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EFFECT OF HEATING TEMPERATURE ON THE PROPERTIES OF CHARS AND ACTIVATED CARBONS PREPARED FROM OIL PALM STONES

J. Guo and A. C. Lua

Division of Thermal and Fluids Engineering, School of Mechanical and Production Engineering
Nanyang Technological University, Nanyang Avenue, 639798 Singapore

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Abstract

The effects of heating temperature of pyrolysis and activation processes on the textural and chemical properties of the chars and activated carbons prepared from oil palm stones, an abundant palm-oil mill solid waste, were studied. For both pyrolysis and activation, relatively high temperature was essential to develop pore structures in the chars and activated carbons. However, too high temperature would cause pore narrowing and pore enlargement during pyrolysis and activation, respectively. The temperature had an insignificant effect on the inorganic components of the chars and activated carbons, but affected their surface organic functional groups significantly.

Keywords: activated carbon, char, heating temperature, surface area and porosity, surface chemistry

Introduction

Preparation of activated carbons from carbonaceous materials (e.g. coal, lignite, wood, coconut shell and some agricultural by-products) normally involves two stages, i.e., pyrolysis (or called carbonisation) and activation. In the first stage, the starting materials are pyrolysed at a moderate temperature (about 700–900°C) to remove the volatile matters and produce chars with rudimentary pore structures. Subsequently, in the second stage, the resulting chars are subjected to a partial gasification at a higher temperature (usually around 900°C) with oxidising gases, such as carbon dioxide, to produce final products with well-developed and accessible internal porosity [1]. In fact, a large amount of studies have been reported on the preparation and characterisation of activated carbons from various starting materials under different conditions [2–6].

However, no reports about the effects of heating temperature on the properties, especially the chemical structures of chars and activated carbons prepared from oil palm stones have been found in the literature. In Malaysia, which is the largest palm oil producer in the world, more than one million tons of oil palm stones are estimated to be generated annually [7]. Preparation of activated carbons from oil palm stones is

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considered to be an economical way to utilise these cheap and abundant agricultural by-products [8]. The aim of this study was to investigate the effect of heating temperature on the textural and chemical properties of activated carbons in order to optimise the preparation conditions.

Experimental

Sample preparation

Raw oil palm stones were obtained from an oil palm mill in Selangor, Malaysia. As received stones were crushed and sieved to 2.0–2.8 mm size fraction. Table 1 shows the characteristics of raw oil palm stones. These agricultural solid wastes appear to be suitable materials for high quality activated carbons because of their inherent high solid density and relatively high fixed-carbon but low ash contents. Both pyrolysis of the raw oil palm stones and activation of the resulting chars were carried out in a stainless-steel vertical reactor (length of 550 mm and 38 mm internal diameter) which was placed in a tube furnace (818P, Lenton) with a programmable PID controller. The starting materials were pyrolysed at 400–900°C for 3 h under a nitrogen gas (99.9995% purity) flow of 150 $cm^3\ min^{-1}$. The resulting chars were then activated with carbon dioxide gas (99.998% purity, 100 $cm^3\ min^{-1}$) at 750–950°C for 2 h.

Table 1 Characteristics of raw oil palm stones

Density and porosity			Proximate analysis				Surface area	
ρ_s/g cm^{-3}	ρ_a/g cm^{-3}	ε/%	M/wt%	VM/wt%	FC/wt%	A/wt%	S_{BET}/$m^2\ g^{-1}$	S_M/$m^2 g^{-1}$
1.53	1.47	3.9	5.3	76.5	16.4	1.8	1.5	0.3

