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Effect of Activation Temperature and Heating Duration on Physical Characteristics of Activated Carbon Prepared from Agriculture Waste

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Abstract

This study was conducted to determine the physical characteristics of activated carbon prepared from durian shell in varied heating durations from 10 min to 30 min and activation temperatures of 400°C and 500°C. Durian shells have been characterized in term of ultimate and proximate analysis, chemical composition and thermal behaviour with a view to be used as activated carbon precursor. Durian shell activated carbon was prepared by impregnating 10g of sample in 10% (v/v) concentration of phosphoric acid for 24 h, followed by carbonization at 400°C and 500°C with different heating durations under nitrogen atmosphere. The results showed that various treatment conditions affect the percentage of yield, BET surface area, micropore volume, and average pore diameter. The highest surface area (S_{BET}) 1024 m^2/g was obtained at 500°C and 20 min of heating duration with 63% of yield and 0.21 cm^3/g micropore volume.

Keywords: durian shell; activation temperature; heating duration; phosphoric acid; BET surface area

1. Introduction

Today, the idea of utilizing biomass from agricultural and livestock wastes as a raw material for production of activated carbons has attracted the interest of researchers especially in agricultural-practicing countries. Malaysia has an abundance of agriculture by-products available which are usually directly discharged as solid waste; causing environmental issues. Many agriculture residues such as coconut husk (Tan *et al.*, 2008), rice husk (Kalderis *et al.*, 2008), oil palm shell (Guo and Lua, 2000), rubber wood saw-dust (Srinivasakannan and Abu Bakar, 2004), jackfruit peel (Prahas *et al.*, 2008), cherry stones (Jaramillo *et al.*, 2009), bamboo (Asada *et al.*, 2006), cow dung (Demiral and Demiral, 2008) and turkey manure (Lima and Marshall, 2005) have been proven to be suitable feedstock for production of activated carbon.

Durian (*Durio zibethinus* Murray) is the most popular seasonal fruit in South East Asia countries. Durian is a tropical fruit of trees species of Malvales order in Bombaceae family and genus of *Durio* (Nanthachai, 1994). It also widely known to the locals as the "King of Fruits". There are a lot of species of durian but only *Durio zibethinus* is of economic importance and commercially grown. In Malaysia, approximately 376,273 metric tonne of durian are produced in year 2008 (Department of Agriculture Malaysia, 2009).

There are a few methods in preparation of activated carbons from biomass, mainly being chemical activation techniques and physical activation. Chemical activation is carried out by the impregnation of chemical agents and the raw materials follow by pyrolisis in an inert atmosphere at high temperature. The chemical activation of lignocellulosic material with phosphoric acid has been done by many other researchers. It proved to be an effective activating agent. According to Patnukao and Pavasant, 2008, activated carbon prepared by phosphoric acid activation produced high BET surface area and iodine adsorption. Physical activation comprise of two stage processes of carbonization of raw material in inert atmosphere and activation of the char in high temperature in the presence of carbon dioxide or steam (Ahmad *et al.*, 2007). Combination of chemical and physical activation seems to be a promising preparation for effective carbon adsorbents too (Budinova *et al.*, 2006).

A lot of literature on preparation of activated carbon and its application from different materials can be found but there is not much information on production and utilization of durian shell as activated carbon precursor. Thus, this study is aimed to evaluate the physical characteristics of activated carbon prepared from durian shell in varied heating durations from 10 min to 30 min and activation temperatures of 400°C and 500°C.

2. Methodology

2.1. Materials

The durian shells were acquired from the market in Serdang, Selangor. The shells were washed and crushed into 1-2 cm particle size before being dried in an oven overnight to reduce the moisture content. The activation agent of choice was *ortho*-phosphoric acid of 85% purity (MERCK). Aqueous solution with concentration of 10% (v/v) was prepared for the impregnation of the sample. Nitrogen gas with purity of 99.995% in a compressed gas cylinder was used to provide inert gas atmosphere during carbonization stage.

2.2. Ultimate and proximate analysis

The moisture content of the samples will be determined by drying the sample in an oven at 135°C for 2 h until a constant weight was obtained (AOAC, 2000). Ash content was determined by dry-ashing in a furnace at 600°C for 2 h (AOAC, 2000). The proximate analysis of C, H, N, and S on the raw material was carried out using Elemental analyzer (LICO-CHNS 932). The oxygen content was calculated by the difference. Durian shell was subjected to thermogravimetric analysis (TGA) in N_2 atmosphere by using a thermal analyzer (Mettler Toledo TGA/STDA 851^e)

