CHAPTER IV

RESULTS AND DISCUSSION

4.1 Raw material

The raw material was prepared from used tires by cutting into pieces with the size of 5 x 5 x 5 mm.

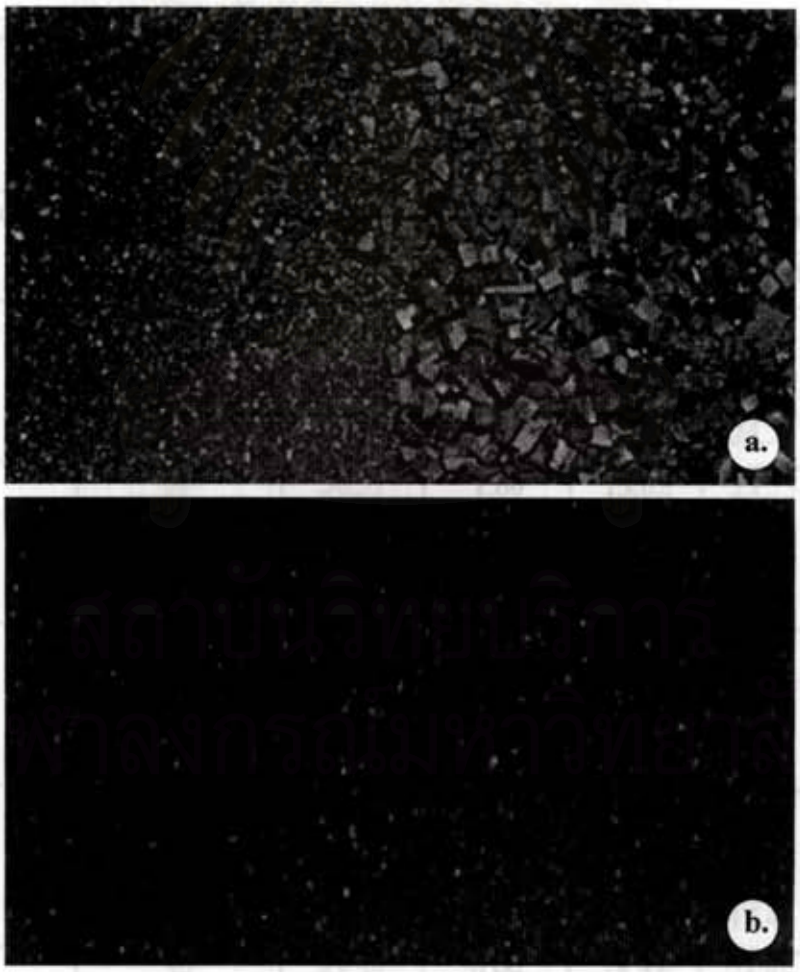

Figure 4.1 **(a)** char from used tires and **(b)** activated carbon from used tires.

4.2 Results and discussion of the experiments

4.2.1 Carbonization

The 500 g of cut pieces (about 5 x 5 x 5 mm in size) of used tires were charged into the carbonizer with the air flow rate of 0.52 nl/min. This experiment was carried out at the temperature of 300, 350, 400, 450 and 500°C, with each temperature, we varied time of 30, 60 and 90 min for carbonization. The final products of this step are called "chars". The proximate analysis of chars are shown in **Table 4.1** and **Figures 4.2-4.9.**

Table 4.1 Characteristics of tire chars from carbonized at different temperatures and times (size 5 x 5 x 5 mm, 500 g, air 0.52 nl/min).

Temperature (°C)	Time (min)	% Y	% M	on dry basis		
				% Ash	% VM	% FC
300	30	52.61	1.04	14.45	28.51	57.04
	60	47.66	1.39	14.63	26.12	59.25
	90	41.26	1.61	14.75	24.23	61.02
350	30	50.51	1.66	15.02	25.25	59.73
	60	41.40	1.63	15.30	22.13	62.57
	90	38.96	1.26	15.50	20.29	64.21
400	30	46.65	1.14	15.99	23.55	60.46
	60	40.29	1.56	16.31	21.45	62.24
	90	37.04	1.11	17.69	19.08	63.23
450	30	45.42	1.01	18.10	22.14	59.76
	60	40.20	0.76	18.59	19.39	62.02
	90	36.48	0.84	19.46	17.42	63.12
500	30	43.55	0.99	18.48	21.85	59.67
	60	37.29	0.65	19.51	18.53	61.96
	90	34.26	0.53	20.53	17.12	62.35

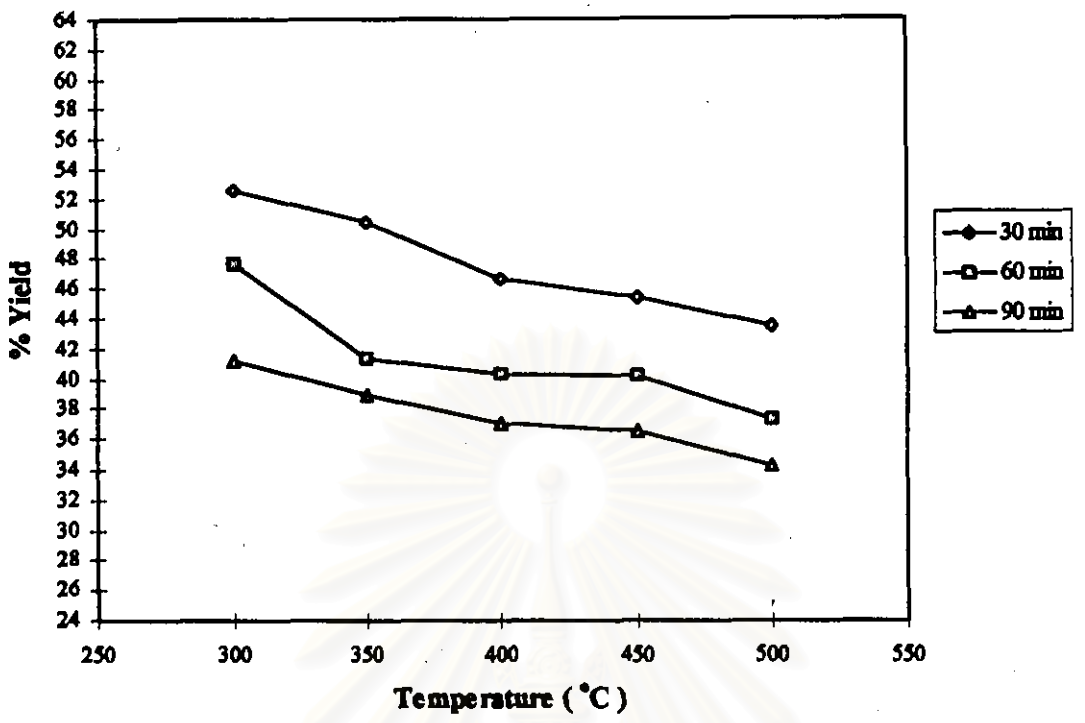

Figure 4.2 Effect of temperature on % yield at different times (size 5 x 5 x 5 mm, 500 g, air 0.52 nl/min).

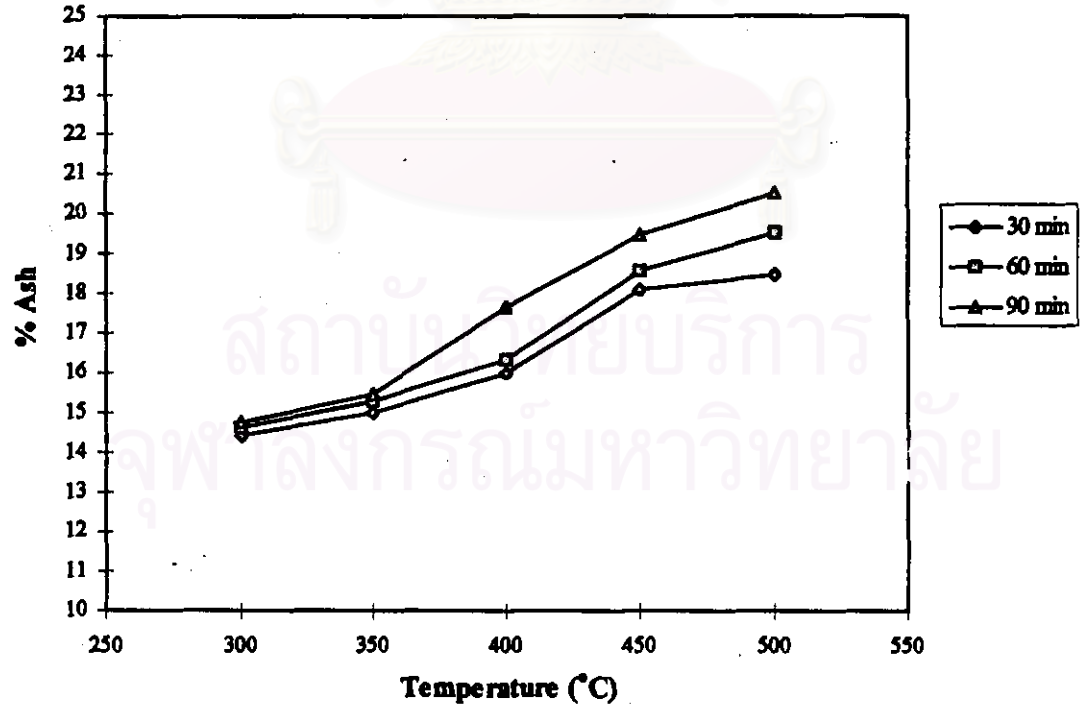

Figure 4.3 Effect of temperature on % ash at different times (size 5 x 5 x 5 mm, 500 g, air 0.52 nl/min).

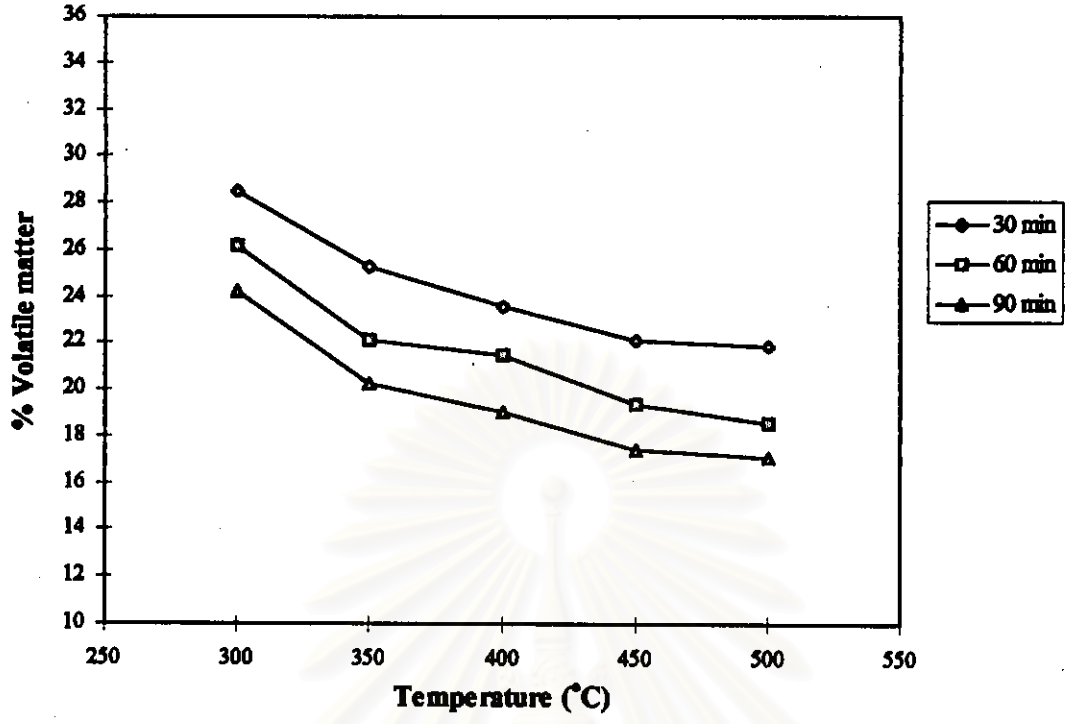

Figure 4.4 Effect of temperature on % volatile matter at different times (size 5 x 5 x 5 mm, 500 g, air 0.52 nl/min).

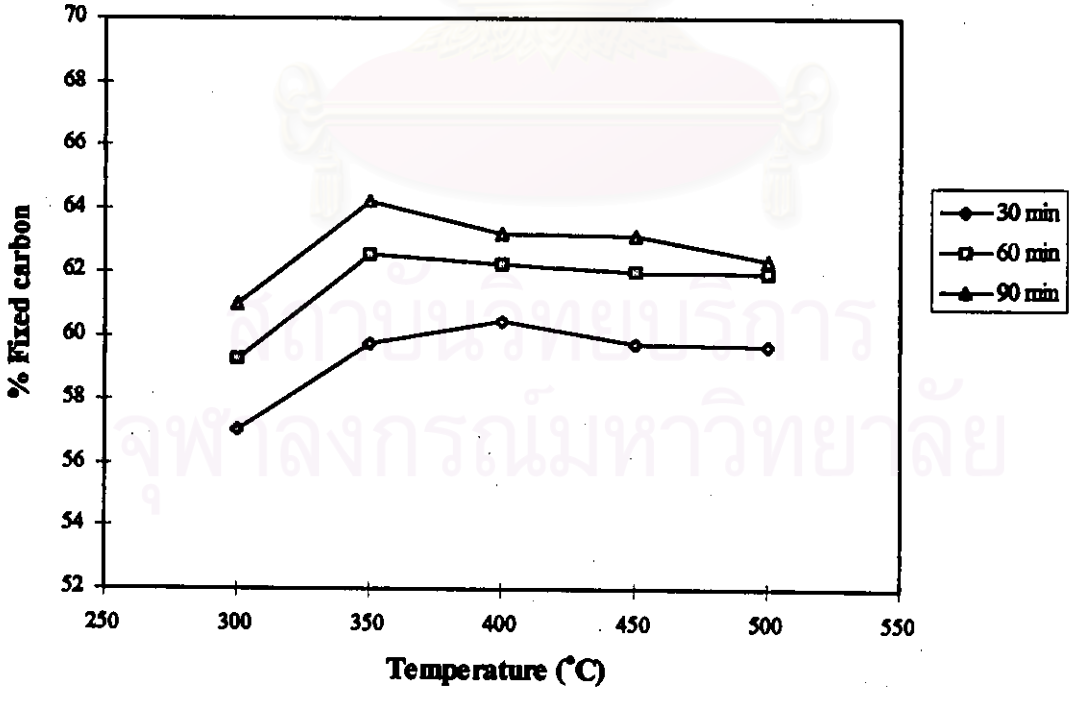

Figure 4.5 Effect of temperature on % fixed carbon at different times (size 5 x 5 x 5 mm, 500 g, air 0.52 nl/min).

