CHAPTER IV

RESULTS AND DISCUSSION

4.1 Raw material

In this experiment palm-oil shells were used for the production of activated carbon by pyrolysis and steam activation in one stage. They were crushed and seived to six particles with the 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 proximate analysis of palm-oil shells is shown in **Table 4.1.**

Table 4.1 Proximate analysis of palm-oil shells.

Palm-oil shell sizes (mm)	%M	on dry basis			
		BD (g/cm^3)	% Ash	% VM	% FC
< 0.60	4.10	0.6799	6.84	76.45	16.71
0.60 - 1.18	3.39	0.6650	2.54	79.12	18.34
1.18 - 2.36	4.97	0.6099	2.05	79.66	18.29
2.36 - 4.75	5.73	0.5770	2.08	79.28	18.64
4.75 - 6.00	6.13	0.5170	2.26	82.67	15.07
6.00 - 8.00	6.28	0.4557	1.57	82.23	16.20

4.2 Results and discussion of the experiments

4.2.1 The optimum temperature and time for pyrolysis and steam activation

The 200 g of 2.36-4.75 mm of the palm-oil shells were used for each batch. The fixed bed reactor had been heated to the final temperature of 600, 650, 700 and 750°C before the palm-oil shells sample were charged into the reactor. After charging, the excess steam continued was passing up through the bed with air at a fixed flow rate of 0.72 nl/min for 1, 2 and 3 hr. The results of this experiment are shown in **Table 4.2** and **Figure 4.1-4.10**

Table 4.2 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	%M	on dry basis			
				BD (g/cm^3)	%Ash	IA (mg/g)	MB (mg/g)
600	1	29.02	6.70	0.5447	4.71	338.08	146.76
	2	27.44	7.31	0.5345	4.79	367.99	153.12
	3	26.71	7.05	0.5303	4.97	439.88	155.04
650	1	27.75	7.62	0.5416	4.85	362.74	152.14
	2	23.78	7.29	0.5305	4.92	401.45	159.42
	3	23.10	8.89	0.5244	5.46	466.01	165.69
700	1	24.63	8.35	0.5293	5.13	452.79	161.71
	2	21.89	8.80	0.5219	5.32	472.87	163.88
	3	21.13	9.27	0.5088	5.84	515.20	169.79
750	1	22.36	10.02	0.5244	5.54	508.10	165.16
	2	20.81	9.79	0.5141	5.73	524.18	171.74
	3	16.90	10.92	0.5047	6.52	543.64	176.06

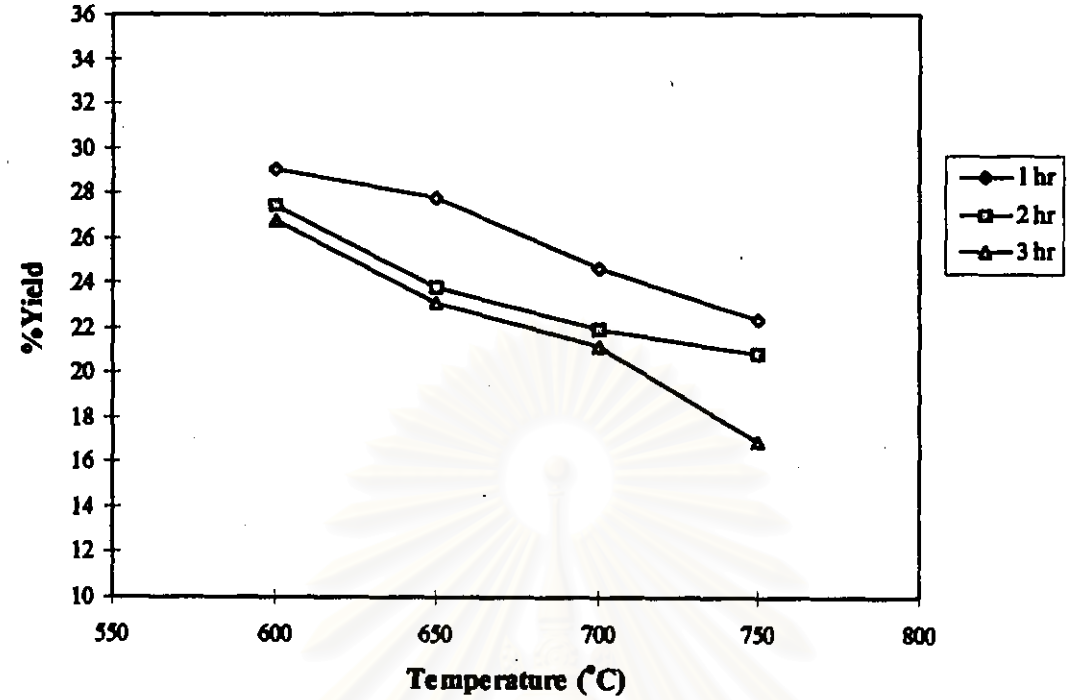

Figure 4.1 Effect of temperature on % yield at different times (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

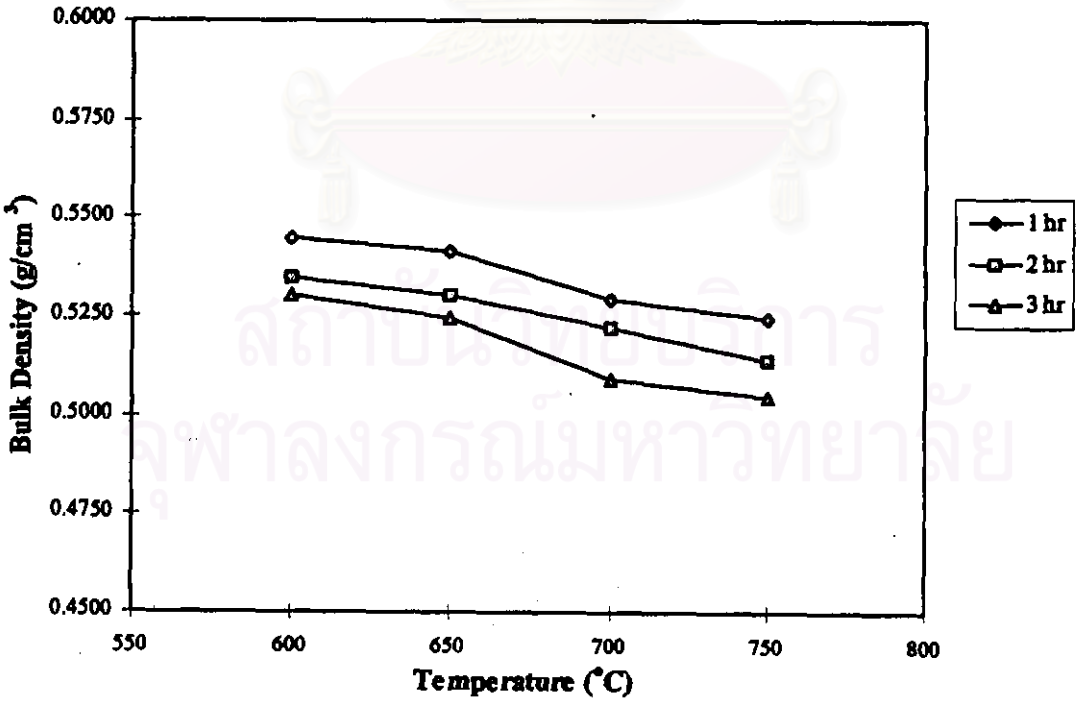

Figure 4.2 Effect of temperature on bulk density at different times (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

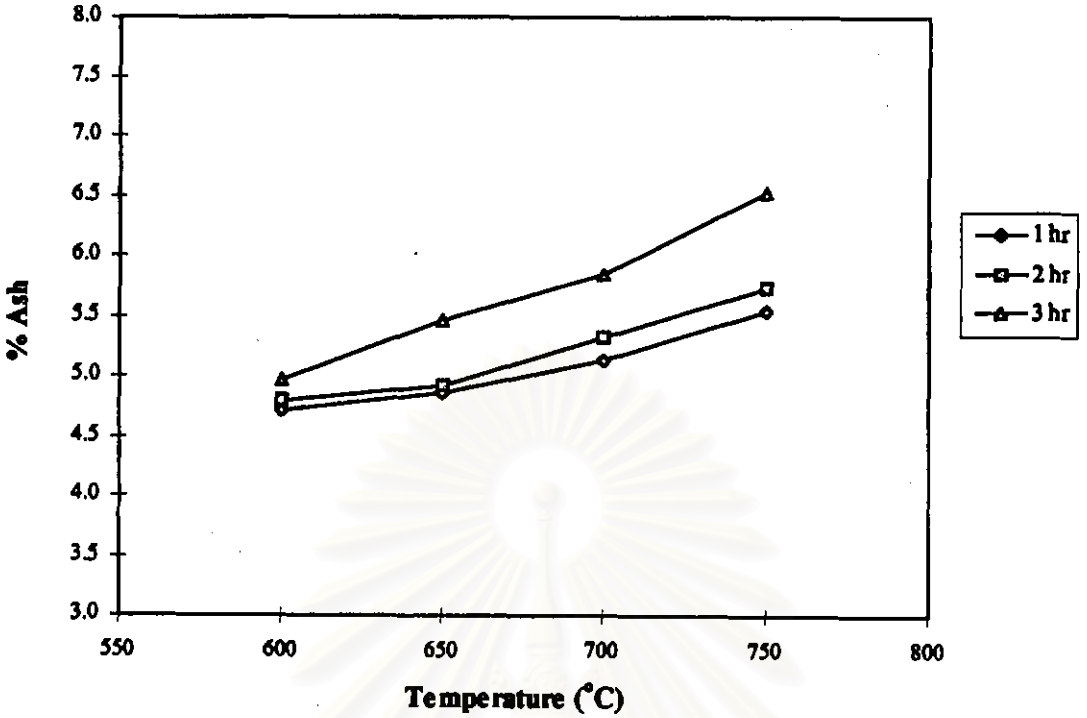

Figure 4.3 Effect of temperature on % ash at different times (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

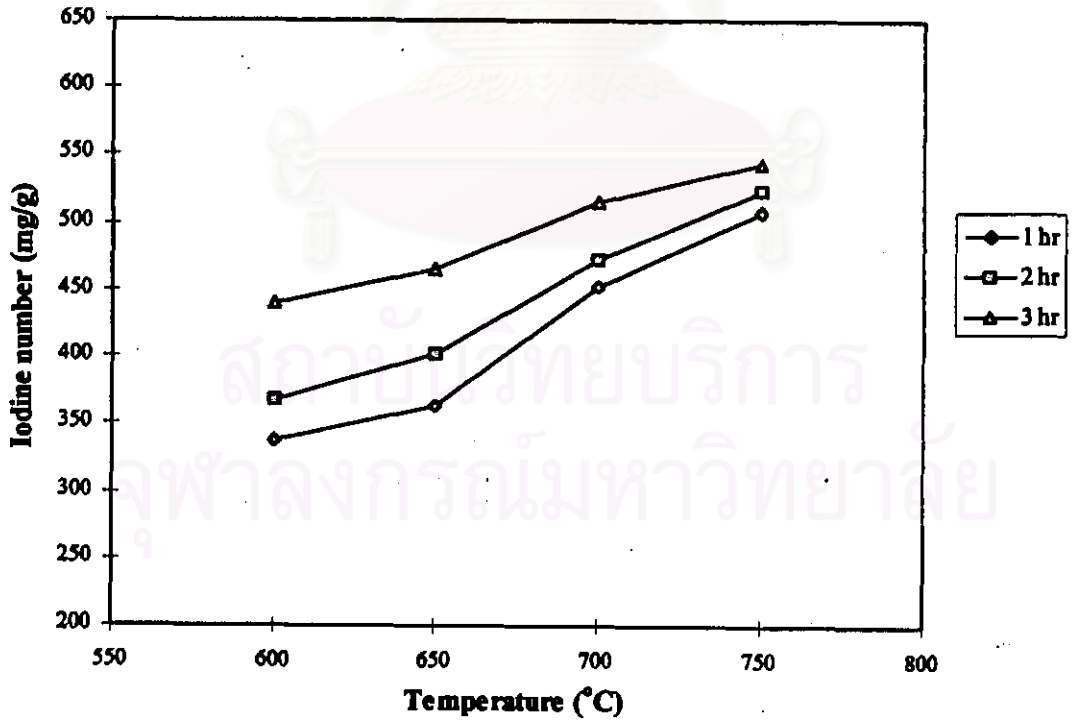

Figure 4.4 Effect of temperature on iodine number at different times (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

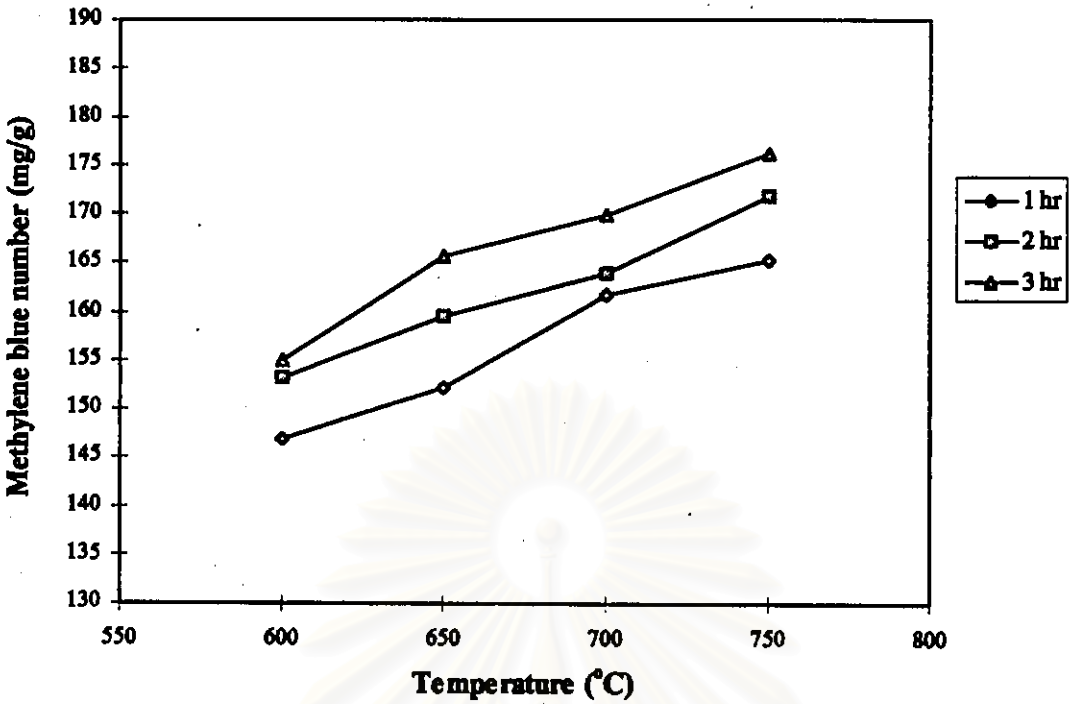

Figure 4.5 Effect of temperature on methylene blue number at different times (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

