EFFECT OF CARBONIZATION TEMPERATURE ON PROPERTIES OF CHAR AND ACTIVATED CARBON FROM COCONUT SHELL

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Abstract

This research focused on investigating the effect of the carbonization temperature on the porous properties (surface area, pore volume, and mean pore size) of coconut shell based activated carbon prepared by physical activation with carbon dioxide. The carbonization temperature was varied in the range from 250-750ºC and the derived chars were activated in CO_2 at 850ºC for 60 and 120 min. The porous properties of the activated carbons obtained including the Brunauer-Emmett-Teller (BET) surface area, pore volume, pore size distribution, and average pore diameter were determined by nitrogen adsorption isotherms at -196ºC. The experimental results showed that most pores occurred during the activation predominantly as micropores with a small proportion of mesopores. The porous properties of the activated carbon decreased with the increase in the carbonization temperature, with the char prepared at the lowest carbonization temperature of 250ºC and activated at 850ºC for 120 min giving activated carbon with the highest BET surface area and pore volume of 1056 m^2/g and 0.533 cm^3/g, respectively. From the obtained results, it is feasible to produce activated carbon with high porous properties from coconut shell by selecting the appropriate conditions for the carbonization and activation steps.

Keywords: Coconut shell chars, carbonization, activated carbon, porous properties

Introduction

Activated carbon is one of the most widely used adsorbents for separation and purification processes. It can be produced froma variety of carbonaceous materials such as coals, polymers, and biomass and, with proper control of the preparation conditions, a wide range of adsorbent porous properties can be well achieved. Nowadays, the demand for activated carbon inindustries has increased steadily, with the majority being used in liquid-phase adsorption systems. Worldwide demand for virgin activated carbon for the year 2010 amounts to 1.2 million metric tons with the following market shares: Asia/Pacific 50%, North America 26%, Western Europe 14%, and other regions 10% (The Freedonia Group, Inc., 2006).

Coconut shell was chosen as the

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starting carbonaceous materialin this study because it is the by-product from coconut palm which is an important economic crop of Thailand. In addition, therelatively large amount left from coconut fruit utilization, in the order of 150000 tons/year (National Food Institute, 2012), is considered to be a potential precursor for industrial production of activated carbon. Coconut shell is a carbonaceous material which has aninherently strongstructure and contains a high fixed carbon content (about 21%) with very low ash content (less than 1.0 wt%) (Li *et al.*, 2008). Moreover, its contaminant is less harmful compared with activated carbon that is produced from raw coal. In the production of activated carbon, there are 2 general methods, namely physical activation and chemical activation. In physical activation, a raw material is first carbonized and then activated with an oxidizing gas such as steam or carbon dioxide to develop internal porosity by gasification reaction. In chemical activation, a raw precursor is impregnated with aninorganic additive and carbonized in an inert atmosphere. This work is focused on physical activation since it is widely adopted in commercial production and is friendly to the environment. Generally, the porous properties of activated carbon are dependent onboth the conditions of carbonization and activation. Most researches have mainly focused on studying the activation conditions such as the activation temperature and activation time. However, the present study was directed towards studying the effect of the carbonization temperature on the resulting porosity of produced activated carbons, the topic of which has not been widely investigated in detail. There have been some previous works reporting on the effect of the carbonization temperature but mostly these were performed at the high temperature range of 400-800°C (Wan Daud *et al.*, 2000; Guo *et al.*, 2009). To study the effect of the carbonization temperature in more detail, a wider range of carbonization temperatures from 250-750°C is specifically focused on and investigated in the present work.

Materials and Methods

Raw material preparation was first commenced by drying the as-received coconut shell in an oven at 110°C for 48 h to remove excess moistureand was then crushed and sieved to obtain a sample of 2.1 mm in average screen size. The pre-dried coconut shell was kept for the proximate and thermal analyses and the subsequent char preparation.

