Production of Activated Carbon from Palm-oil Shell by Pyrolysis and Steam Activation in a Fixed Bed Reactor

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Received 3 May 1999

ABSTRACT The research objective was to produce activated carbon from palm-oil shells by one step pyrolysis and steam activation in a fixed bed reactor with the diameter of 100 mm. The studied variables were activation temperature, activation time, palm-oil shell sizes and flow rate of air. The results showed that the optimum condition was 1.18-2.36 mm of palm-oil shells at 750°C for 2 hr with air flow rate of 0.72 nl/min, using steam as an activating agent. The characteristics of the prepared activated carbon with the yield of 19.66 % were bulk density of 0.5160 g/cm^3, 6.03 % ash, iodine number of 620.16 mg/g, methylene blue number of 176.75 mg/g and 559.48 m^2/g of BET surface area. In addition, it had been found that when there was an addition of pyrolysis time with air before steam activation led to higher porosity development than one step pyrolysis and steam activation. From these experimental data, it was observed that the maximum surface area and adsorption capacity could be obtained from using 200 g of 1.18-2.36 mm of palm-oil shells at 750°C for 3 hr by addition pyrolysis with air for 30 min (0.72 nl/min) before steam activation. The resulting characteristics of the final product with the yield of 12.18 % were bulk density of 0.5048 g/cm^3, 7.54 % ash, iodine number of 766.99 mg/g, methylene blue number of 189.20 mg/g and 669.75 m^2/g BET surface area.

KEYWORDS: palm-oil shell, activated carbon, pyrolysis and steam activation.

INTRODUCTION

Activated carbons are widely used as adsorbents in gas and liquid-phase separation processes, purification of products and water cleaning operations. One of the most important fields in terms of consumption is in water and wastewater treatment, where activated carbons with a relatively high surface area and a well developed porosity are needed. Usually the production of activated carbons involves two stages[1] : the carbonization of the raw materials followed by a high temperature activation, at 800-1000°C, of the resulting chars. The method used in this study combines the two stage into a single one, while the treatment temperature is considerably lower, 600-800°C. This method is preferable to the two-stage treatment from an economic point of view.[2]

Palm-oil cultivation in Thailand has shown increasing economic significance with its expanding market demand at an average growth rate of 15% a year.[3] Expansion of the palm oil industry was followed by the generation of enormous amounts of by-products at plantation grounds, oil press and refineries. It has been estimated that the pressing process produces about 292,367 tons of palm mesocarp fiber, 157,428 tons of palm-oil shells and 742,163 tons of empty fruit bunches as waste in 1997.[4]

Commercial processes to produce activated carbon used a variety of raw material including peat, coal, wood and coconut shell. Among these, palm-oil shell is the interesting raw material because of its enormous amounts as by-products in palm oil industry. From proximate analysis (Table 1), it was observed that palm-oil shells have properties similar to coconut shell but palm-oil shell has more ash than coconut shell and BET surface area showed that palm-oil shell has higher number of external pore than coconut shell, so palm-oil shell is likely to be a precursor for the production of activated carbon. Conversion of the palm-oil shell to value-added product such as activated carbon will directly solve part of the environmental problems and turning the by-product into a resource for another industry.

Gergova *et al*. (1993)[2] used a one step pyrolysis/steam activation to produce activated carbons from coal and agricultural by-products. 50 g sample was

Table 1. The proximate analysis and the BET surface area, compared of coconut shell and palm-oil shell.

Raw material	%VM	% Ash	% FC	Surface area (m^2/g)		
				S_{total}	S_{Micro}	$S_{External}$
Coconut shell	80.80	0.40	18.80	0.9	0.0	0.9
Palm-oil shell	79.66	2.05	18.29	12.2	0.0	12.2

heated in a tube furnace at a heating rate 10°C/min, at atmospheric pressure and a steam flow rate of 0.5 dm^3/hr. The experiments were carried out in a temperature range of 600-700°C. The samples were heated at the final temperature for 1, 2 and 3 hr. Activated carbons were produced from apricot stones at 700°C for 2 hr, had the highest surface area (1,175 m^2/g).

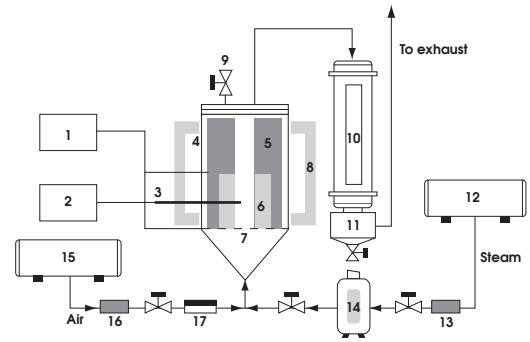
Patra Panyawatanakit (1997)[5] produced activated carbon from palm oil shell. The processes of carbonization and activation with superheated steam were studied. The palm-oil shells were carbonized at 400°C for 1 hr. Next, the charcoal was activated with superheated steam. The optimum condition for activation was 0.850-0.355 mm of charcoal size at 900°C for 1 hr. The resulting characteristics were yield of 19.31%, iodine number of 779.0 mg/g, methylene blue number of 136.96 mg/g, total surface area of 670.1 m^2/g.

The objectives of this study were to find the influence of parameters and optimum conditions for the production of activated carbon by one step pyrolysis and steam activation in a fixed bed reactor, and to study physical and chemical properties of the produced activated carbon.

Experimental

This experiment used palm-oil shells for the production of activated carbon by pyrolysis and steam activation in one stage. The palm-oil shells were crushed and sieved to six particle sizes of < 0.60, 0.60-1.18, 1.18-2.36, 2.36-4.75, 4.75-6.00 and 6.00-8.00 mm before being treated. The various parameters which had the effect in the production of the activated carbon: activation temperatures (600-800°C), activation times (1-3 hr), sizes of the raw material, flow rates of air and addition of pyrolysis with air before steam activation were studied in order to determine the optimum condition.