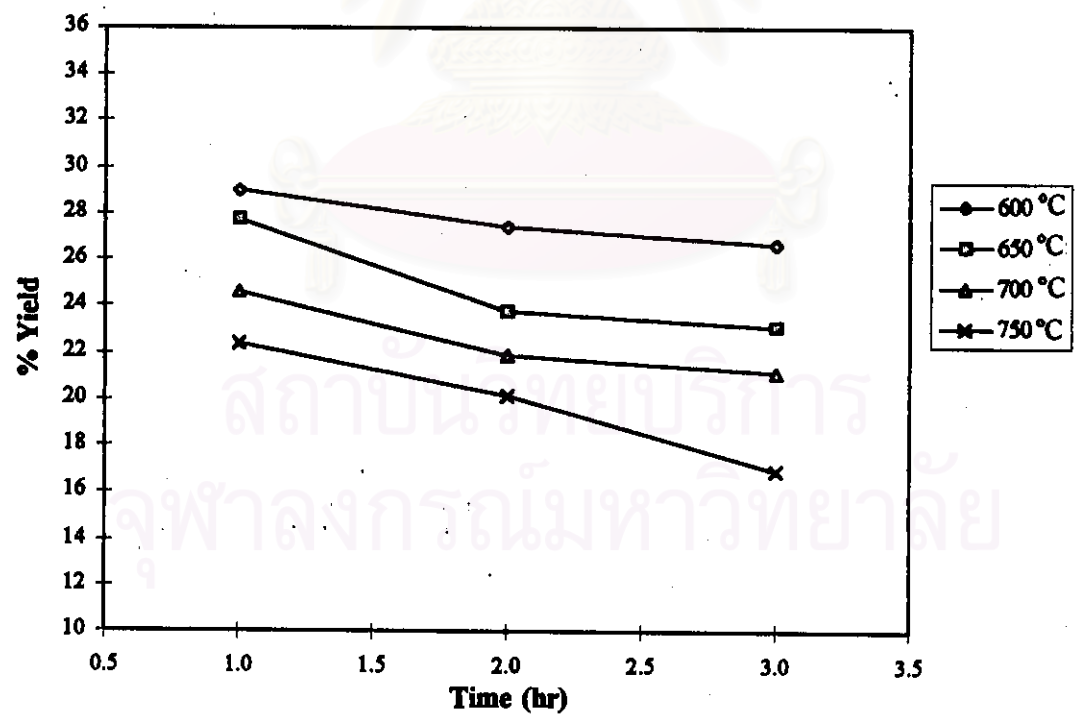

Figure 4.6 Effect of time on % yield at different temperatures (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

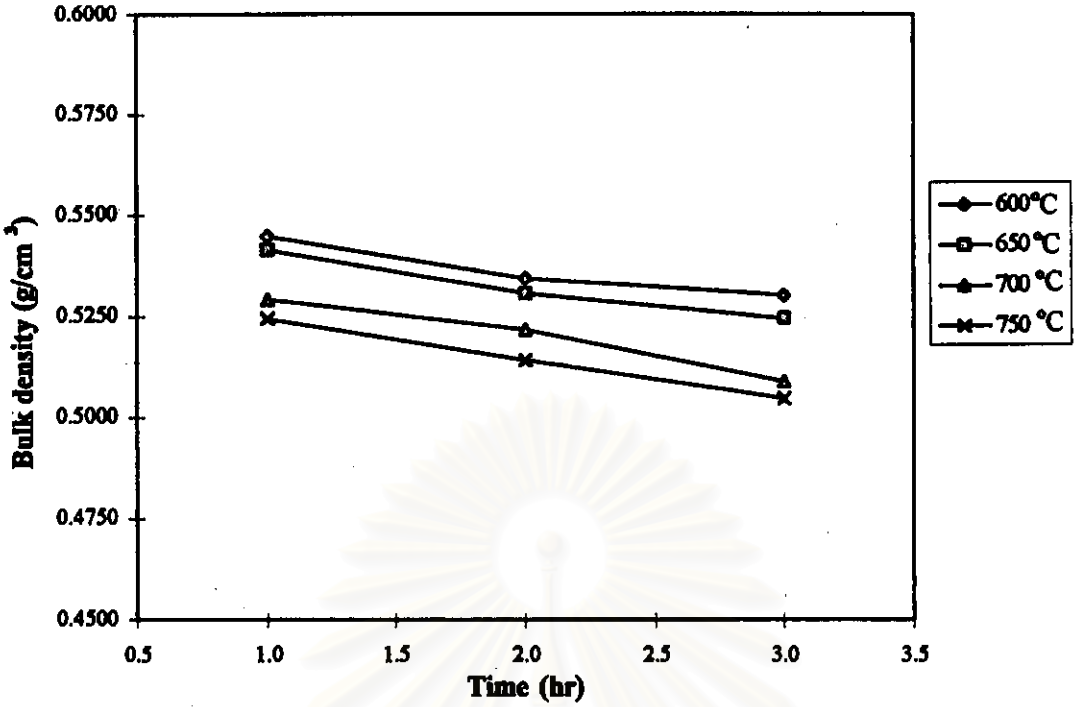

Figure 4.7 Effect of time on bulk density at different temperatures (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

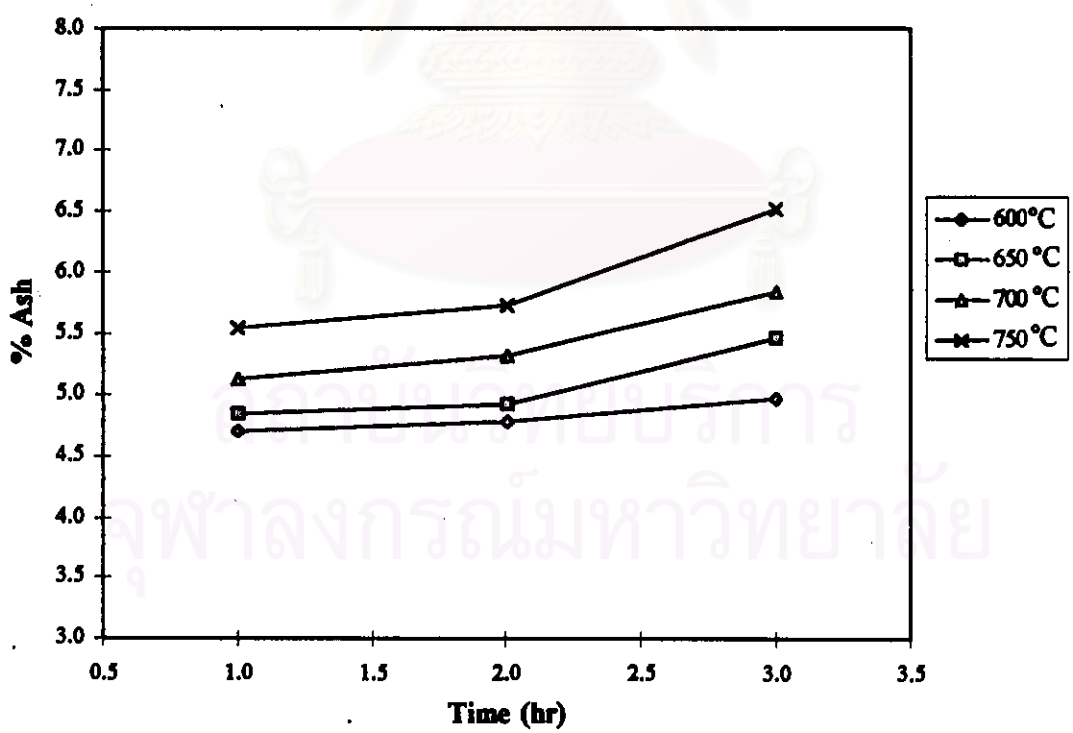

Figure 4.8 Effect of time on % ash at different temperatures (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

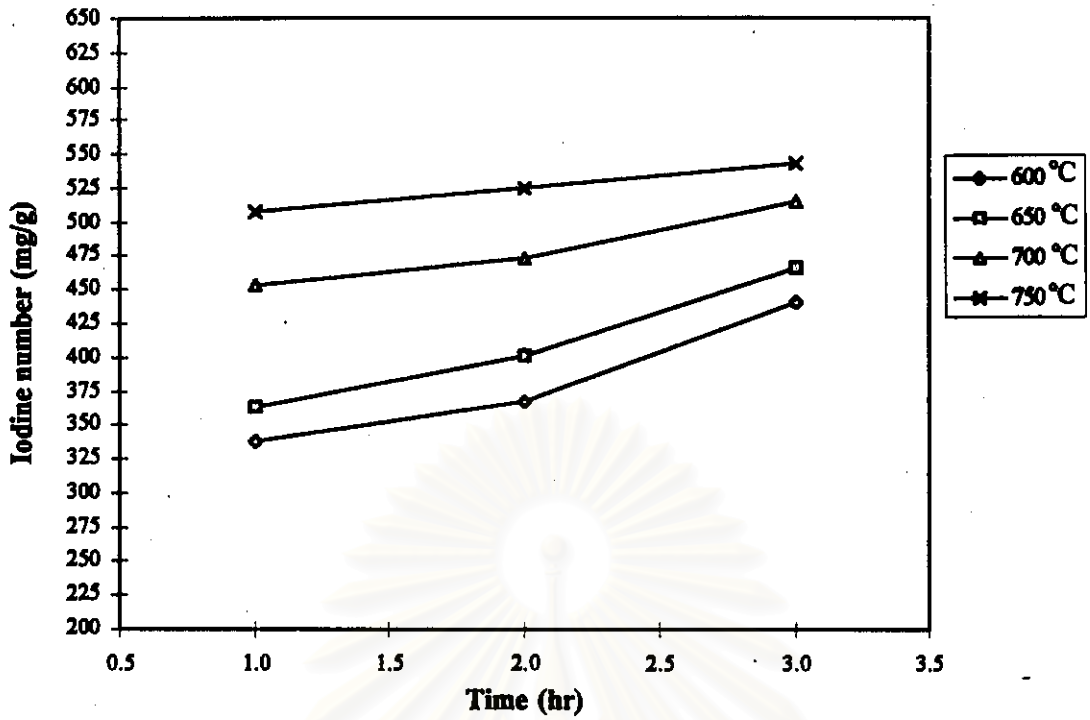

Figure 4.9 Effect of time on iodine number at different temperatures (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

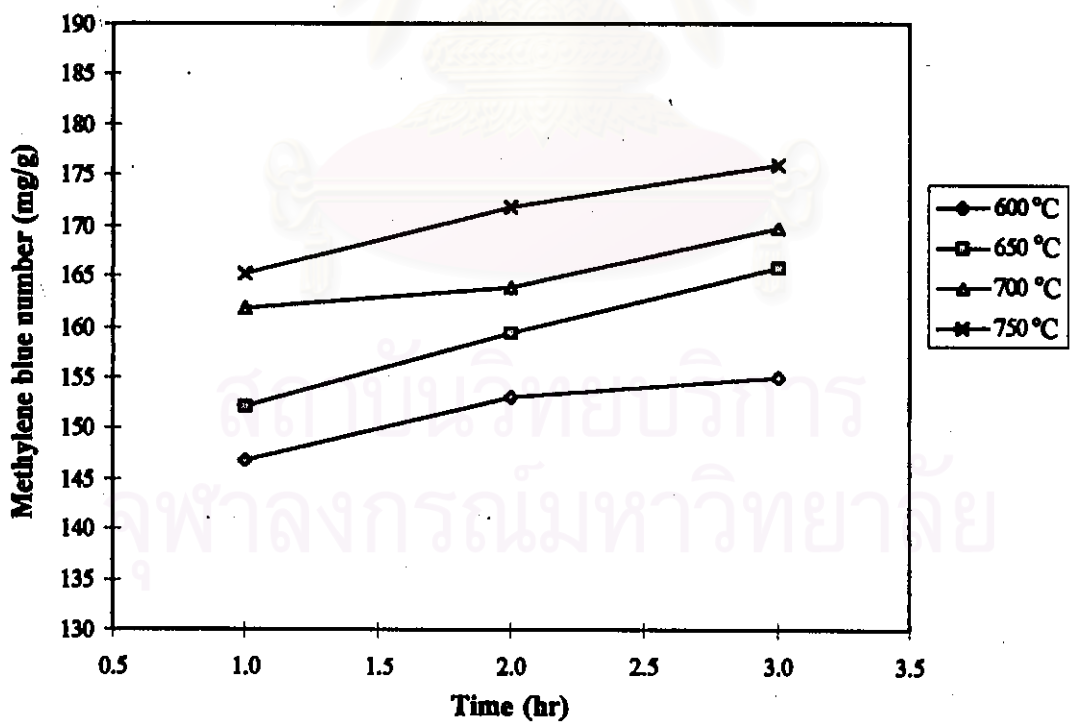

Figure 4.10 Effect of time on methylene blue number at different temperatures (size 2.36 - 4.75 mm, 200 g, air 0.72 nl/min and steam).