Proximate and Thermal Analyses of Coconut Shell

The proximate analysis and thermal decomposition behavior of the coconut shell sample were analyzed using a thermogravimetric analyzer (SDT 2960, TA Instruments, New Castle, DE, USA). The proximate analysis was performed using the procedure as outlined by Luaand Guo (1998). About 30 mg of the sample were placed in the alumina crucible of the analyzer and the heating was carried out at the rate of 5°C/min from room temperature to 110°C under an inert atmosphere of nitrogen flowing at the rate of 100 cm^3/min until the dehydration was completed. Then the temperature was increased to 850°C at a constant heating rate and held for 7 min to determine the volatile matters from the weight loss. After that, the temperature was lowered to 800°C and the inert gas was changed to air flowing at 100 cm^3/min, and the sample was maintained at this temperature until the weight remained constant due to complete combustion. This final weight is the amount of the ash residue and the fixed carbon content in the analyzed sample is calculated by mass balance (%FC=100-%ash-%VM, on a dry basis). For the thermal analysis, coconut shell weighing 30 mg was placed in an alumina crucible and the heating scheme was carried out at the rate of 5°C/min from room temperature to 800°C with nitrogen flowing at 100 ml/min. The weight of the sample was automatically collected as a function of the heating time and temperature.

Carbonization of Coconut Shells

A batch of 15 g of pre-dried coconut shell wasloaded intoa ceramic boat which was placedin an electrically heated horizontal tube furnace(CTF 12/75, Carbolite Ltd., Hope Valley, UK) and then heated up to the desired carbonization temperature of 250, 350, 450, 550, 650, and 750°C, at a heating rate of 5°C/min and held at that temperature for 120 min under the flow of nitrogen at 100 cm^3/min. The proximate analyses of the resulting char samples were also determined by the thermogravimetric technique previously outlined and the surface characteristics of the char products were studied by scanning electron microscopy (SEM) instrument (JEOL JSM-6400 Scanning Microscope, JEOL Ltd., Tokyo, Japan).

Activation of the Carbonized Chars

About 3 g of the char from the carbonization step were loaded on a wire-mesh boat and placed in the tube furnace, and then heated up to the required activation temperature (850°C) at a heating rate of 5°C/min under thenitrogen flow at 100 cm^3/min. When the final activation temperature of 850°C was reached, the nitrogen flow was switched to CO_2 flowing at the rate of 100 cm^3/min and the system was kept at this temperature for the activation times of 60 and 120 min. When the activation was completed, the sample was cooled down to room temperature under the nitrogen flow. The obtained sample was then kept in a desiccator for further analysis. Carbon dioxide rather than steam was employed as an oxidizing gas for the activated carbon production in this work because both gases are commonly used by a number of investigators but CO_2 can be supplied and regulated conveniently from a gas cylinder without the need to include a steam generator and a metering pump as in the case of using steam.

The structural and porous properties of the prepared activated carbons were characterized by nitrogen adsorption at -196°C using an accelerated surface area and porosimetry system (ASAP-2010, Micromeritics Instrument Corp., Norcross, GA, USA). Prior to the measurements, the activated carbon was degassed at 200°C under high vacuum (< 0.05 torr) for 5 h. The BET surface area was calculated from the derived isotherms by applying the well-known Brunauer-Emmett-Teller (BET) equation (Brunauer et al., 1938). The Dubinin–Astakhov (DA) equation (Dubinin and Astakhov, 1971) was used to calculate the micropore volume. The totalpore volume was determined from the amount of nitrogen adsorbed at a relative pressure (P/P^o) of 0.98 and converted to nitrogen volume in liquid state.

Results and Discussion

Proximate and Thermal Analyses of Coconut Shell

The result of the proximate analysis of coconut shell is shown in Table 1. As can be seen, the fixed carbon content of coconut shell has a value of 23.64%, which is higher than those of some biomass precursors such as longanseed (19.6%) (Junpirom et al., 2007), oil palm fibers (18.23%) (Lua and Guo, 1998), and eucalyptus wood (18.3%) (Ngernyen et al., 2006).