2.3. Preparation of activated carbon

Chemical activation method using phosphoric acid was used to activate the raw material. Ten gram of raw material was weighed. The weighed raw sample was impregnated in 100ml 10% (v/v) concentration of acid phosphoric overnight. The calculated impregnation ratio, X_p was 1:1.4. Impregnation ratio was defined as the amount of phosphoric acid incorporated with the sample (Molina-Sabio and Rodrigues-Reinoso, 2004). After impregnation, the wet samples were dried in an oven for 12 h (~100°C) and subsequently activated in nitrogen atmosphere at 400°C and 500°C with a heating rate of 5°C/min. The soaking duration at final temperature was 10 min , 20 min and 30 min, respectively. The activated samples were cooled in a stream of gaseous nitrogen to room temperature. Then, the samples were washed batchwise at ambient temperature with distilled water until the filtrate reached approximately pH6-7. The samples were then dried at 85°C in an oven overnight to make sure they were moisture-free. Finally, the samples were kept in desiccators for further use.

The yield of the activated carbon was calculated:

$$\text{Yield} = \frac{W_1}{W_0} \times 100\% \quad (1)$$

W_1 is the mass of the unwashed carbon after activation while W_0 is the original mass of the precursor on dry basis.

2.4. Characterization

The activated carbon was degassed at 350°C in a vacuum condition for 24 h. The porous structure parameters were determined from the nitrogen adsorption isotherm measured at -196°C using an automatic Micromeritics ASAP 2010 volumetric sorption analyzer. The specific surface area was calculated using (Brunauer, Emmett and Teller) BET method. Total pore volume was determined by estimating the amount of nitrogen adsorbed at a relative pressure of P/P_o 0.95.

3. Results and Discussion

3.1. Raw material analysis

The ultimate and proximate analysis of raw material was shown in Table 1. Moisture content and ash content for the durian shell is 11.27% and 4.84%. Ultimate analysis showed that durian shell has 39.3% of carbon and 53.74% of oxygen. The analysis of chemical properties for durian shell (Khedari *et al.*, 2004) as in Table 2 showed that it contains 13.09% of hemi-cellulose and 15.45% of lignin. Porosity of activated carbons not only depends on the experimental conditions of the carbonization and activation steps but also preponderantly on the original nature and structure

Table 1. Proximate and ultimate analysis for durian shell

	Result (%)
Proximate	
Moisture Content [a]	11.27
Ash Content [b]	4.84
Ultimate [b]	
C	39.30
H	5.90
N	1.00
S	0.06
O	53.74

a = wet basis
b = dry basis

Table 2. Chemical composition of raw durian shell (Khedari *et al.*, 2004)

Chemical Composition	Result (%)
Lignin	15.45
Holocellulose	73.54
α - cellulose	60.45
Hemi-cellulose	13.09

of the involved material. Cagnon *et al.*, 2009, has demonstrated that lignin is the major contributor of activated carbons. The high carbon percentage and low ash content also suggested that durian shell has the potential to be activated carbon precursor.

Fig. 1 illustrates the TG-DTG curve of raw durian shell which represented the three stages of thermal decomposition behavior of raw durian shell. The TGA of raw durian shell was conducted in air flow with temperature range of 25 to 1000°C. The heating rate was 10°C min^{-1}. The first stage range from 59 to 200°C and presents a 4.5 % weight loss due to moisture release from the material. Between 200 to around 300°C the mass loss is as high as 14%. In the temperature range of 300 to 400°C, a weight of 46% of weight loss was observed. This weight loss is attributed to the decomposition or oxidation of organic compounds such as lignin and cellulose in the raw durian shell. There is not much change in weight when the temperature was heated above 400°C. Therefore, 400°C and 500°C was selected as the activation temperature for this study.

3.2. Effects of activation temperature and heating duration on physical properties

3.2.1. Yield

Fig. 2 presents the percentage of yield obtained from the production of activated carbon in different activation temperature and heating time prior to washing. Range of 51.78% to 57.27% of yield is obtained from activated carbons prepared from 400°C. At 500°C the yield decreased as the heating duration increase, range from 68.10% to 58.54%. The yield obtained is relatively higher than expected. Phosphoric acid as activating agent plays an important role in high yield. The presence of phosphoric acid during activation promotes depolymerization, dehydration, and redistribution of constituent biopolymers and also favoring the conversion of aliphatic to aromatic compounds (Prahas *et al.*, 2008 and Rodrigues-Reinoso and Molina-Sabio, 1992).