4.2.1.1 The optimum temperature for pyrolysis and steam activation

From **Table 4.2** and **Figure 4.1**, when the temperature is at 600 to 750°C for 1, 2 and 3 hr, the decrease of % yield can be attributed to the loss of volatile matter with the increase of temperature or partial combustion with air and the porosity development in granules. From these reasons, ash would increase (**Figure 4.3**) with an increase in temperature. The % ash in the first stage (600-650°C) between 1 and 2 hr increases slowly because only the volatile matter at the surface is removed, hence the % ash is rather constant. When time is increased to 3 hr, the % ash would increase quickly. But when the temperature increases from 650 to 750°C for 1 and 2 hr, the % ash in this stage would increase faster than the % ash in the first stage (600-650°C). The % ash at 650-750°C for 3 hr increases the fastest of all. These results show that time has an effect into change of the % ash at the low activation temperature. The % change of the % yield and the % ash are shown in **Table 4.3**.

From **Table 4.2**, the bulk density decreases with an increase in temperature from 600 to 750°C for 1, 2 and 3 hr (**Figure 4.2**) because at high temperature, porosity is highly developed. The % change of bulk density is shown in **Table 4.3**. The bulk density remains fairly constant while the temperature is raised from 600 to 650°C. At the same time, there is a small increase of iodine number. However the bulk density decreases quickly whereas the temperature increases from 650 to 750°C; as a result of high development of porosity which can be seen from increasing of the iodine number and the methylene blue number.

Table 4.2 shows that the iodine number (**Figure 4.4**) and the methylene blue number (**Figure 4.5**) increase when the temperature increases from 600 to 750°C for 1, 2 and 3 hr. The % changes of the iodine number and the methylene blue are shown in **Table 4.3**. In the first stage (600-650°C), the iodine number increases slowly because the diffusion of volatile matter hinders the penetration of steam into the surface of palm-oil shells; as a result, the development of porosity is less. When the

Table 4.3 The % change of characteristics of activated carbon from palm-oil shells when activation temperature increases from 600 to 750°C for 1, 2 and 3 hr.

t (hr)	T (°C)	% Y	BD (g/cm^3)	% Ash	IA (mg/g)	MB (mg/g)
1	600	29.02	0.5447	4.71	338.08	146.76
	↓	↓	↓	↑	↑	↑
	750	22.36	0.5244	5.54	508.10	169.16
	% Change	-22.95	-3.73	+17.62	+50.29	+15.26
2	600	27.44	0.5345	4.79	397.99	153.12
	↓	↓	↓	↑	↑	↑
	750	20.81	0.5141	5.73	524.18	171.74
	% Change	-24.16	-3.82	+19.62	+31.71	+12.16
3	600	26.71	0.5303	4.97	439.88	155.04
	↓	↓	↓	↑	↑	↑
	750	16.90	0.5047	6.52	543.64	176.06
	% Change	-36.73	-4.83	+31.19	+23.59	+13.56

↑ : increase ↓ : decrease

temperature increases from 650 to 700°C, the iodine number increases quickly, because most of volatile matter is diffused from granules in the first stage, so the steam penetrates easily into the surface of palm-oil shells; as a result, the high development of porosity. When the temperature increases from 700 to 750°C, the iodine number increases more slowly than in the first temperature range while the methylene blue number still increases because micropores would have coalesced, resulting in mesopores thus reducing the iodine number.

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

4.2.1.2 The optimum time for pyrolysis and steam activation

From **Table 4.2** and **Figure 4.9**, with the time range of 1-3 hr at 600, 650, 700 and 750°C, the iodine number increases. At the same time and temperature, the methylene blue number **(Figure 4.10)** increases too. The % changes of the iodine number and the methylene blue are shown in **Table 4.4.**

Table 4.4 The % change of characteristics of activated carbon from palm-oil shells in the time range of 1-3 hr for 600, 650, 700 and 750°C.

T (°C)	t (hr)	% Y	BD (g/cm^3)	% Ash	IA (mg/g)	MB (mg/g)
600	1	29.02	0.5447	4.71	338.08	146.76
	↓	↓	↓	↑	↑	↑
	3	26.71	0.5303	4.97	439.88	155.04
	% Change	-7.96	-2.64	+5.52	+30.11	+5.64
650	1	27.75	0.5416	4.85	362.74	152.14
	↓	↓	↓	↑	↑	↑
	3	23.10	0.5244	5.46	466.01	165.69
	% Change	-16.46	-3.17	+12.58	+28.47	+8.91
700	1	24.63	0.5293	5.13	452.79	161.71
	↓	↓	↓	↑	↑	↑
	3	21.13	0.5088	5.84	515.20	169.79
	% Change	-14.21	-3.87	+13.84	+13.78	+4.99
750	1	22.36	0.5244	5.54	508.10	169.16
	↓	↓	↓	↑	↑	↑
	3	16.90	0.5047	6.52	543.64	176.06
	% Change	-24.42	-3.76	+17.69	+6.99	+4.07

↑ : increase ↓ : decrease

Figure 4.9, the iodine number with the time range of 1-2 hr increases lower than 2-3 hr, because at 1-2 hr the diffusion of volatile matter hinders the penetration of steam into the surface of palm-oil shells; as a result, the pores are low developed. At the time range of 2-3 hr, the iodine number and the methylene blue number increase in the near rate because most of volatile matter is diffused in the first stage, so the steam penetrates easily with the surface of palm-oil shells; as a result, the porosity development increases. The high development of porosity makes the bulk density decrease in the time range of 1-3 hr at 600, 650, 700 and 750°C (**Figure 4.7**). The % change of bulk density is shown in **Table 4.4**.

Table 4.2 and **Figure 4.6**, in time range of 1-3 hr for 600, 650, 700 and 750 °C, the % yield decreases because of the loss of volatile matter and partial combustion with air, so the % yield decreases which is the opposite of the % ash of the product (**Figure 4.8**). The % ash in the first stage (1-2 hr) increases slowly because only the volatile matter at the surface is diffused. But time increases to 3 hr, the % ash increases quickly because most of the volatile matter is diffused in the first stage and air helps high partial combustion.

These result in having the maximum of iodine number and methylene blue number at the time of 3 hr. Therefore, the optimum condition ought to be 750°C for 3 hr. But the % yield in this condition is lower than that of 750°C for 2 hr which their iodine number and methylene blue number are not different. Thus the optimum time is 2 hr because it saves more time for activation than 750°C for 3 hr.

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.

4.2.2 The optimum size of palm-oil shells for pyrolysis and steam activation

Six sizes of the palm-oil shells were used to study the optimum size. They were <0.60, 0.60-1.18, 1.18-2.36, 2.36-4.75, 4.75-6.00 and 6.00-8.00 mm. Approximate 200 g of each of the palm-oil shells sample were treated at 750 ^{0}C for 2 hr with steam and air at the flow rate of 0.72 nl/min in the fixed bed reactor. The results are shown in **Table 4.3** and **Figures 4.11-4.14**

Table 4.5 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	%M	on dry basis				Surface area		
			BD (g/cm^3)	% Ash	IA (mg/g)	MB (mg/g)	$S_{B.E.T.}$ (m^2/g)	S_{Micro} (m^2/g)	$S_{External}$ (m^2/g)
< 0.60	17.34	5.97	0.5737	38.54	308.52	156.55	364.65	274.98	89.67
0.60 - 1.18	18.35	8.97	0.5424	11.08	585.15	169.97	534.41	334.12	109.29
1.18 - 2.36	19.66	8.68	0.5160	6.03	620.16	176.75	559.48	432.02	127.46
2.36 - 4.75	20.81	7.05	0.5141	5.73	524.18	171.16	498.52	378.64	119.88
4.75 - 6.00	21.27	9.56	0.4637	5.33	480.51	165.56	462.23	362.28	100.95
6.00 - 8.00	23.38	8.91	0.4374	5.67	455.73	162.91	427.38	329.02	98.36

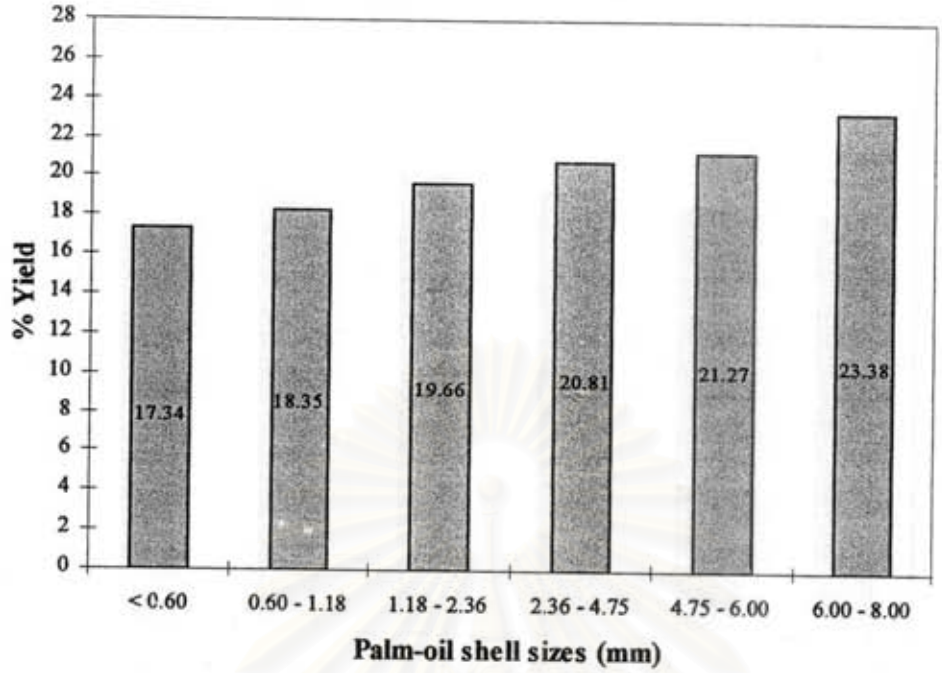

Figure 4.11 Effect of size on %yield (750°C for 2 hr, 200 g, air 0.72 nl/min and steam).

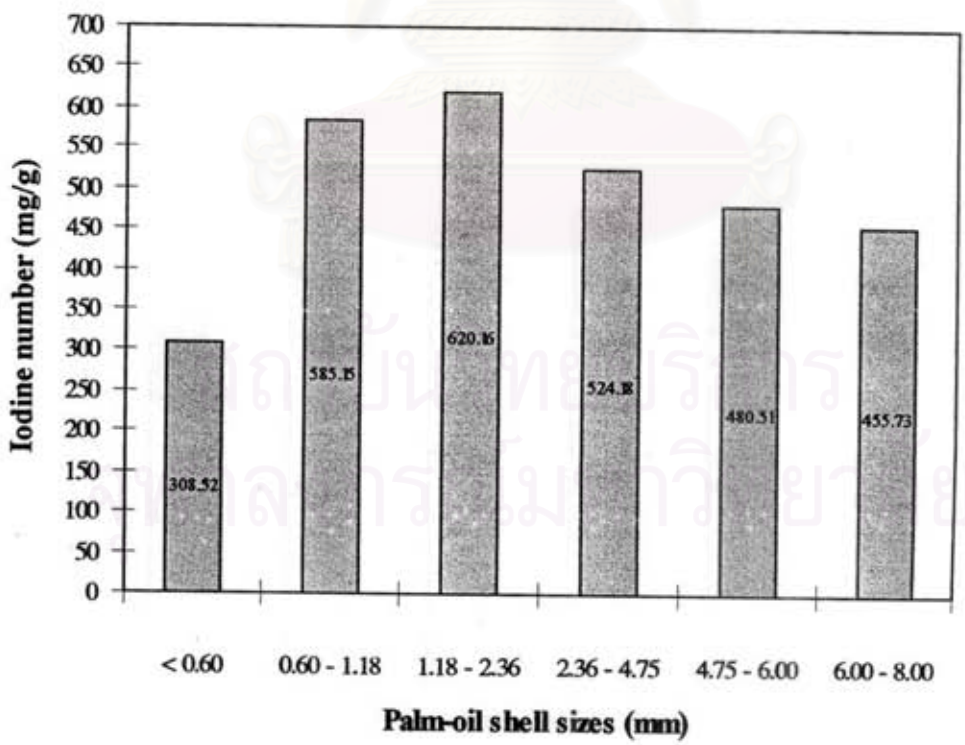

Figure 4.12 Effect of size on iodine number (750°C for 2 hr, 200 g, air 0.72 nl/min and steam).

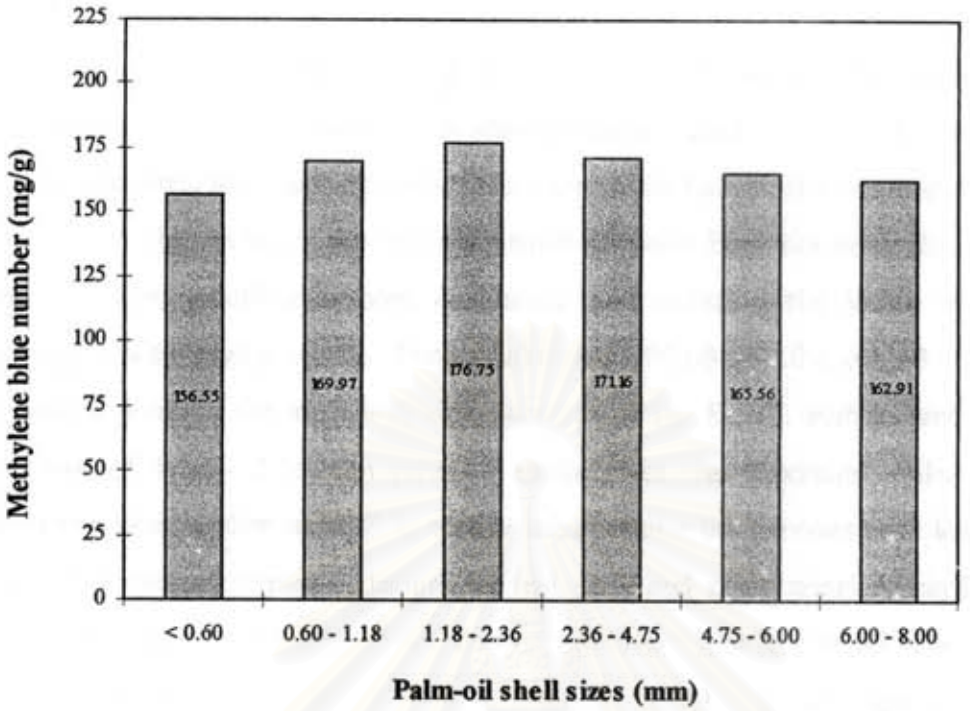

Figure 4.13 Effect of size on methylene blue number (750°C for 2 hr, 200 g, air 0.72 nl/min and steam).

