

## CHAPTER V

### RESULTS AND DISCUSSION

#### 5.1 Porous properties of prepared chars from waste tires

As shown in Table 5.1.1, the carbonization yields obtained through the carbonization of waste tires at 500°C were around 35 wt%, and the prepared chars had ash content about 15%. It was found that the heating rate had no significant effect on the carbonization yield and the ash content in our experiments.

Table 5.1.1 Porous properties of chars from waste tires carbonized at 500°C at the heating rate of 0.5, 5, and 20°C/min

Sample	Carbonization yield (%)	Ash content (%)	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
C 500_0.5	35.07	14.7	0.32	N.D.	75
C 500_5	35.10	15.0	0.36	N.D.	81
C 500_20	35.08	14.6	0.42	N.D.	90

Figure 5.1.1 shows the N<sub>2</sub> adsorption-desorption isotherms on chars obtained at different heating rates, where  $q$  and  $P/P^0$  are the amount of N<sub>2</sub> adsorbed and relative pressure, respectively. Interestingly, a slight hysteresis was observed in the isotherms which suggests the existence of mesoporous structure in the chars. The pore size distributions of obtained chars were shown in Figure 5.1.2 which indicate that chars carbonized from waste tires at 500°C possess mainly mesopores whose pore radius are larger than 4 nm.

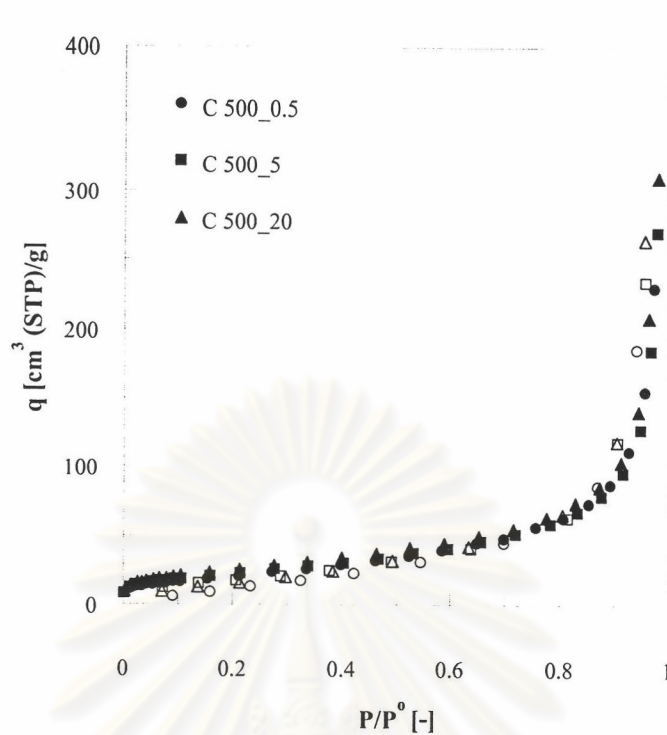


Figure 5.1.1  $\text{N}_2$  adsorption-desorption isotherms on chars from waste tires carbonized at  $500^\circ\text{C}$  at the heating rate of 0.5, 5, and  $20^\circ\text{C}/\text{min}$ ; closed symbols: adsorption, open symbols: desorption

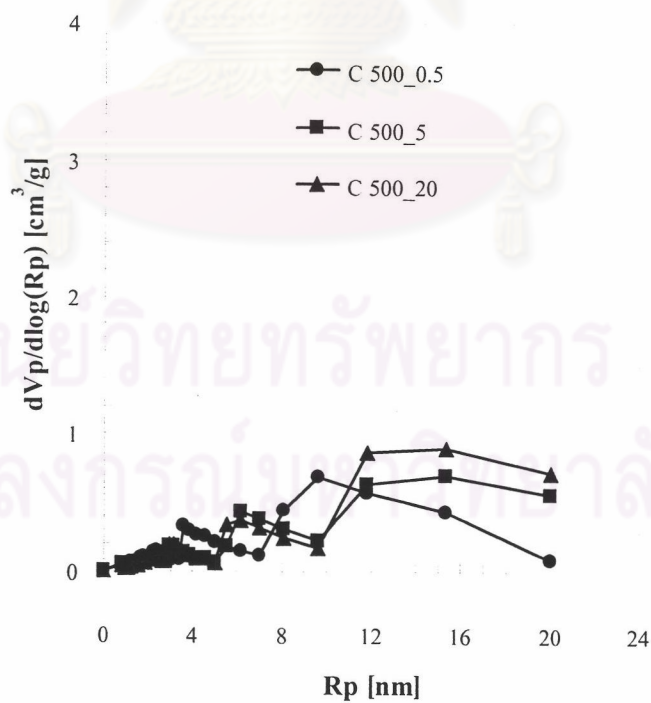


Figure 5.1.2 Pore size distribution of chars from waste tires carbonized at  $500^\circ\text{C}$  at the heating rate of 0.5, 5, and  $20^\circ\text{C}/\text{min}$

The porous properties calculated using the isotherms in Figure 5.1.1 are also summarized in Table 5.1.1. The  $S_{BET}$  values of the obtained chars were around 75-90 m<sup>2</sup>/g which slightly increased with the increase in the heating rate during carbonization. The existence of mesoporous structure in the chars can be confirmed from their  $V_{meso}$  values, which also slightly increased with increasing heating rate. However, the  $V_{micro}$  values in chars could not be detected by applying the t-plot method to the N<sub>2</sub> adsorption isotherms.

In Table 5.1.2, when increased the carbonization temperature, it was found that the carbonization yield decreased down to about 34%, but over 700°C it seems to be constant. The increase in the ash content in char is due to the decrease in the carbonization yield obtained at higher carbonization temperature.