The fixed bed pyrolysis and steam activation reactor was a stainless steel tube of 100 mm inside diameter, 4.50 mm wall thickness and 300 mm in length. The tube was fitted with a perforated stainless steel gas distributor. The distributor had 0.5 mm diameter holes on a triangular pitch. The fixed bed was heated by an electric coil (1000 watt), and the bed temperature was measured by type K thermocouple. The bed could be operated between ambient temperature and 900°C, and the temperature was controlled to an accuracy of ± 5°C by means of a temperature controller. Air flew into the bed which was controlled by using a rotameter. Steam



1. AC Arc welder
2. Temperature controller
3. Thermocouple
4. Stainless steel tube
5. Castable
6. Heating coil
7. Distributor plate
8. Insulator
9. Sample feed and removal port
10. Condenser
11. Separator
12. Boiler
13. Steam trap
14. Preheater
15. Air pump
16. Moisture separation
17. Rotameter

Fig 1. A schematic of the experimental setup.

was preheated by burner before flowing into the bed. A schematic of the experimental setup are shown in Figures 1.

The fixed bed reactor was heated until the bed temperature reached 600°C. The 200 g of the palm-oil shells about 3 cm.of depth were charged into the reactor with 10% of air. Then, the temperature in the fixed bed reactor was raised and maintain at the final temperature 600, 650, 700 and 750°C. The excess steam was continued on, passing up through the bed for 1, 2 and 3 hr. The addition of pyrolysis time with air before steam activation, the palm-oil shells were pyrolysed with air for 30 min at final temperature (600, 650, 700, 750 and 800°C) before activation with steam for 1, 2 and 3 hr. The products were characterized as % yield, % ash, bulk density, iodine number, methylene blue number and BET surface area.

Results and Discussion

The optimum temperature for pyrolysis and steam activation

From Table 2 and Figure 2, when the temperature is at 600 to 750°C for 1, 2 and 3 hr, the decrease of % yield can be attributed to remove light volatile matter first following by big molecules with the increase of temperature or partial combustion with air that is according to the results of the experiment (from 29% down to 22% at 1 hour). When divided by the amount of substance which has been left out as lesser

which look like that the % ash increases (Figure 4). Moreover, the higher temperature makes the substances which stays deeply in the particle has the chance to disintegrate and explode. Therefore, the type of pores which is called mesopores would be formed more, noticed by the increased number of MB about 13-15 %, from 600 °C changing to 750 °C.

Table 2 the bulk density (Figure 3) decreased, the iodine number (Figure 5) and the metyhlene blue number (Figure 6) increase with an increased in temperature from at 600 to 750°C and for all activation time of 1, 2 and 3 hr. In the first stage (600-650°C), The bulk density remained constant while the iodine number and the metyhlene blue number increased slowly because the diffusion of volatile matter hindered the penetration of steam into the surface of palm-oil shells; as a result, the development of porosity is less. When the temperature increased from 650 to 700°C, the bulk density decreased quickly while the iodine number and the metyhlene blue number increased inversely, because most of volatile matter was diffused from granules in the first stage, so the steam penetrated easily into the surface of palm-oil shells; as a result, the high development of porosity. When the temperature increased from 700 to 750°C, the bulk density decreased and the iodine number increases more slowly than in the first temperature range while the metyhlene blue number still increased because micropores would have coalesced, resulting in mesopores reducing the iodine numbers.

From these results, the optimum temperature was 750°C since the iodine number and the methylene blue number of the resulted activated carbon were the highest of values.

Table 2. Characteristics of activated carbon from palm-oil shells at different temperatures and times (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

T (°C)	t (hr)	%Y	On dry basis			
			BD (g/cm³)	%Ash	IA (mg/g)	MB (mg/g)
600	1	29.02	0.5447	4.71	338.08	146.76
	2	27.44	0.5345	4.79	367.99	153.12
	3	26.71	0.5303	4.97	439.88	155.04
650	1	27.75	0.5416	4.85	362.74	152.14
	2	23.78	0.5305	4.92	401.45	159.42
	3	23.10	0.5244	5.46	466.01	165.69
700	1	24.63	0.5293	5.13	452.79	161.71
	2	21.89	0.5219	5.32	472.87	163.88
	3	21.13	0.5088	5.84	515.20	169.79
750	1	22.36	0.5244	5.54	508.10	165.16
	2	20.81	0.5141	5.73	524.18	171.74
	3	16.90	0.5047	6.52	543.64	176.06

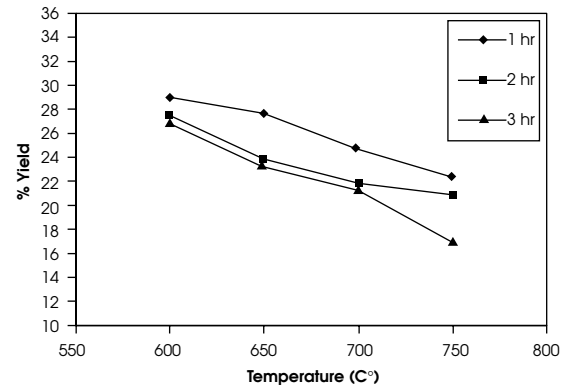


Fig 2. Effect of temperature on % yield at different times (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

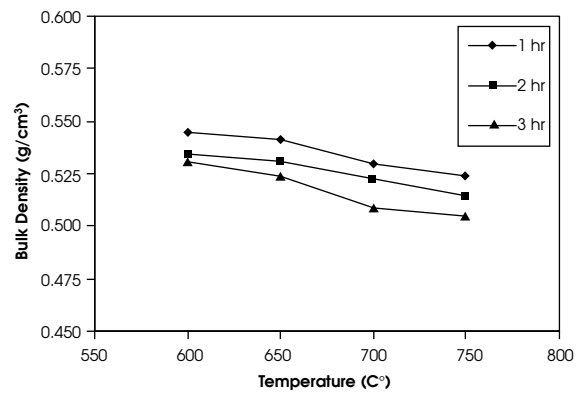


Fig 3. Effect of temperature on bulk density at different times (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

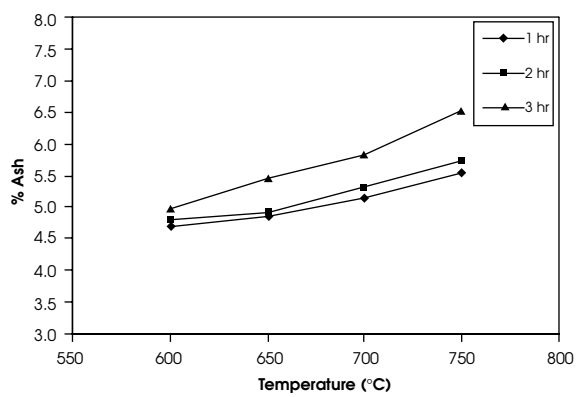


Fig 4. Effect of temperature on % ash at different times (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