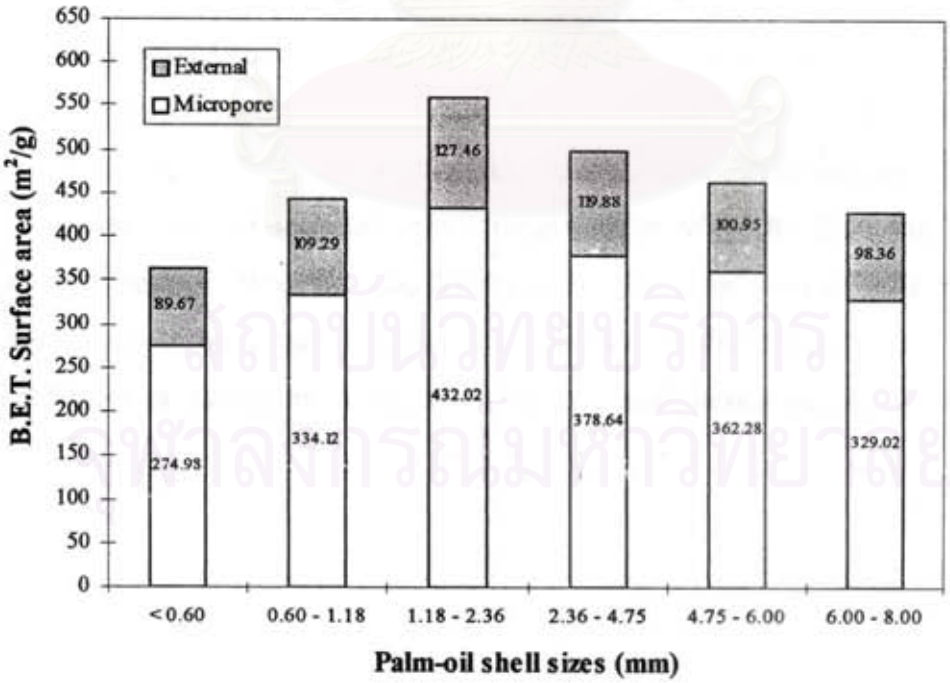

Figure 4.14 Effect of size on B.E.T. surface area (750°C for 2 hr, 200 g, air 0.72 nl/min and steam).

From **Table 4.5** and Figures **4.12 - 4.14**, the iodine number, the methylene blue number and the B.E.T. surface area of small palm-oil shells (< 0.60 mm in size) are less because the small size palm-oil shells pack tight in the bed, so the steam is difficult to penetrate in the surface. Furthermore, small particles burn out early due to faster reaction rates, resulting in pore coalesence and reducing the iodine number as comparing with large particles. For particle sizes of 0.60 - 1.18 and 1.18 - 2.36 mm, the iodine number, the methylene blue number and the B.E.T. surface area increase. The size of 1.18 - 2.36 mm palm-oil shells gives the maximum iodine number, methylene blue number and B.E.T. surface area because the particles pack loose in the bed, so the steam penetrates through the bed easily and could attack all particles; as a result, the porosity development of this size is higher than the small size. For the particle sizes of 2.36 - 4.75, 4.75 - 6.00 and 6.00 - 8.00 mm, the iodine number, the methylene blue number and the B.E.T. surface area decrease because these particles pack too loose, so the steam passes suddenly and could not contact completely with the surface of palm-oil shell particles.

These results show that the optimum size of palm-oil shells for production is 1.18 - 2.36 mm because it gives the highest iodine number, methylene blue number and B.E.T. surface area, besides the % yield of this size is not different that of the large size. Characteristics of activated carbon from the size of 1.18 - 2.36 mm palm-oil shells were yield of 19.66 %, bulk density of 0.5160 g/cm^3, ash of 6.03 %, iodine number of 620.16 mg/g and methylene blue number of 176.75 mg/g, B.E.T. surface area of 559.48 m^2/g, micropore area of 432.02 m^2/g and external area of 127.46 m^2/g.

4.2.3 The optimum flow rate of air for pyrolysis and steam activation

Four flow rates of air were used in this investigation: 0.20, 0.49, 0.72 and 0.97 nl/min. They were used to study optimum flow rate for production of activated carbon. Approximate 200 g of 1.18-2.36 mm of the palm-oil shells were treated at 750°C for 2 hr with steam and various flow rates of air. The results are shown in **Table 4.6** and **Figures 4.15 - 4.18.**

Table 4.6 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	%M	on dry basis			
			BD (g/cm^3)	% Ash	IA (mg/g)	MB (mg/g)
0.20	25.19	8.55	0.5357	5.12	492.14	171.26
0.49	23.04	7.48	0.5118	5.53	540.76	173.47
0.72	19.66	7.03	0.5160	6.03	620.16	176.75
0.97	15.62	7.67	0.5104	7.67	635.42	182.28

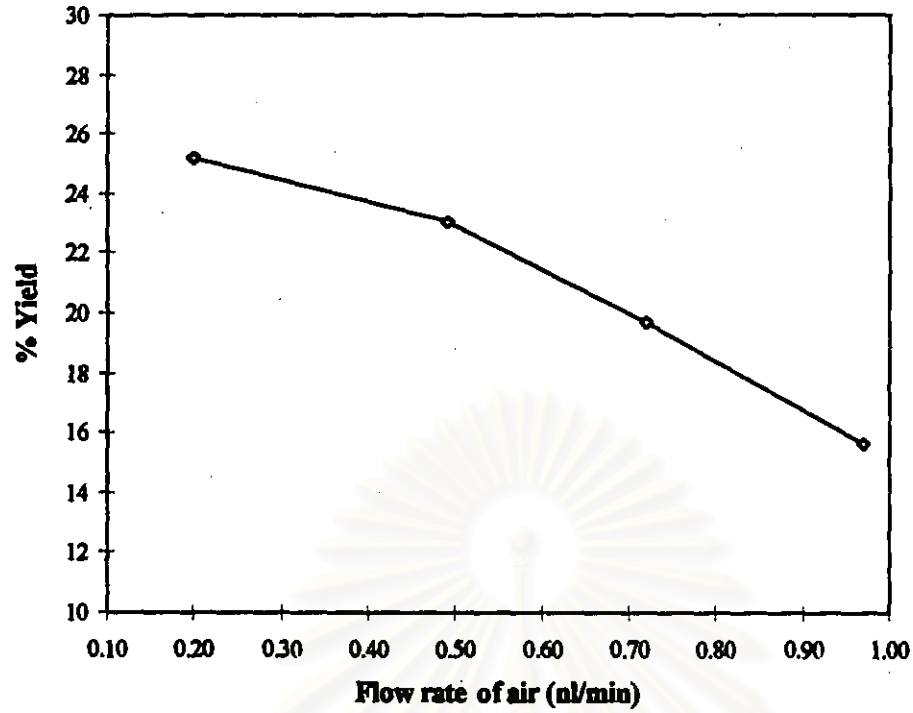

Figure 4.15 Effect of air flow rate on %yield (750°C for 2 hr, size 1.18 - 2.36 mm, 200 g and steam).

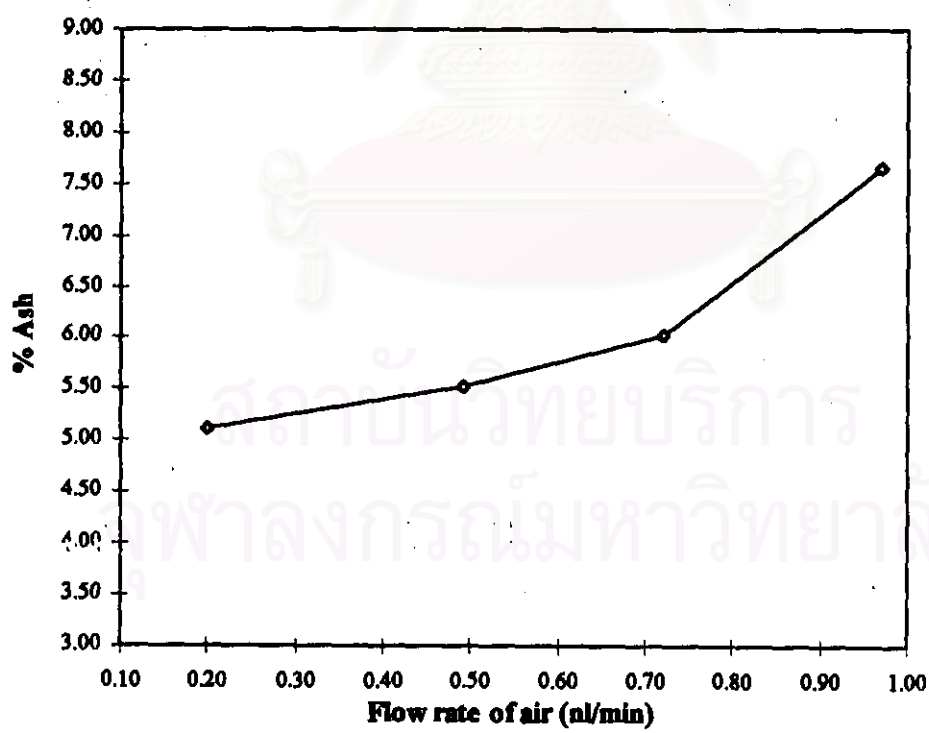

Figure 4.16 Effect of air flow rate on %ash (750°C for 2 hr, size 1.18 - 2.36 mm, 200 g and steam).

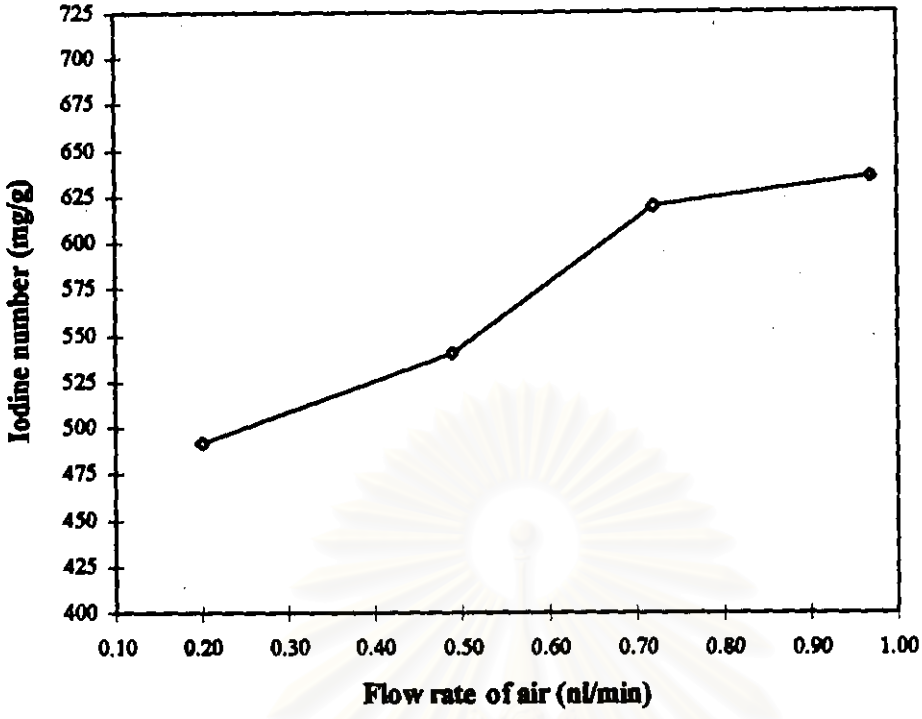

Figure 4.17 Effect of air flow rate on iodine number (750°C for 2 hr, size 1.18 - 2.36 mm, 200 g and steam).

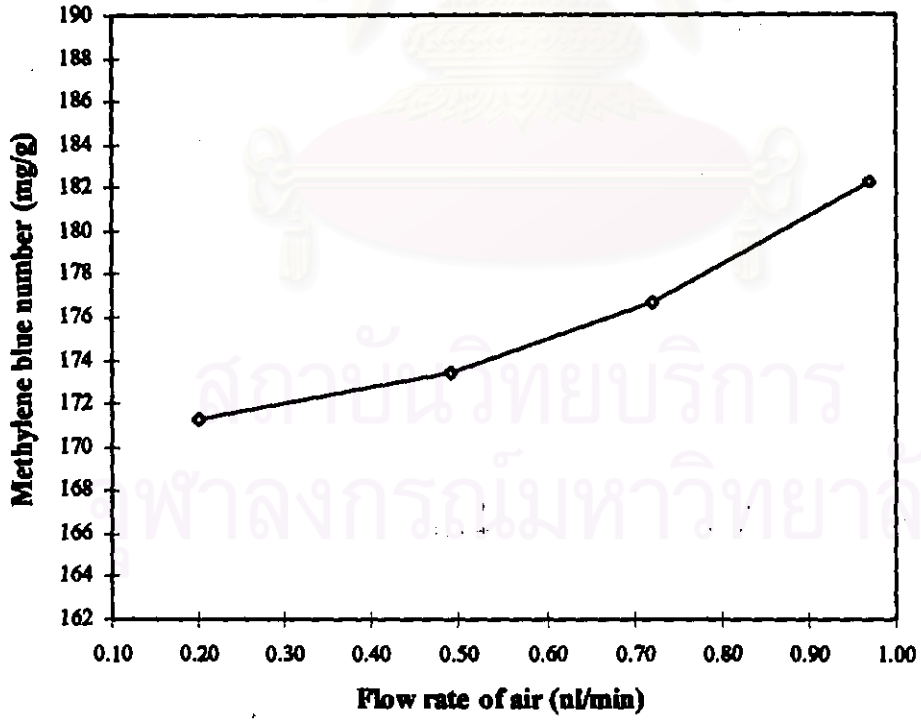

Figure 4.18 Effect of air flow rate on methylene blue number (750°C for 2 hr, size 1.18 - 2.36 mm, 200 g and steam).

