Porous properties of activated carbon produced from Eucalyptus and Wattle wood by carbon dioxide activation

Yuvarat Ngernyen, Chaiyot Tangsathitkulchai† and Malee Tangsathitkulchai*

School of Chemical Engineering, Institute of Engineering,
Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand
*School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand
(Received 6 February 2006 • accepted 2 May 2006)

Porous properties of activated carbon produced from Eucalyptus and Wattle wood by carbon dioxide activation

Yuvarat Ngernyen, Chaiyot Tangsathitkulchai† and Malee Tangsathitkulchai*

School of Chemical Engineering, Institute of Engineering,
Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand
*School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand
(Received 6 February 2006 • accepted 2 May 2006)

Abstract—This work focused on the preparation of activated carbon from eucalyptus and wattle wood by physical activation with CO_2 . The preparation process consisted of carbonization of the wood samples under the flow of N_2 at 400 °C and 60 min followed by activating the derived chars with CO_2 . The activation temperature was varied from 600 to 900 °C and activation time from 60 to 300 min, giving char burn-off in the range of 20-83%. The effect of CO_2 concentration during activation was also studied. The porous properties of the resultant activated carbons were characterized based on the analysis of N_2 adsorption isotherms at -196 °C. Experimental results showed that surface area, micropore volume and total pore volume of the activated carbon increased with the increase in activation time and temperature with temperature exerting the larger effect. The activated carbons produced from eucalyptus and wattle wood had the BET surface area ranging from 460 to 1,490 m²/g and 430 to 1,030 m²/g, respectively. The optimum activation conditions that gave the maximum in surface area and total pore volume occurred at 900 °C and 60 min for eucalyptus and 800 °C and 300 min for wattle wood. Under the conditions tested, the obtained activated carbons were dominated with micropore structure (\sim 80% of total pore volume).

Key words: Activated Carbon, Eucalyptus, Wattle Wood, Physical Activation, Porous Properties

INTRODUCTION

Activated carbon is a highly porous material which is widely used as an adsorbent for separation, purification and recovery processes. Activated carbon can be produced from a variety of carbonaceous materials such as bituminous coal [Ahmadpour and Do, 1996], heavyoil fly ash [Caramuscio et al., 2003], coconut shell [Daud and Ali, 2004], oil-palm stone [Lua and Guo, 2000], corn hull [Zhang et al., 2004], rice straw [Oh and Park, 2002], sugar cane bagasse [Darmstadt et al., 2001], pistachio-nut shell [Yang and Lua, 2003], candlenut shell [Turmuzi et al., 2004], macadamia nutshell [Ahmadpour and Do, 1997] and other agricultural or industrial wastes materials. Approximately half of the raw materials used for activated carbon production are lignocellulosic materials [Durán-Valle et al., 2005]. Porous properties of activated carbon depend on the types of starting materials as well as the method and conditions of preparation. There are generally two processes for the preparation of activated carbon: physical activation and chemical activation. Chemical activation is performed in a single step of combined carbonization and activation by using chemical activating agents such as ZnCl₂, KOH or H₃PO₄ at temperatures in the range from 400-800 °C. These chemical activating agents are known to act as dehydrating agents that inhibit the formation of tar and other by-products thus enhancing the yield of carbon [Howe-Grant, 1992]. Physical activation involves the carbonization of a carbonaceous material in an inert atmosphere followed by the activation of the resulting char at higher temperatures (800-1,100 °C) in the presence of activating agents such as

Activated carbon has been used as an all-purpose sorbent. It finds extensive applications in the removal of organic and inorganic contaminants from solutions as well as in gas purification processes. Some of the related works that have been recently reported in the literature are the removal of metsulfuron-methyl (synthetic organic herbicide) from aqueous solution [Kim et al., 2001], the removal of surfactants (octanoic acid and dodecanoic acid) from industrial process streams [Kim et al., 2005], the adsorption of heavy metal ions (Cu²⁺, Cd²⁺, Ca²⁺, Pb²⁺ and Hg²⁺) from aqueous solutions [Xiao and Thomas, 2005], and the adsorption of volatile organic compounds such as chloropentafluoroethane (CFC-115) [Moon et al., 1998], 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) [Kim et al., 2002] and dichloromethane [Kim et al., 2002] from gaseous wastes.

Eucalyptus and wattle wood, which were used as raw materials in this work, are one type of lignocellulosic carbonaceous materials. These woods are fast growing and abundantly available in Thailand. Over the past decade, there has been considerable interest in producing activated carbon from woods by physical activation. For example, Sainz-Diaz and Griffiths [2000], Sánchez et al. [2001] and Zhang et al. [2004] prepared activated carbons by CO₂ activation from wood furniture waste, *Quercus agrifolia* wood waste and oak wood waste, respectively. The results showed that CO₂ activation produced mostly micropores (more than 78%) within woodbased activated carbon. Tancredi et al. [1996] prepared activated carbons by CO₂, CO₂-O₂ and steam activation from *Eucalyptus grandis* sawdust. They found that the presence of O₂ in the CO₂ atmo-

 $^{{\}rm CO}_2$, air, steam or a mixture of these gases. The advantages of chemical activation are lower energy cost, shorter activation time, and higher product yield and surface area as compared to the method of physical activation.