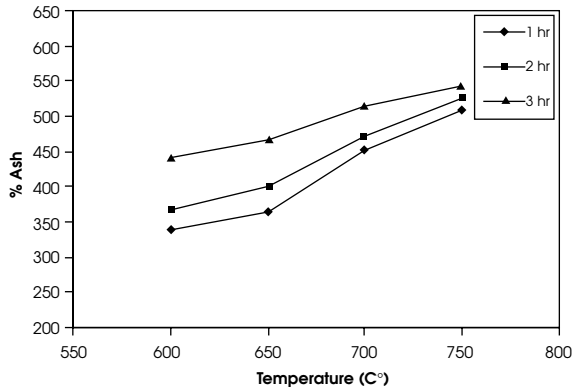


Fig 5. Effect of temperature on iodine number at different times (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

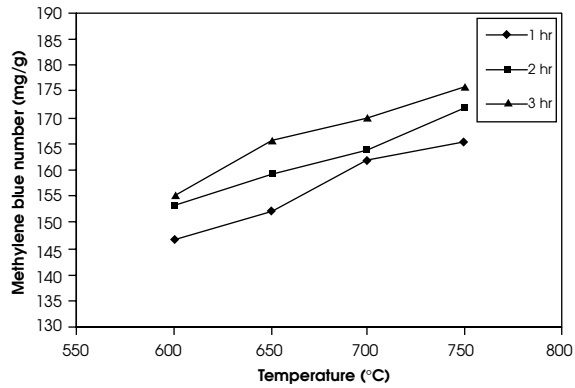


Fig 6. Effect of temperature on methylene blue number at different times (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam)

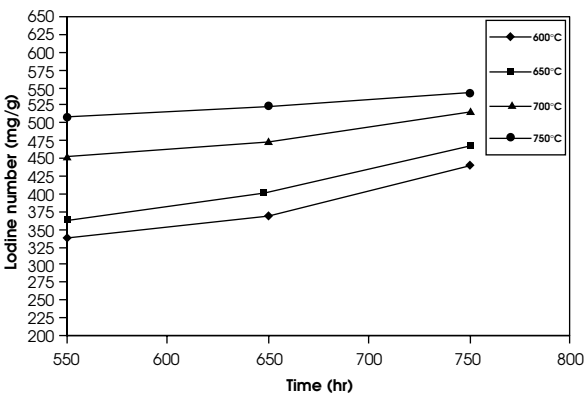


Fig 7. Effect of time on iodine number at different temperatures (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min

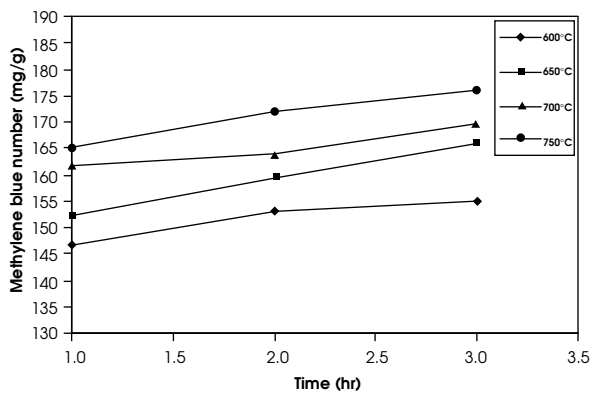


Fig 8. Effect of time on methylene blue number at different temperatures (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

Influence of time on pyrolysis and steam activation

From Table 2 and Figure 7, when increasing the time on pyrolysis and steam activation range of 1-3 hr at 600, 650, 700 and 750°C, the iodine number increased. At the same time and temperature, the methylene blue number (Figure 8) increased too.

We could explain in the same way that when increasing the time on pyrolysis and steam activation (Figure7), some volatile compounds which were in the inner part of particle could evaporate more with long activation. The steam would bring out substance in the pore to diffuse to exterior of the particle. Therefore, the surface area increased, shown from the number of iodine which increased about 13.7% per increasing 1 hour of activation at 600°C, and 5% at 750°C. When there was a reaction of partial oxidation during pyrolysis and steam activation the temperature increased very rapidly. Thus, the carbon on the surface and compounds which were easily evaporated and fallen of , reacted with oxygen fast which caused small pores gathering together and became large pores. That could be seen from the increased number of MB with the average of 4% per increasing 1 hour of activation (Figure 7-8).

The optimum condition for pyrolysis and steam activation was 750°C for 2 hr. Characteristics of activated carbon with the yield of 20.81 % were bulk density of 0.5141 g/cm^3, ash of 5.73 %, iodine number of 524.18 mg/g and methylene blue number of 171.74 mg/g. This optimum condition will be used for the study of other variables after this.

Table 3. Characteristics and surface area of activated carbon from palm-oil shells at different sizes (750°C for 2 hr, 200 g, air 0.72 nl/min and steam).

Palm-oil shell sizes (mm)	%Y	on dry basis				S_{BET} (m^2/g)
		BD (g/cm^3)	% Ash	IA (mg/g)	MB (mg/g)	
< 0.60	17.34	0.5737	38.54	308.52	156.55	364.65
0.60 - 1.18	18.35	0.5424	11.08	585.15	169.97	534.41
1.18 - 2.36	19.66	0.5160	6.03	620.16	176.75	559.48
2.36 - 4.75	20.81	0.5141	5.73	524.18	171.16	498.52
4.75 - 6.00	21.27	0.4637	5.33	480.51	165.56	462.23
6.00 - 8.00	23.38	0.4374	5.67	455.73	162.91	427.38

Influence of size of palm-oil shells for pyrolysis and steam activation on characteristic of activated carbon