From **Table 4.6** and **Figures 4.15 - 4.16**, the % yield decreases while the % ash increases with the increase of air flow rates because air reacts more with palm-oil shells, the volatile matter is diffused quickly out of the surface of particles, so the % yield decreases and the % ash increases.

Table 4.6 and **Figure 4.17 - 4.18**, the iodine number and the methylene blue number increase when the flow rate of air increases from 0.20 to 0.97 nl/min because while the flow rate of air increases, the air quickly carries steam to penetrate, so the porosity development increases. At the flow rate of air 0.97 nl/min, the iodine number increases slowly and the methylene blue number still increases, because the air carries a lot of steam with extreme penetration, so the micropores would have coaleseced, resulting in mesopores development in the surface of particles.

These results show that the optimum flow rate of air is 0.72 nl/min. Characteristics of activated carbon with the yield of 19.66 % were bulk density of 0.5160 g/cm^3, ash of 6.03 %, iodine number of 620.16 mg/g and methylene blue number of 176.75 mg/g, B.E.T. surface area of 559.48 m^2/g, micropore area of 432.02 m^2/g and external area of 127.46 m^2/g.

4.2.4 Pyrolysis with air 30 min before steam activation

Approximate 200 g of 1.18-2.36 mm of the palm-oil shells were pyrolysed with air at 600, 650, 700, 750 or 800 °C for 30 min before activation with steam. After 30 min pyrolysis, the sample was activated at 600, 650, 700, 750 and 800 °C for 1, 2 or 3 hr with steam and air flow at a rate of 0.72 nl/min. The results of this experiment are shown in **Table 4.7** and **Figures 4.19 - 4.31.**

Table 4.7 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				Surface area		
				BD (g/cm^3)	%Ash	IA (mg/g)	MB (mg/g)	$S_{B.E.T.}$ (m^2/g)	S_{Micro} (m^2/g)	$S_{External}$ (m^2/g)
600	1	22.53	8.35	0.5277	4.88	467.17	160.49	434.41	349.12	85.29
	2	20.06	6.83	0.5234	4.95	499.63	165.53	480.43	381.42	99.01
	3	15.59	9.56	0.5201	6.03	553.02	169.47	497.74	399.83	97.91
650	1	19.70	9.08	0.5240	5.45	515.22	170.15	486.95	390.71	96.24
	2	18.47	9.32	0.5165	5.81	542.23	175.34	507.89	410.53	97.37
	3	13.47	10.44	0.5143	6.73	630.58	178.71	554.26	455.28	98.98
700	1	19.28	9.47	0.5198	5.90	586.20	172.95	511.72	419.90	91.82
	2	17.08	9.64	0.5105	6.42	602.98	180.94	531.62	430.73	100.89
	3	12.48	11.38	0.5060	7.33	679.41	183.44	583.52	477.55	105.97
750	1	18.71	10.64	0.5178	6.06	635.16	177.58	557.38	458.97	98.41
	2	14.18	10.48	0.5069	6.63	667.14	182.61	572.93	469.03	103.90
	3	12.18	12.19	0.5017	7.54	766.99	189.20	669.75	547.21	122.54
800	1	16.75	10.38	0.5162	6.23	577.57	188.00	556.26	437.13	119.12
	2	12.90	10.05	0.5051	6.61	604.27	198.00	585.34	444.41	140.93
	3	10.34	10.22	0.4996	7.72	735.31	200.91	660.85	529.67	131.18

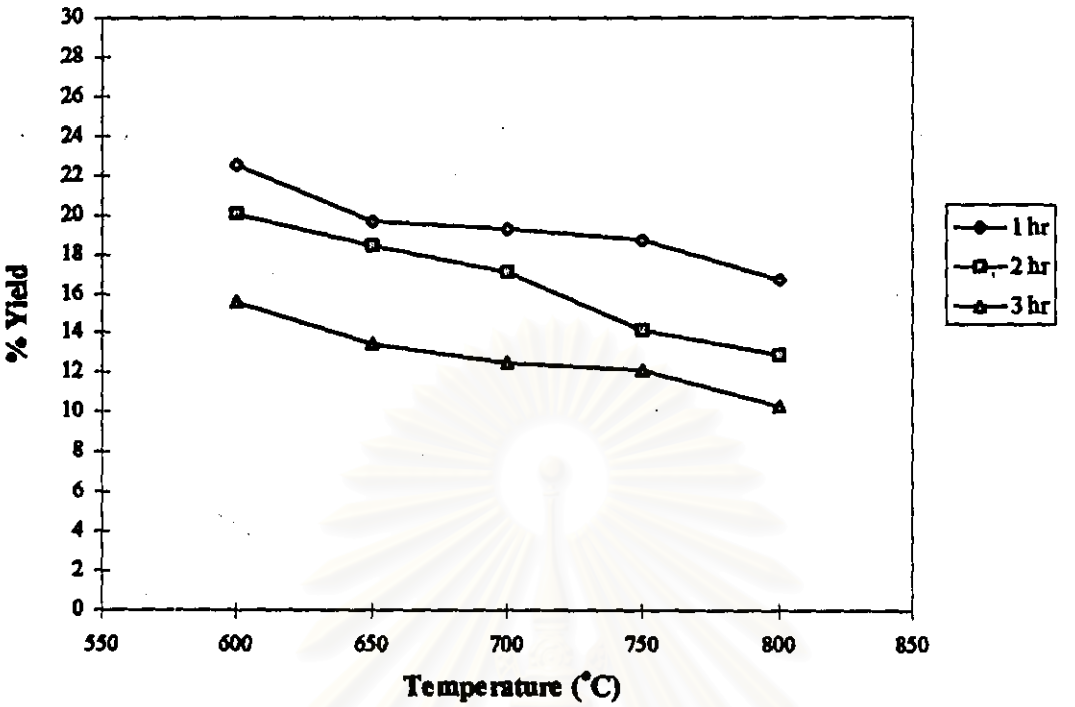

Figure 4.19 Effect of temperature on %yield at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

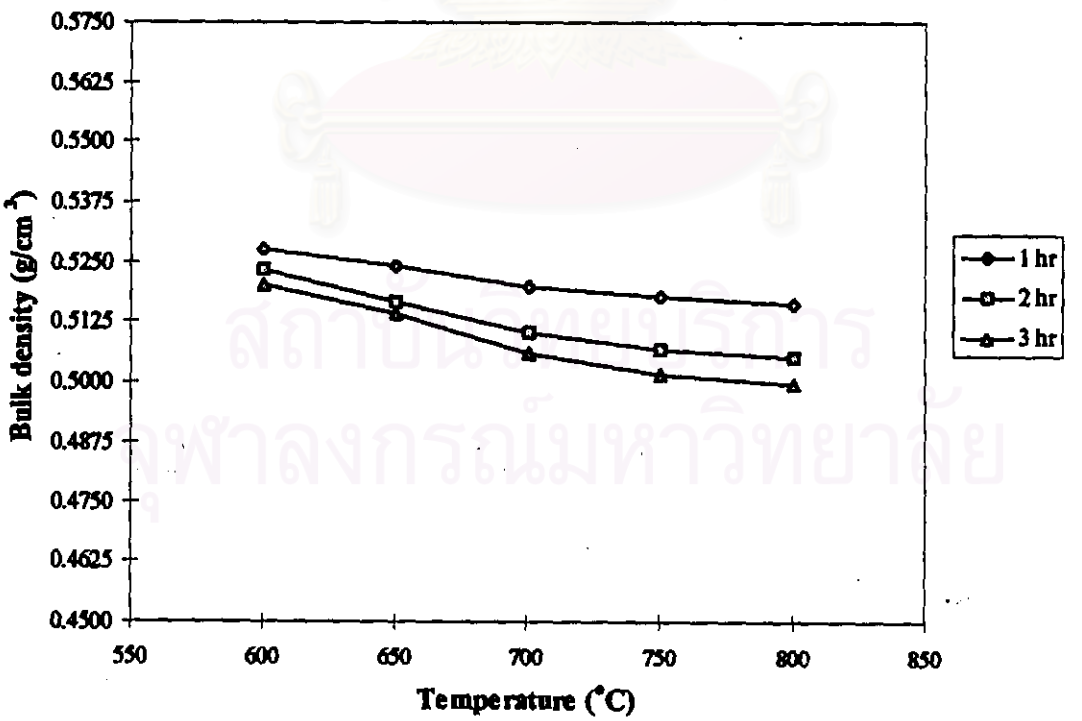

Figure 4.20 Effect of temperature on bulk density at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

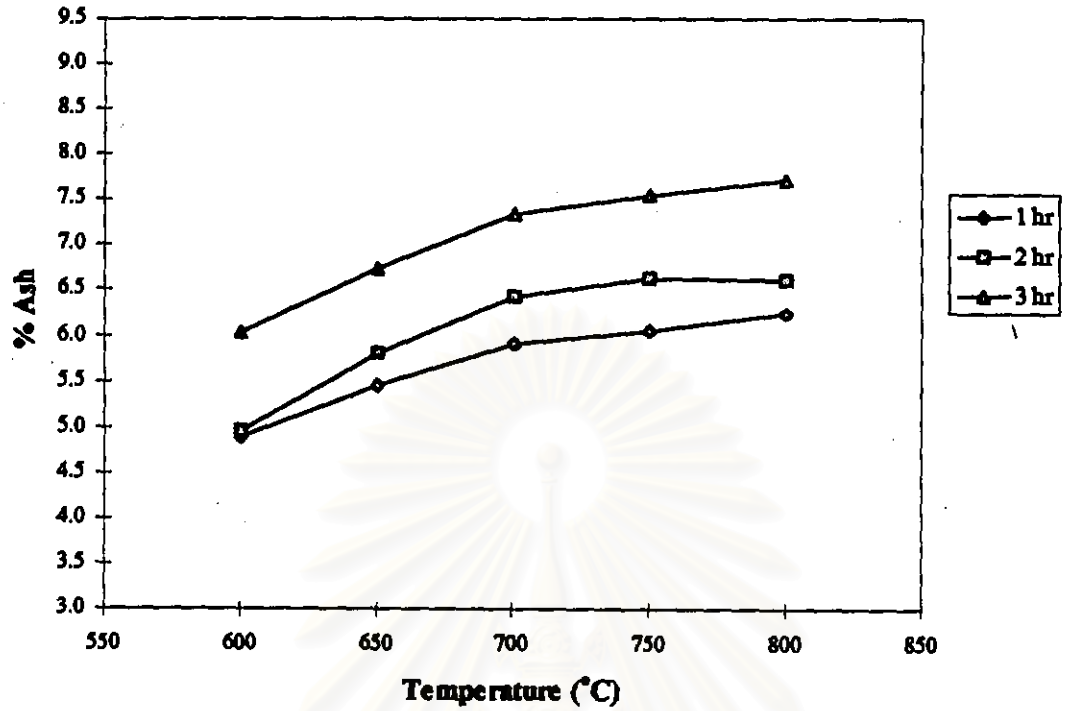

Figure 4.21 Effect of temperature on %ash at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

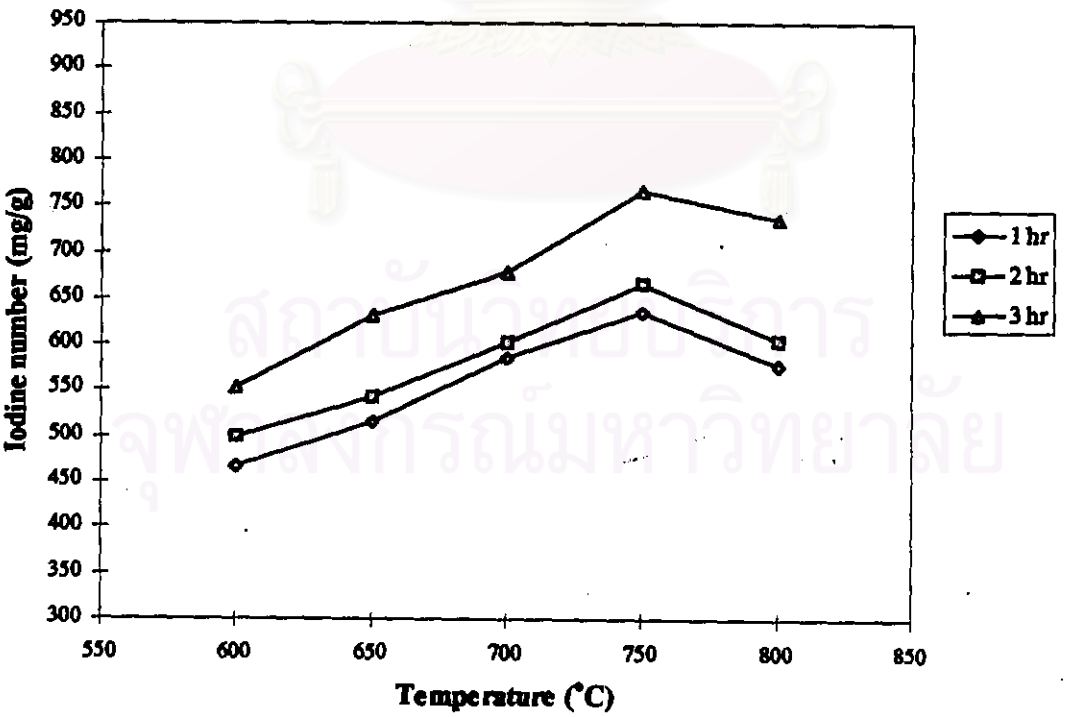

Figure 4.22 Effect of temperature on iodine number at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