[†]To whom correspondence should be addressed. E-mail: chaiyot@ccs.sut.ac.th

sphere increased the micropore and macropore volume, but had no effect on mesopore development. On the other hand, steam activation led to a higher development of mesopore and macropore volume. Arriagada et al. [1997] and Ismadji et al. [2005] prepared activated carbons by steam activation using *Eucalyptus globulus* chips and teak sawdust, respectively. They found that steam activation produced carbons with high macroporosity.

The aim of this work is to study the preparation and characterization of activated carbons from eucalyptus and wattle wood by physical activation with CO₂. The effects of activation temperature, activation time and CO₂ concentration were investigated. The porous properties of the prepared activated carbons including BET surface area, micropore volume, total pore volume and pore size distribution were determined.

Table 1. Analysis of raw materials

	Eucalyptus	Wattle wood	
Proximate analysis (wt%)			
Fixed carbon	18.3	16.6	
Volatile matters	76.4	78.3	
Ash	1.2	1.9	
Moisture	4.1	3.2	
Lignocellulosic composition (wt%)			
Cellulose	57.3	62.0	
Hemicelluloses	16.8	12.6	
Lignin	25.9	25.4	

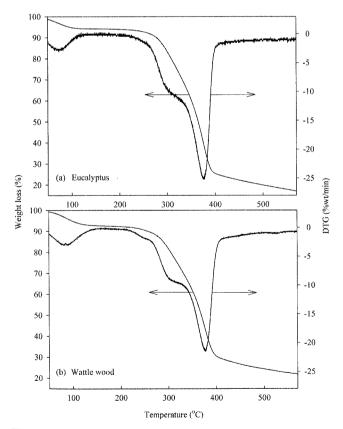


Fig. 1. TGA and DTG curves of (a) eucalyptus and (b) wattle wood heated at 25 °C/min under nitrogen atmosphere.

MATERIALS AND METHODS

Eucalyptus and wattle wood chip were used as the starting precursors for activated carbon production in this work. Each raw material was milled and sieved to obtain the 20×30 mesh size fractions (average size of 0.714 mm). Next, the obtained wood samples were dried at 110 °C for 24 h in an oven to remove excess moisture in the raw materials. The proximate analysis and lignocellulosic composition of the pre-dried woods were determined. The proximate analysis was carried out by a thermogravimetric analyzer (SDT 2960 Simultaneous DSC-TGA). The cellulose and hemicelluloses contents were determined by using the method of Browing [Lee and Rowell, 2004]. The lignin content was determined by using TAPPI

Table 2. Properties of derived char

	Eucalyptus	Wattle wood	
Proximate analysis (wt%)			
Fixed carbon	65.4	64.9	
Volatile matters	30.1	30.7	
Ash	0.2	1.3	
Moisture	4.3	3.1	
S_{BET} (m ² /g)	4.9	4.7	
$V_T(cm^3/g)$	0.03	0.02	

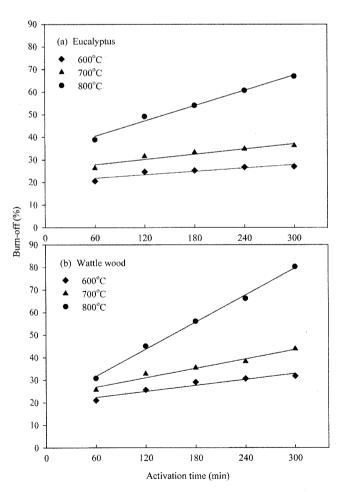


Fig. 2. Burn-off of the chars at various times and temperatures of activation (a) eucalyptus and (b) wattle wood.

Korean J. Chem. Eng.(Vol. 23, No. 6)

Standard Test Method (T222-om-98), available from the Technical Association of the Pulp and Paper Industry [Jiménez et al., 2001]. Thermal analysis of both woods were also performed by using a thermogravimetric analyzer (SDT 2960 Simultaneous DSC-TGA) under N_2 atmosphere. In this experiment, the temperature was programmed to increase from room temperature to 600 $^{\circ}\mathrm{C}$ at the heating rate of 25 $^{\circ}\mathrm{C/min}$.

On the carbonization step, about 7 g of the dried wood sample was loaded into a ceramic boat and placed in the heated zone of a horizontal ceramic tube furnace (Carbolite CTF12/75/700/201) with N_2 flowing through at a constant rate of 100 cm³/min. The furnace was heated from room temperature to 400 °C at the heating rate of 25 °C/min and held at this temperature for 60 min. Then, the carbonized char was cooled down to room temperature under the flow of N_2 . Both woods gave approximately the same char yields of 33% by weight.