**Table 5.1.2** Porous properties of chars from waste tires carbonized at 500, 700, and 850°C at the heating rate of 5°C/min

Sample	Carbonization yield (%)	Ash content (%)	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
C_500_5	35.10	15.0	0.36	N.D.	81
C_700_5	33.95	17.3	0.39	N.D.	185
C_850_5	33.56	16.9	0.31	N.D.	174

The N<sub>2</sub> adsorption-desorption isotherms and pore size distribution on chars carbonized at different temperatures at the heating rate of 5°C/min are shown in Figures 5.1.3 and 5.1.4, respectively.

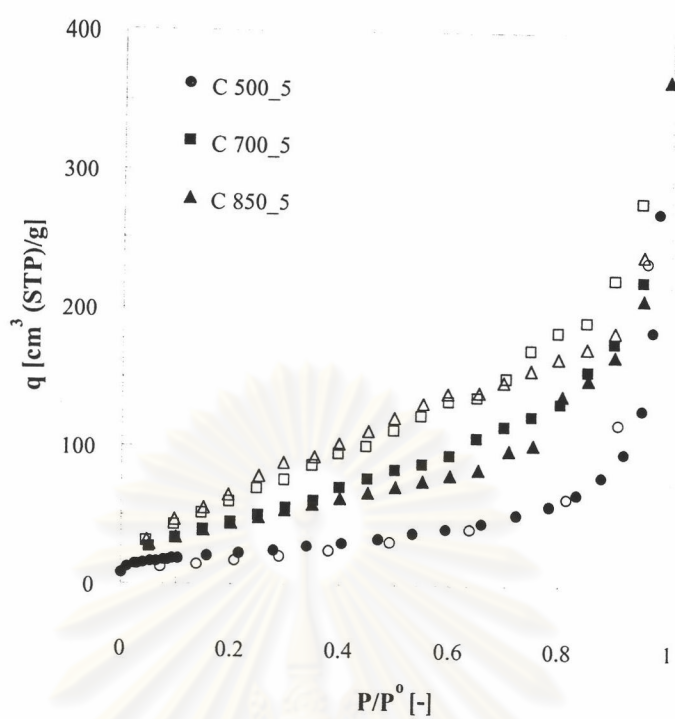


Figure 5.1.3  $N_2$  adsorption-desorption isotherms on chars from waste tires carbonized at 500, 700, and 850°C at the heating rate of 5°C/min; closed symbols: adsorption, open symbols: desorption

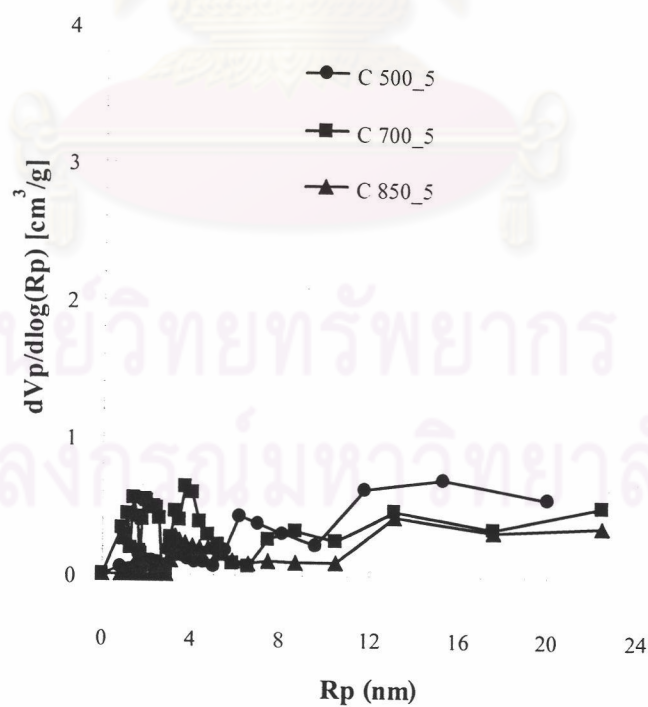


Figure 5.1.4 Pore size distribution of chars from waste tires carbonized at 500, 700, and 850°C at the heating rate of 5°C/min

It was indicated that chars from waste tires carbonized at the varied temperatures have mesoporous structure which can be observed from the hysteresis in their isotherms. It was found in Figure 5.1.4 that chars carbonized at 700 and 850°C possess the mesopores of which the radius are smaller than 4 nm, which can not be observed in char carbonized at 500°C.

The porous properties of these chars are given in Table 5.1.2. The  $S_{BET}$  value of char increased with increasing carbonization temperature up to 700°C, but when the temperature increased until 850°C, no significant increase was observed. It was assumed that the increasing in  $S_{BET}$  value when the char was carbonized at the temperature over 500°C is due to the existence of the small mesopores, pore radius < 4 nm. Nevertheless, the  $V_{meso}$  value of chars did not obviously change at the investigated carbonization temperatures. However, the  $V_{micro}$  values in chars prepared in the range of 500-850°C were found to be essentially zero through the t-plot calculation.

### Conclusion for Section 5.1

- Heating rate during carbonization has negligible effect on the carbonization yield.
- The  $V_{meso}$  and  $S_{BET}$  values of the prepared char slightly increase with the increasing heating rate.
- The carbonization yield decreases a little bit when the carbonization temperature increases but over 700°C the yield seems to be constant.
- The  $V_{meso}$  values of the prepared chars obtained at investigated carbonization temperatures are nearly the same.

- In contrast to the yield, when the carbonization temperature increases, the  $S_{BET}$  value of the char increases but over 700°C it trends to be constant.
- The  $V_{micro}$  values of the chars from vulcanized waste tires at all investigated heating rates and carbonization temperatures are essentially zero.



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## 5.2 Porous properties of prepared activated carbons from waste tires

As expected, in Table 5.2.1, the % burn-off during activation increased with the increase of activation time. However, the activation rates of chars carbonized at 500°C by using different heating rates were almost the same.