From Table 3 and Figures 9, the size of particles was an important parameter. Whether we could get good quality activated carbon depends on this parameter. When we used small particle (0.60 –1.18 mm in size), the bed packed very tight. The air and steam passed difficulty through the bed. Heat and mass transfer was not good and caused less evaporation of compound, which could be noticed from the high number of bulk density. But if we let the air and steam pass through very small particles bed, the entrainment of fine particles would cause less product yield. From the Table 3, the particle size of <0.6 mm. gave %yield only 17, high %ash of 38%and more bulk density, which was different from the particle size of >4 mm. gave 21%. When the particle size were bigger (2.36-8.00 mm), there was less entrainment, cracking or evaporation of compounds from pores inside particles were more. The smaller the size, the more the loss, we obtained high specific area (S_{BET}); for example, the average size of 3.00mm. would get more number of (S_{BET}) than that of 5.00mm.10%. While large particles gave more product yield, the amount of volatile matter was driven out less which cause less number of (S_{BET}), such as the size 7.00 mm. has less (S_{BET}) than that 5.00mm. by 10%. Therefore, the size of the optimum was around 1.18 to 2.36mm.

Influence of air flow rate on air for pyrolysis and steam activation

In Table 4 and Figures 10, the increased air flow rate effected the quality of the products less, due to the happening of partial oxidation in all of the conditions of experiment, the temperature did not relatively increase rapidly. Because the faster the air flow rate , the faster the removal of the heat out of the bed, more ash was left on the particles. There might be more turbulence in the bed which would make more diffusion of the volatile matter from particles pores. Table 4 shown small different in characteristic of activated carbon of all used flow rate of air. The optimum flow rate of air is 0.72 nl/min. which could be determined from Figure 10.

Table 4. Characteristics of activated carbon from palm-oil shells at different flow rate of air (750°C for 2 hr, size 1.18 - 2.36 mm, 200 g and steam).

Flow rate of air (nl/min)	%Y	on dry basis			
		BD (g/cm^3)	% Ash	IA (mg/g)	MB (mg/g)
0.20	25.19	0.5357	5.12	492.14	171.26
0.49	23.04	0.5118	5.53	540.76	173.47
0.72	19.66	0.5160	6.03	620.16	176.75
0.97	15.62	0.5104	7.67	635.42	182.28

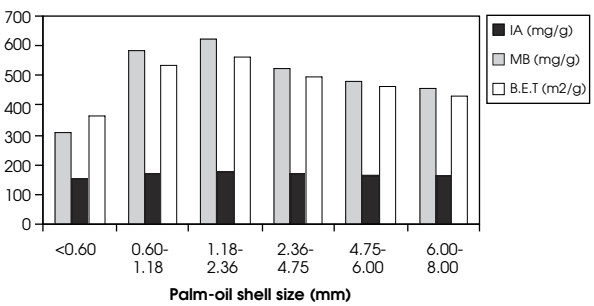


Fig 9. Effect of size on iodine number, methylene blue number and B.E.T surface (750°C for 2 hr, 200 g, air 0.72 nl/min and steam).

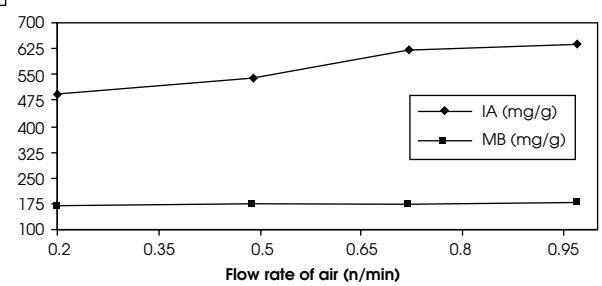


Fig 10. Effect of air flow rate on iodine number and methylene blue number (750°C for 2 hr, size 1.18 - 2.36 mm, 200 g and steam).

Table 5. Characteristics and surface area of activated carbon from palm-oil shells at different temperatures and times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

T (°C)	t (hr)	%Y	%M	on dry basis				S_{BET} (m^2/g)
				BD (g/cm^3)	%Ash	IA (mg/g)	MB (mg/g)	
600	1	22.53	8.35	0.5277	4.88	467.17	160.49	434.41
	2	20.06	6.83	0.5234	4.95	499.63	165.53	480.43
	3	15.59	9.56	0.5201	6.03	553.02	169.47	497.74
650	1	19.70	9.08	0.5240	5.45	515.22	170.15	486.95
	2	18.47	9.32	0.5165	5.81	542.23	175.34	507.89
	3	13.47	10.44	0.5143	6.73	630.58	178.71	554.26
700	1	19.28	9.47	0.5198	5.90	586.20	172.95	511.72
	2	17.08	9.64	0.5105	6.42	602.98	180.94	531.62
	3	12.48	11.38	0.5060	7.33	679.41	183.44	583.52
750	1	18.71	10.64	0.5178	6.06	635.16	177.58	557.38
	2	14.18	10.48	0.5069	6.63	667.14	182.61	572.93
	3	12.18	12.19	0.5017	7.54	766.99	189.20	669.75
800	1	16.75	10.38	0.5162	6.23	577.57	188.00	556.26
	2	12.90	10.05	0.5051	6.61	604.27	198.00	585.34
	3	10.34	10.22	0.4996	7.72	735.31	200.91	660.85

The optimum temperature for pyrolysis with air 30 min before steam activation

Table 5, when the temperature increased from 600 to 800°C for 1, 2 and 3 hr, the % yield decreased (Figure 11) while the % ash increased (Figure 13). Because at high temperature, the volatile matter was removed suddenly and the partial oxidation of some carbon in particles develop quickly; with this result, some carbon in the surface changes into ash and the porosity was developed highly in granules at the same time. We could see that the temperature 800°C could get less yield than at 600°C by 40%and more ash by 3.5 % at 2 hr of activation .

Table 5 and Figure 12, the bulk density decreases with the increasing temperature from 600 to 800°C for 1, 2 and 3 hr. The bulk density decreased quickly because the steam easily penetrated into the surface of palm-oil shell particles, so it meant that the porosity development of activated carbon increased. As a result, the weight of activated carbon decreased, thus the bulk density in this temperature range decreased.

From Table 5 and Figure 14, the temperature increased from 600 to 750°C for 1, 2 and 3 hr, the iodine number increased. But when the temperature increased to 800°C, the iodine number decreased, which was the same trend as that BETsurface area (Figure 16). When the temperature increased from 600 to 800°C for 1, 2 and 3 hr (Figure 15) the methylene blue number would increase.