The char derived from the carbonization step was further activated in a packed-bed reactor (2.5 cm diameter and 10 cm long) made of stainless steel. The reactor was packed with char particles, placed inside the horizontal ceramic tube furnace and heated from room temperature to the desired activation temperature under the constant flow of $N_{\rm 2}$ at 100 cm³/min using the heating rate of 25 °C/min. When the desired activation temperature was reached, the $\rm CO_2$ was allowed to flow into the reactor at the rate of 100 cm³/min, giving

50 vol% of CO_2 concentration in the gas mixture, and the furnace was kept at the set temperature for the required activation time. When the activation period was completed, the flow of CO_2 was stopped and the activated carbon product was cooled down to room temperature under the flow of N_2 . The activation was performed at temperatures varying from 600 to 900 °C and activation time from 60 to 300 min, giving activated carbons with various degrees of char burn-off. The burn-off is defined as the weight difference between the weight of the original char, W_0 , and that of the activated carbon, W_0 , divided by the weight of the original char with both weights being on a dry basis. That is, on a percentage basis,

% burn-off=
$$\frac{W_0 - W}{W_0} \times 100\%$$
 (1)

In studying the effect of CO_2 concentration, the flow of CO_2 was varied from 50 to $200~\rm cm^3/min$ and N_2 flow rate was correspondingly varied from 150 to $0~\rm cm^3/min$ to maintain a constant total gas flow rate at $200~\rm cm^3/min$, thus giving CO_2 concentration to vary from 25-100% by volume. For these tests, the activation temperature and activation time were fixed at $800~\rm ^{\circ}C$ and $120~\rm min$, respectively.

Specific surface area and pore volume of the resulting char and activated carbons were determined using N_2 gas adsorption data at $-196\,^{\circ}\text{C}$ obtained by employing an automated adsorption apparatus

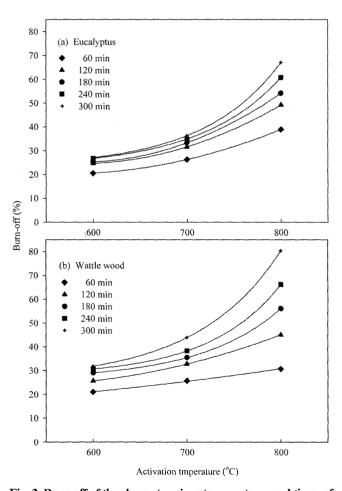


Fig. 3. Burn-off of the chars at various temperatures and times of activation (a) eucalyptus and (b) wattle wood.

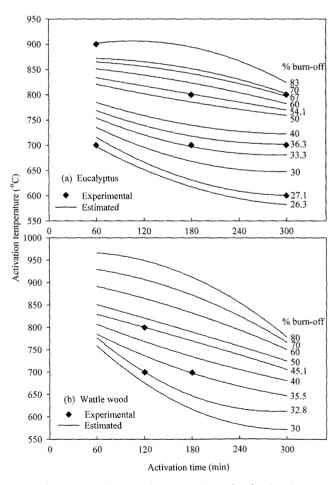


Fig. 4. Contour of % burn-off as a function of activation time and temperature (a) eucalyptus and (b) wattle wood.

(Micromeritics ASAP 2010). Prior to the adsorption measurement, the char or activated carbon was first degassed at 300 °C under vacuum (<50 mmHg) for 12 h to remove moisture and other volatiles. The specific surface area, S_{BET} , was estimated by applying Brunauer-Emmett-Teller (BET) equation [Do, 1998]. The micropore volume, V_{mic} , was calculated by using Dubinin-Radushkevich (DR) equation [Do, 1998]. The total pore volume, V_{T} , was found from the amount of N_2 gas adsorbed at the relative pressure of 0.99 and converted it to the corresponding volume of liquid state. Average pore diameter, D, was calculated from $4V_T/S_{BET}$. Pore size distributions were computed by applying the Density Functional Theory (DFT) method [Olivier, 1995].

RESULTS AND DISCUSSION

1. Properties of Raw Materials and Chars

The proximate analysis and lignocellulosic composition of the wood samples are shown in Table 1. The results show that eucalyptus and wattle wood have fixed carbon content of 18.3 and 16.6%, respectively, and contain a high proportion of volatile matter but with low ash content. These fixed carbon content are comparable with other biomass materials used to produce activated carbons such as corn cob (16.1%) [Chang et al., 2000], sugar cane bagasse (16.2%)

500 (a) Eucalyptus 400 300 200 Volume adsorbed (cm³/g STP) 100 600°C - 700°C → 900°C 800°C 0 .2 .4 8. 1.0 0.0 .6 (b) Wattle wood 400 300 200 100 600°C ─**■** 850°C 700°C +--- 900°C - 800°C .2 1.0 0.0 Relative pressure (P/P⁰)

Fig. 5. Adsorption and desorption isothems of N_2 at $-196\,^{\circ}\mathrm{C}$ of activated carbons prepared from (a) eucalyptus and (b) wattle wood at different activation temperatures (activation time 60 min).