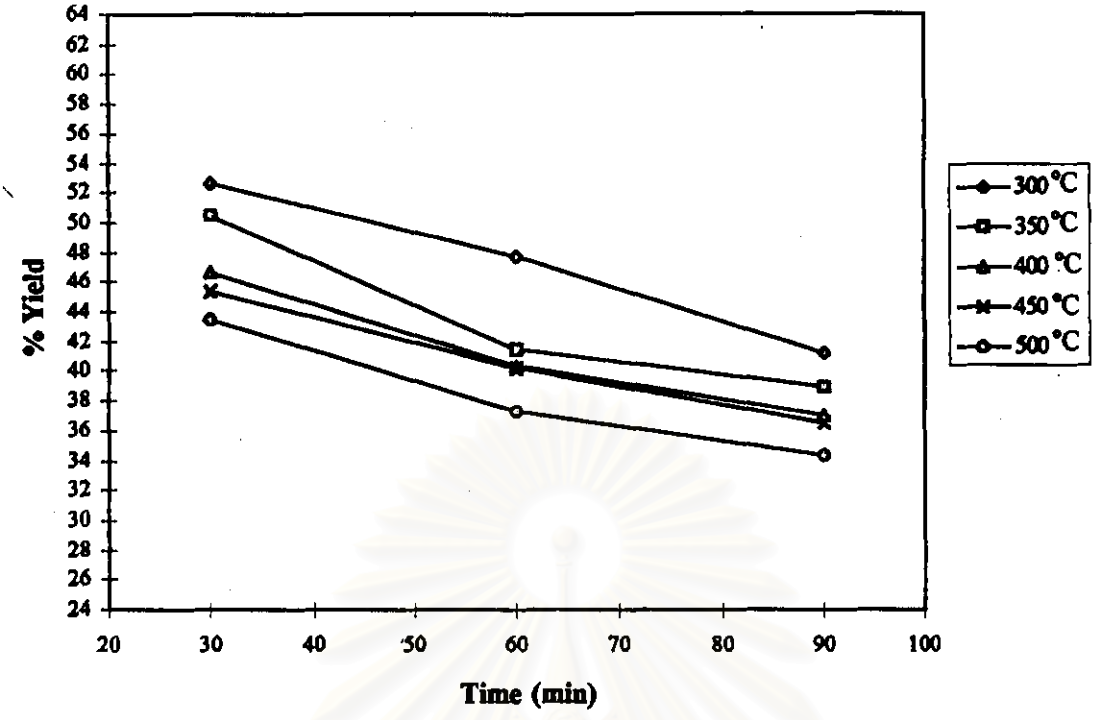

Figure 4.6 Effect of time on % yield at different temperature (size 5 x 5 x 5 mm, 500 g, air 0.52 nl/min).

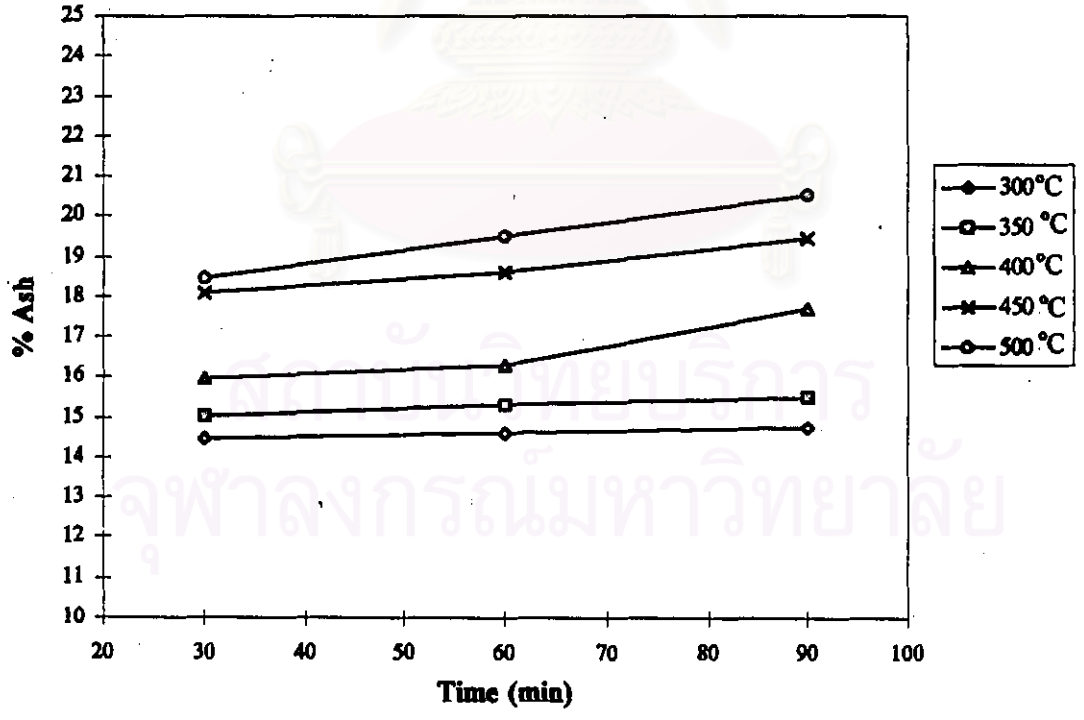

Figure 4.7 Effect of time on % ash at different temperature (size 5 x 5 x 5 mm, 500 g, air 0.52 nl/min).

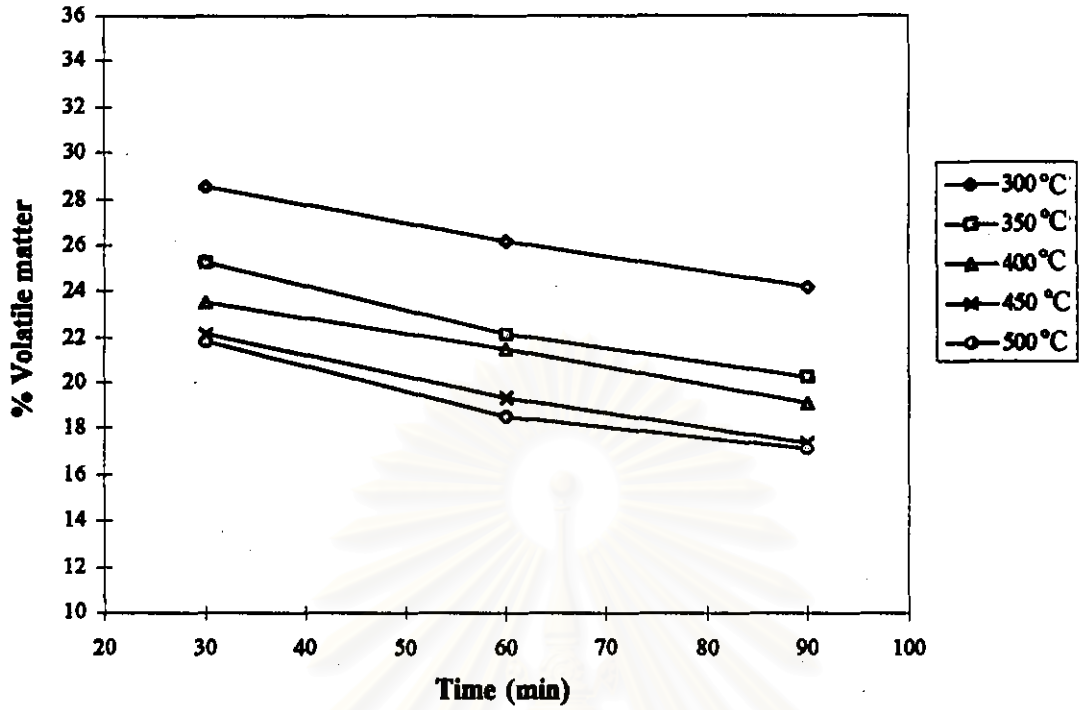

Figure 4.8 Effect of time on % volatile matter at different temperature (size 5 x 5 x 5 mm, 500 g, air 0.52 nl/min).

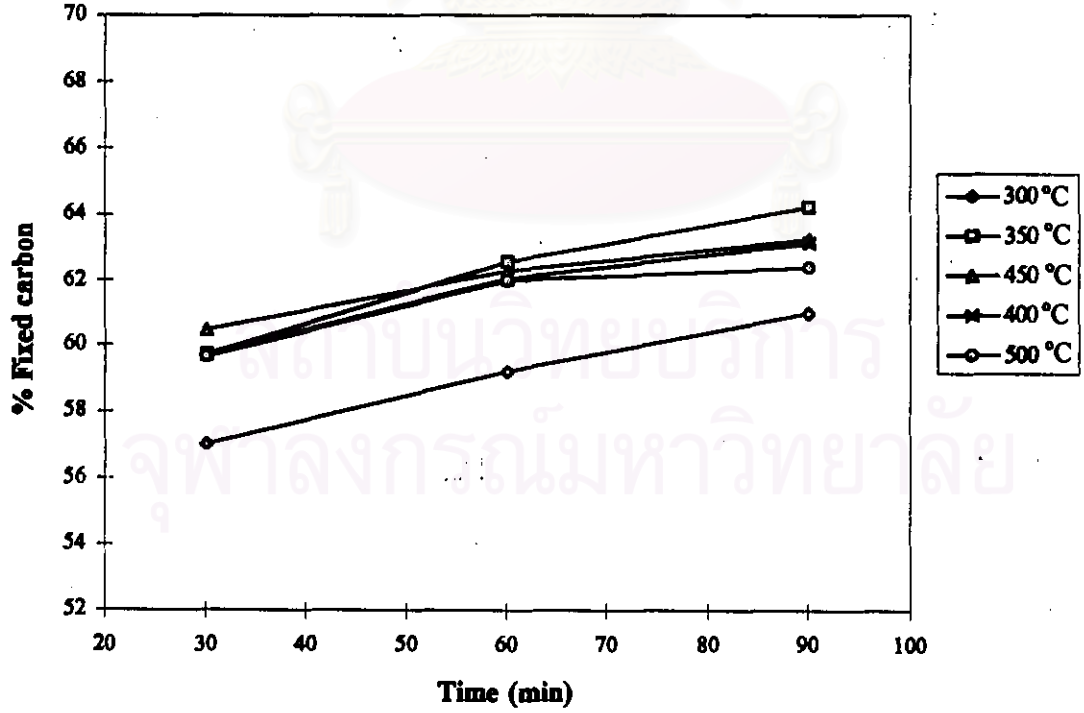

Figure 4.9 Effect of time on % fixed carbon at different temperature (size 5 x 5 x 5 mm, 500 g, air 0.52 nl/min).

4.2.1.1 The optimum temperature for carbonization

Table 4.1 and **Figure 4.2** show that the % yields of various carbonization decrease while the temperature increases because at high temperature, the carbon in used tires is progressively gasified and diffused with volatile, so the volatile in the products decreases, resulting in the decrease of % yield. The % change of % yield is shown in **Table 4.2.**

Table 4.2 The % change of characteristics of char from used tires when carbonization temperature increases from 300 to 500°C for 30, 60 and 90 min.

t (min)	T (°C)	% Y	% Ash	% VM
30	300	52.61	14.45	28.51
	↓	↓	↑	↓
	500	43.55	18.48	21.85
	% Change	-17.22	+27.89	-23.36
60	300	47.66	14.63	26.12
	↓	↓	↑	↓
	500	37.29	19.51	18.53
	% Change	-21.76	+33.36	-29.06
90	300	41.26	14.75	24.23
	↓	↓	↑	↓
	500	34.26	20.53	17.12
	% Change	-16.97	+39.19	-29.34

↑ : increase ↓ : decrease

From **Table 4.1** and **Figure 4.3**, the change of the % ash in temperature range of 300-400°C is small because at low temperature, only the volatile is removed. But at high temperature, some tires react with air too extremely and change into ash. Thus, when the temperature increases from 400 to 500°C, the % ash increases quickly. The increasing of the % change of the % ash in range of these temperatures is shown in **Table 4.2.**

Table 4.1 and **Figure 4.4**, the volatile matter in the temperature range of 300-400°C decreases quickly because the low temperature has largely effected the rate of diffusion of the volatile out of the surface of particle. In contrast, this effect is less when the temperature is above 400°C. With this less effect, the rate of diffusion is more or less stable, and the % change is small. The % change of volatile matter for 300-500°C is shown in **Table 4.2**.

Table 4.1 and **Figure 4.5**, while the temperature increases from 300 to 350°C, the % fixed carbon increases largely owing to immediately taking place of carbonization. The % fixed carbon has the highest increase at 350°C. But above 350 °C , it would decrease, due to the reason that the tires contain carbon black, inorganic and SBR which has straight chain polymer as a structure. When the temperature increases above 350°C, some C-C bond in this structure is broken. Then, carbon can react more with air and changes finally into ash, thus the % fixed carbon has a trend to decrease. At 450-500°C, the % fixed carbon's trend is constant.

The optimum condition for carbonization of used tires in this experiment is 350 °C because the characteristic of chars at this temperature has 20-25 % of volatile matter[22] which is appropriate for activation. These carbonized used tires, or chars, have high fixed carbon, low ash and suitable yield.