**Table 5.2.1** Porous properties of activated carbons prepared at 850°C from waste tires derived chars carbonized at 500°C at the heating rate of 0.5, 5, and 20°C/min

Sample	Burn-off (%)	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
AC 850_1 500_0.5	33.2	0.23	0.13	430
AC 850_3 500_0.5	67.7	0.53	0.21	718
AC 850_4 500_0.5	76.1	0.98	0.26	743
AC 850_1 500_5	34.3	0.32	0.13	435
AC 850_3 500_5	67.3	0.82	0.22	752
AC 850_4 500_5	75.8	1.09	0.26	737
AC 850_1 500_20	32.2	0.21	0.12	386
AC 850_3 500_20	68.6	0.68	0.22	755
AC 850_4 500_20	73.7	0.62	0.25	722

Figures 5.2.1-5.2.3 show the N<sub>2</sub> adsorption-desorption isotherms on the activated carbons obtained through the steam activation at 850°C of the chars carbonized at the heating rate of 0.5, 5, 20°C/min, respectively. Considering the shape of isotherm and the N<sub>2</sub> adsorption capacity, the development of micropores and mesopores during activation could be clearly observed.

From these isotherms, the pore size distributions of obtained activated carbons are shown in Figures 5.2.4-5.2.6.

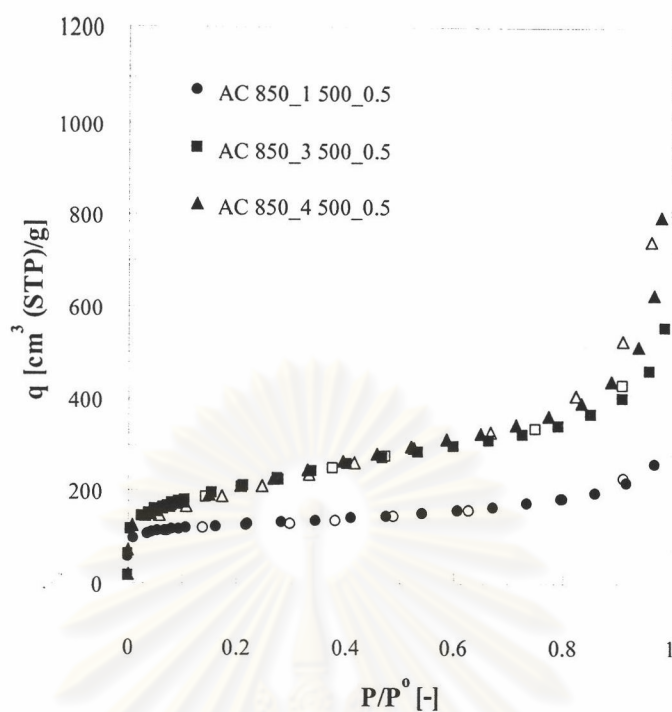


Figure 5.2.1  $N_2$  adsorption-desorption isotherms on activated carbons prepared at  $850^\circ\text{C}$  from waste tires derived chars carbonized at  $500^\circ\text{C}$  at the heating rate of  $0.5^\circ\text{C}/\text{min}$ ;  
closed symbols: adsorption, open symbols: desorption

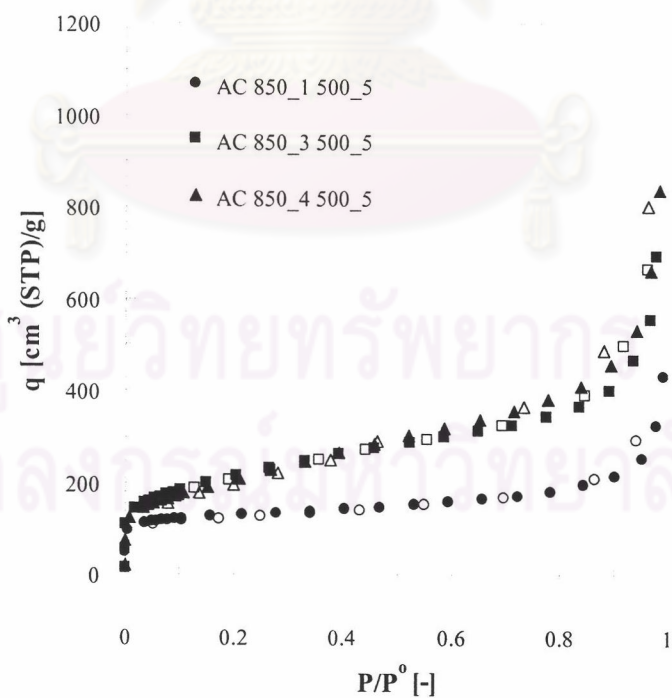


Figure 5.2.2  $N_2$  adsorption-desorption isotherms on activated carbons prepared at  $850^\circ\text{C}$  from waste tires derived chars carbonized at  $500^\circ\text{C}$  at the heating rate  $5^\circ\text{C}/\text{min}$ ;  
closed symbols: adsorption, open symbols: desorption



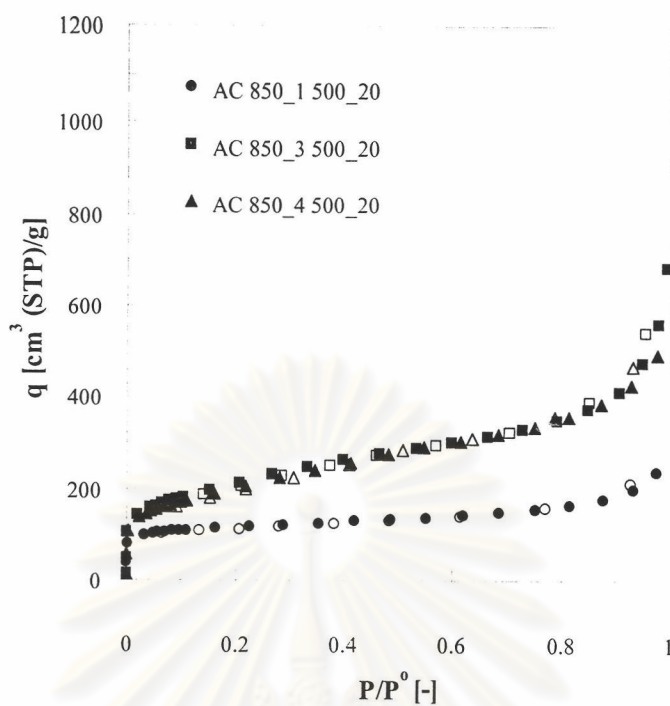


Figure 5.2.3  $N_2$  adsorption-desorption isotherms on activated carbons prepared at  $850^\circ C$  from waste tires derived chars carbonized at  $500^\circ C$  at the heating rate of  $20^\circ C/min$ ;  
closed symbols: adsorption, open symbols: desorption