[Darmstadt et al., 2001], oil-palm stone (16.4%) [Lua and Guo, 2000], rice straw (17.8%) [Oh and Park, 2002], coconut shell (18.6%) [Daud and Ali, 2004] and pistachio-nut shell (21.6%) [Yang and Lua, 2003]. The results indicate that both eucalyptus and wattle wood are potential precursors for the preparation of activated carbons. According to Jagtoyen and Derbyshire [1998], hard woods have cellulose content about 52%, hemicellulose content about 14-25% and lignin content about 25-34%. Thus, both eucalyptus and wattle wood used in this work are classified as hard wood type.

The thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) curves of both woods under $\rm N_2$ atmosphere are presented in Fig. 1. The DTG curves show an initial peak between 60 and 110 °C, which corresponds to the mass loss of absorbed moisture of approximately 5%. Following this peak, the DTG curves showed two decomposition steps: the first decomposition shoulder peak at about 280-320 °C is attributed to the thermal depolymerization of hemicelluloses [Ouajai and Shanks, 2005] (mass loss 25%); the major second decomposition peak at about 370-380 °C is attributed to cellulose decomposition [Ouajai and Shanks, 2005] (mass loss 30%). It should be noted that the carbonization temperature of 400 °C was chosen based on the thermogravimetric analysis results to ensure the complete devolatilization process, thus forming char with high carbon content.

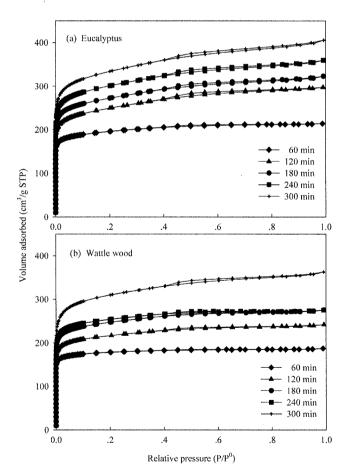


Fig. 6. Adsorption and desorption isothems of N_2 at $-196\,^{\circ}\mathrm{C}$ of activated carbons prepared from (a) eucalyptus and (b) wattle wood at different activation times (activation temperature $800\,^{\circ}\mathrm{C}$).

Table 2 lists the results of proximate analysis of the resulting char obtained from each wood. It is clear that the fixed carbon content of char was significantly increased after carbonization. The surface area of the chars before activation were extremely low as shown in Table 2, partly due to the pore blockage by tarry products after the carbonization process.

2. Char Burn-off

Fig. 2 and Fig. 3 shows, respectively, the effect of activation time and temperature on the extent of char burn-off due to $C\text{-}CO_2$ gasification reaction. For both woods, the results show that the burn-off increases linearly with increasing the time of activation. Below 700 °C the char gasification rate, which is proportional to the slope of the curve, is relatively constant but at higher temperature of 800 °C the rate increases by about twice for eucalyptus and three times for wattle wood. It also appears that the rate of gasification during activation

at the same temperature is higher for wattle wood, although the lignocellulosic compositions of both woods are not so different. Fig. 3 shows that temperature has a marked effect on the extent of burnoff, particularly at temperatures higher than 700 °C and activation time longer than 120 min where the burn-off increases rapidly with temperature. The removal of carbon atom by the effect of time and temperature during the activation step would lead to the creation of new pores and enlargement of existing pores, with temperature of activation exerting the most effect. Fig. 4 illustrates the dependence of char burn-off, which is indicative of extent of gasification reaction and hence the pore development, on the activation time and temperature for eucalyptus and wattle wood-derived chars. These burn-off contours were prepared directly from Fig. 2 and Fig. 3 by interpolation and are useful for the selection of preparation conditions (time and temperature) to obtain a specified burn-off.

Table 3. Effect of activation temperature and time on the porous properties of prepared activated carbons (CO₂ flow rate of 100 cm³/min, N₂ flow rate of 100 cm³/min and heating rate of 25 °C/min)