4.2.1.2 The optimum time for carbonization

Table 4.1 and **Figure 4.6**, the increase of carbonization time leads to the decrease of the % yield because carbon in used tires is progressively gasified and diffused out with volatile. The % change of % yield is shown in **Table 4.3**.

Table 4.3 The % change of characteristics of chars from used tires when carbonization time increases from 30 to 90 min for 300, 350, 400, 450 and 500°C.

T (°C)	t (min)	% Y	% Ash	% VM	% FC
300	30	52.61	14.45	28.51	57.04
	↓	↓	↑	↓	↑
	90	41.26	14.75	24.23	61.02
	% Change	-21.57	+2.08	-15.01	+6.98
350	30	50.51	15.02	25.25	59.73
	↓	↓	↑	↓	↑
	90	38.96	15.50	20.29	64.21
	% Change	-22.87	+3.20	-19.64	+7.50
400	30	46.65	15.99	23.55	60.46
	↓	↓	↑	↓	↑
	90	37.04	17.69	19.08	63.23
	% Change	-20.60	+10.63	-18.98	+4.58
450	30	45.42	18.10	22.14	59.76
	↓	↓	↑	↓	↑
	90	36.48	19.46	17.42	63.13
	% Change	-19.68	+7.51	-21.32	+5.62
500	30	43.55	18.48	21.85	59.67
	↓	↓	↑	↓	↑
	90	34.26	20.53	17.21	62.35
	% Change	-21.33	+11.09	-21.65	+4.49

↑ : increase ↓ : decrease

Table 4.1 and **Figure 4.7**, the % ash increases with an increase in time because at long time, carbon in used tires is higher progressively gasified than at short time. The % change of % ash is shown in **Table 4.3**.

Table 4.1 and **Figure 4.8**, the decrease of volatile matter in the time range of 30-60 min is faster than at 60-90 min because in the first time range (30-60 min), only

volatile at the surface is removed. When time increases above 60 min, volatile in the interior particle would be removed, but with more difficulty than volatile at the surface The % change of volatile matter is shown in **Table 4.3.**

Table 4.1 and **Figure 4.9**, the % fixed carbon increases with an increase in time because the increase of time leads to the increase of volatile diffusion.

Considering from these results and characteristics, 30 and 60 min are better time for carbonization than 90 min. But 60 min is the best, because the chars with have been carbonized in 60 min will have the highest % fixed carbon. Thus the optimum time for carbonization of used tires is 60 min.

The optimum condition for carbonization of used tires in this experiment was 350°C for 60 min. The chars in this condition odtained yield of 41.40 %, ash of 15.30 %, volatile matter of 22.13 % and fixed carbon of 62.57 %.

4.2.2 Activation

The chars obtained from the optimum in carbonization step was crushed and sieved to the particle sizes of 0.25-0.60, 0.60-1.18, 1.18-2.36 and 2.36-4.75 mm. The proximate analysis of used tires and used tires char are shown in **Table 4.4.**

Table 4.4 Proximate analysis of used tires and used tires char.

Tires char sizes (mm)	% M	on dry basis					
		BD (g/cm^3)	% Ash	% VM	% FC	IA (mg/g)	MB (mg/g)
Used tires	1.07	-	9.84	59.86	30.30	-	-
0.25 - 0.60	1.02	0.4286	16.58	20.67	62.75	87.31	165.96
0.60 - 1.18	1.15	0.4202	16.37	21.03	62.60	66.22	163.57
1.18 - 2.36	1.04	0.3925	15.92	23.65	60.43	53.75	163.80
2.36 - 4.75	1.01	0.3969	15.83	23.68	60.49	45.73	159.23

4.2.2.1 The optimum temperature and time for activation

The 200 g of 1.18-2.36 mm of chars were charged into the fixed bed reactor followed with CO_2 and air at the flow rate of 5.0 nl/min and 0.27 nl/min, at 750, 800, 850 and 900°C, respectively. Then the superheated steam was passed through the reactor for 30, 45 and 60 min. The results are shown in **Table 4.5** and **Figures 4.10-4.22.**

Table 4.5 Characteristics of activated carbon from used tires at different temperatures and times (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

T (°C)	t (min)	%Y	%M	on dry basis				Surface area (m^2/g)		
				BD (g/cm^3)	Ash (%)	IA (mg/g)	MB (mg/g)	$S_{B.E.T.}$	S_{Micro}	$S_{External}$
750	30	50.63	6.65	0.3580	16.75	289.38	215.71	351.71	145.57	206.14
	45	48.37	6.75	0.3560	17.08	330.48	222.67	378.25	165.89	212.36
	60	46.23	7.89	0.3521	17.16	425.39	226.27	502.21	279.45	222.76
800	30	47.83	7.16	0.3489	17.86	414.35	224.64	491.66	271.71	219.95
	45	44.67	6.83	0.3475	18.59	445.24	230.14	519.32	293.74	225.58
	60	41.36	6.38	0.3462	19.95	531.12	235.95	609.72	378.24	231.48
850	30	46.32	7.05	0.3464	18.06	507.08	229.95	572.50	349.20	224.30
	45	40.59	7.59	0.3370	19.96	543.21	234.38	613.09	384.71	228.38
	60	36.21	8.21	0.3356	20.55	549.64	242.93	619.49	387.12	232.37
900	30	39.94	7.21	0.3361	19.21	532.33	244.07	615.25	380.40	234.85
	45	35.05	8.69	0.3221	20.75	570.45	253.95	644.94	399.19	245.75
	60	30.12	8.22	0.3191	21.79	558.55	259.82	639.94	389.33	250.61

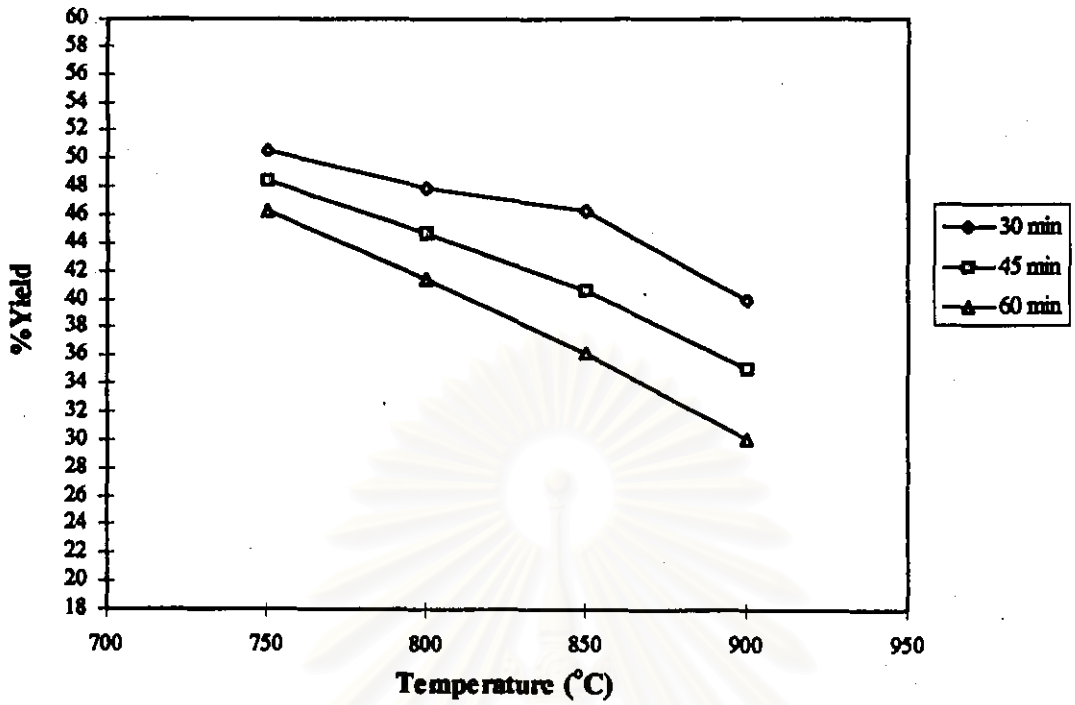

Figure 4.10 Effect of temperature on % yield at different time (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

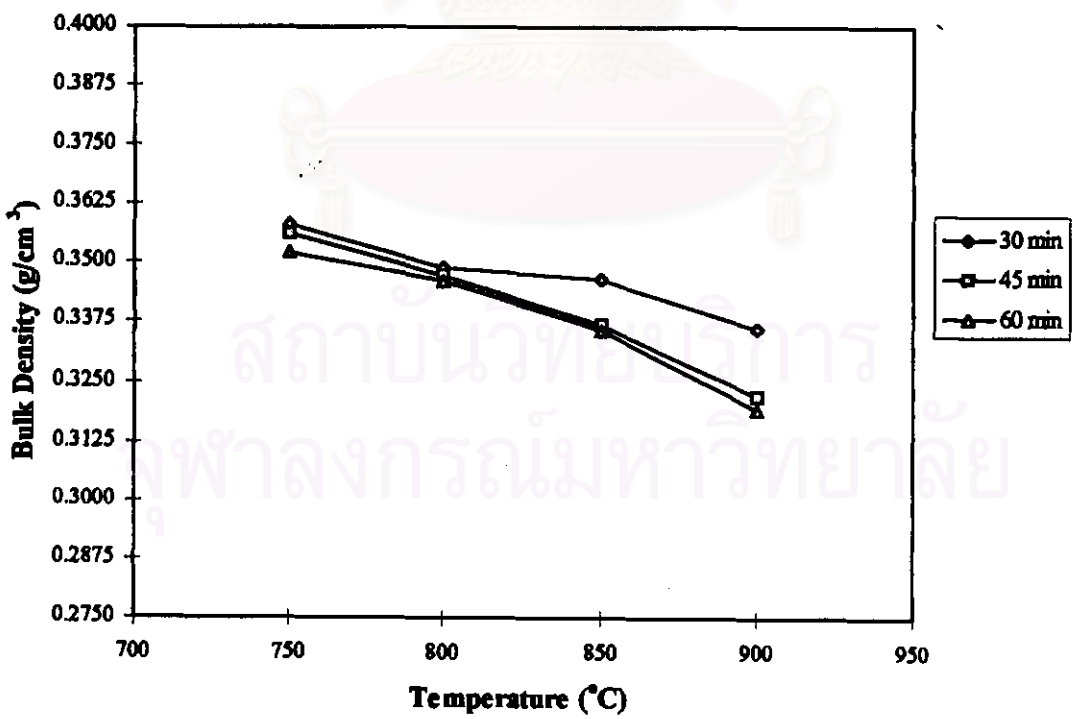

Figure 4.11 Effect of temperature on bulk density at different time (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

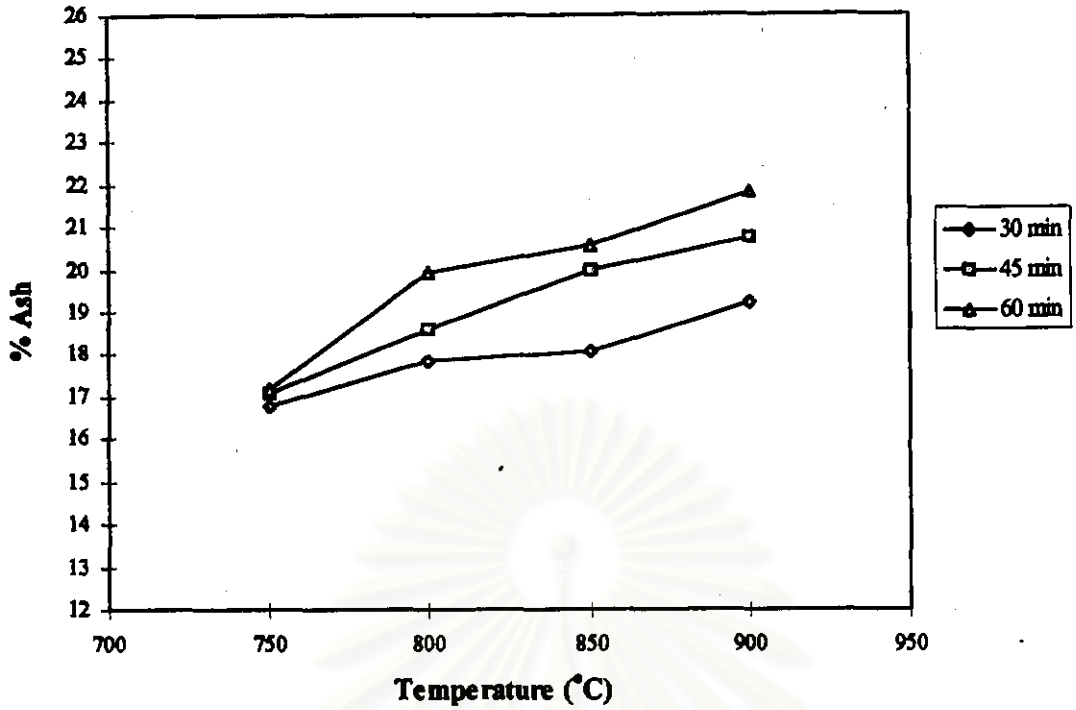

Figure 4.12 Effect of temperature on % ash at different time (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