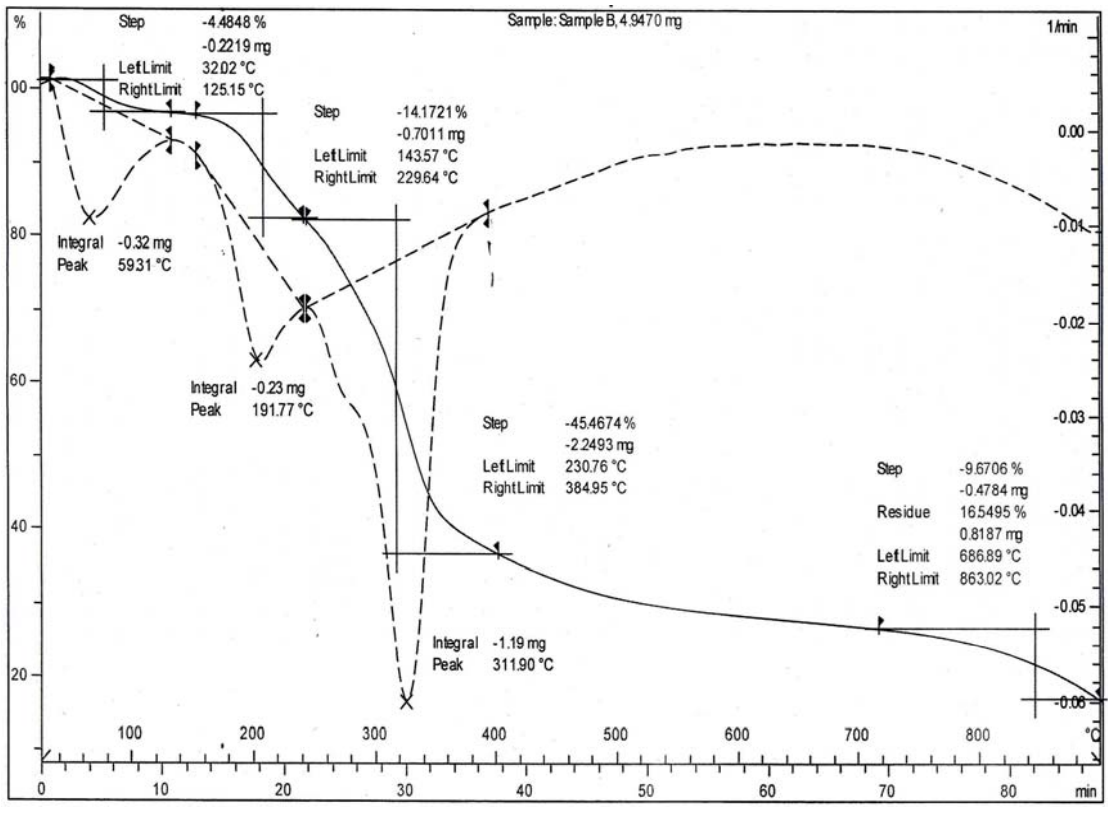

Figure 1. TG-DTG curve of raw durian shell.

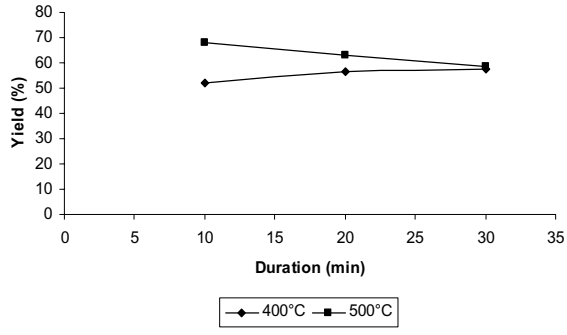

Figure 2. Percentage of yield from activated carbon prepared from durian shell.

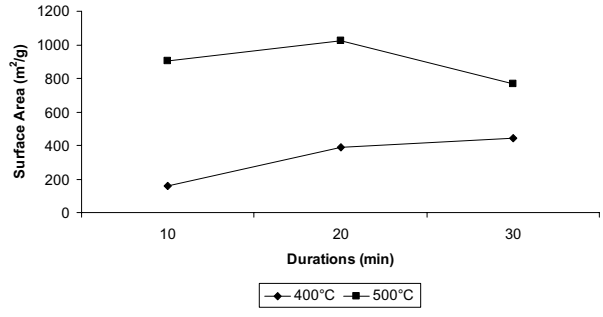

Figure 3. Effects of soaking durations on BET surface area of activated carbons prepared with 10% acid concentration and different activation temperatures.

3.2.2. Surface area and pore structure

Fig. 3 shows the effects of soaking time and activation temperature on the BET surface area (S_{BET}). Obviously, BET surface area for 400°C is much lower than the BET surface area of 500°C. Increasing of activation temperature contributed to formation of new pores because more volatile organic compounds are being released from precursor (Demiral *et al.*, 2007). Note that when activation duration lengthened from 20 min to 30 min at 500°C, surface area decreased from 1024 m^2/g to 768 m^2/g, which amounted to 25%. This is because longer heating duration caused some of the pores become larger or even collapse, thus contributed to the reduction of surface area (Diao *et al.*, 2001).