Sample characterisation

A thermogravimetric analyser (TA-50, Shimadzu) was used to carry out the proximate analysis which was expressed in terms of moisture (M), volatile matter (VM), fixed carbon (FC) and ash (A) contents [9]. An ultra-pycnometer (UPY-1000, Quantachrome) and a mercury intrusion porosimeter (Poresizer-9320, Micromeritics) were used to measure the solid and apparent densities of the samples, respectively. For known solid density ρ_s and apparent density ρ_a, the porosity ε can be calculated as follows:

$$\varepsilon=(\rho_s-\rho_a)/\rho_s\times 100\% \tag{1}$$

Adsorption characterisations of the chars and activated carbons were determined by nitrogen adsorption at –196°C with an accelerated surface area and porosimetry system (ASAP-2000, Micromeritics). The BET surface area (S_{BET}) was calculated from the adsorption isotherms by using the Brunauer-Emmett-Teller (BET) equation [10]. The Dubinin-Radushkevich (DR) equation was used to calculate the micropore volume and micropore surface area (S_M) [11]. The pore size distribution was determined using the BJH model [12].

An X-ray diffractometer (PW-1830, Philips) was used to determine the inorganic components of the chars and activated carbons. The X-ray patterns were recorded in the scan range 2θ=10–70°, at a scan rate of 0.1 degree per min. The surface organic structures of the samples were studied by Fourier transform infrared spectroscopy (FTIR-2000, Perkin Elmer). The spectra were recorded from 4000 to 400 cm^{-1}.

Results and discussion

Proximate analysis

The proximate analyses (dry basis) of chars pyrolysed at different pyrolysis temperatures for a retention time of 3 h are listed in Table 2. As the pyrolysis temperature increased from 400 to 900°C, the volatile content of the chars decreased progressively from 64.6 to 2.2% whilst both the fixed carbon and ash content increased. This was to be expected because increased devolatilisation during pyrolysis resulted in the char to be predominantly carbon. Table 3 shows the proximate analyses (dry basis) of activated carbons prepared at different temperatures for a retention time of 2 h. For all samples investigated here, their volatile contents were negligible because the remains in the chars had been released during the activation stage. As the activation temperature increased from 750 to 950°C, the fixed carbon contents decreased significantly due to the conversion of carbon into gaseous products by carbon dioxide gasification, resulting in relatively higher ash contents in the final products.

Table 2 Proximate analyses of chars pyrolysed at various temperatures for 3 h (dry basis)

Pyrolysis temp./°C	VM/	FC/	A/
		%	
400	64.6	31.5	3.9
500	46.5	48.9	4.6
600	30.6	63.4	6.0
700	15.6	76.9	7.5
800	7.9	83.7	8.4
900	2.2	88.6	9.2

Density and porosity

The density of the activated carbon depends not only on the nature of the starting material and char but also the preparation process [13]. Densities and porosity of the chars pyrolysed at 400–900°C for 3 h are shown in Table 4. As seen from Table 4, increasing the pyrolysis temperature up to 800°C would increase the solid densities of the chars and decrease their apparent densities, resulting in development of the porosity from 8.3 to 24.0%. However, when the temperature was further increased to 900°C, the apparent density of the char increased and the porosity decreased. This was probably due to the sintering effect, which resulted in the shrinkage of the char particle and consequently narrowing or even closing some pores. Table 5 shows the densities and porosity of the activated carbons prepared at 750–950°C for 2 h. As the activation temperature increased, the porosity increased progressively since activation process not only enlarged the pores created during the pyrolysis but also generated some new pores [14].

Table 3 Proximate analyses of carbons activated at various temperatures for 2 h (dry basis)

Activation temp./°C	VM/	FC/	A/
		%	
750	0.5	90.4	9.1
800	0.4	88.2	11.4
850	0.2	87.3	12.5
900	0.2	85.6	14.2
950	0.1	80.4	19.5

Table 4 Densities and porosity of chars pyrolysed at various temperatures for 3 h

Pyrolysis temp./°C	ρ_s/	ρ_a/	ε/%
	g cm^{-3}		
400	1.57	1.44	8.3
500	1.60	1.40	12.5
600	1.63	1.35	17.2
700	1.64	1.32	19.5
800	1.67	1.27	24.0
900	1.69	1.31	22.5