In general, biomass contains 3 main cellulosic components, that is, hemicellulose, cellulose, and lignin. During the carbonization of biomass, the hemicellulose and cellulose will decompose mostlyinto volatile products, while the lignin content is more difficult to decompose and contributes to the formation of a solid residue called char. For thermal

Table 1. Proximate analysis of coconut shell (dry basis)

	wt% (dry basis)
Volatile matter	76.23
Fixed carbon	23.64
Ash	0.13

analysis, the thermal degradation of lignocellulosic materials was investigated using the technique of thermogravimetric analysis. The pyrolysis results obtained as reported in weight percent remaining of coconut shell (TG curve) and its corresponding first derivative (DTG curve) are shown in Figure 1. Forthe DTG curve, the small peak occurring at the temperature below 120°C corresponds to the removal of water (dehydration), giving the weight loss of about 2.8%. As the temperature was increased, the main pyrolysis decomposition of lignocelluloses occurred as 2 peaks in the range of 200-385°C, which agreed with the result of Antal (1983) in that lignocelluloses' decomposition usually occurs over a wide range of temperatures from 200-400°C. For the 2-peak characteristic of the decomposition curve, the first peak appeared in the range of 200-315°C and the second peak occurred in the range of 315-385°C. As reported by Yang *et al.* (2007) and Gašparovič *et al.* (2010), the decomposition of hemicellulose and cellulose started over the range from 200-380°C and 250-400°C, respectively, while the decomposition of lignin occurred over a wider range of 160-900°C. Therefore, the appearance of the first-peak decomposition should correspond to the decomposition of hemicellulose with the weight loss of about 28.5%, followed by the decomposition of cellulose which occurred as the second peak, giving the weight loss of about 26.6%. Lignin

should decompose over the wider range of temperatures, by starting to decompose at the lowest temperature and continuing up to the final temperature of around 750°C at which the weight remaining becomes almost constant.

Effect of Carbonization Temperature on Physical Properties of Char

Coconut shell was carbonized at temperatures in the range from 250-750°C. The effect of the carbonization temperature on char yield is delineated in Figure 2. It was found that the char yield decreased with an increase in the carbonization temperature. The yield significantly decreased from 250 to 350°C and then gradually decreased at temperatures higher than 350°C. This result indicates that the loweryield obtainedat a higher temperature is caused bya much larger release of volatile matters, thus giving the lower content of volatile matters in the derived char as can be seen in Figure 3. This figure also shows the proximate analyses of chars prepared at different carbonization temperatures. It is observed that the fixed carbon and ash content increased with increases in the carbonization temperature over the range from 31.41-88.42% and 0.23-1.32%, respectively, while the volatile content decreasedfrom 68.35 to10.26%.

In addition, the effect of the carbonization temperature on the surface morphology of charsby SEM is presented in Figure 4. The raw coconut shell result (Figure 4(a)) is
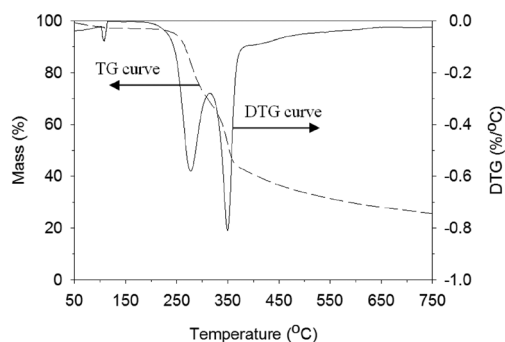

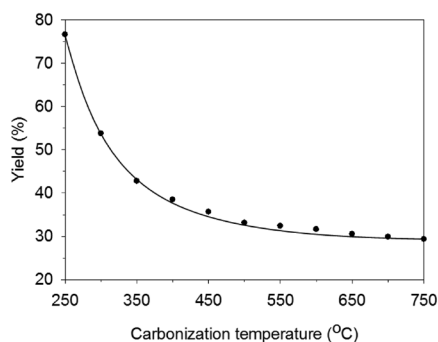**Figure 1. TG/DTG curves of raw coconut shell**

Figure 2. Effect of carbonization temperature on the yield of coconut shell char

also included for the sake of comparison. It is observed that the external surface of raw coconut shell is quite smooth, and appears to consist of a stack of ordered layering flakes. When the coconut shell is carbonized, the external surface shows an increase in the degree of surface roughness as the carbonization temperature is increased, as displayed in Figure 4(b) to 4(g). The increased surface roughness is attributed to the rupture of the biomass structure resulting from the release of more volatile species as the heat treatment temperature is increased.