min, N ₂ flow rate of 100 cm ³ /min and heating rate of 25 °C/min)								
Activation temperature (°C)	Activation time (min)	Burn-off (%)	S_{BET} (m ² /g)	V_{mic} (cm ³ /g)	V_T (cm ³ /g)	$%V_{mic}$	D (nm)	
Eucalyptus								
600	60	20.6	460	0.21	0.23	91.3	2.00	
	120	24.7	463	0.21	0.23	91.3	1.99	
	180	25.3	467	0.21	0.23	91.3	1.97	
	240	26.8	471	0.21	0.23	91.3	1.95	
	300	27.1	473	0.21	0.23	91.3	1.94	
700	60	26.3	507	0.23	0.25	92.0	1.97	
	120	31.6	556	0.25	0.28	89.3	2.01	
	180	33.3	560	0.25	0.28	89.3	2.00	
	240	34.9	577	0.26	0.30	86.7	2.08	
	300	36.3	589	0.26	0.31	84.0	2.10	
800	60	38.9	651	0.29	0.33	87.9	2.03	
	120	49.2	828	0.36	0.43	83.7	2.08	
	180	54.1	907	0.40	0.50	80.0	2.20	
	240	60.7	1003	0.44	0.56	78.6	2.23	
	300	67.0	1110	0.49	0.63	77.8	2.27	
850	60	66.1	1016	0.44	0.53	83.0	2.09	
900	60	83.0	1491	0.66	0.80	82.5	2.15	
Wattle wood								
600	60	21.0	433	0.20	0.21	95.2	1.94	
•	120	25.7	439	0.20	0.21	95.2	1.91	
	180	29.1	451	0.21	0.23	91.3	2.04	
	240	30.7	454	0.21	0.23	91.3	2.03	
	300	31.9	512	0.23	0.26	88.5	2.03	
700	60	25.7	473	0.22	0.23	95.6	1.94	
	120	32.8	511	0.24	0.26	92.3	2.04	
	180	35.5	548	0.25	0.28	89.3	2.04	
	240	38.3	580	0.26	0.30	86.7	2.07	
	300	43.9	606	0.27	0.32	84.4	2.11	
800	60	30.8	591	0.27	0.29	93.1	1.96	
	120	45.1	719	0.32	0.37	86.5	2.06	
	180	56.1	823	0.37	0.43	86.0	2.09	
	240	66.2	846	0.38	0.45	84.4	2.13	
	300	80.3	1032	0.46	0.56	82.1	2.17	
850	60	56.8	828	0.37	0.44	84.1	2.16	
900	60	67.1	1000	0.44	0.54	81.5	2.16	

 S_{BET} =BET surface area, V_{mic} =micropore volume, V_T =total pore volume, D=average pore diameter

3. Adsorption Isotherms

Adsorption and desorption isotherms of N_2 at -196 °C for activated carbons prepared at different activation temperatures and activation times are shown in Fig. 5 and Fig. 6, respectively. As shown in Fig. 5, the activated carbon prepared at 900 °C has the highest adsorption capacity for both woods. For the activated carbons prepared at 600-800 °C, the nitrogen uptake is significant only in the low-pressure range, i.e., for the relative pressure less than 0.2. In the high-pressure range, slight increase in adsorption is observed. According to the IUPAC classification [Patrick, 1995] this shape of isotherm is of Type I, indicating that the prepared activated carbons contain predominantly micropores. At higher activation temperatures (>800 °C), the adsorption-desorption curves show closed hysteresis loops at relative pressure higher than about 0.4, indicating an increased proportion of mesopore volume. Fig. 5 also reveals that at the same activation time (60 min), the increase in activation temperature can produce activated carbon with higher adsorption capacity from eucalyptus wood than that obtained from wattle wood.

As shown in Fig. 6 for activation temperature of 800 °C, the activated carbon prepared at 300 min has the highest adsorption capacity for both woods. For the activated carbon prepared at 60 min, the isotherm is still of Type I isotherm. However, at higher activation times (>120 min), the adsorption-desorption curves for both woods start to show small hysteresis loops at relative pressure greater than 0.4. This tends to change the isotherms from Type I to Type IV, although the effect is not so pronounced.

4. Porous Properties of Activated Carbons

Table 3 and Fig. 7 show the effect of the activation temperature

and activation time on the porous properties of the obtained carbons. From Table 3 and Fig. 7, for both carbon series with activation time 60 min, the increase in activation temperature leads to an increase in BET surface area, micropore volume and total pore volume. Increasing in activation temperature from 600 to 700 °C leads to an increase in the percentage of micropore volume. However, at temperatures higher than 700 °C, the percentage of micropore volume decreases while BET surface area, micropore volume and total pore volume increase with the increase in activation temperature. This signifies that at higher temperatures there were not only the development of micropore by C-CO₂ reaction and the opening of blocked pores by devolatilization process, resulting in the formation of new micropores, but also the widening of existing micropore by gasification reaction and possibly by the collapse of adjacent pore walls. For carbon samples with activation time longer than 60 min, the BET surface area, micropore volume and total pore volume also increases with activation temperature but the percentage of micropore volume decreases. This again is caused by the corresponding increase in the extent of gasification reaction for long activation time. It is also observed that at temperatures greater than 700 °C, the relative increase in the surface area with increasing temperature is higher for longer activation time.

At any activation temperature, the effect of increasing activation time is to increase BET surface area, micropore volume and total pore volume but the proportional increase is much greater at higher activation temperatures. There is also a tendency for the percentage of micropore volume to decrease as the time of activation is increased, with higher temperatures having the larger effect (see Table 3).

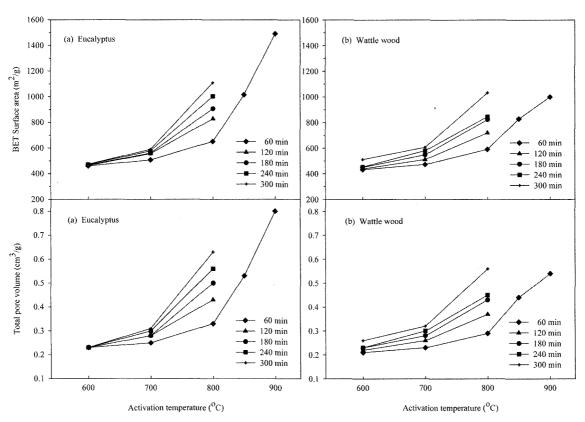


Fig. 7. Effect of the activation temperature and activation time on the porous properties of the activated carbon prepared from (a) eucalyptus and (b) wattle wood.