Figures 14-16, the iodine number, the methylene blue number and the BET surface area would increase when the temperature increased from 600 to 650°C. Increasing of the BET surface area, the iodine number and the methylene blue number in this step were more than those without pyrolysis with air. The main reason for this preliminary pyrolysis was to form some large pores in the palm-oil shells surface which could be used as transport arteries. These large pores would allow the diffusion of low-molecular weight compounds of the volatile matter and easy penetration of steam into the interior of the palm-oil shells particles; as a result, the porosity was developed quickly at low temperature.[6] After the temperature has been increased from 650 to 750°C, the increasing of the iodine number and the methylene blue number of pyrolysis with air 30 min were in the vicinity with increasing of the iodine number and the methylene blue number of those without pyrolysis with air. At 750 to 800°C, the iodine number decreased, while the methylene blue number still increased. And the BETsurface area decreased until it was constant because the reaction in this temperature range, was too extreme, so the micropores would have coalesced, resulting in mesopores. These results could be observed from the decreasing of micropore surface area and the increasing of external surface area, while the BET surface area was nearly constant. The 24% more of the iodine number and 15% more of MB (Figure 14 and 15) shown that there was diffusion of

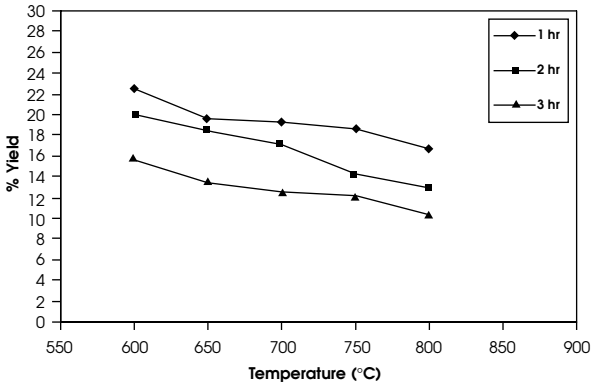


Fig 11. Effect of temperature on %yield at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

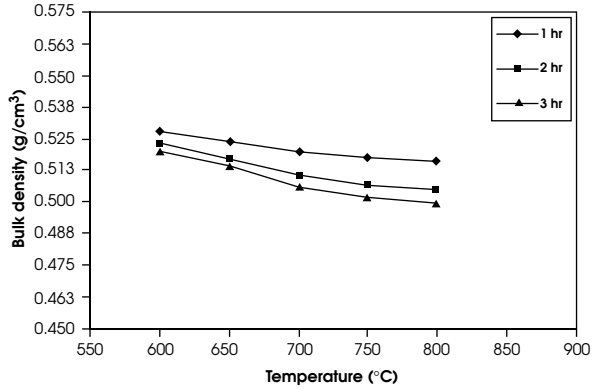


Fig 12. Effect of temperature on bulk density at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

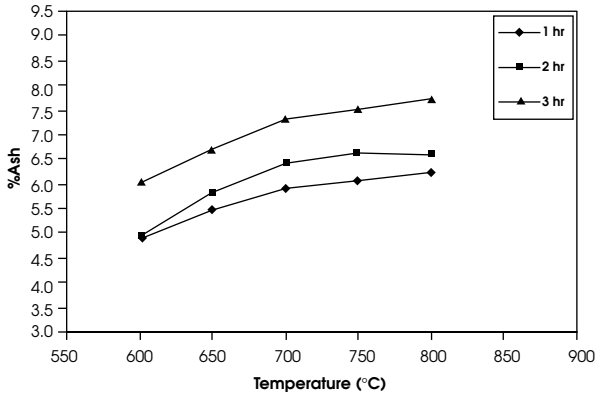


Fig 13. Effect of temperature on %ash at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

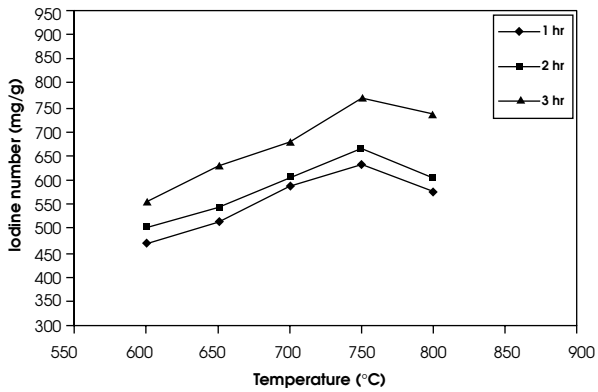


Fig 14. Effect of temperature on iodine number at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

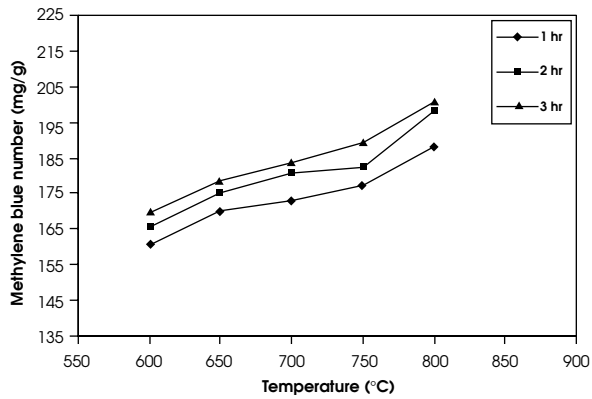


Fig 15. Effect of temperature on methylene blue number at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

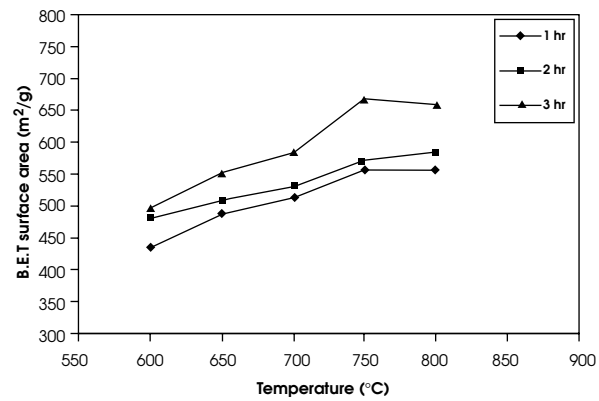


Fig 16. Effect of temperature on BET surface area at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

compounds out of pore, and that there was expansion of pores at the same time as we increased the temperature of the pyrolysis. About the increased time of the activation from 1 hour to 3 hours, it could be seen clearly that the compounds in the particles fell off with the steam which has been brought in after pyrolysis. It was noticeable that the BET surface increased with the average of 18% of each temperature, the % yield decreases 40% as well. Therefore, the hypothesis that the volatile matter which was inside of the particles fall of could be seen from the increasing of iodine number by the average of 15% which was different from the methyl blue number which increased only 5% (Table 5).