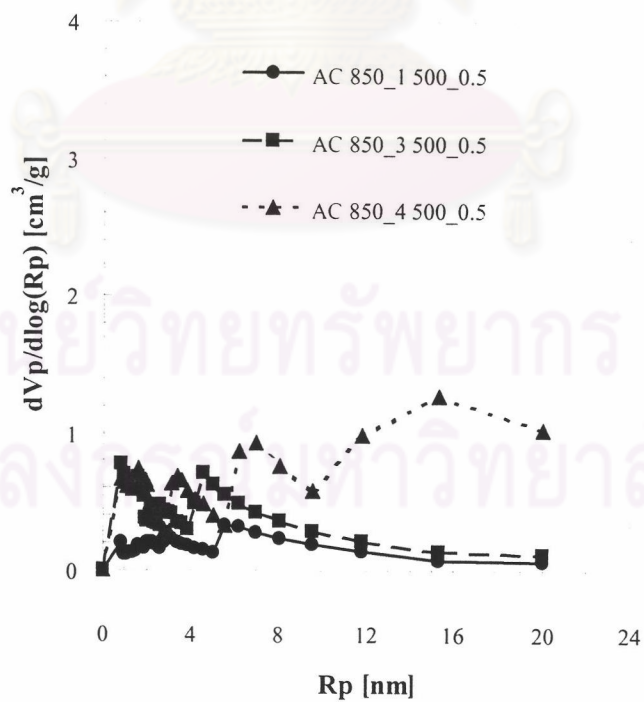


Figure 5.2.4 Pore size distribution of activated carbons prepared at  $850^\circ C$  from waste tires derived chars carbonized at  $500^\circ C$  at the heating rate of  $0.5^\circ C/min$

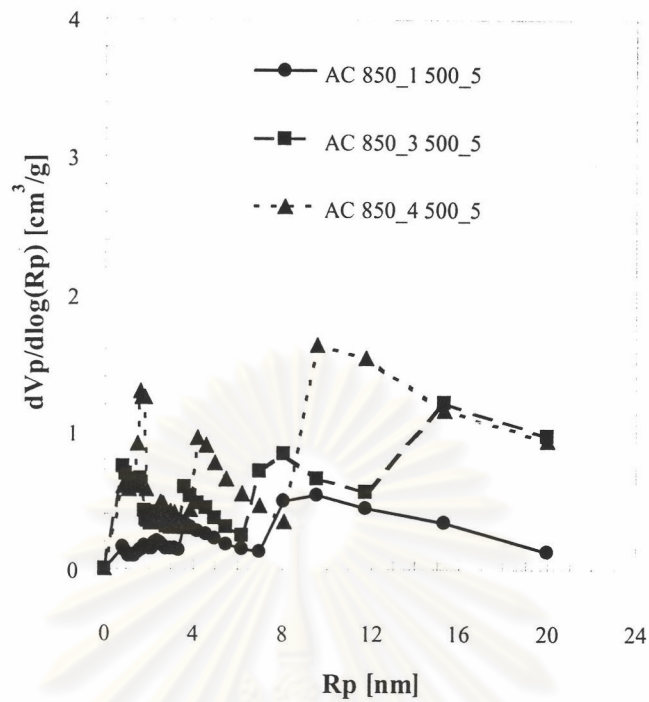


Figure 5.2.5 Pore size distribution of activated carbons prepared at 850°C from waste tires derived chars carbonized at 500°C at the heating rate of 5°C/min

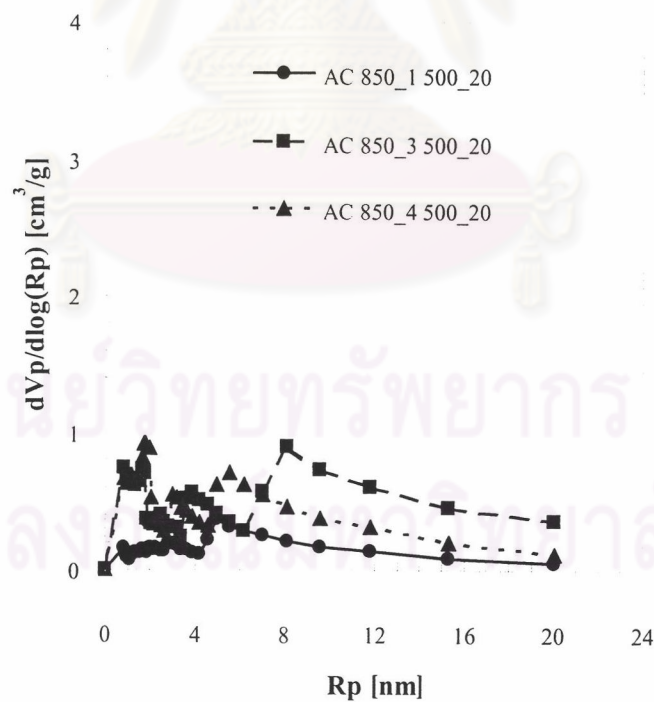


Figure 5.2.6 Pore size distribution of activated carbons prepared at 850°C from waste tires derived chars carbonized at 500°C at the heating rate of 20°C/min

It was found that both mesoporosity and microporosity are improved by steam activation. From these pore size distributions, it was indicated that the pore development mechanism consists of micropore creation followed by pore widening into mesopores.