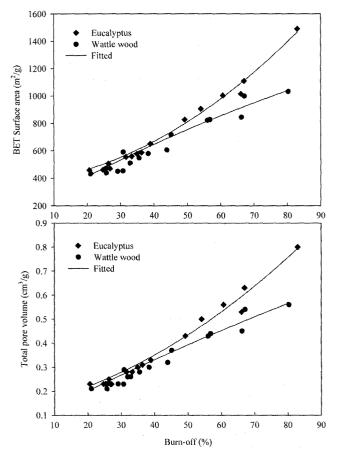


Fig. 8. Effect of char burn-off on the porous properties of the activated carbon.

Fig. 8 shows the correlation between char burn-off and the BET surface area and total pore volume. It is observed that, both the BET surface area and total pore volume increase with the increase in the degree of burn-off as expected. Wattle wood carbon shows an approximate linear relationship over the entire range of burn-off up to 80%. The eucalyptus carbon gives approximately the same surface area and total pore volume as wattle wood carbon up to about 40% burn-off but gives higher porous property values at higher burn-off with the difference becoming greater at higher burn-off levels. Table 4 lists the fitted parameters for estimating the porous properties of activated carbons from both woods, using the following quadratic equation:

$$y=a_1+a_2x+a_3x^2$$
 (2)

where y represents BET surface area or total pore volume and x is the % burn-off, covering burn-off up to about 80%.

Fig. 9 shows typical pore size distribution of activated carbon

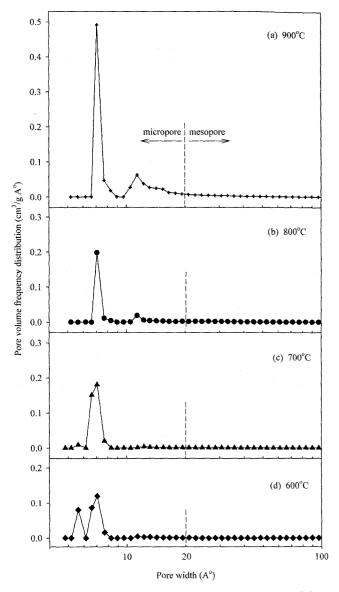


Fig. 9. Pore size distribution of activated carbons prepared from eucalyptus wood at different activation temperature (a) 900 °C, (b) 800 °C, (c) 700 °C and (d) 600 °C (activation time 60 min).

prepared from eucalyptus wood at activation time 60 min and temperature varying from 600-900 °C by applying the Density Functional Theory (DFT) method. The curves of pore size distribution show the main peak around 7 Å for all carbons, which corresponds to the ultramicropore size (pore size ≤7 Å) [Lastoskie et al., 1993]. The second smaller peak appears at 12 Å for 800 and 900 °C activation temperatures corresponding to the supermicropore (pore size

Table 4. Parameters of empirical equations for estimating porous properties of activated carbon from % burn-off

W	BET surface area (m²/g)				olume (cm³/g)			
Wood type a_1 a_2 a_3	\mathbb{R}^2	a_1	a_2	a_3	\mathbb{R}^2			
Eucalyptus	364.67	2.33	-0.13	0.9989	0.14	2.96×10^{-3}	5.99×10 ⁻⁵	0.9972
Wattle wood	153.64	13.63	-0.03	0.9955	0.06	7.12×10^{-3}	-1.07×10^{-5}	0.9967

November, 2006

Table 5. Effect of CO ₂ concentration on the porous properties of prepared activated carbons (heating rate of 25 °C/min, activation temperature 800 °C and activation time 120 min)									
Wood type	CO ₂ concentration (%)	Burn-off (%)	S_{BET} (m ² /g)	V_{mic} (cm ³ /g)	V_T (cm ³ /g)	$% V_{mic}$	D (nm)		
Eucalyptus	25	44.4	753	0.33	0.40	82.5	2.12		

Wood type	CO ₂ concentration (%)	Burn-off (%)	S_{BET} (m ² /g)	V_{mic} (cm ³ /g)	V_T (cm ³ /g)	$% V_{mic}$	D (nm)
Eucalyptus	25	44.4	753	0.33	0.40	82.5	2.12
71	50	49.2	828	0.36	0.43	83.7	2.08
	75	54.8	841	0.37	0.45	82.2	2.14
	100	56.8	980	0.43	0.55	78.2	2.24
Wattle	25	44.0	684	0.30	0.35	85.7	2.05
	50	45.1	719	0.32	0.37	86.5	2.06
	75	52.0	806	0.36	0.42	85.7	2.08
	100	62.1	833	0.37	0.45	82.2	2.16

between 7 to 20 Å) [Lastoskie et al., 1993]. The curves also show that the micropore volume (area under the curve) present in the activated carbon products varies in the sequence: 600 °C<700 °C<800 °C < 900 °C, which is in agreement with V_{mic} as shown in Table 3.