From these results, when there was pyrolysis with air for 30 min before the steam activation, the BET surface area, the iodine number and the methylene blue number increased more than without having pyrolysis with air. With the temperature range of 600-750°C, the reaction was developed in the particles well. And the BET surface area, the iodine number and the methylene blue number would be reached a maximum at 750°C. But at 800°C, the iodine number decreased, while the methylene blue number still increases and the BET surface area was constant because of the widen of micropores. Therefore, the optimum temperature for pyrolysis with air 30 min before steam activation was 750°C.

Influence of time on pyrolysis with air 30 min before steam activation

Table 5, with the time range of 1-3 hr for 600, 650, 700, 750 and 800°C, the % yield decreased (Figure 17) but the % ash increasesd(Figure 19) because at long time activation, the volatile matter was removed more from particles, the partial combustion of some carbon in particle reacting more with air caused increasing % ash .

Figure 18, the bulk density decreased while the increasing of activation time because the steam could penetrate inside the surface of particles for a long time, the porosity development increased, so the weight of activated carbon would be less; as a result, bulk density decreases. From Table 5, with the time range of 1 to 3 hr for 600, 650, 700, 750 and 800°C, the iodine number (Figure 20), the methylene blue number (Figure 21) and the BET surface area (Figure 22) were all increased. At long time activation, the steam penetrated deeper inside of particles than at short time, so the porosity development at long time was higher than at short time, resulting in the increase of the iodine number, the methylene blue number and the BET surface area.

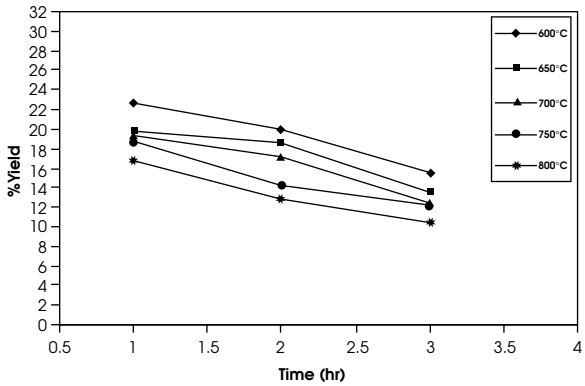


Fig 17. Effect of time on %yield at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

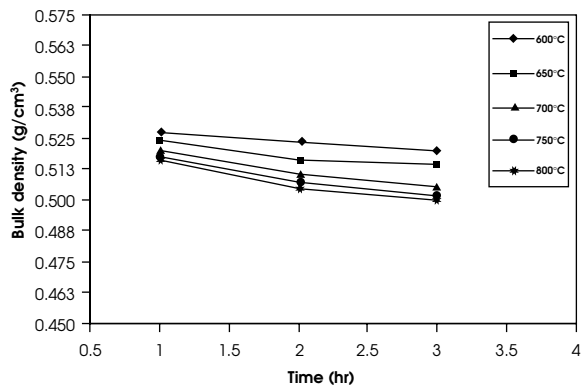


Fig 18. Effect of time on bulk density at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

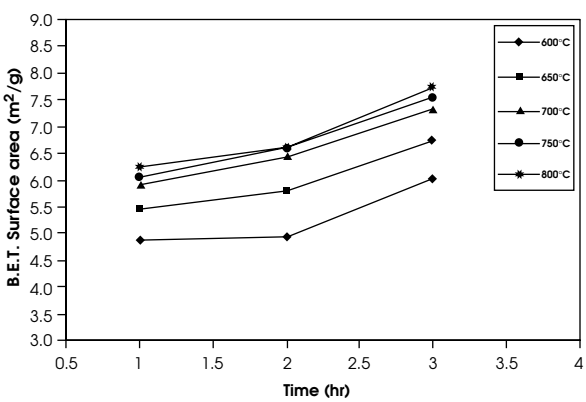


Fig 19. Effect of time on %ash at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36mm, 200 g, air 0.72 nl/min and steam).

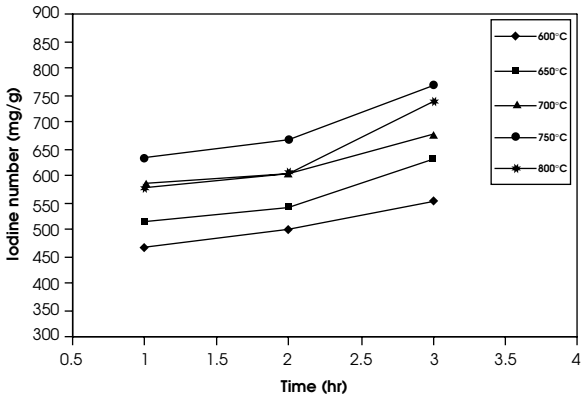


Fig 20. Effect of time on iodine number at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

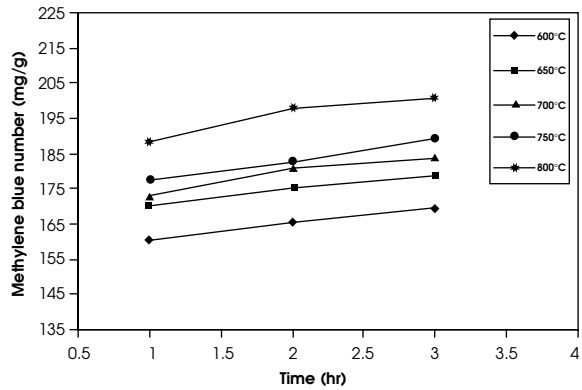


Fig 21. Effect of time on methylene blue number at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