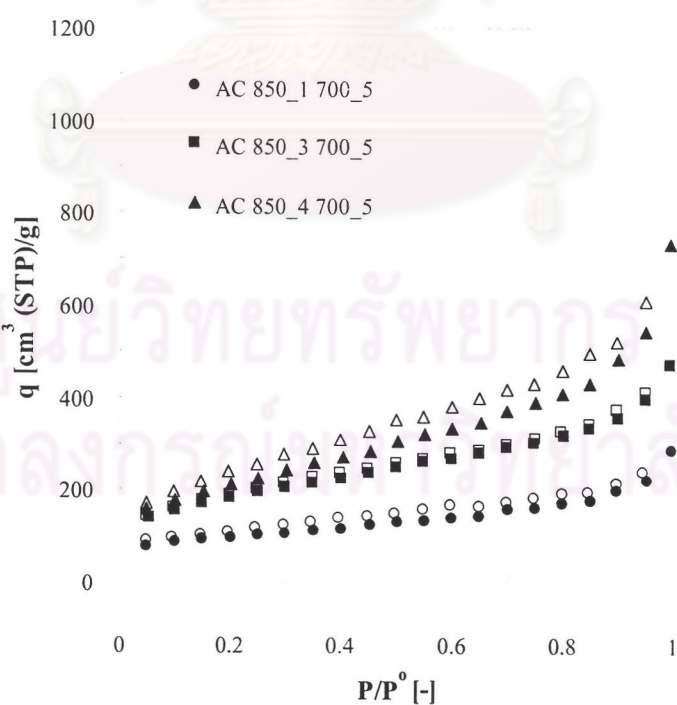
Table 5.2.1 also provides the porous properties of obtained activated carbons calculated from above isotherms. The prepared activated carbons had the  $V_{meso}$  and  $V_{micro}$  values up to 1.09 and 0.26 cm<sup>3</sup>/g, respectively, and possessed the  $S_{BET}$  value up to 750 m<sup>2</sup>/g. It was found that the higher  $V_{meso}$  value of prepared activated carbons can be obtained at higher % burn-off, while the  $V_{micro}$  and  $S_{BET}$  values increase until about 70 % burn-off and then tend to be constant. It was indicated that the heating rate in carbonization step does not show obvious influence on the porous properties of activated carbons.

As shown in Table 5.2.2, a slight decrease in rate of steam activation was observed in char carbonized at higher temperature. It was suggested that the char prepared at higher carbonization temperature has less disorganized carbons and the activation rate decreases.

The N<sub>2</sub> adsorption-desorption isotherms on activated carbons carbonized at 700 and 850°C and steam-activated at 850°C are presented in Figures 5.2.7-5.2.8, respectively. The shape of these isotherms was similar to that of activated carbons in Figure 5.2.2, which showed both mesopores and micropores developments.

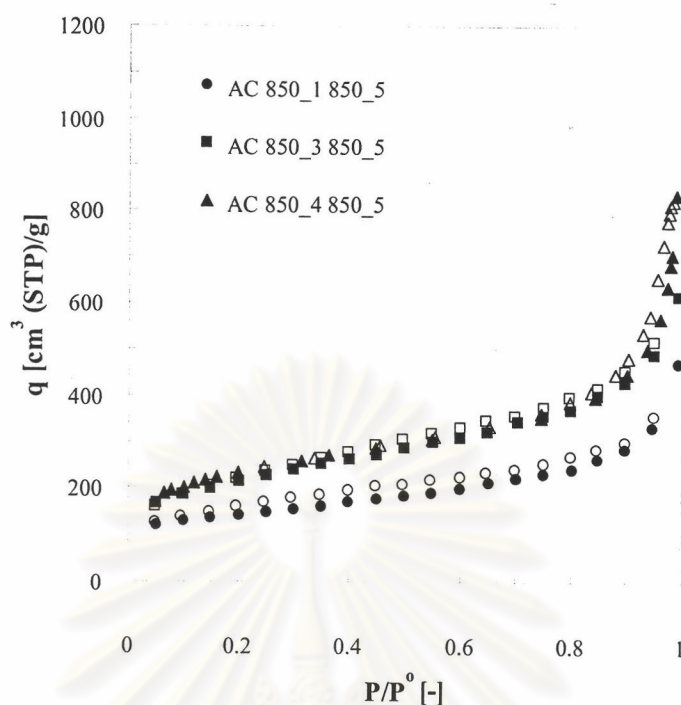
**Table 5.2.2** Porous properties of activated carbons prepared at 850°C from waste tires derived chars carbonized at 500, 700, and 850°C at the heating rate of 5°C/min

Sample	Burn-off (%)	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
AC 850_1 500_5	34.3	0.32	0.13	435
AC 850_3 500_5	67.3	0.82	0.22	752
AC 850_4 500_5	75.8	1.09	0.26	737
AC 850_1 700_5	30.0	0.16	0.14	317
AC 850_3 700_5	60.2	0.53	0.26	639
AC 850_4 700_5	74.1	0.87	0.23	752
AC 850_1 850_5	26.3	0.45	0.13	469
AC 850_3 850_5	53.4	0.69	0.24	743
AC 850_4 850_5	61.1	0.74	0.23	781



**Figure 5.2.7** N<sub>2</sub> adsorption-desorption isotherms on activated carbons prepared at 850°C from waste tires derived chars carbonized at 700°C at the heating rate of 5°C/min;

closed symbols: adsorption, open symbols: desorption



**Figure 5.2.8** N<sub>2</sub> adsorption-desorption isotherms on activated carbons prepared at 850°C from waste tires derived chars carbonized at 850°C at the heating rate of 5°C/min; closed symbols: adsorption, open symbols: desorption

Figures 5.2.9-5.2.10 show the pore size distributions of activated carbons calculated from these isotherms. It was observed that activated carbons obtained from chars carbonized at 700 and 850°C do not have the large size of mesopores as much as in activated carbons prepared from char carbonized at 500°C.