In this work, activated carbon prepared from eucalyptus and wattle wood gave the highest BET surface area of 1,491 m²/g and 1,032 m²/g, respectively, and this occurred at the highest burn-off level for both woods (83% for eucalyptus and 80.3% for wattle wood). These surface area are comparable with other activated carbons prepared by CO₂ activation, for example, from corn hull (1,010 m²/g) [Zhang et al., 2004], candlenut shell (1,050 m²/g) [Turmuzi et al., 2004], pistachio-nut shell (1,064 m²/g) [Yang and Lua, 2003] or oil-palm stone (1,410 m²/g) [Lua and Guo, 2000]. In addition, as seen in Table 3, the percentage of micropore volume of activated carbons is more than 78%. This indicates that CO₂ activation develops mostly micropores within wood-based activated carbon. This result is also in agreement with the work of Tancredi et al. [1996], Sainz-Diaz and Griffiths [2000], Sánchez et al. [2001] and Zhang et al. [2004].

5. Effect of CO₂ Concentration

Table 5 shows the effect of CO₂ concentration on the burn-off, BET surface area, micropore volume, total pore volume and percentage of micropore volume. The increase in CO₂ concentration from 25-100% by volume leads to an increase in burn-off, BET surface area, micropore volume and total pore volume in the order of 30% and 22% for eucalyptus and wattle wood, respectively. There is a tendency for the average pore size of the prepared activated carbons to increase with the increase in CO₂ concentration, except for the eucalyptus-based activated carbon prepared at 50 vol% CO₂. The activated carbon prepared from eucalyptus wood gave larger average pore size than that of the activated carbon prepared from wattle wood. The increased CO₂ concentration enhances the C-CO₂ reaction, which results in an increase in the burn-off level and hence better pore development of the activated carbons.

CONCLUSIONS

The results obtained from this work showed that highly porous activated carbon can be produced from eucalyptus and wattle wood by carbon dioxide activation. The effect of activation temperature, activation time and CO₂ concentration on the porous properties of activated carbon were investigated. The increase in activation temperature, activation time and CO₂ concentration led to an increase in BET surface area, micropore volume and total pore volume with

temperature showing the largest effect. The effects of activation time and temperature on these porous properties can be represented by the burn-off level of char during activation. Eucalyptus-based activated carbon gave maximum surface area and total pore volume of 1,491 m²/g and 0.80 cm³/g, respectively, which occurred at 900 °C and 60 min of activation conditions. In comparison, wattle woodbased activated carbon gave maximum BET surface area and total pore volume at 800 °C and 300 min with corresponding values of 1,032 m²/g and 0.56 cm³/g. The activated carbons derived from both eucalyptus and wattle wood by CO2 activation produced internal pores mainly in the micropore size range, constituting about 80% of total pore volume. Overall, both eucalyptus and wattle woodbased activated carbons showed similar adsorptive behavior and porous characteristics with eucalyptus giving relatively better pore development under the preparation conditions studied.

ACKNOWLEDGEMENT

This work was supported by The Royal Golden Jubilee (RGJ) Ph.D. Program under The Thailand Research Fund (TRF) and is gratefully acknowledged (Grant 1.C.TS/45/A.1 PHD/0132/2545).

REFERENCES

Ahmadpour, A. and Do, D. D., "The preparation of activated carbons from coal by chemical and physical activation," Carbon, 34, 471 (1996).

Ahmadpour, A. and Do, D. D., "The preparation of activated carbon from macadamia nutshell by chemical activation," Carbon, 35, 1723

Arriagada, R., García, R., Molina-Sabio, M. and Rodríguez-Reinoso, F., "Effect of steam activation on the porosity and chemical nature of activated carbons from Eucalyptus globulus and peach stones," Microporous Mater., 8, 123 (1997).

Caramuscio, P., Stefano, L. D., Seggiani, M., Vitolo, S. and Narducci, P., "Preparation of activated carbons from heavy-oil fly ashes," Waste Manag., 23, 345 (2003).

Chang, C. F., Chang, C. Y. and Tsai, W. T., "Effects of burn-off and activation temperature on preparation of activated carbon from corn Cob agrowaste by CO₂ and steam," J. Coll. Int. Sci., 232, 45 (2000).

Darmstadt, H., Garcia-Perez, M., Chaala, A., Cao, N. Z. and Roy, C., "Co-pyrolysis under vacuum of sugar cane bagasse and petroleum residue properties of the char and activated char products," Carbon, 39, 815 (2001).