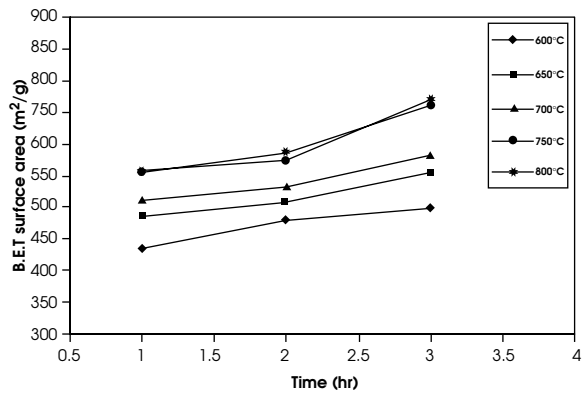


Fig 22. Effect of time on BET surface area at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

With these results, the optimum range of time for activation is 2-3 hr from which 3 hr was the best of all because it gave the maximum BET surface area, iodine number and methylene blue number.

The optimum condition for pyrolysis with air 30 min before steam activation was 750°C for 3 hr. The characteristics of activated carbon at 750°C for 3 hr with the yield of 12.18 % were bulk density of 0.5017 g/cm^3, ash of 7.54 %, iodine number of 766.99 mg/g and methylene blue number of 189.20 mg/g, BET surface area of 669.75 m^2/g, micropore area of 547.21 m^2/g and external area of 122.54 m^2/g.

Comparison of this work with other work

The comparison of this work with Patra Panyawathanakit[5] (1997) and Gergova *et al.*[2] (1993) is presented with respect to the maximum surface area obtained (Table 6).

Table 6. Comparison of this work with Patra Panya-wathanakit[5] (1997) and Gergova *et al*[2] (1993).

	This work (1998)	Patra (1997)	Gergova *et al* (1993)
Raw material	**Palm-oil shell**	**Palm-oil shell**	**Coconut shell**
Carbonization	Pyrolysis with air 30 min and 750°C for 3 hr	400°C for 1 hr with air	700°C for 2 hr
Activation		900°C for 1 hr with air	
Activating agent	Steam	Steam	Steam
% Yield	12.18 %	19.31 %	-
IA	766.99 mg/g	779.00 mg/g	-
MB	189.20 mg/g	136.96 mg/g	-
S_{BET}	669.75 m^2/g	670.10 m^2/g	700 m^2/g

Patra[5] produced the activated carbon from palm-oil shells by carbonization and activation with steam at 900°C for 1 hr and reportes the maximum surface area of 670.10 m^2/g, iodine number of 779.00 mg/g and methylene blue number of 136.96 mg/g. In this work with the same raw material, the surface area of 669.75 m^2/g, iodine number of 766.99 mg/g and methylene blue number of 189.20 mg/g were obtained at 750°C for 3 hr with pyrolysis in air for 30 min. It also observed that the surface area and iodine number are similar to Patra's. But the methylene blue number of this work is higher than Patra's, because of more overall time than Patra's; as a result, the micropores would have coalesced to mesopores, thus the methylene blue numbers increases. The % yield comparing to Patra's is lower because of more time activation in this work. Since this work has only one step pyrolysis and steam activation, the diffusion of volatile hinders the penetration of steam into the surface of palm-oil shells. Therefore, the development of porosity is less. The activation temperature for production in this work is 750°C which is lower than Patra's (900°C). Hence, it ends up using more overall time than Patra's. Even adding pyrolysis time 30 min before steam activation, but the increase of surface area and adsorption capacity of activated carbon are not much because the time and temperature for pyrolysis are not suitable. Chakrin Nithechan[9] proposes that the optimum volatile in char obtaining from carbonized step is in the range of 20-30 % in order to obtain high surface area activated carbon after being activated by steam. The two step method, the % volatile can be controlled by the optimum conditions in carbonization step but in the one step method for this work, we can not control the % volatile in raw material before steam activation; as a result, activated carbon has low surface area and adsorption capacity. In addition, the experiment takes place in the fixed bed reactor, so some particles of palm-oil shells can not be attacked by steam. If the production is in the fluidization technique, activated carbon will have higher surface area and adsorption capacity.

From the results, the advantages of production of activated carbon by the one step pyrolysis and steam activation are (i) lower activation temperature than that of two step method, (ii) reducing of step for production and (iii) using only one reactor, while the two step method using two reactors (carbonizer and activator). However, time of the one step production for activation spent more time.

Gergova *et al*, which used the same method (one step pyrolysis/steam activation) to produce the activated carbon from coconut shells, they reported that the maximum surface area was about 700 m^2/g at 700°C for 2 hr with steam as the activating agent in furnace tube on a laboratory condition. Comparing with this work, their temperature and time for production of activated carbon are lower, with the same surface area, because of their smaller reactor and only 50 g of sample for each experiment, being used. But the reactor in this work has 100 mm diameter and 200 g of sample is used for each production.

Correlation between % burn-off and the BET surface area as a function of the activation temperature

Figure 23 showed the change in the % burn-off and in the BET surface area as a function of the activation temperature, using data from pyrolysis with air 30 min before steam activation section. While the % burn-off increased, the BET surface area reached a maximum at 750°C and then decreased. This observed behaviour of the BET surface area at large % burn-off was well known and was attributed to the transformation of micropores into mesopores by a burn-off mechanism in the internal wall of the micropores.[7]

Correlation between the iodine number and the BET surface area

The iodine number was correlated in terms of the BET surface area, using representative samples from the experiments covering the range of parameters in this study as shown in Figure 24. The iodine number showed the same trend as that for the BET surface area(7). The iodine number increased with the increase of BET surface area. The iodine number gives an indication of the adsorption capacity of activated carbon in micropores(8). The surface area of activated carbon was dependent on micropores area, so the iodine number provided a good indication of the surface area of an activated carbon.

$$y = 0.687x + 131.8$$

where : y = BET surface area (m^2/g)
x = iodine number (mg/g)
R^2 = 0.9453

Correlation between the methylene blue number and the BET surface area

The methylene blue number gave an indication of the adsorption capacity of an activated carbon for molecules having similar dimensions to methylene