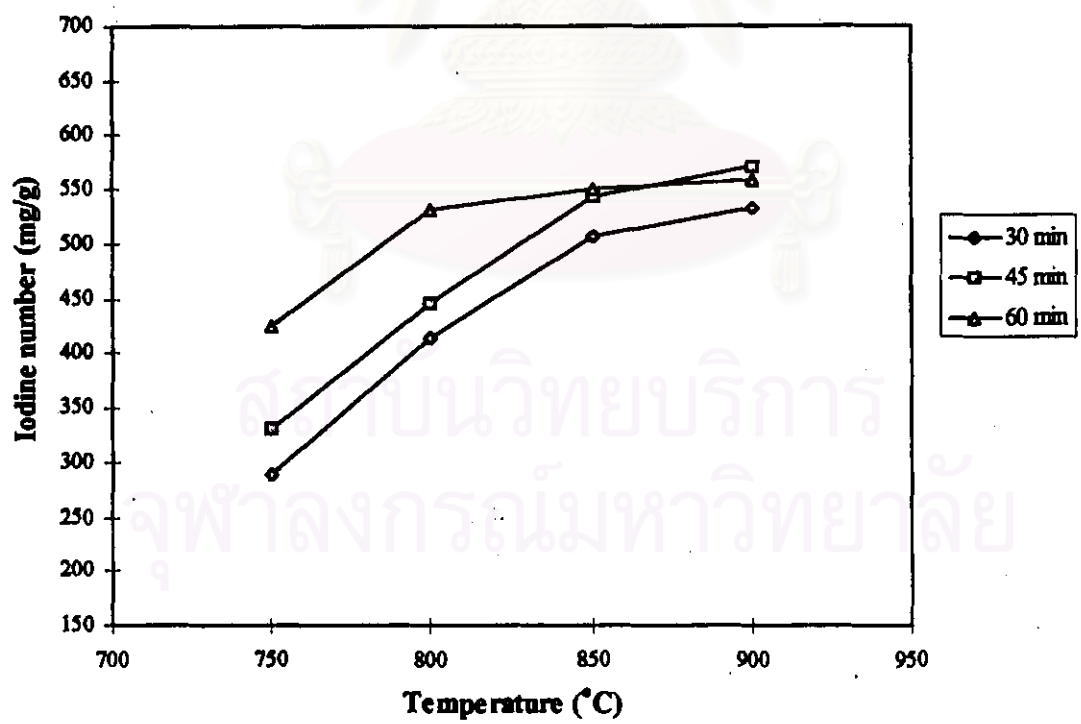

Figure 4.13 Effect of temperature on iodine number at different time (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

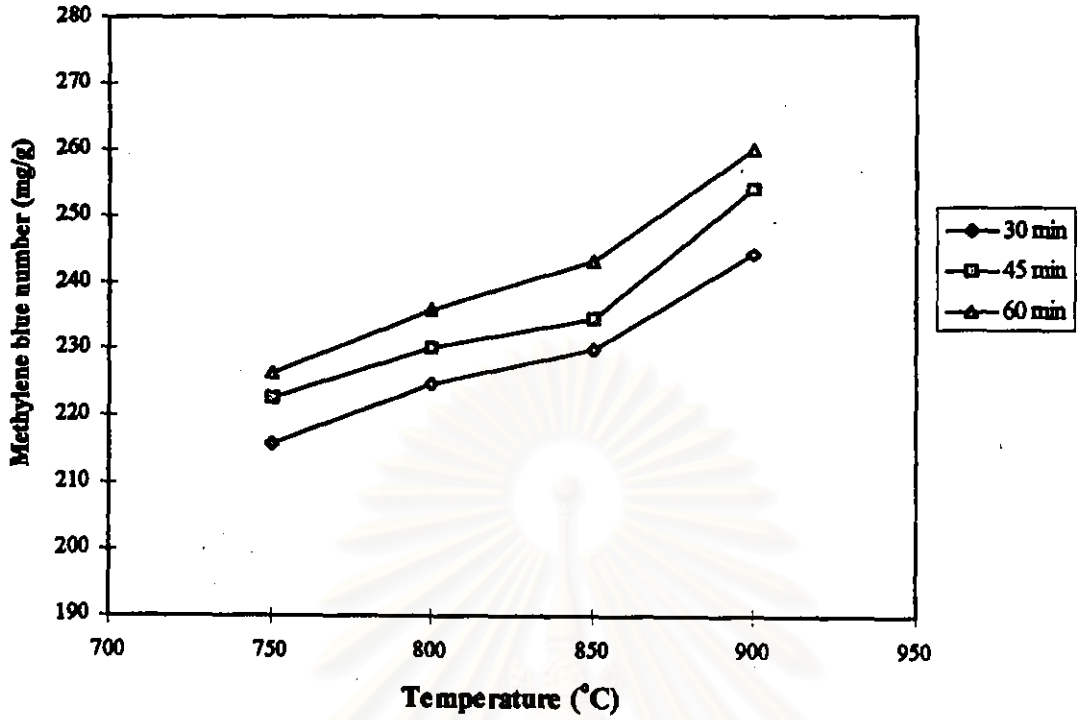

Figure 4.14 Effect of temperature on methylene blue number at different time (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

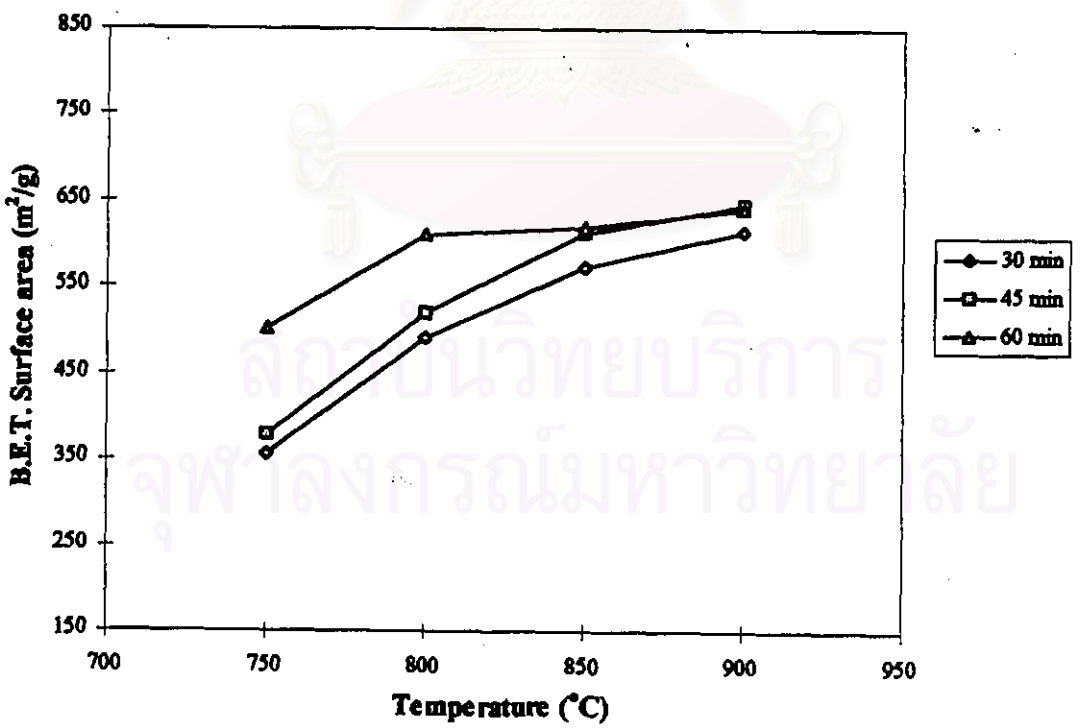

Figure 4.15 Effect of temperature on B.E.T. surface area at different time (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

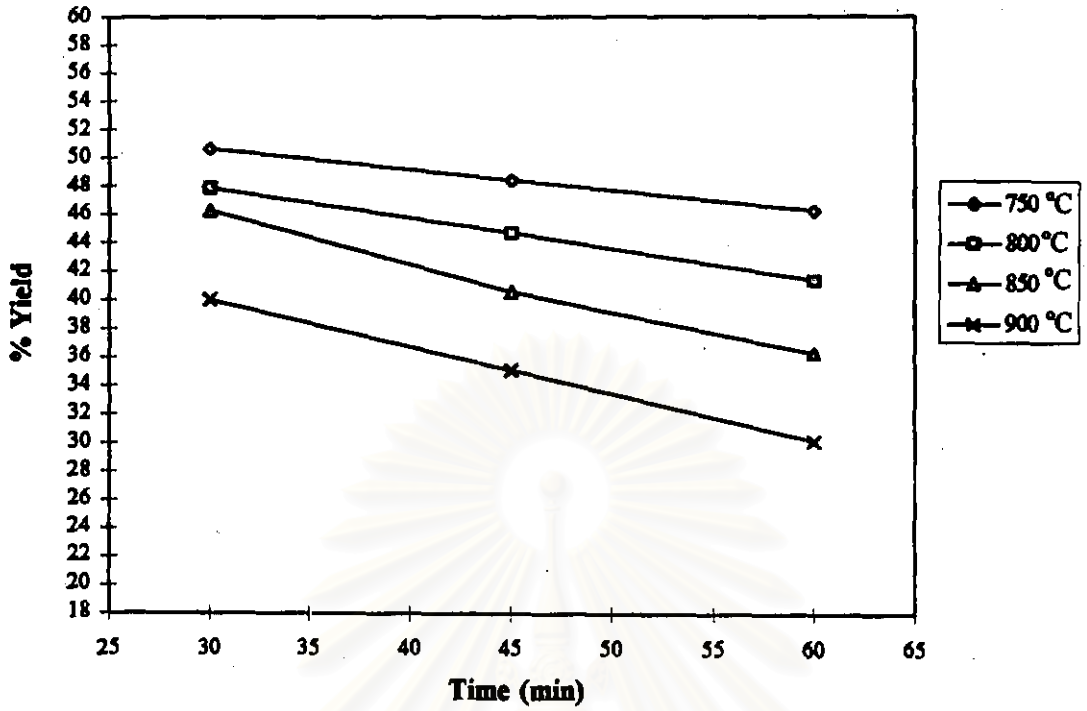

Figure 4.16 Effect of time on % yield at different temperature (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

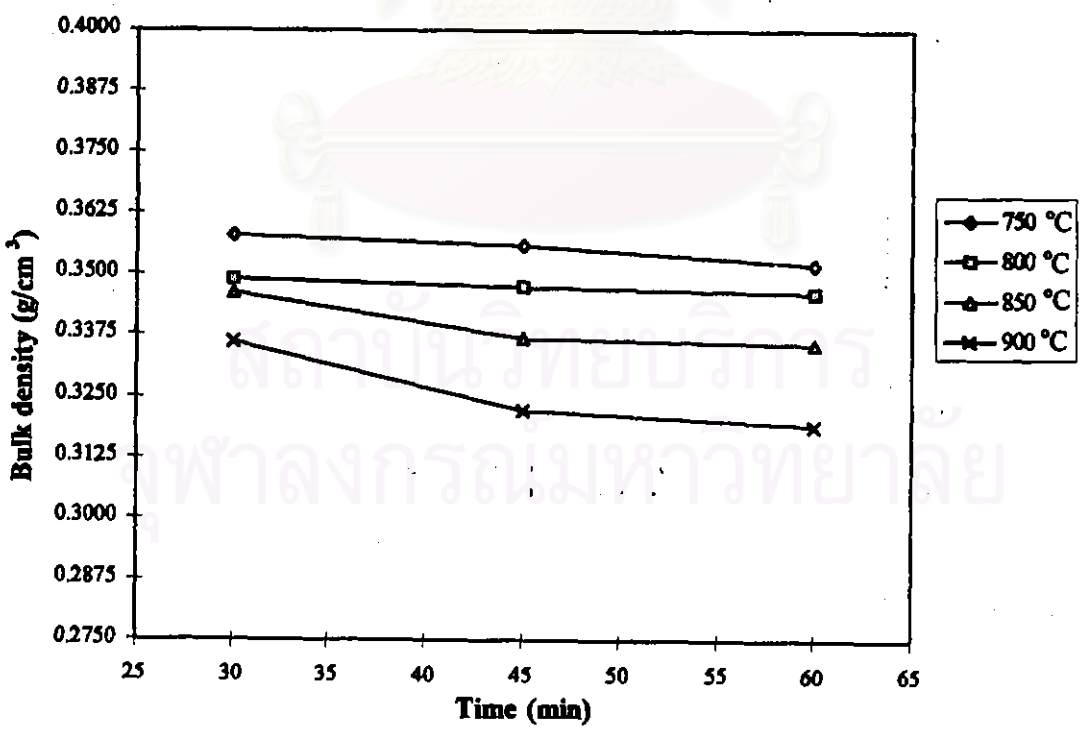

Figure 4.17 Effect of time on bulk density at different temperature (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

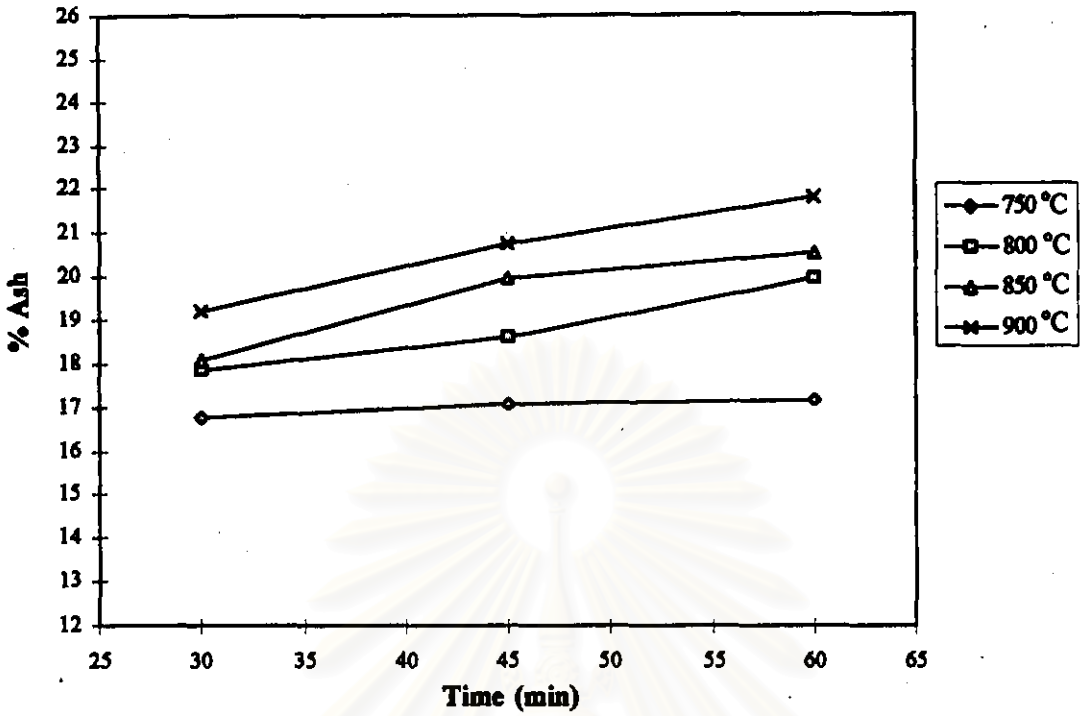

Figure 4.18 Effect of time on % ash at different temperature (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