Table 5 Densities and porosity of carbons activated at various temperatures for 2 h

Activation temp./°C	ρ_s/	ρ_a/	ε/%
	g cm^{-3}		
750	1.73	1.09	37.0
800	1.87	0.98	47.6
850	1.91	0.92	51.8
900	1.95	0.90	53.8
950	2.04	0.85	58.3

Surface area and pore size distribution

The most important property of the activated carbon is its adsorptive capacity, which is related to the specific surface area and pore structure [15]. The effect of pyrolysis temperature on the BET and micropore surface areas of the chars is shown in Fig. 1. When the pyrolysis temperature was 400°C, pyrolysis reactions had just commenced, thereby producing very small BET surface area. This phenomenon was due to the inadequacy of heat energy to drive away any substantial amounts of volatile. As the temperature was increased from 500 to 800°C, increasingly greater volatile matters were released progressively during pyrolysis thereby resulting in the development of some new porosities, and hence the BET surface areas increased progressively. With further increase of temperature to 900°C, the BET surface area decreased due to some of the pores being sealed off as a result of the sintering effect at such a high temperature. Generally, a high pyrolysis temperature is needed to remove volatile matters and enhance porosity before detrimental effects set in at a higher temperature. As seen from Fig. 1, the micropore surface area shows a similar trend to that for the BET surface area.

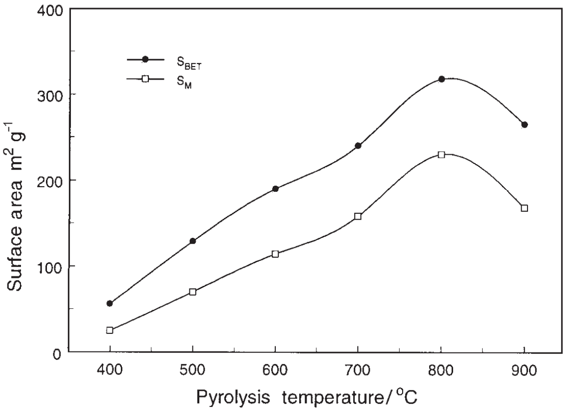

Fig. 1 Effect of pyrolysis temperature on the BET and micropore surface areas of the chars

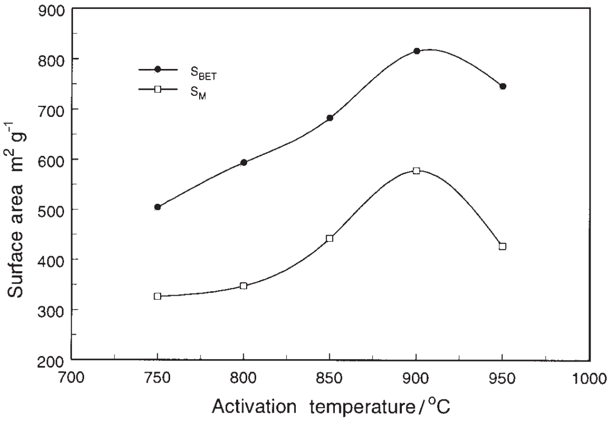

Fig. 2 Effect of activation temperature on the BET and micropore surface areas of the activated carbons

The effect of activation temperature on the BET and micropore surface areas of the activated carbons is shown in Fig. 2. The BET and micropore surface areas increased continuously with increasing activation temperature from 750 to 900°C. However, for the activation temperature of 950°C, the BET surface area decreased due to the over-reaction of carbon with carbon dioxide gas, resulting in the conversion of microporosity into mesoporosity or even macroporosity. This was confirmed by a more significant decrease of micropore surface area, indicating an extended conversion of micropores into meso- and macropores.