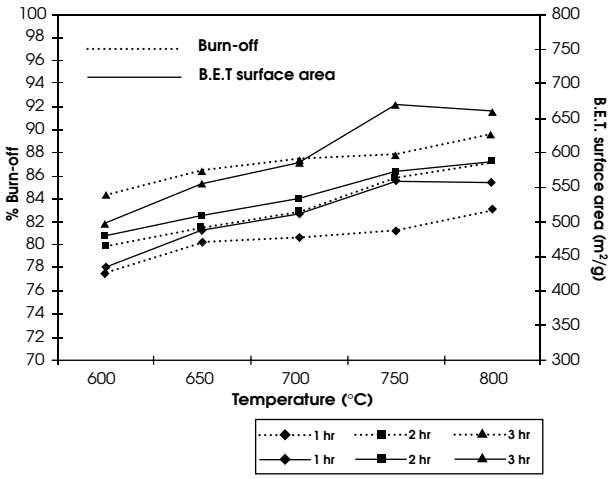


Fig 23. Correlation between % burn-off and the BET surface area as a function of the activation temperature.

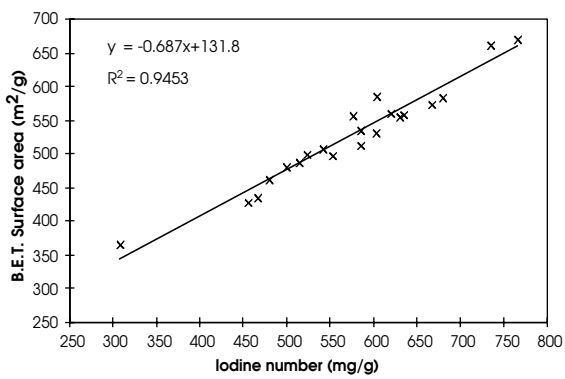


Fig 24. Correlation between the iodine number and the BET surface area.

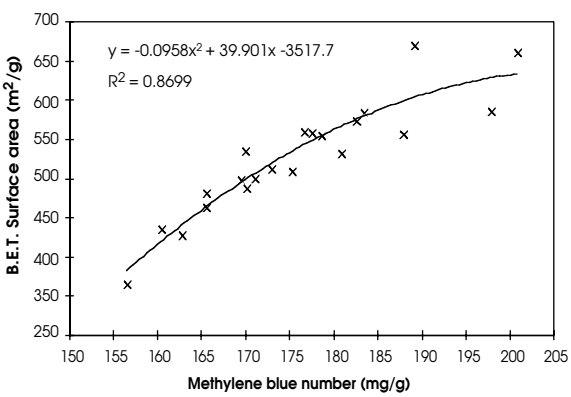


Fig 25. Correlation between methylene blue number and the BET surface area.

blue. It also gave an indication of the surface area of the activated carbon which results from the existence of mesopores of dimensions over than 1.5 nm[8]. The methylene blue number was correlated in terms of the BET surface area, using representative samples from the experiments covering the range of parameters in this study as shown in Figure 25. At the high value of methylene blue number, the BET surface area increased slowly. The experiment data showed that methylene blue number was higher when the temperature and time for activation increased. Under fast reaction condition for activation, micropores would become mesopores or macropores which would result in a reduction of the BET surface area.

$$y = -0.0958x^2 + 39.901x - 3517.7$$

where : y = BET surface area (m^2/g)
x = methylene blue numbe (mg/g)
R^2 = 0.8699

Conclusions

The experimental results showed the possibility for the production of activated carbon with well developed pore structure, high specific surface area and adsorption capacity from palm-oil shells by one step pyrolysis and steam activation. Experimental data showed that the increase in temperature and time resulted in a better activation. However, at the higher temperature, the decrease in micropores was observed, which was due to coalescence or widening of already formed pores. The activated carbon from palm-oil shells in medium size (1.18-2.36 mm) had the highest adsorption capacity and surface area.

When the flow rate of air was excess, the adsorption capacity and the surface area decreased. The optimum condition for the production of activated carbon from palm-oil shells by one step pyrolysis and steam activation in a fixed reactor was 200 g of palm-oil shells in size of 1.18-2.36 mm at 750oC for 2 hr with air at a flow rate of 0.72 nl/min and steam. The resulting characteristics were yield of 19.66%, bulk density of 0.5160 g/cm3, ash of 6.03%, iodine number of 620.16 mg/g, methylene blue number of 176.75 mg/g, BET surface area of 559.48 m2/g, micropore area of 432.02 m2/g, external area of 127.46 m2/g and average pore diameter of 15.53 .

In addition, it had been found that when there was an adding of pyrolysis time with air before steam activation, it would be led to higher porosity

development than one step pyrolysis and steam activation. From these experimental data, it was observed that the maximum surface area and the adsorption capacity could be obtained from using 200 g of palm-oil shells in size of 1.18-2.36 mm at 750oC for 3 hr by add pyrolysis with air for 30 min (0.72 nl/min) before steam activation. The resulting characteristics of final product were yield of 12.18 %, bulk density of 0.5017 g/cm3, ash of 7.54 %, iodine number of 766.99 mg/g, methylene blue number of 189.20 mg/g, BET surface area of 669.75m2/g, micropore area of 547.21 m2/g, external area of 122.54 m2/g and average pore diameter of 16.20. The above iodine number, more or less meets the standard of the commercial activated carbon of TIS 900-1989(10), that is over 600 mg/g.

The experiments in this work would help valuing the by-products from palm oil industry, instead of only using as fuel for steam generation in palm oil factory. From worthless by-products, they would become activated carbon after having been produced, using one step pyrolysis and steam activation, experimented in this work. It would be worth investing money in producing activated carbon as a mass product in the long run.

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Abbreviations

T	:	Temperature (°C)
t	:	Time (hr)
% Y	:	% Yield
% VM	:	% Volatile matter
% FC	:	% Fixed carbon
BD	:	Bulk density (g/cm^3)
IA	:	Iodine number (mg/g)
MB	:	Methylene blue number (mg/g)
S_{BET}	:	BET surface area (m^2/g)
S_{micro}	:	Micropore area (m^2/g)
$S_{external}$	:	External surface area (m^2/g)
nl	:	Normal liter (volume at standard condition)