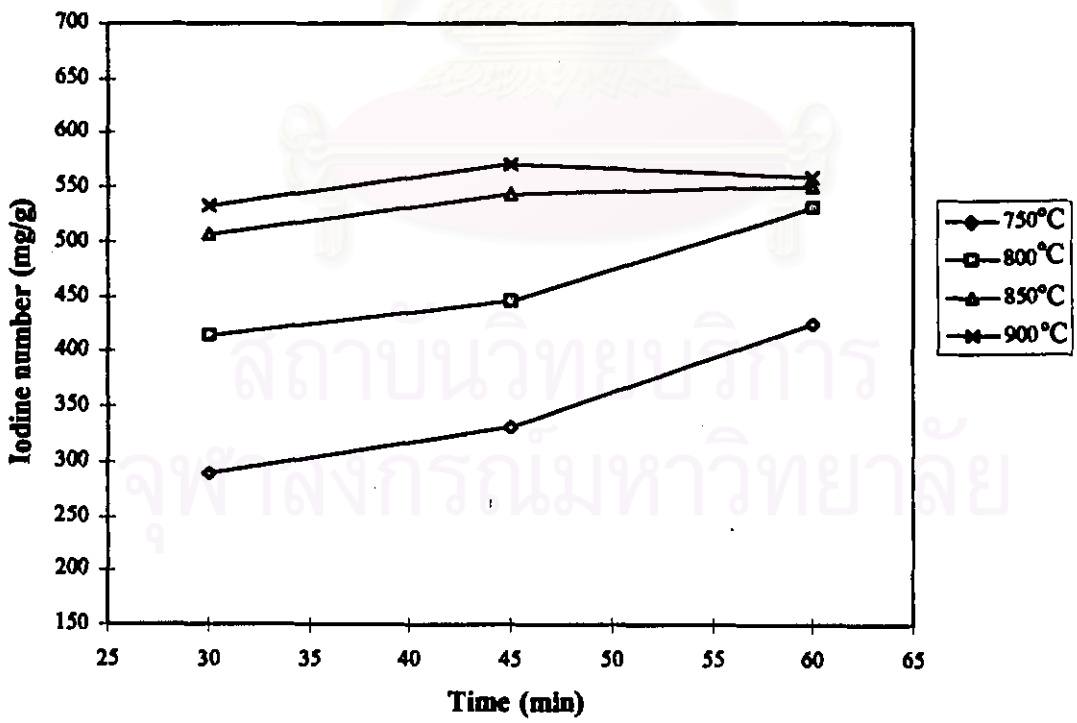

Figure 4.19 Effect of time on iodine number at different temperature (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

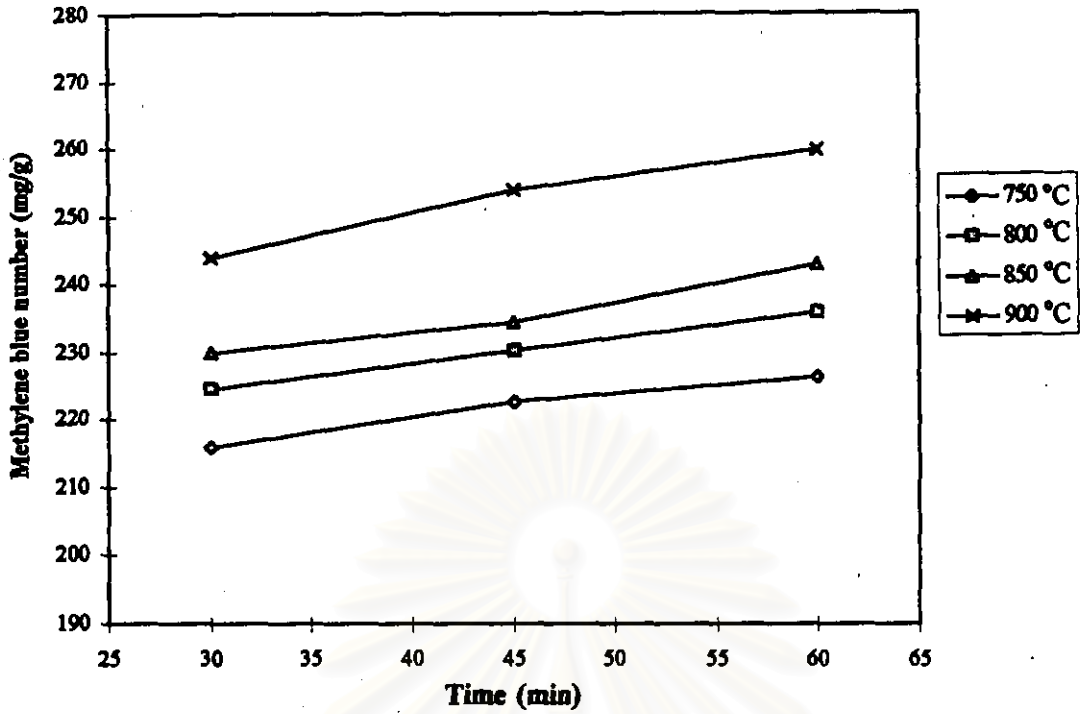

Figure 4.20 Effect of time on methylene blue at different temperature (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

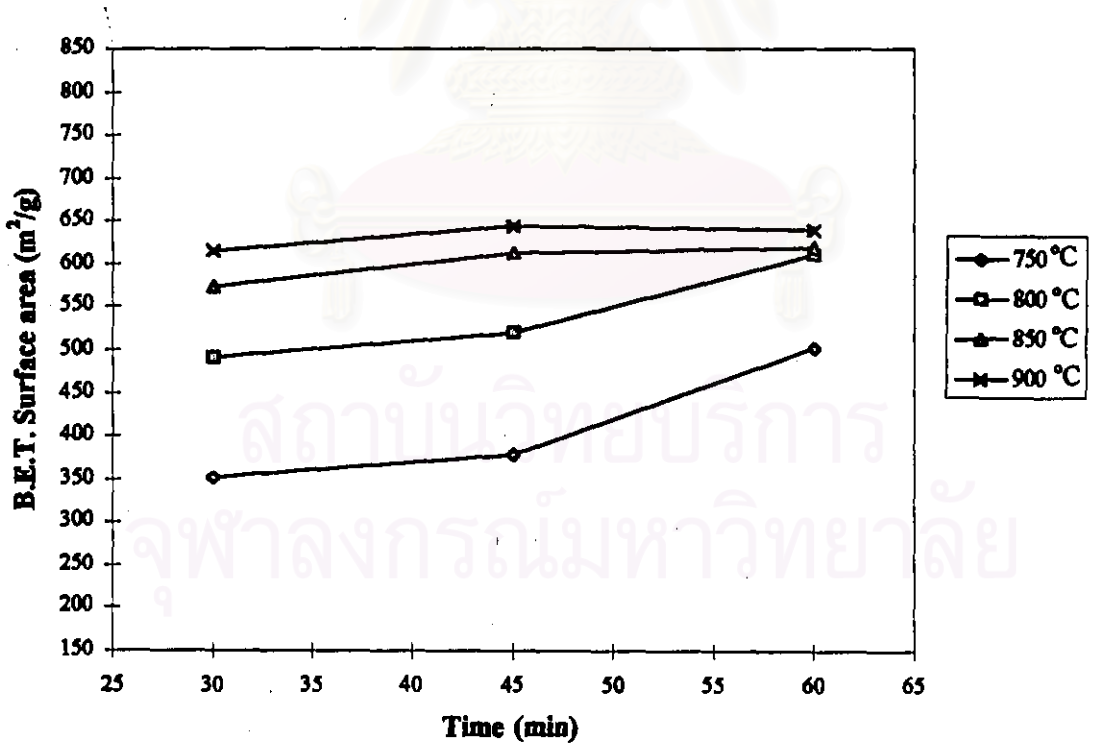

Figure 4.21 Effect of time on B.E.T. surface area at different temperature (size 1.18 - 2.36 mm, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

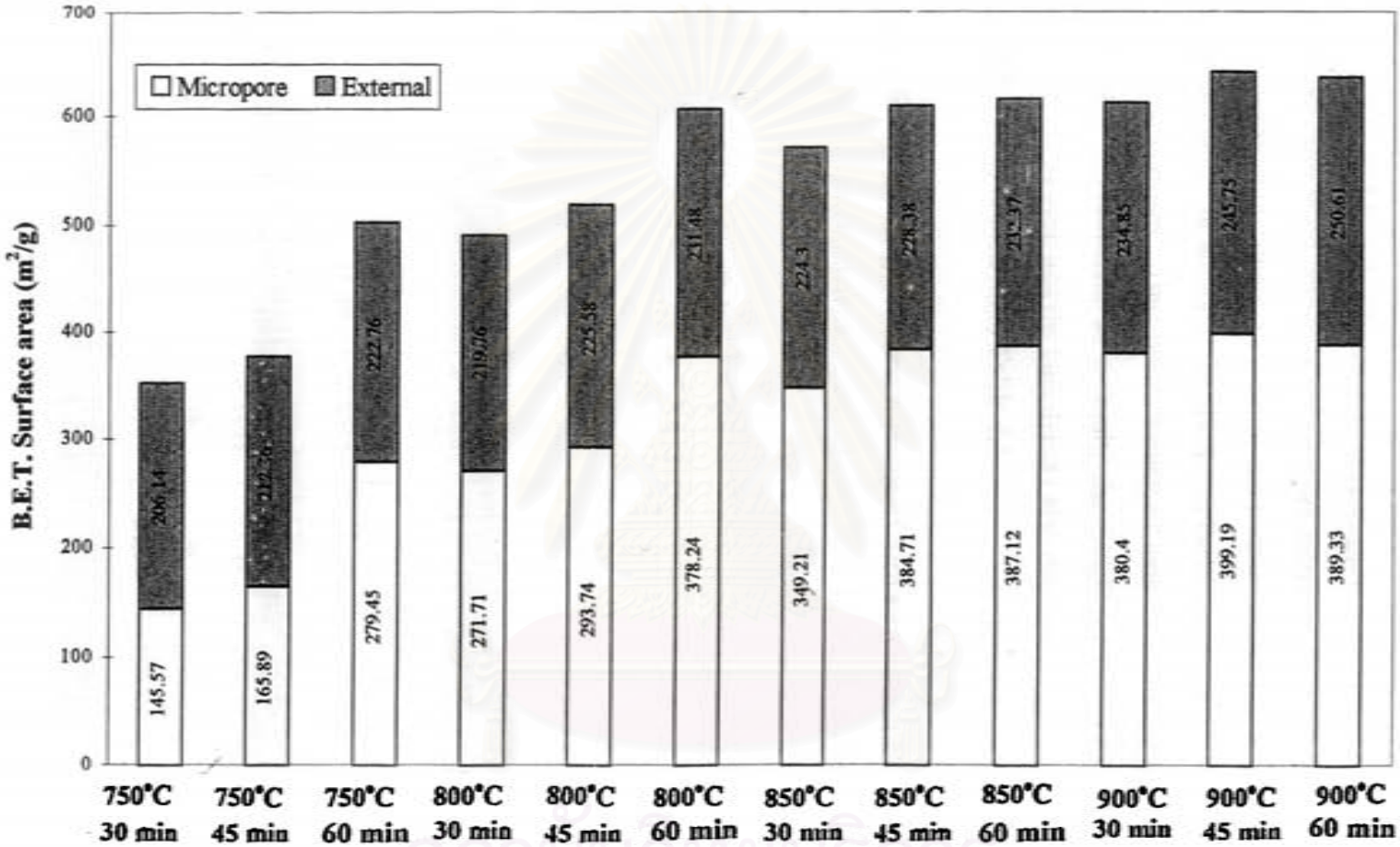

Figure 4.22 Effect of temperature and time on B.E.T. suface area (size 1.18-2.36 mm, 200.0 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

- The optimum temperature for activation

From **Table 4.5, Figure 4.10** and **Figure 4.11**, the % yield and the bulk density decrease when activation temperature increases from 750 to 900°C. Because at high temperature, superheated steam and carbon dioxide attack chars better than at low temperature. In addition, the change of carbon in the chars structure into oxide compounds increases. Thus the increasing of temperature leads to the increasing of the porosity development; as a result, the weight of activated carbon decreases. Moreover, the % yield and the bulk density also decrease. The % changes of % yield and bulk density are shown in **Table 4.6.**

Table 4.6 The % change of characteristics of activated carbon from used tires when activation temperature increases from 750 to 900°C for 30, 45 and 60 min.

t (min)	T (°C)	% Y	BD (g/cm^3)	% Ash	IA (mg/g)	MB (mg/g)	$S_{B.E.T.}$ (m^2/g)
30	750	50.63	0.3580	16.75	289.38	215.78	351.71
	↓	↓	↓	↑	↑	↑	↑
	900	39.94	0.3361	19.21	532.33	244.07	615.25
	% Change	-21.11	-6.12	+14.69	+83.96	+13.19	+74.93
45	750	48.37	0.3560	17.08	330.48	222.67	378.25
	↓	↓	↓	↑	↑	↑	↑
	900	35.05	0.3221	20.75	570.45	253.95	644.94
	% Change	-27.54	-9.52	+21.49	+72.61	+14.05	+70.51
60	750	46.23	0.3521	17.16	425.39	226.27	502.21
	↓	↓	↓	↑	↑	↑	↑
	900	30.12	0.3191	21.79	558.55	259.82	639.94
	% Change	-34.85	-9.37	+26.98	+31.30	+14.83	+27.42

↑ : increase ↓ : decrease

From **Table 4.5** and **Figure 4.12**, the increasing of activation temperature leads to the increase of the % ash because at high temperature, the carbon in chars structure is higher progressively gasified and diffused from particles than at low temperature. But the % change of ash in activation step increases lower than those of with carbonization step, it seems that the steam reduces the change of carbon into ash. Then in the final activation, it is necessary to feed steam into the fixed bed for a moment before finishing the activation. The % change of % ash is shown in **Table 4.6.**

Table 4.5 and **Figures 4.13-4.15**, when the activation temperature increases from 750 to 800°C, the iodine number, the methylene blue number and the B.E.T. surface area increase quickly (see slope **Figures 4.13, 4.14** and **4.15**) because tarry matter and the products of deposition in pores are removed while the superheated steam and the carbon dioxide attack chars; as a result, a lot of new pores are obtained. Even though the temperature increases from 800 to 850°C, the iodine number, the methylene blue number and the B.E.T. surface area still increase but they increase more slowly than in the first temperature range (750-800°C). Above 850°C, the iodine number and the B.E.T. surface area are nearly constant while the methylene blue number still increases because the micropores are changed into the mesopores which can adsorb the methylene blue well, so the methylene blue number increases. The % change of iodine number, methylene blue number and B.E.T. surface area are shown in **Table 4.6.**

These results show that the optimum temperature is 900°C since it has maximum iodine number and B.E.T. surface area.