Effect of Carbonization Temperature on Weight Loss

In general, the production of activated carbon consists of the carbonization of a raw precursor to increase the carbon content, followed by the activation step to generate adsorbent internal porosity. The weight loss of each process indicates the extent of chemical reaction involved, which in turn affects the property of the carbon product in each step. The weight loss of char is defined based on the initial weight of raw coconut
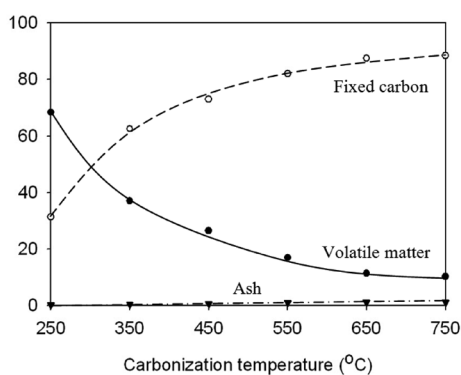

Figure 3. **Effect of carbonization temperature on the proximate analysis of coconut shell chars prepared at various carbonization temperatures**
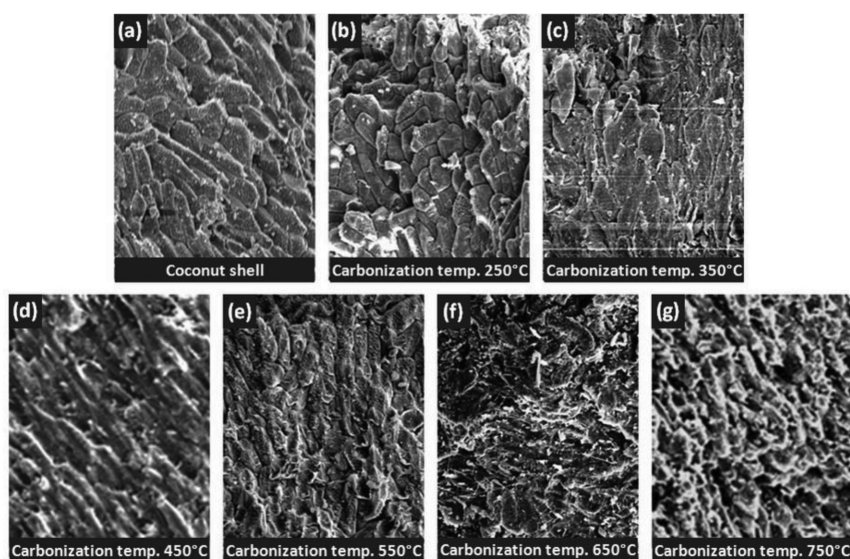

Figure 4. **SEM images of coconut shell and coconut shell chars at various carbonization temperatures**

shell where as that of the activation step is defined based on the weight of the initial char prior to activation. The char derived at each carbonization temperature has a different yield and characteristics which will affect the later stage of char activation with CO_2. As a result, in order to compare the effect of chars prepared at different carbonization temperatures on the properties of produced activated carbon, it is logical to use the total weight loss for the activation step based on the initial weight of coconut shell. That is,

Total fractional weight =

$$1 - \frac{W_{ac}}{W_r} = 1 - (1 - W_{L,car})(1 - W_{L,act}) \qquad (1)$$

where $W_{L,car}$, $W_{L,act}$ are the weight losses during carbonization and activation, respectively, which are defined in terms of weight fraction as

$$W_{L,car} = 1 - \frac{W_{car}}{W_r} \qquad (2)$$

and

$$W_{L,car} = 1 - \frac{W_{ac}}{W_{car}} \qquad (3)$$

where W_r, W_{car}, and W_{ac} are the weight of the starting raw material, the weight of char after carbonization or before activation, and the weight of the obtained activated carbon, respectively.

Figure 5 shows the percent weight loss during carbonization and activation and total weight loss versus carbonization temperature at 2 activation times (60 and 120 min). For a given activation time, the total weight loss and the weight loss during activation tended to decrease with increasingthe carbonization temperature, while the opposite trend was found for the carbonization step. This result implies that the char obtained from a lower carbonization temperature which contains higher amounts of volatile matter favors theproduction of char with higher reactivity toward CO_2 gasification in the activation step. It is hypothesized that the release of more volatiles of this char at a high activation temperature could create more reactive sites