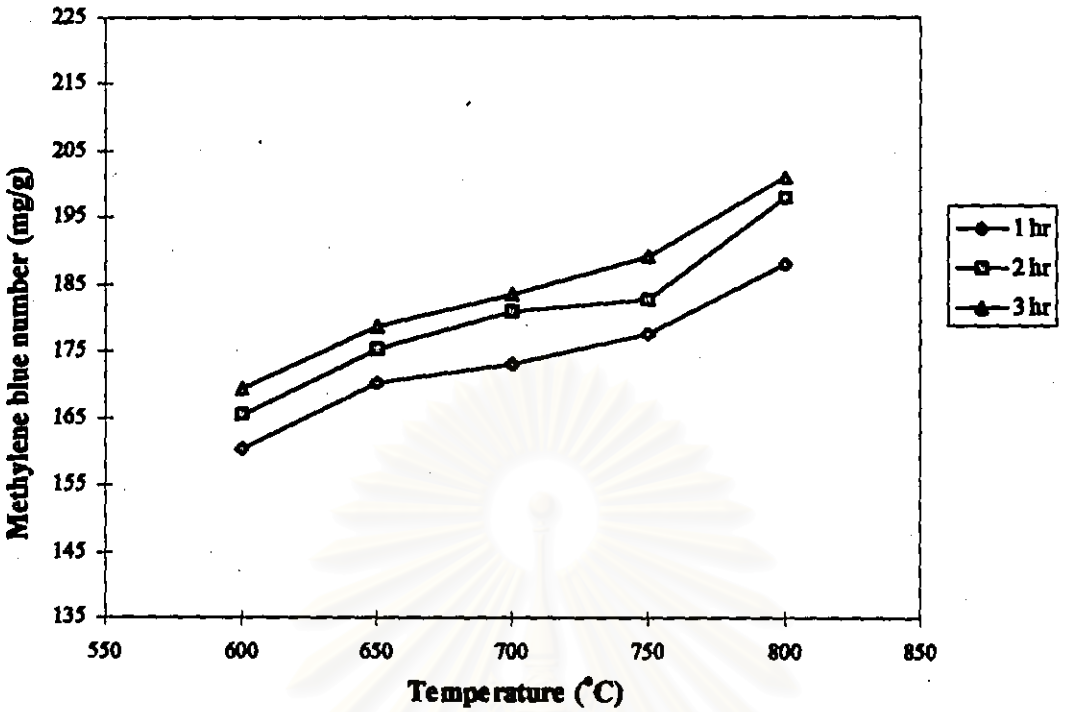

Figure 4.23 Effect of temperature on methylene blue number at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

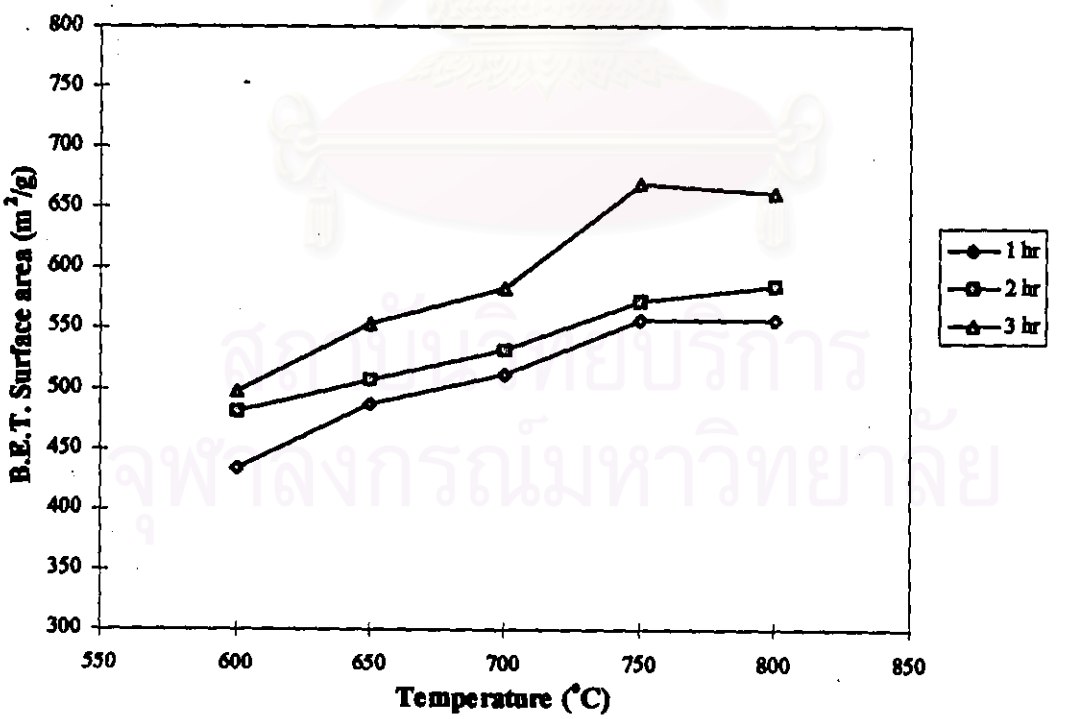

Figure 4.24 Effect of temperature on B.E.T. surface area at different times (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

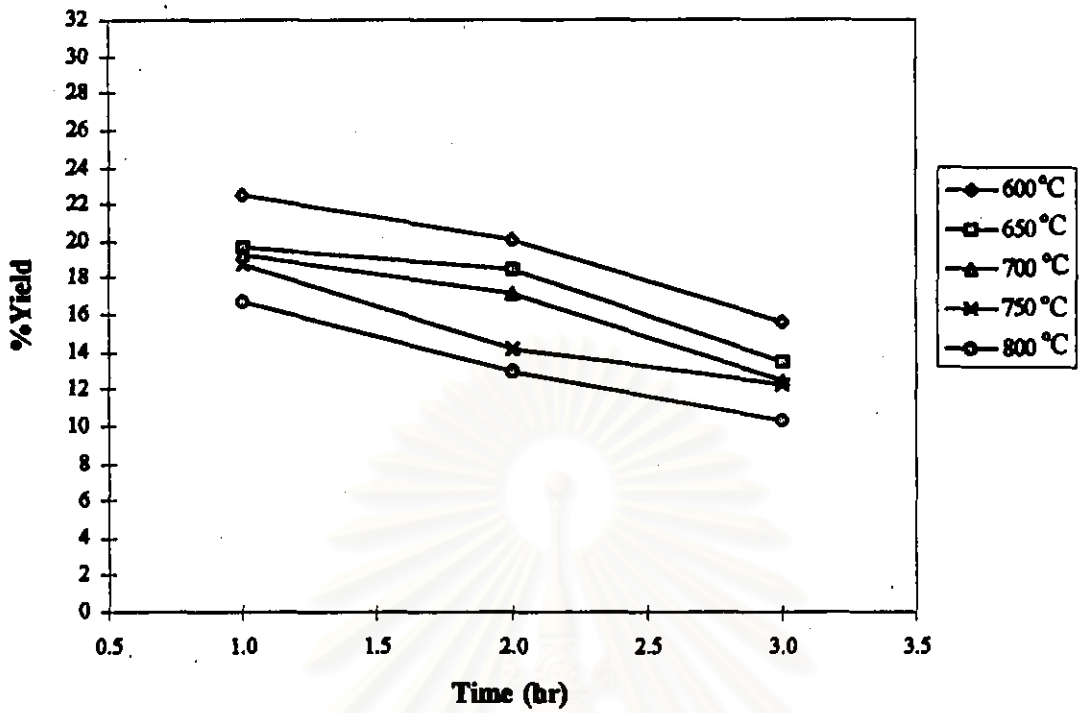

Figure 4.25 Effect of time on %yield at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

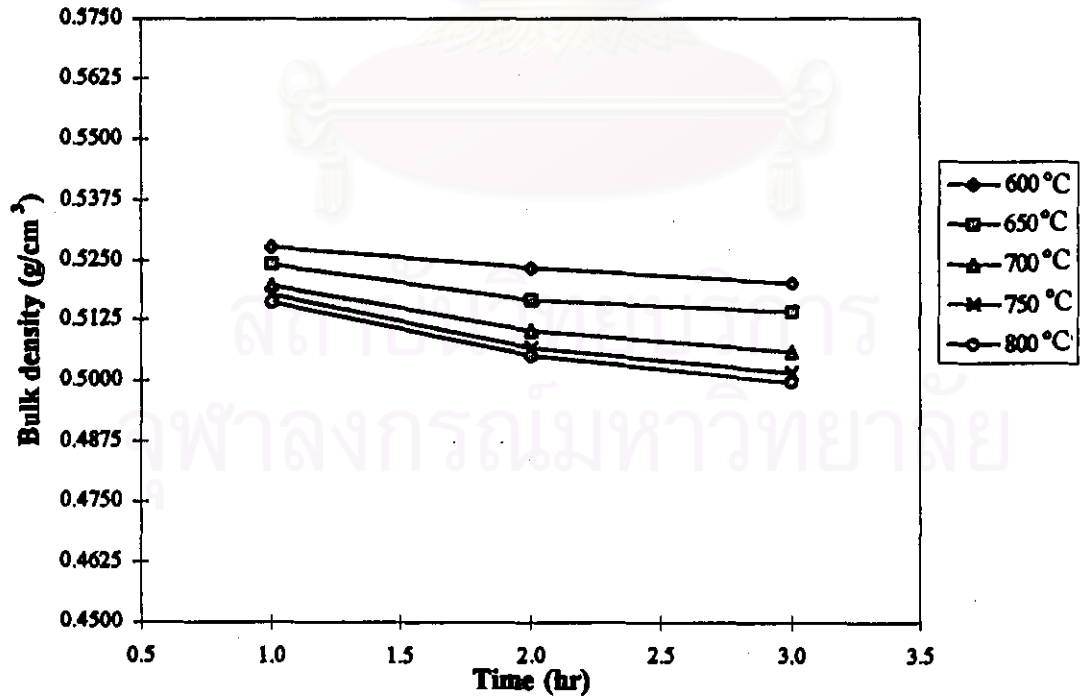

Figure 4.26 Effect of time on bulk density at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

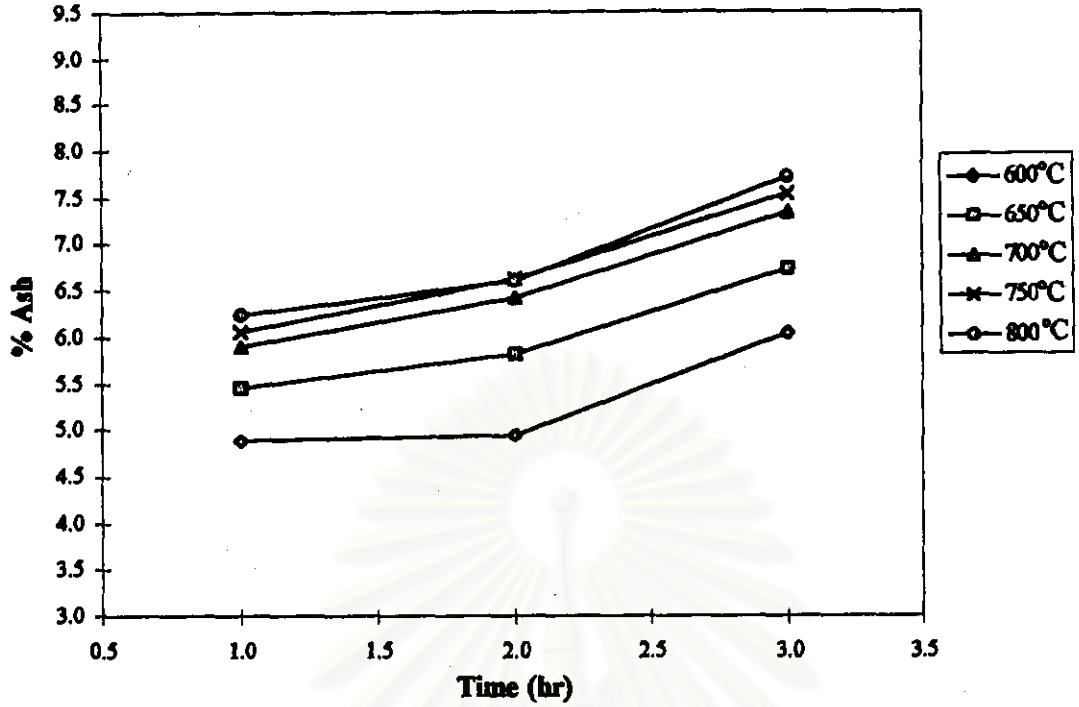

Figure 4.27 Effect of time on %ash at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