- The optimum time for activation

Table 4.5 and **Figure 4.16**, the % yield decreases while activation time increases because the partial chars are progressively gasified by air and the porosity development increases with an increase in time, so the % yield decreases. The % change of % yield is shown in **Table 4.7**.

From **Table 4.5** and **Figure 4.17**, when the activation time increases, the bulk density decreases. Due to increasing of activation time, the chances of superheated steam and carbon dioxide, attacking the surface of chars, also increase. Therefore, the porosity development increases. The % change of the bulk density is shown in **Table 4.7**.

Table 4.5 and **Figure 4.18**, in the time range of 30-60 min, the % ash increases because of the increasing of activation time which made the partial chars reacts with air longer, so the carbons in chars are higher progressively gasified than that in the shorter time. The % change of % ash is shown in **Table 4.6**

Table 4.5 and **Figures 4.19-4.22** show that the iodine number, the methylene blue number and the B.E.T. surface area increase when the activation time increases from 30 to 45 min because the superheated steam and the carbon dioxide highly attack chars, so micropores are obtained. At 750-800°C, when the activation time increases from 45 to 60 min, the iodine number in this time range increases more quickly than at the first time range (30-45 min). But above 850°C for 60 min time of activation, the iodine number and the B.E.T. surface area decrease but the methylene blue number still increases because this condition is too extreme, so the micropores would have coalesced and then the mesopores or macropores are developed. The % changes of iodine number, methylene blue number and B.E.T. surface area are shown in **Table 4.7**.

Table 4.7 The % change of characteristics of activated carbon from used tires when activation time increases from 30 to 60 min for 750, 800, 850 and 900 °C.

T (°C)	t (min)	% Y	BD (g/cm^3)	% Ash	IA (mg/g)	MB (mg/g)	$S_{B.E.T.}$ (m^2/g)
750	30	50.63	0.3580	16.75	289.38	215.78	351.71
	↓	↓	↓	↑	↑	↑	↑
	60	46.23	0.3521	17.16	425.39	226.27	502.21
	% Change	-8.69	-1.67	+2.45	+47.00	+4.86	+42.79
800	30	47.83	0.3489	17.86	414.35	224.64	491.66
	↓	↓	↓	↑	↑	↑	↑
	60	41.36	0.3462	19.95	531.12	235.95	609.72
	% Change	-13.53	-0.77	+11.70	+28.18	+5.03	+24.01
850	30	46.32	0.3464	18.06	507.08	229.95	572.50
	↓	↓	↓	↑	↑	↑	↑
	60	36.21	0.3356	20.55	549.64	242.93	619.25
	% Change	-21.83	-3.12	+13.79	+8.39	+5.64	+8.20
900	30	39.94	0.3361	19.21	532.33	224.07	615.25
	↓	↓	↓	↑	↑	↑	↑
	60	30.12	0.3191	21.79	558.55	259.82	639.94
	% Change	-24.59	-5.06	+13.43	+7.92	+6.45	+4.01

↑ : increase ↓ : decrease

The above results show that the optimum time for activation is 45 min because the activated carbon obtained the maximum of iodine number and B.E.T. surface area. Moreover, it also obtained the optimum methylene blue number and yield. Thus, the optimum condition for activation was 900°C for 45 min. The properties of the activated carbon in this optimum condition obtained yield of 35.05 %, bulk density of 0.3221 g/cm^3, ash of 20.75 %, iodine number of 570.45 mg/g, methylene blue number of 253.95 mg/g, B.E.T. surface area of 644.94 m^2/g, micropore area of 399.19 m^2/g and external area of 245.75 m^2/g.

4.2.2.2 The optimum size for activation

This experiment used four sizes of chars to study the optimum size for production of activated carbon. These sizes were 0.25-0.60, 0.60-1.18, 1.18-2.36 and 2.36-4.75 mm. Approximate 200 g of sample was charged into the fixed bed reactor followed CO_2 and air at the flow rate of 5.0 nl/min and 0.27 nl/min at 900°C while superheated steam was passed through reactor for 45 min. The results are shown in **Table 4.8** and **Figures 4.23-4.26.**

Table 4.8 Characteristics of activated carbon from used tires at different sizes (900°C for 45 min, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

Tires char sizes (mm)	%Y	%M	on dry basis				Surface area (m^2/g)		
			BD (g/cm^3)	Ash (%)	IA (mg/g)	MB (mg/g)	$S_{B.E.T.}$	S_{Micro}	$S_{External}$
0.25 - 0.60	25.56	5.59	0.3602	28.09	484.14	235.99	516.83	289.60	227.23
0.60 - 1.18	29.31	8.61	0.3578	20.44	594.55	245.78	654.17	418.22	235.95
1.18 - 2.36	35.05	8.69	0.3221	20.75	570.45	253.95	644.94	399.19	245.75
2.36 - 4.75	37.82	5.01	0.3069	17.15	344.50	210.23	383.13	181.55	201.58

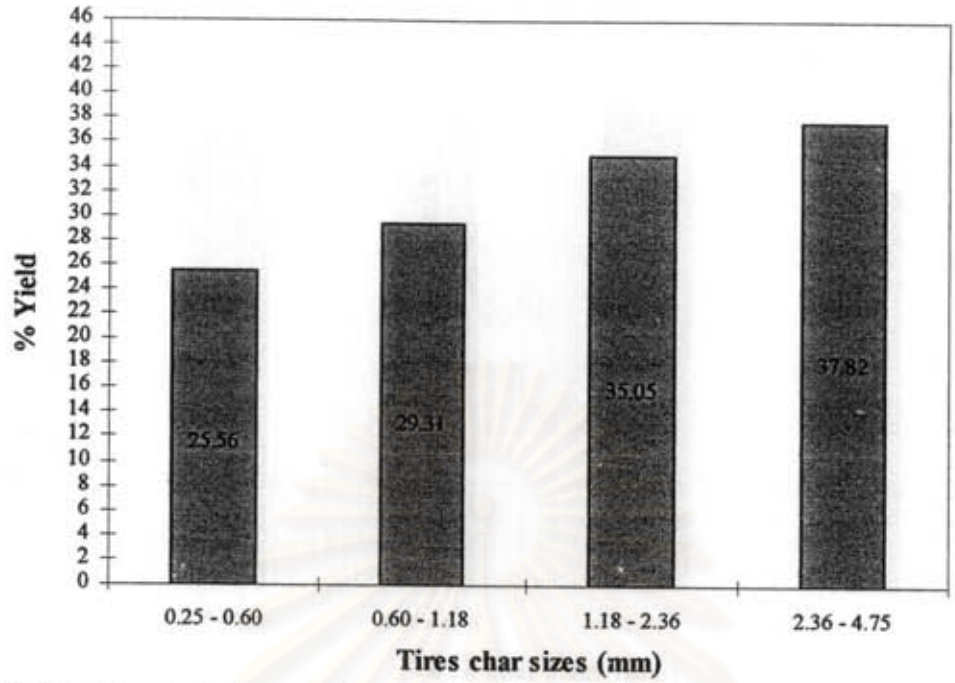

Figure 4.23 Effect of size on % yield (900°C for 45 min, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

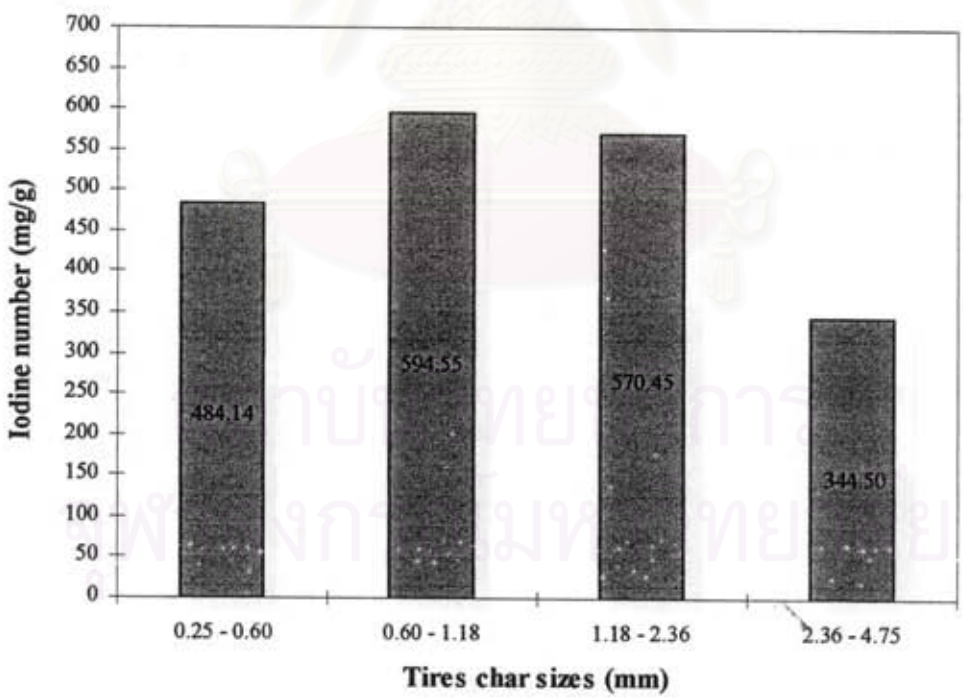

Figure 4.24 Effect of size on iodine number (900°C for 45 min, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

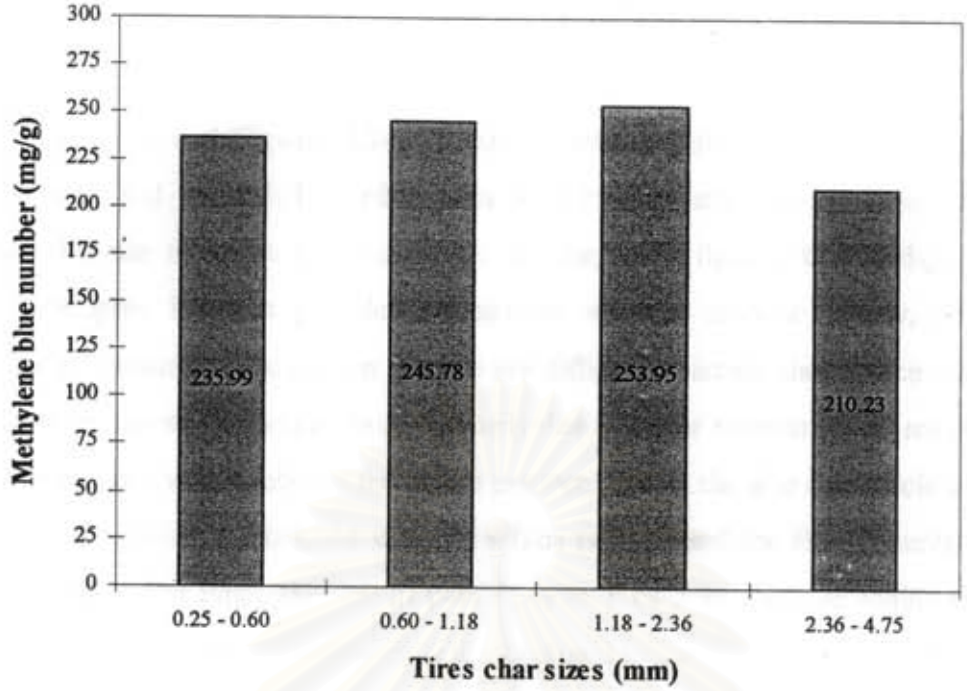

Figure 4.25 Effect of size on methylene blue number (900°C for 45 min, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

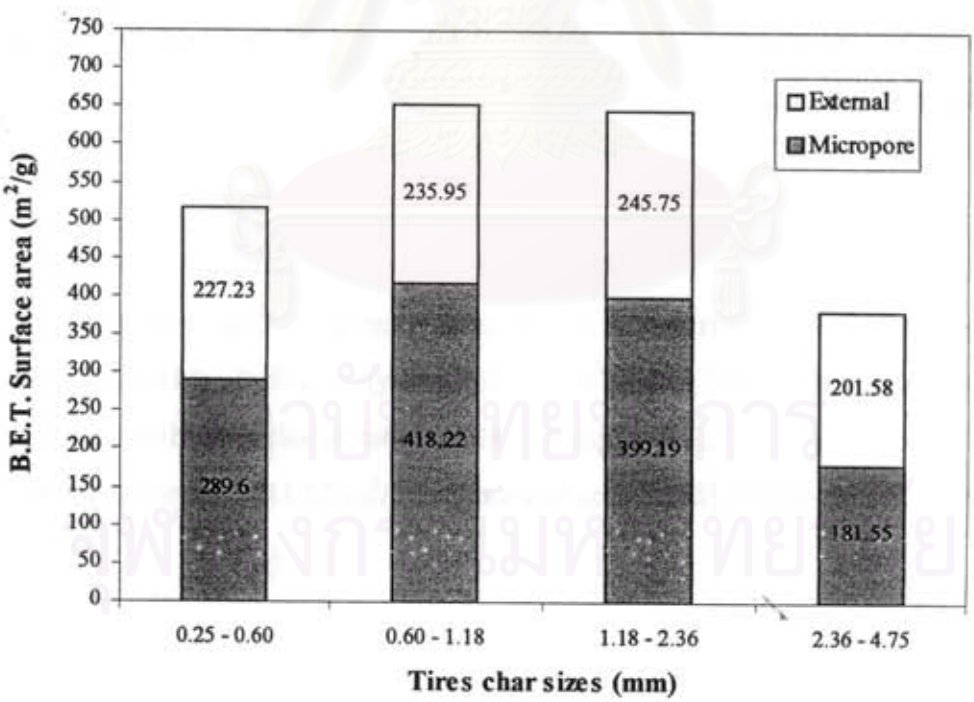

Figure 4.26 Effect of size on B.E.T. surface area (900°C for 45 min, 200 g, air 0.27 nl/min, CO_2 5.0 nl/min and superheated steam).