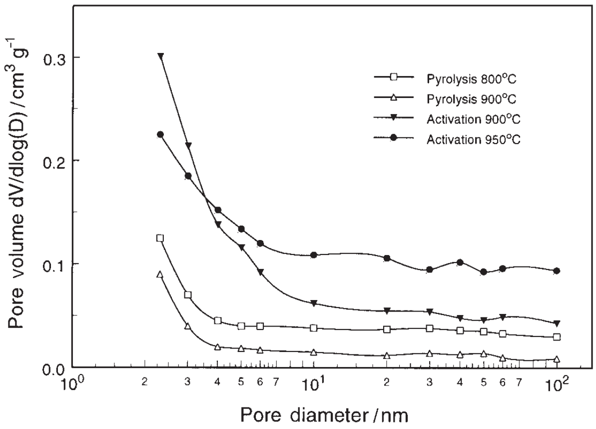

Fig. 3 Pore size distributions of chars and activated carbons prepared under different conditions

Figure 3 shows the pore size distribution of chars and activated carbons for different preparation conditions. For the chars pyrolysed at 800 and 900°C, the sharp increase of pore size distribution curves as the pore diameter decreased below 2 nm indicated the formation of micropores. This increase became especially significant in the activated carbons prepared at 900°C, indicating predominant micropores. However, activated carbons prepared at 950°C had less micropores but more mesopores and macropores than those at 900°C because of the over-reaction of carbon with carbon dioxide gas.

Inorganic component

The adsorptive capacity of activated carbons is determined by their physical or porous structure and also strongly influenced by the chemical structure of their surface [16]. The X-ray diffraction (XRD) patterns of chars and activated carbons prepared under different conditions are shown in Fig. 4. For XRD patterns of chars pyrolysed at 800 and 900°C, $CaCO_3$ as calcite (C), $CaSO_4$ as anhydrite (A) and CaO as lime (L) were present; for those of activated carbons prepared at 900 and 950°C, $CaCO_3$ as calcite mainly and also as vaterite (V) and $CaSO_4$ as anhydrite were the dominant components but lime peaks disappeared. For both pyrolysis and activation, the effects

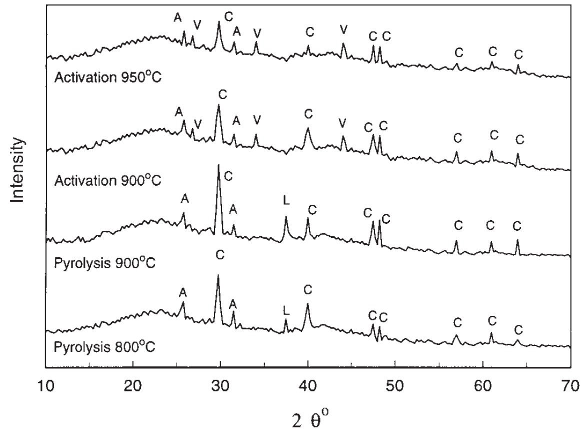

Fig. 4 X-ray diffraction patterns of chars and activated carbons prepared under different conditions

of heating temperatures on the inorganic components of the chars and activated carbons were insignificant. However, activation process changed the inorganic component by transforming lime into vaterite due to the carbon dioxide atmosphere.

Surface organic functional group

The FTIR spectra of raw oil palm stone and chars pyrolysed at different temperatures are shown in Fig. 5. The spectrum of the raw oil palm stone displayed the following bands:
3528 cm^{-1}: O–H stretching vibration in alcohols (assignment range 3700–3000 cm^{-1});
2972 cm^{-1}: C–H stretching vibration in alkane groups (3300–2700 cm^{-1});
1747 cm^{-1}: C=O stretching vibration in ketones (1850–1650 cm^{-1});
1648 cm^{-1}: C=O stretching vibration in quinones (1690–1635 cm^{-1});
1507 cm^{-1}: C=C stretching vibration in aromatic rings (around 1600 or 1500 cm^{-1});
1262 cm^{-1}: C–O stretching vibration in ethers (1300–900 cm^{-1});
817 and 719 cm^{-1}: C–H out-of-plane bending in benzene derivatives (900-600 cm^{-1}).