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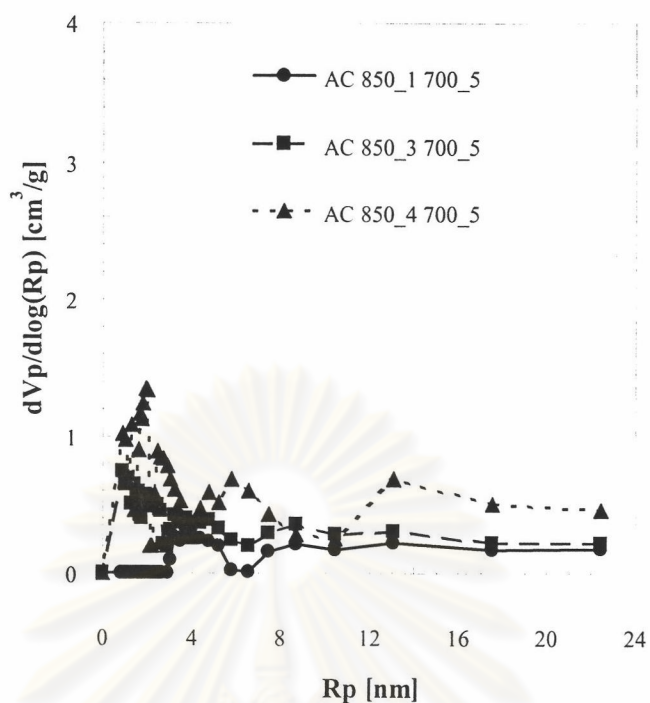


Figure 5.2.9 Pore size distribution of activated carbons prepared at 850°C from waste tires derived chars carbonized at 700°C at the heating rate of 5°C/min

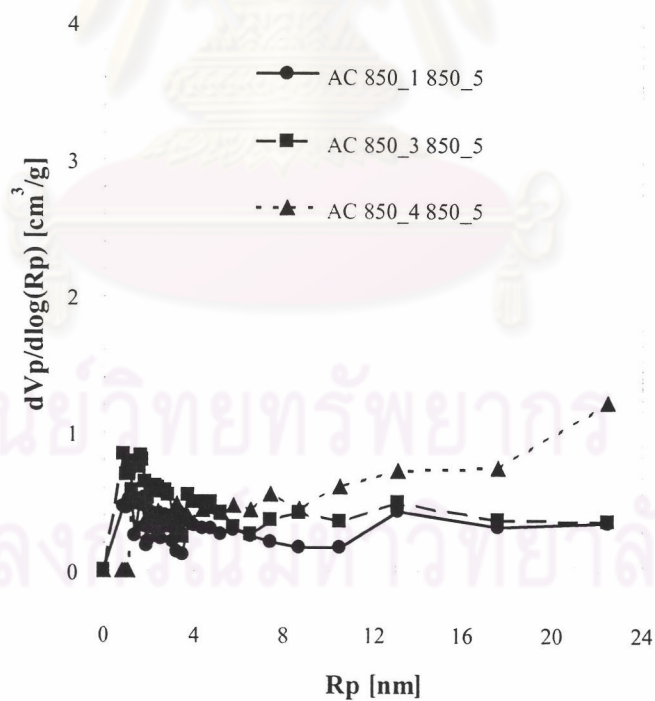


Figure 5.2.10 Pore size distribution of activated carbons prepared at 850°C from waste tires derived chars carbonized at 850°C at the heating rate of 5°C/min

The porous properties of activated carbons obtained at 850°C from chars carbonized at varied temperatures are summarized in Table 5.2.2. Similarly, it was clear that the  $V_{meso}$  value of activated carbons prepared from chars carbonized at different temperature increased with increasing % burn-off. In addition, the  $V_{micro}$  and  $S_{BET}$  values of activated carbons derived from chars obtained at 700 and 850°C had the same trend as those from char carbonized at 500°C. Also, it seems that the  $V_{meso}$ ,  $V_{micro}$ , and  $S_{BET}$  values did not show obvious differences among the activated carbons prepared from chars carbonized at varied carbonization temperatures by comparing them at the same level of the % burn-off achieved.

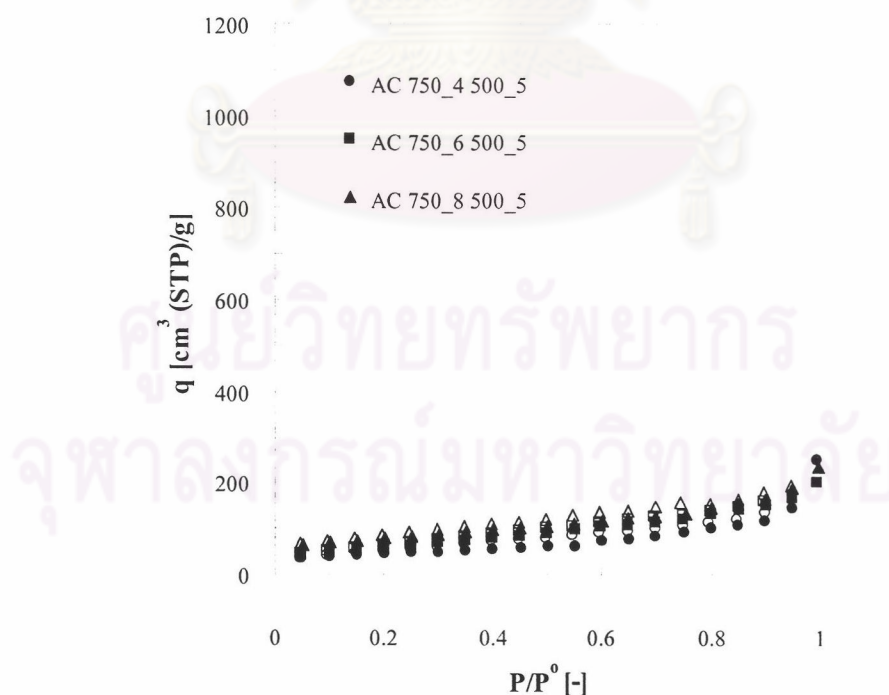
The % burn-off achieved at varied activation times are given in Table 5.2.3. It was found that the activation rate of char increases strongly with increasing activation temperature.