Table 4.8 and **Figures 4.24-4.26** show that the iodine number, the methylene blue number and the B.E.T. surface area of 0.25-0.60 mm size of chars are less because this size of chars is the smallest. So they pack tight in the fixed bed; as a result, the gaps between particles are narrow and the amount is low, thus the superheated steam and the carbon dioxide are difficult to attack the surface of chars. Furthermore, the small particles burn out early due to faster reaction rates, resulting in pore coalescence which reduces the iodine number. When the size of particle is 0.60-1.18 mm, the iodine number, the methylene blue number and the B.E.T. surface area are maximum. But when the size of particle is to 1.18-2.36 mm, the iodine number and the B.E.T. surface area decrease. They decrease to the minimum when the size of particle is 2.36-4.75 mm. Because the bigger chars particles pack loose, so the gaps between big particles are larger than those small particles; as a result, the superheated steam and the carbon dioxide attack easily chars. The reaction time of the bigger particle is less because the superheated steam and the carbon dioxide pass quickly through the bed, thus they can not attack the inner particles. So the reacted surface of big particles is lower than that of the medium particles, resulting in the decreasing of iodine number, methylene blue number and B.E.T. surface area.

Thus the optimum size for activation is 0.60-1.18 mm because the activated carbon obtaines the highest iodine number and B.E.T. surface area. It's properties were yield of 29.31 %, bulk density of 0.3578 g/cm^3, ash of 20.44 %, iodine number of 594.55 mg/g, methylene blue number of 245.78 mg/g, B.E.T. surface area of 654.17 m^2/g, micropore area of 418.22 m^2/g and external area of 235.95 m^2/g.

4.2.2.3 The optimum flow rate of CO_2 for activation

This experiment used CO_2 at a flow rate of 0.0, 2.0, 5.0, 10.0 and 15.0 nl/min. Approximate 200 g of 0.60-1.18 mm of chars were treated at 900°C for 45 min with superheated steam, air at the flow rate of 0.27 nl/min and the various flow rates of CO_2. The results are shown in **Table 4.9** and **Figures 4.27-4.30.**

Table 4.9 Characteristics of activated carbon from used tires at different flow rate of CO_2 (900°C for 45 min, size 0.60 - 1.18 mm, 200 g, air 0.27 nl/min and superheated steam).

CO_2 (nl/min)	%Y	%M	on dry basis				Surface area (m^2/g)		
			BD (g/cm^3)	Ash (%)	IA (mg/g)	MB (mg/g)	$S_{B.E.T.}$	S_{Micro}	$S_{External}$
0.0	27.09	8.76	0.3500	23.95	623.99	258.15	725.31	446.80	278.51
2.0	27.99	8.25	0.3590	21.05	598.79	247.08	658.75	424.27	234.48
5.0	29.31	8.61	0.3578	20.44	594.55	245.78	654.17	418.22	235.95
10.0	30.52	7.37	0.3570	19.43	590.23	242.24	645.09	411.29	233.80
15.0	31.99	8.70	0.3561	18.79	580.05	239.51	634.34	402.46	231.88

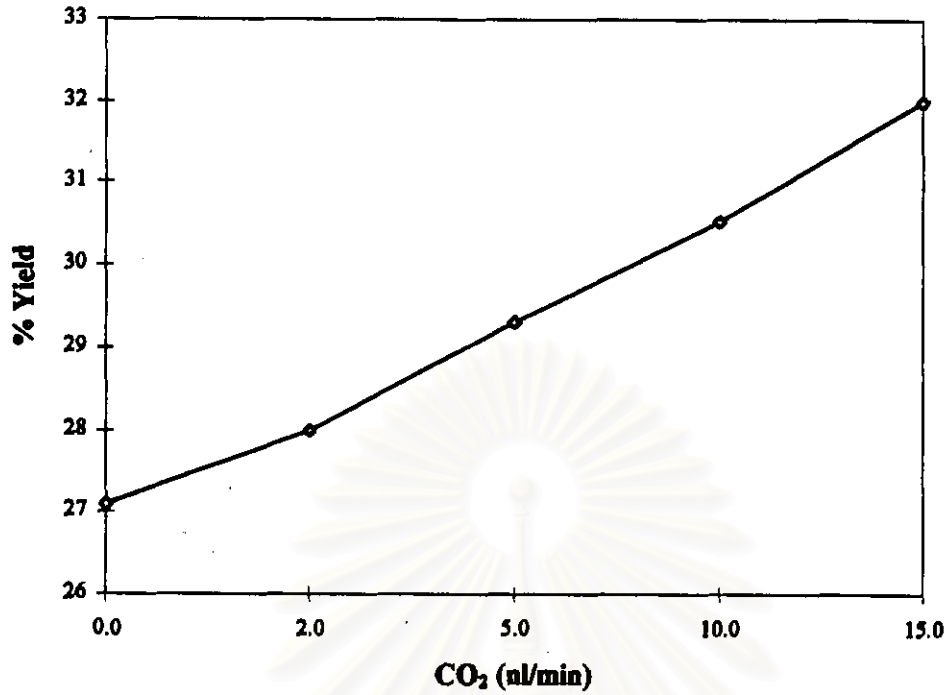

Figure 4.27 Effect of flow rate of CO_2 on % yield at different flow rate of CO_2 (900 °C for 45 min, size 0.60 - 1.18 mm, 200 g, air 0.27 nl/min and superheated steam).

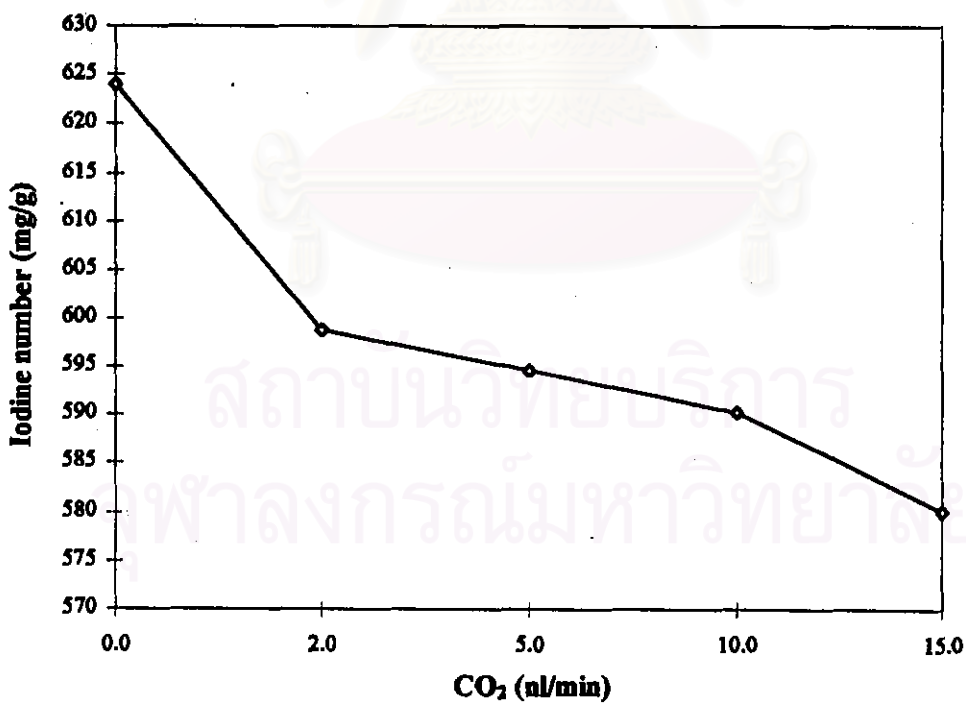

Figure 4.28 Effect of flow rate of CO_2 on iodine number (900°C for 45 min, size 0.60 - 1.18 mm, 200 g, air 0.27 nl/min and superheated steam).

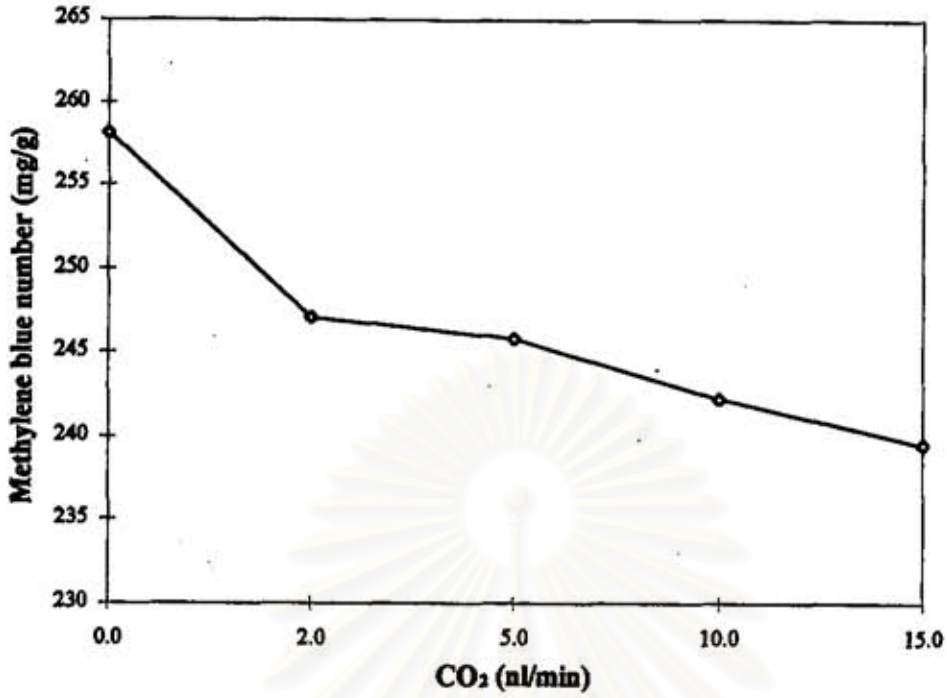

Figure 4.29 Effect of flow rate of CO_2 on methylene blue number (900°C for 45 min, size 0.60 - 1.18 mm, 200 g, air 0.27 nl/min and superheated steam).

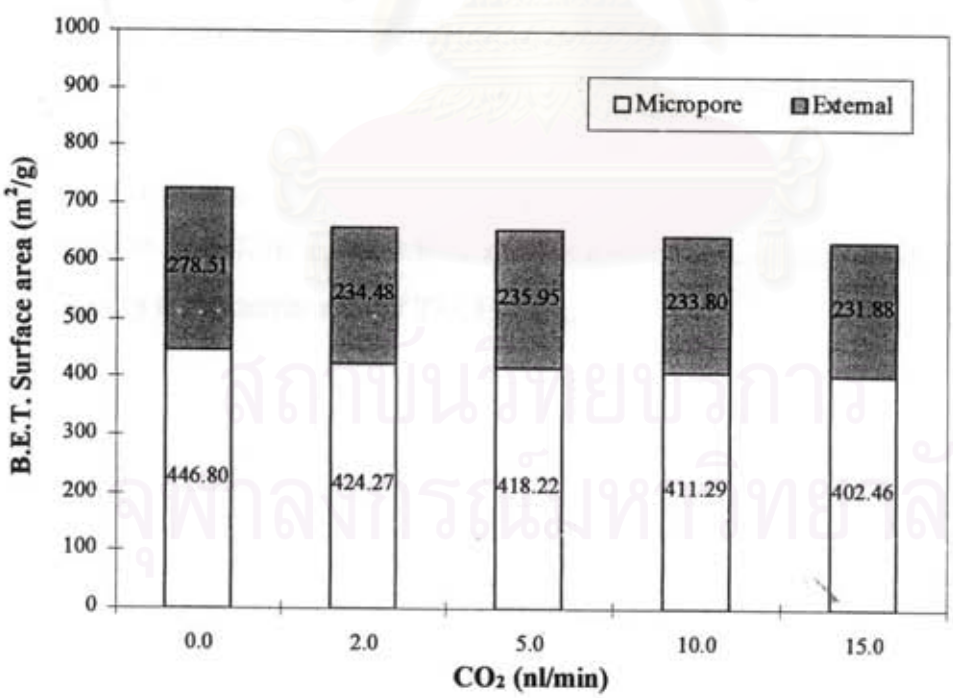

Figure 4.30 Effect of flow rate of CO_2 on B.E.T. surface area (900°C for 45 min, size 0.60 - 1.18 mm, 200 g, air 0.27 nl/min and superheated steam).