The main oxygen groups present in the raw oil palm stone were carbonyl groups (such as ketone and quinone), ethers and alcohols (including phenols). These results are in agreement with the surface chemistries of other agricultural by-products, such as peach stones [17] and rockroses [18]. The spectrum of the char pyrolysed at a low temperature of 400°C was similar to that of the raw material. As the pyrolysis temperature increased to 600 or 800°C, the ether and alcohol structures were not found due to their thermal instabilities. At 900°C, the ketonic groups were absent for the same reason, but the aromatic rings and quinones remained.

The FTIR spectra of char and activated carbons prepared at different temperatures are shown in Fig. 6. After activation, besides aromatic rings and quinones, the band attributed to C≡O stretching vibrations at 2354 cm^{-1} could be found. This was probably due to the enriched carbon dioxide atmosphere during activation process.

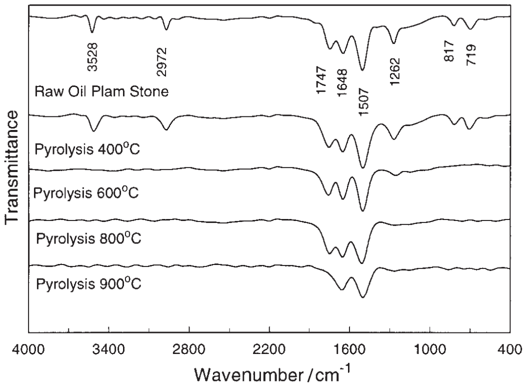

Fig. 5 FTIR spectra of raw oil palm stone and chars pyrolysed at different temperatures

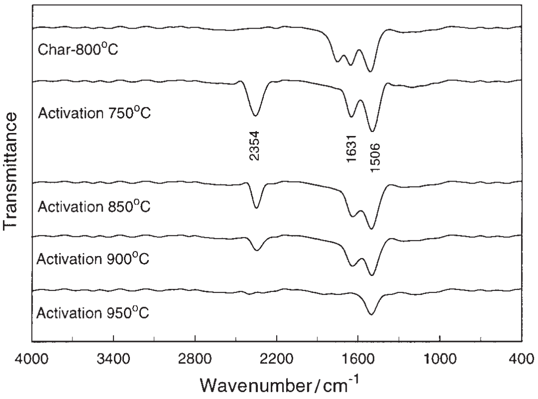

Fig. 6 FTIR spectra of char and activated carbons prepared at different temperatures

As the activation temperature increased, the bands became weaker, indicating lower concentration of the surface organic components. For the activated carbon prepared at 950°C, only aromatic rings remained. In brief, the surface organic functional groups of the chars and activated carbons were markedly affected by the pyrolysis and activation temperatures, respectively.

Conclusions

The experimental results showed that relatively high pyrolysis temperature was essential to remove volatile matters and develop rudimentary pore structures. However, an extreme temperature of 900°C would cause a sintering effect, resulting in a decrease in porosity. As the activation temperature increased from 750 up to 900°C, the BET and micropore surface areas increased progressively since the activation process not only enlarged the pores created during the pyrolysis but also generated some new pores. However, at 950°C, the surface area, especially the micropore surface area dropped dramatically due to the over-reaction of carbon with carbon dioxide. The pore size distributions also confirmed the conversion of microporosity into mesoporosity or even macroporosity at a higher activation temperature.

The temperature had an insignificant effect on the inorganic components of the chars and activated carbons, but activation changed the inorganic component by transforming lime into vaterite due to the carbon dioxide atmosphere. For the surface organic functional groups, as the pyrolysis temperature increased, the ether and alcohol structures and ketonic groups were absent due to their thermal instabilities. After activation at 750°C, the band attributed to C≡O stretching vibrations could be found. For the activated carbon prepared at 950°C, only aromatic rings remained. In brief, the surface organic functional groups of chars and activated carbons were markedly affected by the pyrolysis and activation temperatures, respectively.

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