Korean J. Chem. Eng.(Vol. 23, No. 6)

- Daud, W. M. A. W. and Ali, W. S. W., "Comparison on pore development of activated carbon produced from palm shell and coconut shell," *Biores. Technol.*, **93**, 63 (2004).
- Do, D. D., Adsorption analysis: Equilibria and kinetics, Imperial College Press, Singapore (1998).
- Durán-Valle, C. J., Gómez-Corzo, M., Pastor-Villegas, J. and Gómez-Serrano, V., "Study of cherry stones as raw material in preparation of carbonaceous adsorbents," J. Anal. Appl. Pyrol., 73, 49 (2005).
- Howe-Grant, M., *Encyclopedia of chemical technology*, John Wiley & Sons, New York (1992).
- Ismadji, S., Sudaryanto, Y., Hartono, S. B., Setiawan, L. E. K. and Ayucitra, A., "Activated carbon from char obtained from vacuum pyrolysis of teak sawdust: pore structure development and characterization," *Biores. Technol.*, 96, 1364 (2005).
- Jagtoyen, M. and Derbyshire, F., "Activated carbon from yellow poplar and white oak by H₃PO₄ activation," *Carbon*, **36**, 1085 (1998).
- Jiménez, L., García, J. C., Pérez, I., Ariza, J. and López, F., "Acetone pulping of wheat straw influence of the cooking and beating conditions on the resulting paper sheets," *Ind. Eng. Chem. Res.*, 40, 6201 (2001).
- Kim, S. H., Bidkar, A., Ngo, H. H., Vigneswaran, S. and Moon, H., "Adsorption and mass transfer characteristics of metsulfuron-methyl on activated carbon," *Korean J. Chem. Eng.*, **18**, 163 (2001).
- Kim, S. J., Cho, S. Y. and Kim, T. Y., "Adsorption of chlorinated volatile organic compounds in a fixed bed of activated carbon," *Korean J. Chem. Eng.*, **19**, 61 (2002).
- Kim, J.-H., Wu, S. H. and Pendleton, P., "Effect of surface properties of activated carbons on surfactant adsorption kinetics," *Korean J. Chem. Eng.*, **22**, 705 (2005).
- Lastoskie, C., Gubbins, K. E. and Quirke, N., "Pore size distribution analysis of microporous carbons: A density functional theory approach," *J. Phys. Chem. B*, **97**, 4786 (1993).
- Lee, B.-G and Rowell, R. M., "Removal of heavy metal ions from aqueous solutions using lignocellulosic fibers," *J. Natural Fibers*, **1**, 97 (2004).
- Lua, A. C. and Guo, J., "Activated carbon prepared from oil palm stone

- by one-step CO₂ activation for gaseous pollutant removal," *Carbon*, **38**, 1089 (2000).
- Moon, D. J., Chung, M. J., Kim, H., Lee, B. G, Lee, S. D. and Park, K. Y., "Adsorption equilibria of chloropentafluoroethane on activated carbon powder," *Korean J. Chem. Eng.*, 15, 619 (1998).
- Oh, G.H. and Park, C.R., "Preparation and characteristics of rice-straw-based porous carbons with high adsorption capacity," *Fuel*, **81**, 327 (2002).
- Olivier, J. P., "Modeling physical adsorption on porous and nonporous solids using density functional theory," *J. Porous Mater.*, **2**, 9 (1995).
- Ouajai, S. and Shanks, R. A., "Composition, structure and thermal degradation of hemp cellulose after chemical treatments," *Polym. Degrad. Sta.*, **89**, 327 (2005).
- Patrick, J. W., *Porosity in carbons: characterization and applications*, Edward Arnold, London (1995).
- Sainz-Diaz, C. I. and Griffiths, A. J., "Activated carbon from solid wastes using a pilot-scale batch flaming pyrolyser," *Fuel*, **79**, 1863 (2000).
- Sánchez, A. R., Elguézabal, A. A. and Saenz, L. L. T., "CO₂ activation of char from *Quercus Agrifolia* wood waste," *Carbon*, **39**, 1367 (2001).
- Tancredi, N., Cordero, T., Rodríguez-Mirasol, J. and Rodríguez, J. J., "Activated carbons from uruguayan eucalyptus wood," *Fuel*, 75, 1701 (1996).
- Turmuzi, M., Daud, W. R. W., Tasirin, S. M., Takriff, M. S. and Iyuke, S. E., "Production of activated carbon from candlenut shell by CO₂ activation," *Carbon*, **42**, 453 (2004).
- Xiao, B. and Thomas, K. M., "Adsorption of aqueous metal ions on oxygen and nitrogen functionalized nanoporous activated carbons," *Langmuir*, 21, 3892 (2005).
- Yang, T. and Lua, A. C., "Characteristics of activated carbons prepared from pistachio-nut shells by physical activation," *J. Coll. Int. Sci.*, 267, 408 (2003).
- Zhang, T., Walawender, W. P., Fan, L. T., Fan, M., Daugaard, D. and Brown, R. C., "Preparation of activated carbon from forest and agricultural residues through CO₂ activation," *Chem. Eng. J.*, **105**, 53 (2004).