Table 4.9 and **Figures 4.27-4.30** show that the activation using superheated steam gives the maximum of the iodine number, the methylene blue number and the B.E.T. surface area. But they decrease when using both superheated steam and carbon dioxide as the activating agent. Increasing of the flow rate of carbon dioxide in mixing gases, the iodine number, the methylene blue number and the B.E.T. surface area still decrease until they reach the minimum at the flow rate of CO_2 15.0 nl/min. These results conform the results of Sai, Ahmed and Krishnaian[23], who produced the activated carbon from coconut shell chars in fluidized bed reactor with steam and a mixture of steam and carbon dioxide. His results show that the reaction with steam gives the maximum of the iodine number, and it decreases with increasing of carbon dioxide composition in the reacting gas at any particular time. Therefore, the activation with only steam has the maximum adsorption because steam is better than carbon dioxide for activation.

Thus the optimum flow rate of carbon dioxide is 2.0 nl/min since it gives the highest iodine number, methylene blue number and B.E.T. surface area. The activated carbon from this optimum flow rate of carbon dioxide obtained yield of 27.99 %, bulk density of 0.3590 g/cm^3, ash of 21.05 %, iodine number of 598.79 mg/g, methylene blue number of 247.08 mg/g, B.E.T. surface area of 658.75 m^2/g, micropore area of 424.27 m^2/g and external area of 234.48 m^2/g.

4.3 Comparison of this work with other work

The comparison of this work with that of Ratikorn Isarasaenee (1996), Teng *et al.* (1995), Marchant *et al.* (1993), Ogasawara *et al.* (1987) and Torikai *et al.* (1979) are presented with respect to the maximum surface area obtained (**Table 4.10**).

Table 4.10 Comparison of this work with other work.

	This work (1998)	Ratikorn (1996)	Teng *et al.* (1995)	Marchant (1993)	Ogasawara (1987)	Torikai (1979)
Raw material	Used tires	Used tires	Used tires	Used tires	Used tires	Used tires
Carbonization	350°C for 60 min with air	450°C for 30 min with N_2	700°C with He	530°C for 60 min with He	one stage 900°C for 1 hr with He	550°C for 30 min with He
Activation	900°C for 45 min with air	900°C for 30 min with air	900°C with O_2 pretreat	920°C for 60 min with N_2		900°C with He
Activating agent	steam and CO_2	steam	CO_2	steam	steam	CO_2
% yield	13.97	17.35	16.20	25.55	9.00	-
IA (mg/g)	598.79	891.11	-	-	-	-
MB (mg/g)	247.08	172.03	-	-	-	-
$S_{B.E.T.}$ (m^2/g)	658.75	691.51	952.00	607.00	1,260.00	400.00

The results of this work, comparing to other works show that the temperature of carbonization (350°C) in this work is lower than the others (450-700°C). Because air is used as the medium, while the others use inert gas. Air helps removing volatile matter from raw materials and oxidizes some carbon. The reaction of air oxidizing carbon is exothermic, so it helps increasing the temperature of the bed. But this reaction is too extreme that the volatile matter is removed quickly; as a result, the sizes of the chars's pores in this carbonization are big, which would cause the surface area of the activated carbon to be less.

The temperature of the activation in this work is similar to the others (900°C). Comparing to Ratikorn's[22], her time is less, due to only 50 g of chars being used in the activation, while 200 g of chars is used in this work. When it comes to B.E.T. surface area, ours is higher. But our iodine number is lower due to our longer activation time, which causes the micropores to be widened. Besides, the medium in the carbonization in this work is air but Ratikorn's is nitrogen. Therefore, the pore sizes of chars from air medium are larger than that of the chars from nitrogen medium.

Comparison to Ogasawara's *et al.*[19], the surface area of the activated carbon of Ogasawara's *et al.* is high, because they prepare in a quartz tube reactor (10 mm in diameter) for 1 hr by one stage production, using only 1 g of sample. Thus their B.E.T. surface area is raised 1260.00 m^2/g. But the B.E.T. surface area of this work is only 725.31 m^2/g, since the reactor is 100 mm in diameter which is bigger, and more quantity of chars (200 g). So, the superheated steam can not overall attack chars through the bed; as a result, the B.E.T. surface area of this work is lower than that of Ogasawara's *et al.*

Teng *et al.*[6], observe the maximum surface area of 952.00 m^2/g at 900°C for activated carbon from used tires using carbon dioxide as the activating agent. Whereas Tarikai *et al.*[18], observe different maximum surface area of 400.00 m^2/g at the same temperature and activating agent. Teng's *et al.*, maximum surface area as more because they pretreat the used tires in oxygen by exposing them to air at 140°C for 15 days.

From the above comparisons, it can be seen that by using steam as an activating agent, the B.E.T. surface area of the activated carbon is more than that by using carbon dioxide. Because carbon dioxide widenes the pores of the activated carbon, which causes less B.E.T. surface area.

In this work, the activation process is carried out with the mixture of superheated steam and carbon dioxide as activating agents simular to industrial condition. For economic reasons, we could use less quantity of steam to cut cost of the activated carbon production by mixing steam with carbon dioxide which is one kind of flue gases; this kind of flue gases has high concentrations. The activated carbon of this method obtained B.E.T. surface area of 658.75 m^2/g and iodine number of 598.79 mg/g.

The above iodine number, more or less meets the standard of the commercial activated carbon of TIS 900-1989[24], that is over 600 mg/g. The process condition used in this work is a good starting point from which to optimize a process to convert used tires to activated carbon.

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

Figure 4.31 shows the change in the % burn-off and in the B.E.T. surface area as a function of the activation temperature. While the % burn-off increases, the B.E.T. surface area also increases. Above 850°C for 30 and 45 min, the B.E.T. surface area increases slowly with the increase in the % burn-off because micropores transform into mesopores at high burn-off. For 60 min, the B.E.T. surface area is nearly constant because this time of activation is the highest transformation of micropores to mesopores.

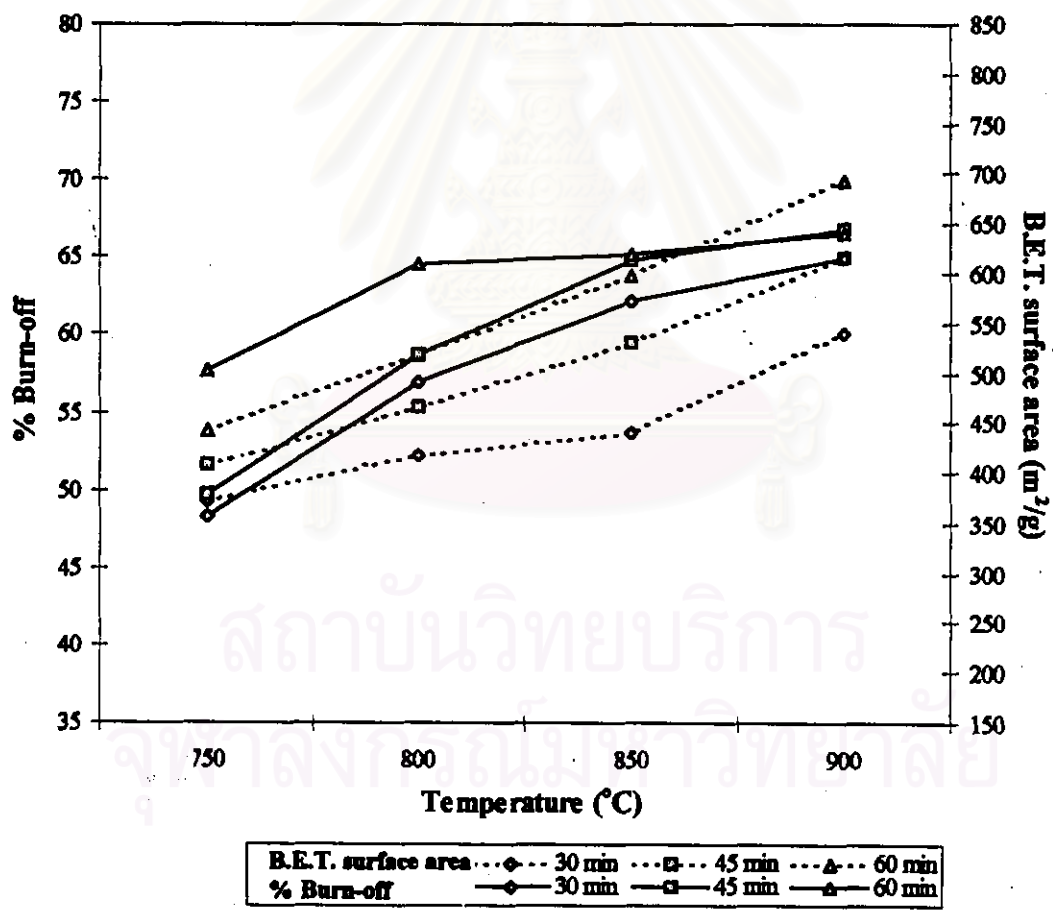

Figure 4.31 Correlation between % burn-off and the B.E.T. surface area as a function of the activation temperature.

4.5 Correlation between 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 4.32.** A linear increase can be observed that the B.E.T. surface area depends directly on the iodine number. The iodine number gives an indication of the adsorption capacity of an activated carbon in micropores[14], so the surface area of activated carbon is depended on micropore area too. The iodine number provides a good indication of the surface area of an activated carbon.

$$y = 1.0591x + 36.834$$

where :

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

x = iodine number (mg/g)

R^2 = 0.979

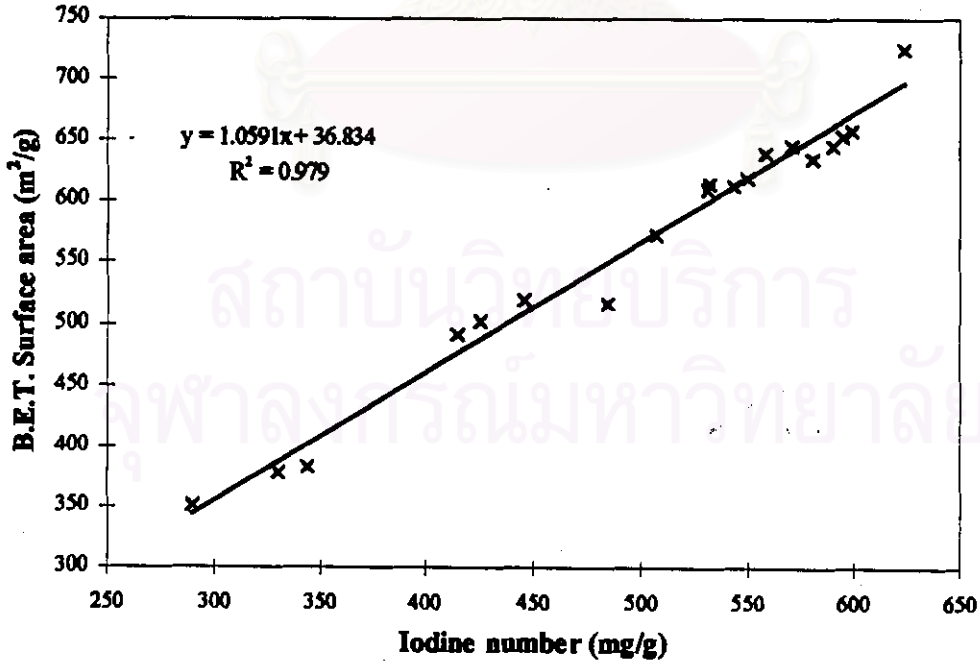

Figure 4.32 Correlation between iodine number and the B.E.T.surface area.

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

The methylene blue number gives an indication of the surface area of the activated carbon which results from the existence of mesopores of dimensions over 1.5 nm[14]. 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 4.33**. At the high value of methylene blue number, the B.E.T. surface area increases slowly. These values of methylene blue numbers are high in the higher temperature and longer time period. Thus the reaction for activation is fast, micropores would have coalescence to mesopores or macropores results in a reduction of the B.E.T. surface area.

$$y = -0.1144x^2 + 61.075x - 7458.7$$

where :

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

x = methylene blue number (mg/g)

R^2 = 0.8599

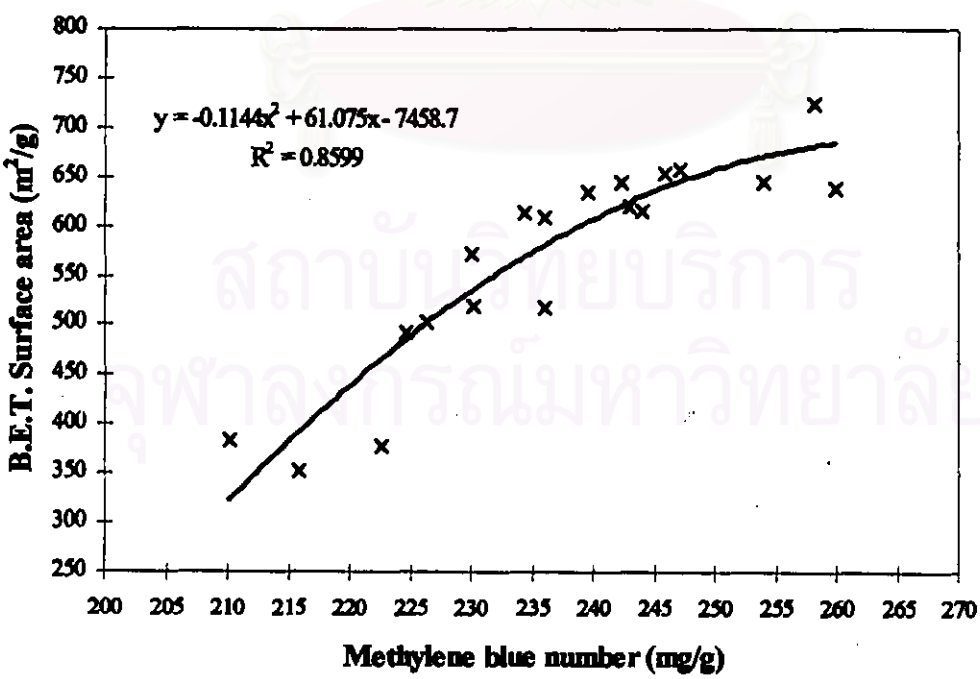

Figure 4.33 Correlation between methylene blue number and the B.E.T.surface area.