for gasification on the carbon surface, hence giving higher weight loss during the activation step. As to the effect of activation time, the extent of char gasification would be increased with increasing the activation time from 60 to 120 min, giving rise to the consequent increase for both the total weight loss and weight loss for the activation process.
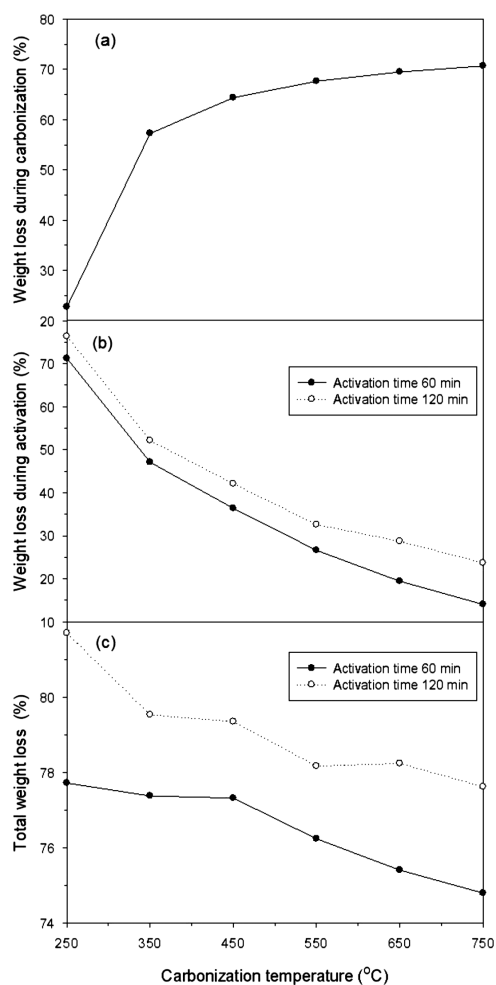

Figure 5. Effect of carbonization temperature on (a) the weight loss of coconut shell during carbonization, (b) weight loss of char during activation, and (c) total weight loss of coconut shell for carbonization and activation (activation temperature 850°C, activation time 60 and 120 min)

Effect of Carbonization Temperature on Porous Properties of Activated Carbon

The porous properties of activated carbon were characterized by using nitrogen adsorption isotherms at -196°C. Figure 6 shows the typical adsorption isotherms of the activated carbon produced from chars carbonized at temperatures of 250 and 750°C and at activation temperature of 850°C. From these results, it isseen that the nitrogen adsorption isotherms display a type I isotherm, according to the BDDT (Brunauer–Deming–Deming–Teller) classification (Gregg and Sing, 1982). The rapid rising of N_2 adsorbed over a low range of relative pressure followed by a plateau of an almost constant adsorbed amount clearlyindicates that the derived activated carbon contains predominantly micropores, by which the adsorption takes place by the pore-filling mechanism. Evidently, the adsorbed amount of N_2 moleculesby the activated carbon is dependent both on the carbonization temperature and activation time.

Figures 7 and 8 show the effect of the carbonization temperature on the porous properties of produced activated carbon. It was found that both BET surface area and pore volume (total and micropores) decreased with an increase in the carbonization temperature. Based on the investigated results, it can be concluded that the extent of gasification and
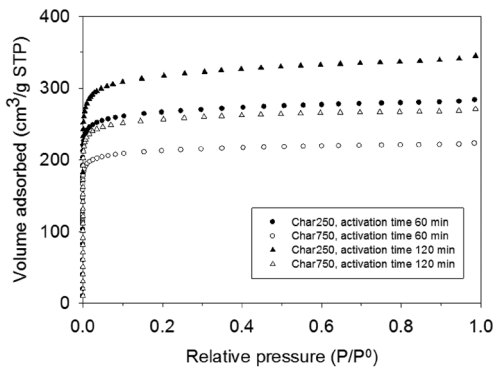

Figure 6. Effects of carbonization temperature and activation time on nitrogen adsorption isotherms of prepared activated carbon from coconut shell at activation temperature of 850°C
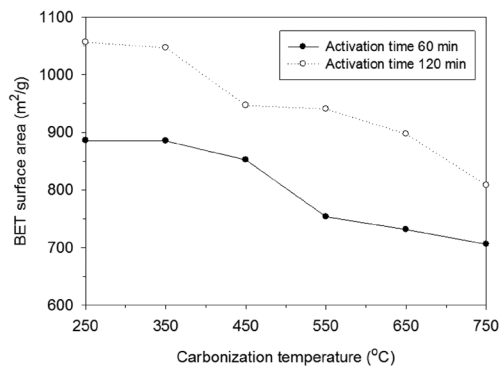