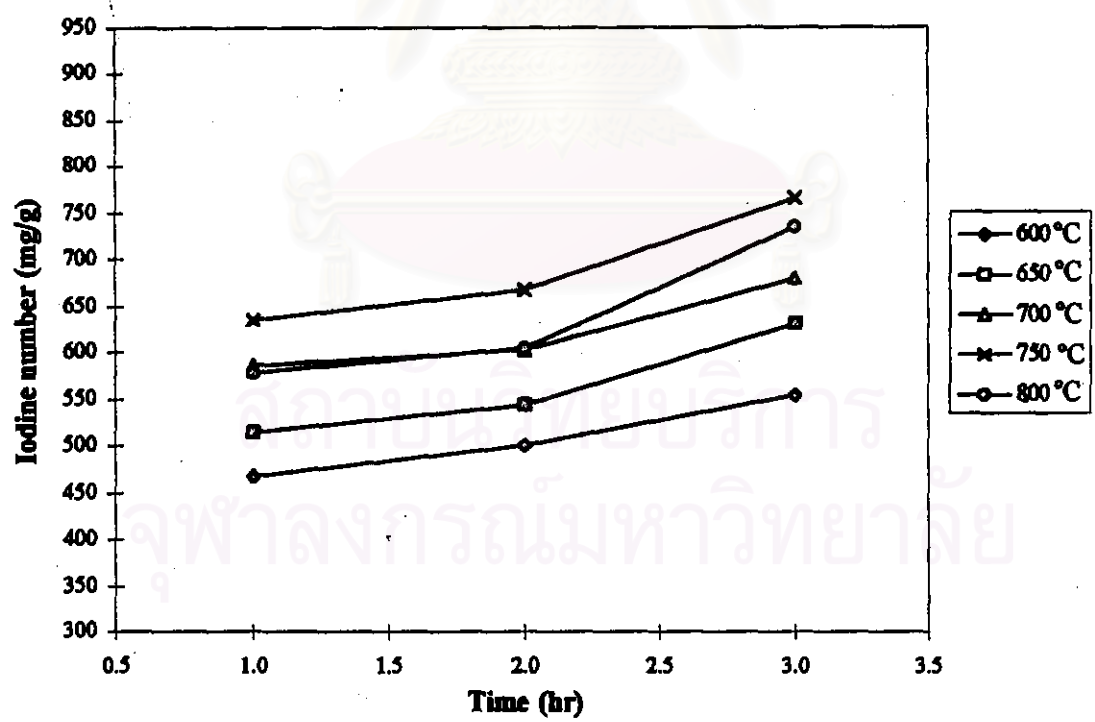

Figure 4.28 Effect of time on iodine number at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

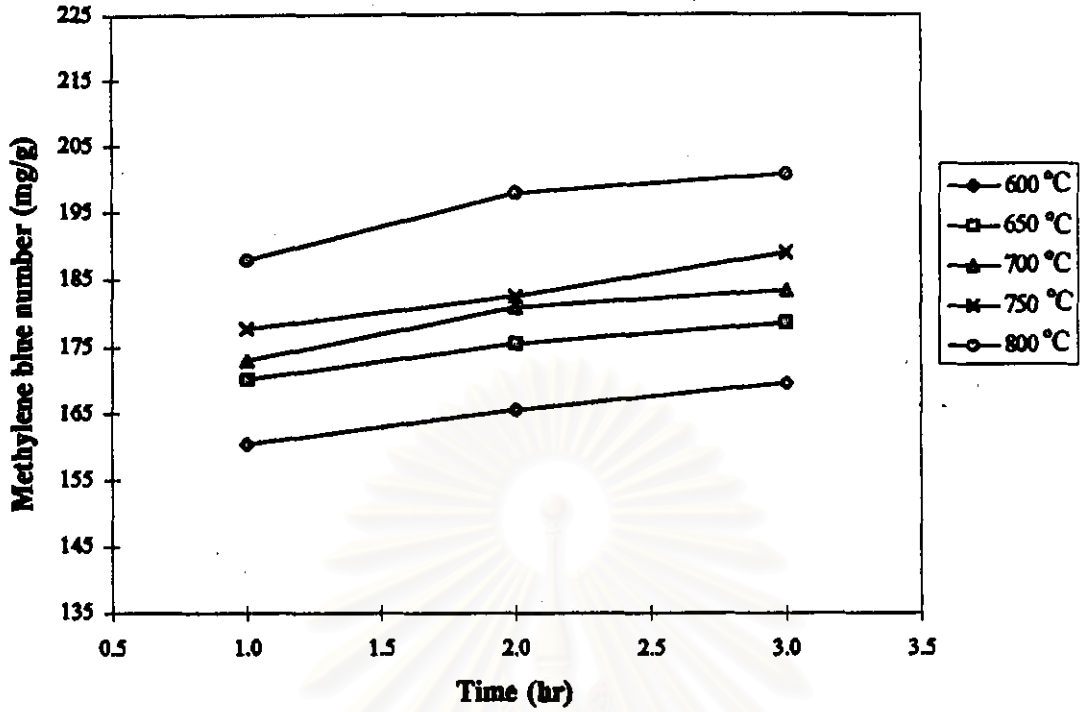

Figure 4.29 Effect of time on methylene blue number at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

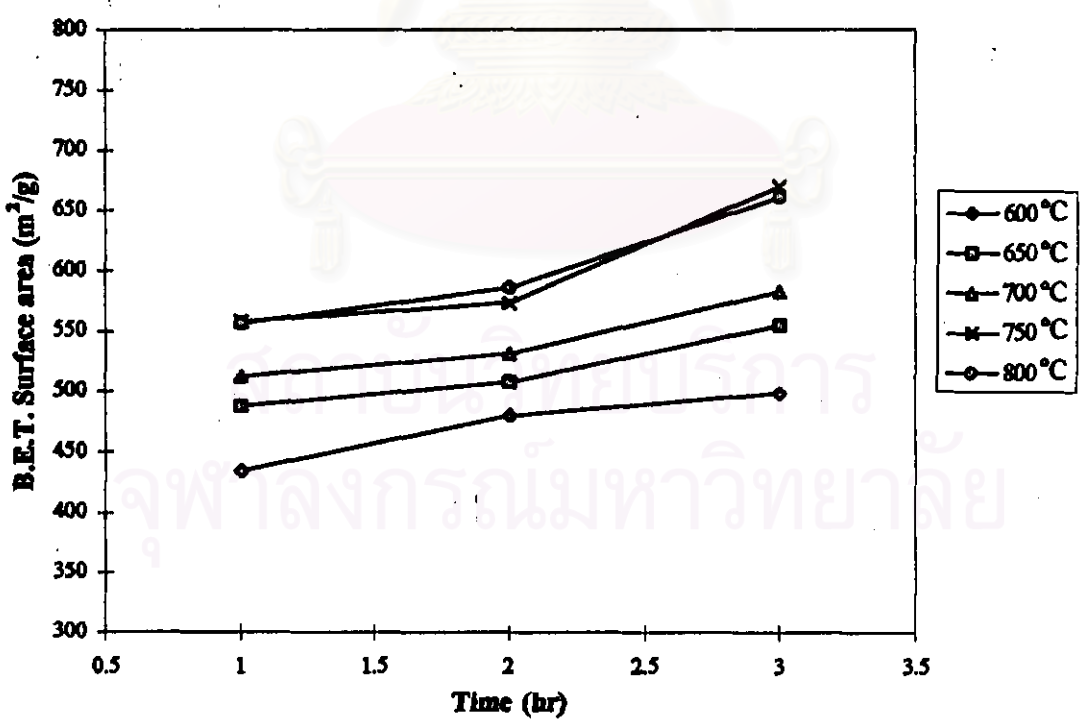

Figure 4.30 Effect of time on B.E.T. surface area at different temperatures (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

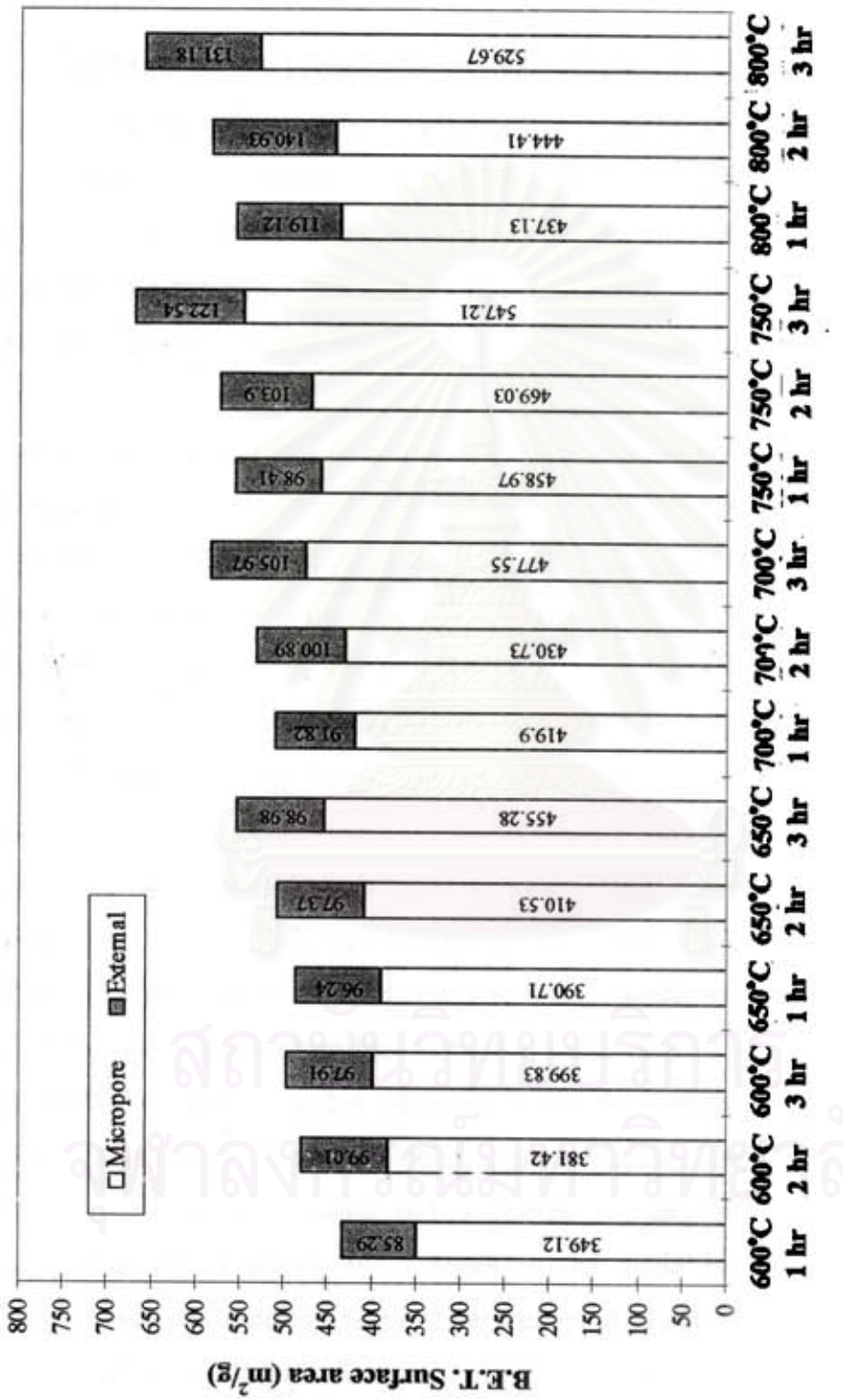

Figure 4.31 Effect of temperature and time on B.E.T. Surface area (pyrolysis with air 30 min, size 1.18 - 2.36 mm, 200 g, air 0.72 nl/min and steam).

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

From **Table 4.7** and **Figure 4.22**, the temperature increases from 600 to 750°C for 1, 2 and 3 hr, the iodine number increases. But when the temperature increases to 800°C, the iodine number decreases, which is the same trend as that B.E.T.surface area (**Figure 4.24**). When the temperature increases from 600 to 800°C for 1, 2 and 3 hr (**Figure 4.23**) the methylene blue number would increase. The % changes of iodine number, methylene blue number and B.E.T.surface area are shown in **Table 4.8**.

Figures 4.22-4.24, the iodine number, the methylene blue number and the B.E.T. surface area would increase when the temperature increases from 600 to 650 °C. Increasing of the B.E.T. surface area, the iodine number and the methylene blue number in this step are 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 is developed quickly at low temperature. 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 are 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 decreases, while the methylene blue number still increases. And the B.E.T.surface area decreases until it is constant because the reaction in this temperature range, is 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 B.E.T. surface area is nearly constant.

Table 4.8 The % change of characteristics of activated carbon from palm-oil shells when activation temperature increases from 600 to 800°C for 1, 2 and 3 hr (pyrolysis with air 30 min before steam activation).

t (hr)	T (°C)	% Y	BD (g/cm^3)	% Ash	IA (mg/g)	MB (mg/g)	S_{BET} (m^2/g)
1	600	22.53	0.5277	4.88	467.17	160.49	434.41
	↓				↑		↑
	750				635.16		557.38
	% Change	↓	↓	↑	+35.96	↑	+28.31
	750				635.16		557.38
	↓				↓		↓
	800	16.75	0.5162	6.23	575.57	188.00	556.26
	% Change	-25.65	-2.18	+27.66	-9.38	+17.14	-0.20
2	600	20.06	0.5234	4.95	499.63	165.53	480.43
	↓				↑		↑
	750				667.14		572.93
	% Change	↓	↓	↑	+33.53	↑	+19.25
	750				667.14		572.93
	↓				↓		↑
	800	12.90	0.5051	6.61	604.27	198.00	585.34
	% Change	-35.69	-3.50	+33.54	-9.42	+19.62	+2.17
3	600	15.59	0.5201	6.03	553.02	169.47	497.74
	↓				↑		↑
	750				766.99		669.75
	% Change	↓	↓	↑	+38.69	↑	+34.56
	750				766.99		669.75
	↓				↓		↓
	800	10.34	0.4996	7.72	735.31	200.91	660.85
	% Change	-33.68	-3.94	+28.03	-4.13	+18.55	-1.33

↑ : increase ↓ : decrease

Table 4.7 and **Figure 4.20**, the bulk density decreases with the increasing of temperature from 600 to 800°C for 1, 2 and 3 hr. The % change of bulk density is shown in **Table 4.8**. The bulk density decreases quickly because the steam easily penetrates into the surface of palm-oil shell particles, so the porosity development of activated carbon increases. As a result, the weight of activated carbon decerases, thus the bulk density in this temperature range decreases.