Respectively, Figures 5.2.11-5.2.12 present the N<sub>2</sub> adsorption-desorption isotherms on activated carbons prepared at 750 and 950°C. Even though a slight hysteresis still occurred in activated carbons obtained at 750°C, the N<sub>2</sub> adsorption capacities were essentially smaller than those of activated carbons obtained at 850°C because of obviously lower achieved % burn-off. In case of activation at 950°C, the mesopores and micropores developments were also observed in the isotherms.

By applying the Dollimore-Heal method to these isotherms, the pore size distributions of prepared activated carbons are shown in Figures 5.2.13-5.2.14.

**Table 5.2.3** Porous properties of activated carbons prepared at 750, 850, and 950°C from waste tires derived chars carbonized at 500°C at the heating rate of 5°C/min

Sample	Burn-off (%)	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
AC 750_4 500_5	18.5	0.27	0.01	146
AC 750_6 500_5	19.5	0.12	0.06	268
AC 750_8 500_5	23.3	0.09	0.08	262
AC 850_1 500_5	34.3	0.32	0.13	435
AC 850_3 500_5	67.3	0.82	0.22	752
AC 850_4 500_5	75.8	1.09	0.26	737
AC 950_0.17 500_5	41.1	0.35	0.17	490
AC 950_0.25 500_5	50.9	0.45	0.22	642
AC 950_0.50 500_5	70.5	0.70	0.24	705



**Figure 5.2.11** N<sub>2</sub> adsorption-desorption isotherms on activated carbons prepared at 750°C from waste tires derived chars carbonized at 500°C at the heating rate of 5°C/min; closed symbols: adsorption, open symbols: desorption



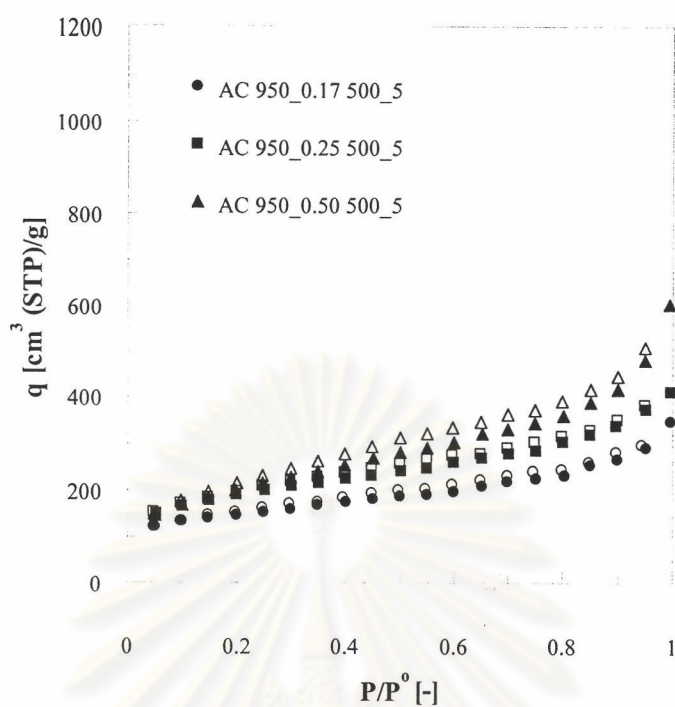


Figure 5.2.12  $N_2$  adsorption-desorption isotherms on activated carbons prepared at 950°C from waste tires derived chars carbonized at 500°C at the heating rate of 5°C/min; closed symbols: adsorption, open symbols: desorption

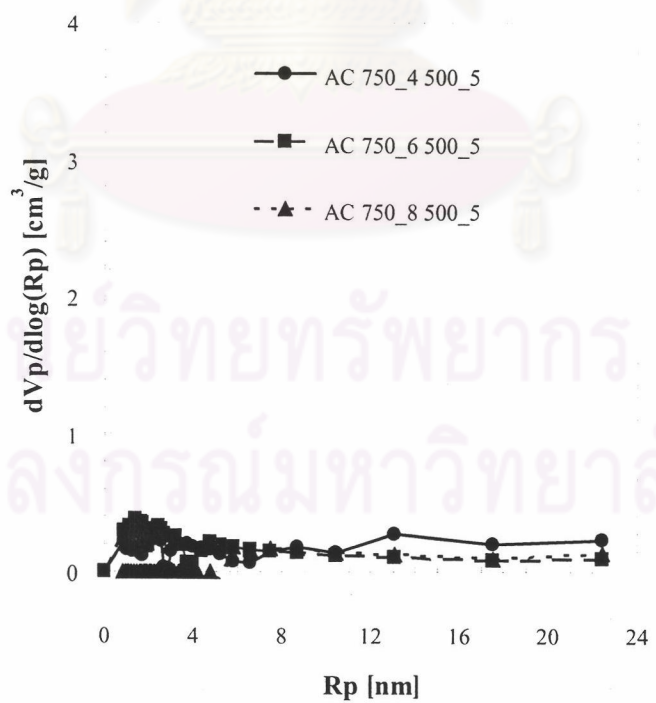
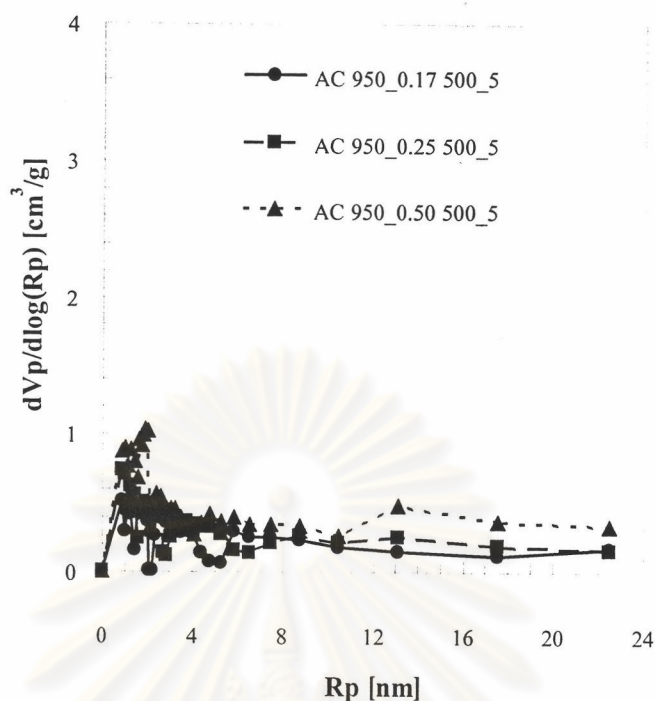