Figure 7. Effect of carbonization temperature on BET surface area of activated carbons from coconut shell at activation temperature 850°C
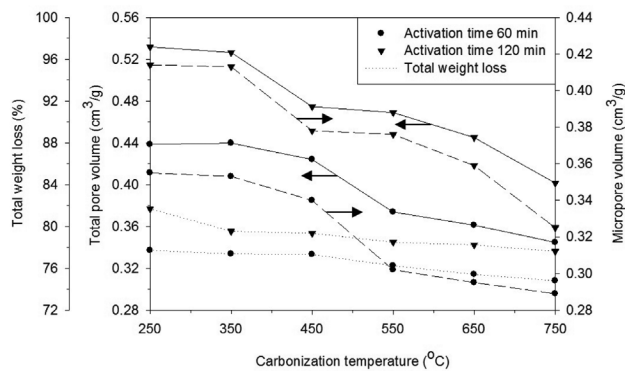

Figure 8. Effect of carbonization temperature on the pore volumes of activated carbons from coconut shell at activation temperature 850°C

pore development are both strongly dependent on the carbonization temperature. The char prepared at the lowest carbonization temperature of 250°C and activated at atemperature of 850°C and time of 120 min gave the activated carbon with the highest BET surface area and pore volume of 1056 m^2/g and 0.533 cm^3/g, respectively. Both the surface area and pore volume decreased slightly from 250 to 350°C but dropped significantly from 350 to 550°C followed by a gradual decrease at higher carbonization temperatures. The highest porous properties of activated carbon from char prepared at the lowest carbonization temperature indicate that this char is most reactive towardsthe gasification reaction of the activation step. A similar gasification study on coconut shell chars was previously

performed in a thermogravimetric analyzer and the kinetic results alsoindicated that char reactivity decreased with increasing the carbonization temperature, with the largest decrease occurring between 250 and 350°C (Tangsathitkulchai *et al.*, 2012). It was hypothesized that the decomposition of hemicellulose over this low carbonization temperature range could be responsible for thisincrease of char reactivity (number of active sites) for the gasification reaction. In addition, it has been reported that, at high carbonization temperatures, a more ordered structure is likely to be developed in the char, leading to a slower rate of gasification during the activation step (Li *et al.*, 2008).

It is discovered that the total weight loss (see Equation (1) for the definition) can be used to represent the combined effect of the carbonization temperature and activation condition (temperature and time) on the porous properties of activated carbons, as displayed in Figure 9. The results show that within the range of total weight loss investigated, as the total weight loss increases the porous properties increase initially almost linearly for total weight loss less than 76%. For higher weight loss, the pore volume rises with the increasing slope, approaching a maximum near the 81% weight loss. It is further noted that the values of total weight loss vary over a rather narrow range from around 75 to 82 wt%. This is attributed to the
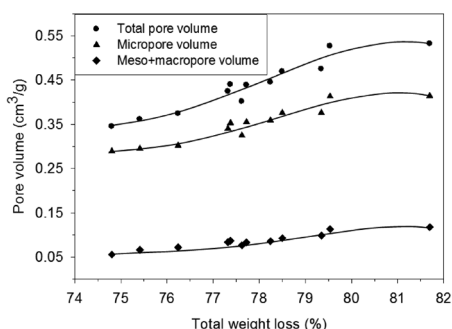