Results for pore characteristics of activated carbon are presented in Table 3. Activated carbon produced at 400°C with heating duration of 10 min and with acid concentration of 10% was named AC1 (refer Table 3). Activated carbons prepared at 400°C and 500°C have increment in term of micropore surface area, micropore volume and total volume as the heating duration increase from 10min to 30min. At 400°C, the total volume of pores is 0.08 cm^3/g, 0.15 cm^3/g, and 0.27 cm^3/g for AC1, AC2 and AC3 respectively. Micropore volume range from 0.05 to 0.16 cm^3/g. Increase of heating duration proved to have enhanced the development of micropores and total volume because longer duration has the possibility for generation of new micropores and mesopores in the carbon. When the activation temperature was increased to 500°C, a larger total volume and micropore volume is observed if compared to activated carbons prepared from 400°C. Adinata *et al.*, 2007, study also showed that micropore volume increased as the temperature increased and after 800°C the micropore volume slightly decreased.

One of the important properties of activated carbon is the adsorption capacity, which directly affected the surface area. Shape of the adsorption isotherm may tell the qualitative information on the adsorption capacity as well as the extent of surface area available to the adsorbate. As shown in Fig. 4, a small hysteresis in the shape means that the mesopores are developed during activation was observed in AC2 and AC6. Larger hysteresis loop was observed for AC4 and AC5 carbons suggest a notable contribution of higher mesopores in their porous structure. This is supported by the average pore diameter which is classified as mesopores carbon. The presence of mesopores together with micropores in the activated carbon enhances their adsorption capacities, especially for larger molecules adsorbates (Chandra *et al.*, 2007). The activated carbon produced at 500°C for 20 min heating duration (AC5) has the highest BET surface area (1024 m^2/g) and largest total pore volume (0.35 cm^3/g). Short heating duration is desirable because it can reduce the manufacturing costs.

Table 3. Pore characteristics of activated carbon prepared from durian shell

Sample Temp / duration	**Average pore diameter** Å	**Micropore surface area** (m^2/g)	**Micropore volume** (cm^3/g)	**Total volume** (cm^3/g)
AC1-400C /10 min	24.66	87	0.05	0.08
AC2-400C /20 min	27.80	136	0.07	0.15
AC3-400C /30 min	26.02	314	0.16	0.27
AC4-500C /10 min	29.27	264	0.14	0.35
AC5-500C /20 min	25.35	404	0.21	0.35
AC6-500C /30 min	23.66	347	0.18	0.22

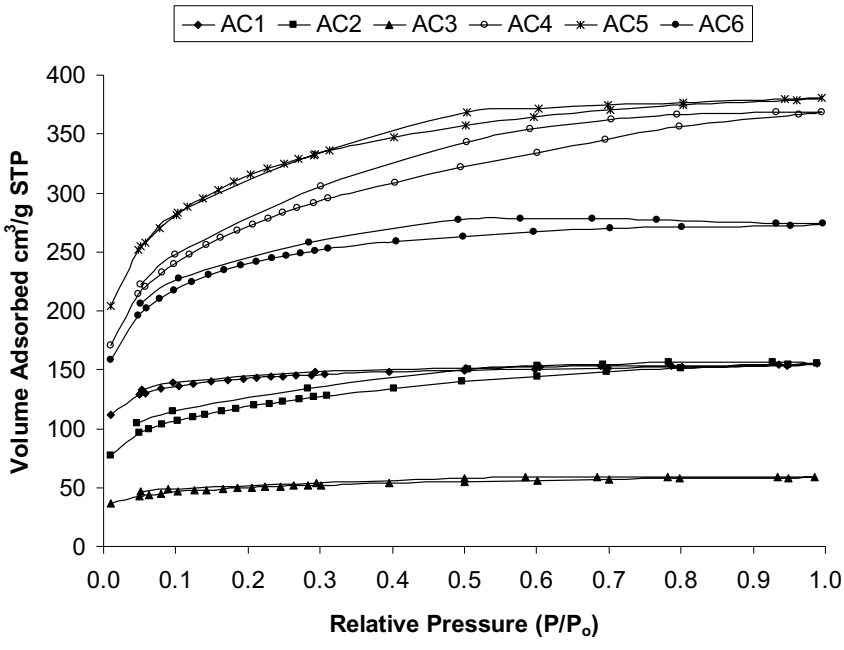

Figure 4. Adsorption/desorption isotherm of N_2 at -196C on activated carbon prepared from different conditions.

4. Conclusion

The results obtained in this study of characterization of raw durian show that it is a promising activated carbon precursor. Activation temperature and heating duration have significant influence on the characteristics of the activated carbon prepared from durian shell. The highest surface area (S_{BET}) 1024 m^2/g was obtained at 500°C and 20 min of heating duration with 63% of yield. Nevertheless, further work on the preparation methods should be done in future.

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