Table 4.7, when the temperautre increases from 600 to 800°C for 1, 2 and 3 hr, the % yield decreases (**Figure 4.19**) while the % ash increases (**Figure 4.21**). Because at high temperature, the volatile matter is removed suddenly and the partial combustion of some carbon in particles develops quickly; with this result, some carbon in the surface changes into ash and the porosity is developed highly in granules at the same time. The % changes of % yield and % ash are shown in **Table 4.8**.

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

4.2.4.2 The optimum time for pyrolysis with air 30 min before steam activation

Table 4.9 The % change of characteristics of activated carbon from palm-oil shells with the time range of 1-3 hr for 600, 650, 700, 750 and 800°C (pyrolysis with air 30 min before steam activation).

T (°C)	t (min)	% Y	BD (g/cm^3)	% Ash	IA (mg/g)	MB (mg/g)	$S_{B.E.T.}$ (m^2/g)
600	1	22.53	0.5277	4.88	467.17	160.49	434.41
	↓	↓	↓	↑	↑	↑	↑
	3	15.59	0.5201	6.03	553.02	169.47	497.74
	% Change	-30.80	-1.44	+23.57	+18.38	+5.60	+14.58
650	1	19.70	0.5240	5.45	515.22	170.15	486.95
	↓	↓	↓	↑	↑	↑	↑
	3	13.47	0.5143	6.73	630.58	178.71	554.26
	% Change	-31.62	-1.85	+23.49	+22.39	+5.03	+13.82
700	1	19.28	0.5198	5.90	586.20	172.95	511.72
	↓	↓	↓	↑	↑	↑	↑
	3	12.48	0.5060	7.33	679.41	183.44	583.52
	% Change	-35.27	-2.65	+24.24	+15.30	+6.07	+14.03
750	1	18.71	0.5178	6.06	635.16	177.58	557.38
	↓	↓	↓	↑	↑	↑	↑
	3	12.18	0.5017	7.54	766.99	189.20	669.75
	% Change	-34.90	-3.11	+24.42	+20.76	+6.54	+20.16
800	1	16.75	0.5162	6.23	577.57	188.00	556.26
	↓	↓	↓	↑	↑	↑	↑
	3	10.34	0.4996	7.72	735.31	200.91	660.85
	% Change	-38.27	-3.22	+23.92	+27.31	+6.87	+18.80

↑ : increase ↓ : decrease

Table 4.7, with the time range of 1-3 hr for 600, 650, 700, 750 and 800°C, the % yield decreases (**Figure 4.25**) but the % ash increases (**Figure 4.27**) because at long time activation, the volatile matter is more removed from particles, the partial combustion of some carbon in particle reacts more with air, and the porosity develops in granules with the increased temperature. The % changes of % yield and % ash are shown in **Table 4.9**.

Figure 4.26, the bulk density decreases while the increasing of activation time because the steam reacts at the surface of particles for a long time, the porosity development increases, so the weight of activated carbon would be less; as a result, bulk density decreases. The % change of bulk density is shown in **Table 4.9**. From **Table 4.7**, with the time range of 1 to 3 hr for 600, 650, 700, 750 and 800°C, the iodine number (**Figure 4.28**), the methylene blue number (**Figure 4.29**) and the B.E.T. surface area (**Figure 4.30**) are all increased. The % changes of these are shown in **Table 4.9**. At long time activation, the steam penetrates deeper than at short time, so the porosity development at long time is higher than at short time, resulting in the increase of the iodine number, the methylene blue number and the B.E.T. surface area.

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

The optimum condition for pyrolysis with air 30 before steam activation is 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, B.E.T. 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.

4.3 Comparison of this work with other work

The comparison of this work with Patra Panyawathanakit[29] (1997) and Gergova *et al.*[13] (1993) is presented with respect to the maximum surface area obtained (**Table 4.10**).

Table 4.10 Comparison of this work with Patra Panyawathanakit (1997) and Gergova *et al.* (1993).

	This work (1998)	Patra (1997)	Gergova *et al.* (1993)
Raw material	Palm-oil shell	Palm-oil shell	Coconut shell
Carbonization	750°C for 3 hr by add pyrolysis with air for 30 min before steam activation	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	-
$S_{B.E.T.}$	669.75 m^2/g	670.10 m^2/g	700 m^2/g

Patra produces 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 are obtained at 750°C for 3 hr with pyrolysis in air for 30 min. It also observes 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[26] proposes that the optimum volatile in chars obtaining from carbonized step is in the range of 20-30 % in order to obtain high quality activated carbon after being activated by steam. The two step method can have the volatile controlled by proximate analysis of chars in carbonized step but in the one step method, 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). Anyhow, time of the one step production for activation spends more time.

Gergova *et al.*, which uses the same method (one step pyrolysis/steam activation) to produce the activated carbon from coconut shells, they reports that the maximum surface area is 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.

The adsorption capacity of the commercial activated carbon follows TIS 900-1989[27], which iodine number is over 600 mg/g. The activated carbon which has been produced in this work, having iodine number of 776.99 mg/g meets the standard of comercial activated carbon.

4.4 Correlation between % burn-off and the B.E.T. surface area as a function of the activation temperature

Figure 4.32 shows the change in the % burn-off and in the B.E.T. 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 increases, the B.E.T. surface area reaches a maximum at 750°C and then decreases. This observed behaviour of the B.E.T. surface area at large % burn-off is well known and is attributed to the transformation of micropores into mesopores by a burn-off mechanism in the internal wall of the micropores[19].

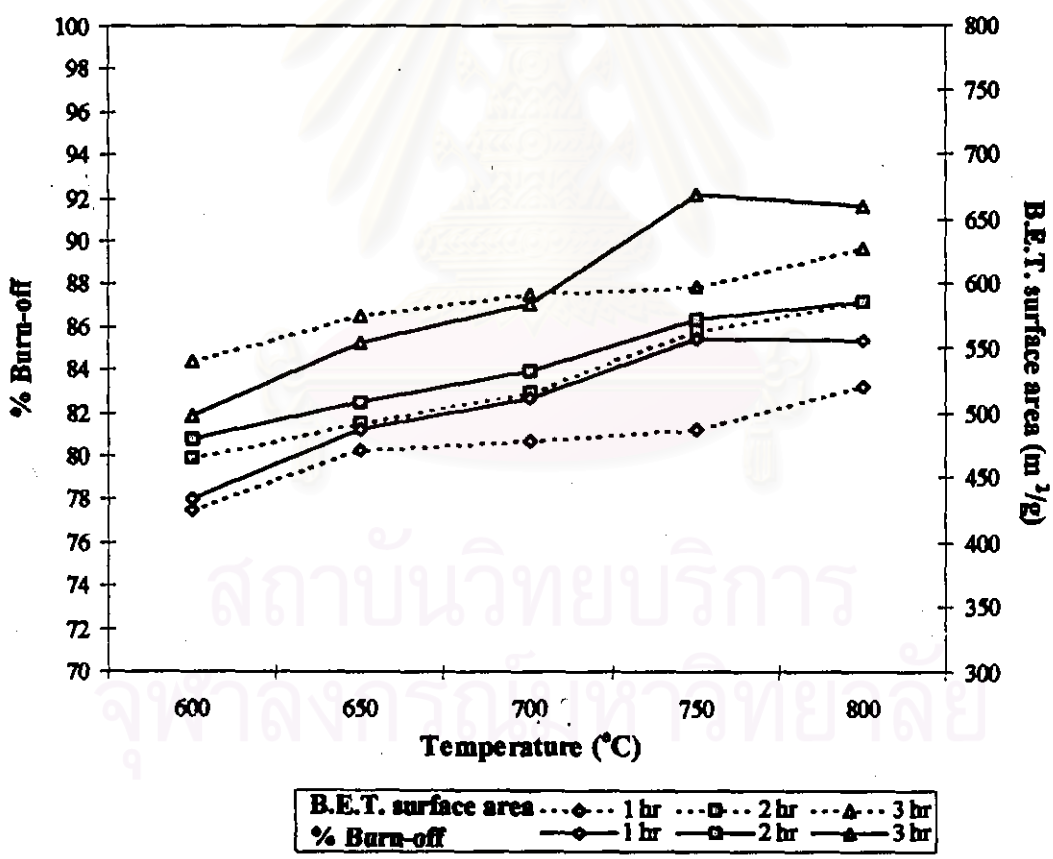

Figure 4.32 Correlation between % burn-off and the B.E.T. surface area as a function of the activation temperature.

4.5 Correlation between the iodine number and the B.E.T. surface area

The iodine number is correlated in terms of the B.E.T. surface area, using representative samples from the experiments covering the range of parameters in this study as shown in **Figure 4.33**. The iodine number shows the same trend as that for the B.E.T. surface area[19]. The iodine number increases with the increase of B.E.T. surface area. The iodine number gives an indication of the adsorption capacity of activated carbon in micropores[9]. The surface area of activated carbon is dependent on micropores area, so the iodine number provides a good indication of the surface area of an activated carbon.

$$y = 0.687x + 131.8$$

where :

y = B.E.T. surface area (m^2/g)

x = iodine number (mg/g)

R^2 = 0.9453

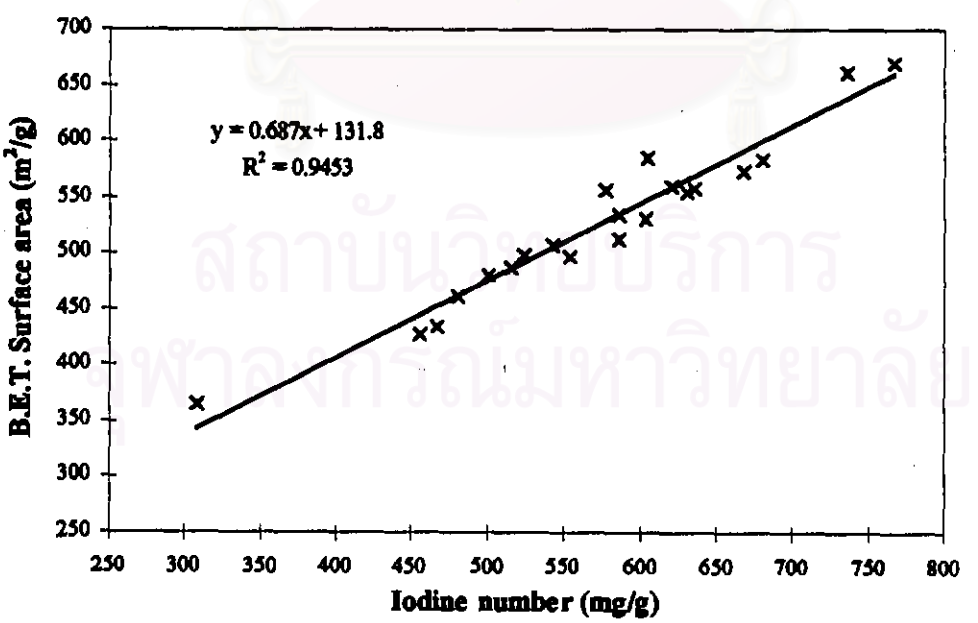

Figure 4.33 Correlation between the iodine number and the B.E.T. surface area.

4.6 Correlation between the methylene blue number and the B.E.T. surface area

The methylene blue number gives an indication of the adsorption capacity of an activated carbon for molecules having similar dimensions to methylene blue. It also gives an indication of the surface area of the activated carbon which results from the existence of mesopores of dimensions over than 1.5 nm[9]. The methylene blue number is correlated in terms of the B.E.T. surface area, using representative samples from the experiments covering the range of parameters in this study as shown in **Figure 4.34**. At the high value of methylene blue number, the B.E.T. surface area increases slowly. The experiment data show that methylene blue number is higher when the temperature and time for activation increase. Under fast reaction condition for activation, micropores would become mesopores or macropores which would result in a reduction of the B.E.T. surface area.

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

where :

y = B.E.T. surface area (m^2/g)

x = methylene blue number (mg/g)

R^2 = 0.8699

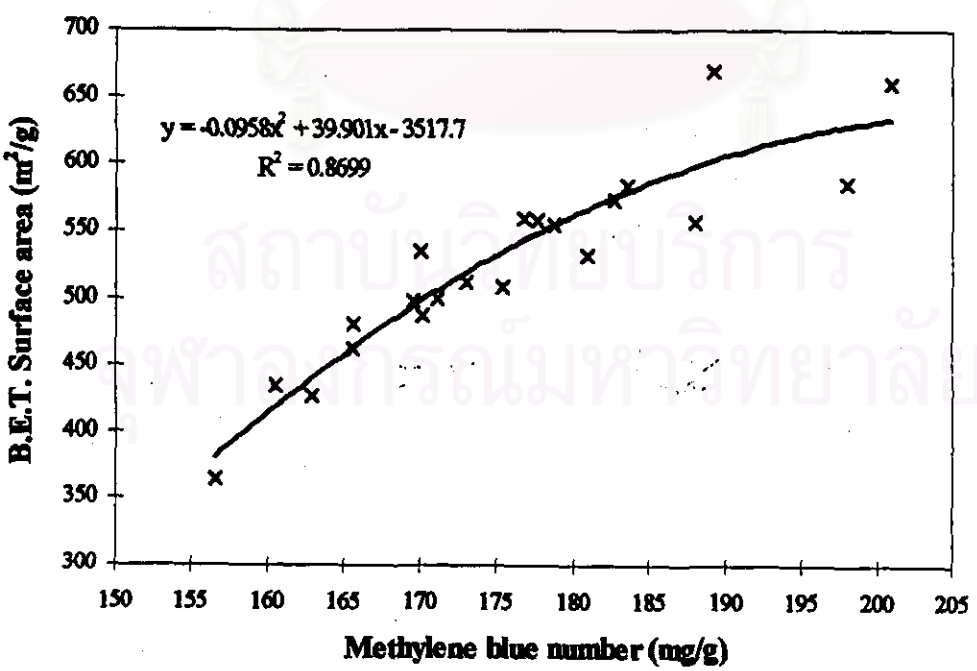

Figure 4.34 Correlation between methylene blue number and the B.E.T. surface area.