Figure 9. Correlation between total weight loss and pore volume of activated carbonfrom coconut shell
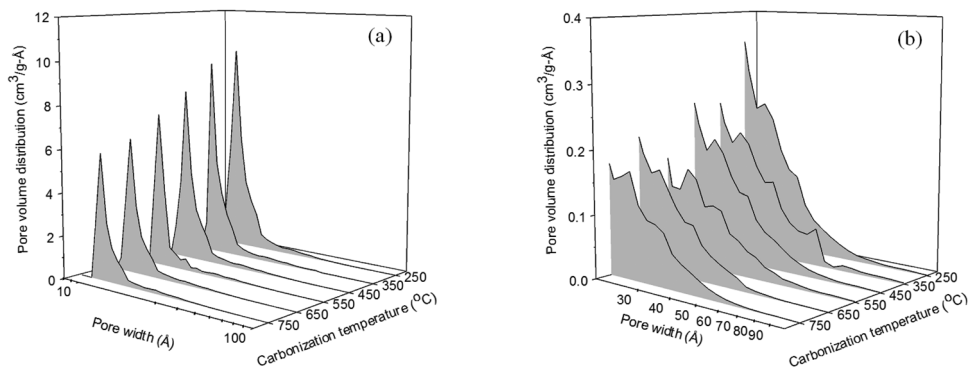

Figure 10. Pore size distribution of activated carbons from coconut shell chars prepared at different carbonization temperatures (activation conditions of 850°C and 120 min)

Table 2. Effect of carbonization temperature on pore size distribution of activated carbon (activation temperature = 850°C and activation time = 120 min)

Carbonization temperature (°C)	Total pore volume (cm³/g)	Micropore volume		Mesopore volume		Macropore volume		Average pore size (Å)
		(cm³/g)	%	(cm³/g)	%	(cm³/g)	%	
250	0.532	0.414	77.84	0.118	22.12	0.00021	0.04	20.14
350	0.526	0.413	78.45	0.113	21.45	0.00053	0.10	20.12
450	0.475	0.376	79.20	0.098	20.66	0.00062	0.14	20.05
550	0.469	0.376	80.18	0.092	19.69	0.00059	0.13	19.94
650	0.445	0.359	80.67	0.085	19.19	0.00063	0.14	19.84
750	0.401	0.325	80.95	0.076	18.89	0.00067	0.16	19.86

compensation effect between the increase of weight loss during carbonization and the decrease of weight loss during activation as the carbonization temperature is increased, as seen in Figure 9.

Figure 10 shows the effect of carbonization temperature on the developed pore size distribution of activated carbons. It is clear that the distribution of pore size is relatively narrow, with the presence of a sharp peak near the pore width of 11.3Å, and confined mainly in the micropore size range of less than 20Å (Figure 10(a)). The pore volume distribution data in the mesopore size (20-500Å) is enlarged and displayed in Figure 10(b). Since the area under the curve represents the value of the pore volume, it is obvious that micropore and mesopore volumes decrease with increasing the carbonization temperature over the range from 250 to 750°C, in agreement with the results shown in Figure 8.

Further examination of Table 2 indicates that the contribution of macropores in terms of pore volume is insignificant, as compared to the micropores and mesopores. The percentage of created micropores increases with an increased carbonization temperature from 77.84 to 80.95%, while the development of mesopores gives the opposite trend; it drops from 22.12 to 18.89%. In addition, the average pore size of activated carbon appears to decrease from 20.14 to 19.86Å as the carbonization temperature is increased. These results tend to suggest that the carbonization

temperature not only has an effect on char reactivity, which results in different values of porous properties, but also on the physical structure of char upon heat treatment during the carbonization step, giving activated carbons with different distribution of pore size. It is probable that the char prepared at a high carbonization temperature, due to a greater loss of volatiles, possesses a more densely packed structure from which it is difficult to enlarge the small pores to larger pores by gasification with the activating gas. From our measured results, this structural change of char is confirmed by the continued increase of char density from 1.194 to 1.853 g/cm³ as the carbonization temperature is increased from 250 to 750°C.

Conclusions

The effect of the carbonization temperature in the range from 250 to 750°C on the properties of char and activated carbon from coconut shell was investigated in this work. It was found that char yield decreased with an increasing carbonization temperature due to the increased amount of volatile being released, giving the corresponding increase of the fixed carbon content. Porous properties of activated carbon including surface area, pore volume, and mean pore size were found to decrease with the increase in the carbonization temperature, with activated carbon produced from char prepared at the

lowest temperature of 250°C giving the largest surface area and pore volume of 1,056 cm^2/g and 0.533 cm^3/g, respectively. Most pores generated in activated carbon are micropores (pore size smaller than 20Å) which accounts for 78-81% of total pore volume. The carbonization temperature has a profound effect on the chemical reactivity and structural change of resulting char which in turn affect the porous texture of produced activated carbons.

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