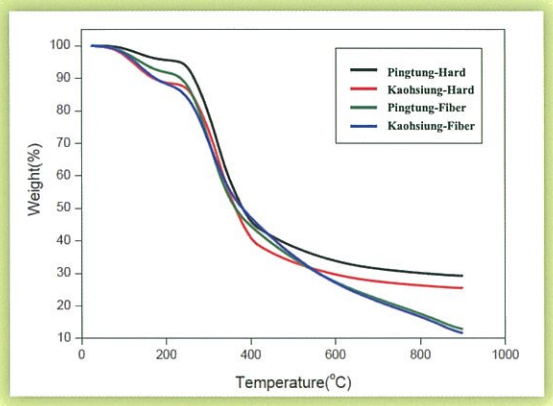

Figure 1.TGA curves of coconut shells (hard and fibrous fractions) obtained from markets in Kaohsiung and Pingtung.

In this study, the Brunauer, Emmett and Teller (BET) surface area and total pore volume obtained from the nitrogen adsorption-desorption isotherms at –196°C were used as comparative factors of determining the degree of pore properties of the physically activated carbon products from the coconut shell residue. The data in Table 2 lists the surface areas and pore volumes of the coconut shell precursor and activated carbon products. As indicated in Table 2, the values of BET surface area and total pore volume increased rapidly with activation temperature ranging from 750 to 1000 °C, and reached a maximum at 1000 °C; i.e. 1,113 m^2/g and 0.9 cm^3/g. Meanwhile, the values of BET surface area and total pore volume increased slightly with holding time (from 120 to 180 min) and CO_2 flow rate (from 100 to 250 cm^3/min). The increase in pore properties by the physical activation could be due to the increase in porosities mainly by gasification reaction of the resulting char. It implies that the activation treatment was more aggressive (i.e., increasing activation temperature, holding time and CO_2 flow rate), resulting in the micropores (<2 nm diameter) /mesopores (2-50 nm diameter) further developed by the progressive gasification in CO_2 environment. As compared to holding time and CO_2 flow rate, the activation temperature seemed to be more suitable for the development of micro- and mesopores of resulting activated product; hence giving a higher surface area and pore volume. These findings were also consistent with the values of iodine number.

Table 2. Pore properties of cylindrical activated carbon derived from carbonized coconut shell

Activation temp. (℃)	Holding time (min)	CO_2 flow rate (cm^3/min)	BET surface area (m^2/g)	Total pore vol. (cm^3/g)	Porosity (-)	True density (g/cm^3)	Iodine No. (mg/g)
750	120	100	457.9	0.253	0.334	1.9854	635
800	120	100	499.1	0.278	0.359	2.0129	697
850	120	100	657.3	0.387	0.451	2.1186	883
900	120	100	822.3	0.515	0.534	2.2219	948
950	120	100	1,032.8	0.715	0.632	2.4005	1,083
1,000	120	100	1,123.2	0.900	0.690	2.4676	1,065
900	120	100	822.3	0.515	0.534	2.2219	948
900	150	100	923.8	0.644	0.591	2.2444	1,065
900	180	100	950.3	0.633	0.603	2.3990	1.036
900	120	100	822.3	0.515	0.534	2.2219	948
900	120	200	979.1	0.595	0.606	2.5804	1,040
900	120	250	993.2	0.604	0.594	2.4232	1,043

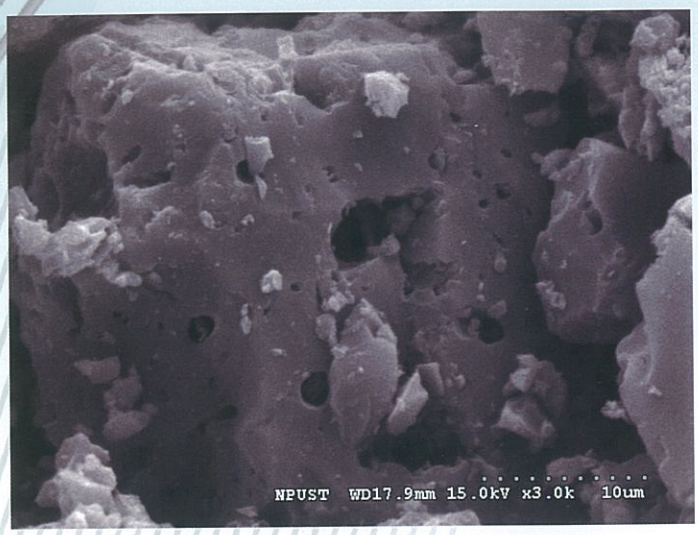

Figure 2. Surface texture observation of activated carbon product derived from coconut shell (BET surface area 822.3 m^2/g).

Figure 2 shows a typical SEM photograph of the activated carbon product prepared by physical activation at 900°C under holding times of 120 min and CO_2 flow rate of 100 cm^3/min, revealing that the porous and disrupted structure examination of the resulting product due mainly to the rigorous activation during the gasification reaction with CO_2. As referred to ASTM D-3467 (Standard Test Method for Carbon Tetrachloride Activity of Activated Carbon), toluene vapor adsorption capacity was also measured in the study (the analytical experiment was not described here), showing that 38% (0.38 g/g) can be obtained, meeting the specifications set by the end user.

4. Conclusions and industrial benefits

Based on the experimental findings, the related properties (i.e., proximate analysis, heating value, elemental analysis and thermogravimetric analysis) of coconut shell samples (including inner hard shell and outer fibrous material) have been evaluated, showing that their variations were not significant. Based on its high carbon and low ash contents, this local biomass can be used as a precursor for activated carbon production. Furthermore, the pore properties (i.e., BET surface area, total pore volume, porosity, or iodine number) of the resulting cylindrical activated carbon products from carbonized coconut shell were on the increasing trend with activation temperature increased. These values exceeded the project's goals/end user's specifications, including BET surface area of 950 m^2/g, iodine number of 1,000 mg/g, and toluene vapor adsorption capacity of 38% (0.38 g/g). However, the yields of these activated carbons were not high, and their ash contents were slightly high ($>$ 10 wt%).

Currently, the market demand on activated carbon products exceeds 16 thousands metric tons in Taiwan, which are mostly imported and belong to high-price cylindrical form. By the industry-academic collaboration research, it shows that the domestic factory can produce cylindrical activated carbon (seen below, left figure), which meets the industrial specifications by end-user. Furthermore, this research also assisted the domestic factory to analyze the pore properties of its activated carbon products for promoting their quality. On the other hand, the hollow activated carbon filter derived from coconut shell (seen below, right figure) was preliminarily produced by this research. This filter core product has been used in the drinking water purification.