Figure 5.2.13 Pore size distribution of activated carbons prepared at 750°C from waste tires derived chars carbonized at 500°C at the heating rate of 5°C/min



**Figure 5.2.14** Pore size distribution of activated carbons prepared at 950°C from waste tires derived chars carbonized at 500°C at the heating rate of 5°C/min

It was observed in Figure 5.2.13 that the carbons prepared at 750°C have slight mesopore distribution which is corresponded to the pore development in which at low % burn-off the mesopores have not been developed yet. On the other hand, the activated carbons obtained at 950°C showed similar mesopore size distribution as those activated at 850°C. However, it was noted that the activated carbons prepared at 950°C do not possess the large size of mesopore radius.

Their porous properties were calculated from these isotherms and shown in Table 5.2.3. Since the activation rate at 750°C was too slow to achieve over 25% burn-off, the porous properties of obtained activated carbons were very low compared with those of activated carbons prepared at higher temperature. It was suggested that the activation at 750°C is not suitable to produce activated carbon. The  $V_{meso}$  value of activated carbons obtained at 950°C was lower than

that of activated carbons prepared at 850°C. On the other hand, the activation at 950°C provided both the  $V_{micro}$  and  $S_{BET}$  values in the same order as at 850°C.

### Conclusion for Section 5.2

- Heating rate during carbonization does not significantly influence the activation rate and the porous properties of the activated carbon.
- Fairly mesoporous activated carbon is obtained from vulcanized waste tires by conventional steam activation.
- Pore development mechanism consists of micropore formation followed by pore widening into mesopore.
- Activation rate of the char decreases as the carbonization temperature increases.
- Carbonization temperature does not have a clear systematic effect on the porous properties of the activated carbon.
- Activation rate greatly depends on the activation temperature.
- Because of very slow activation rate, activation at 750°C is not suitable for preparing the activated carbon.
- Activated carbons prepared at 850°C have higher  $V_{meso}$  values than but nearly the same  $V_{micro}$  and  $S_{BET}$  values as those prepared at 950°C.

### 5.3 Porous properties of acid-treated chars

After carbonization, typical chars obtained were acid-treated with HCl, and the  $N_2$  adsorption-desorption isotherms of the HCl-treated chars carbonized at  $500^\circ\text{C}$  at the varied heating rates are shown in Figure 5.3.1. It was indicated that the shape of isotherms and  $N_2$  adsorption capacity of HCl-treated chars are very similar to those of non-treated chars.

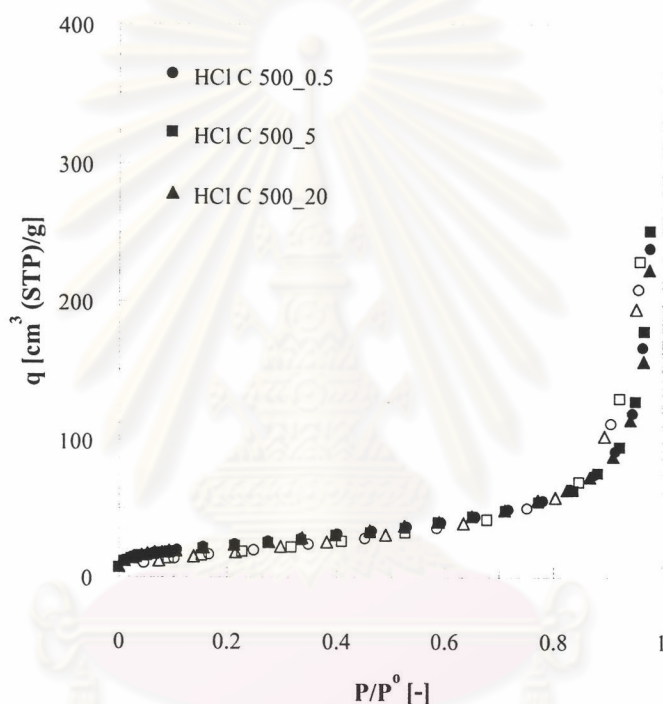


Figure 5.3.1  $N_2$  adsorption-desorption isotherms on HCl-treated chars from waste tires carbonized at  $500^\circ\text{C}$  at the heating rate of 0.5, 5, and  $20^\circ\text{C}/\text{min}$ ; closed symbols: adsorption, open symbols: desorption

Figure 5.3.2 presents the pore size distributions calculated from the isotherms of HCl-treated chars in Figure 5.3.1. It was observed that the pore size distribution of the chars after HCl treatment is almost the same as that of non-treated char.

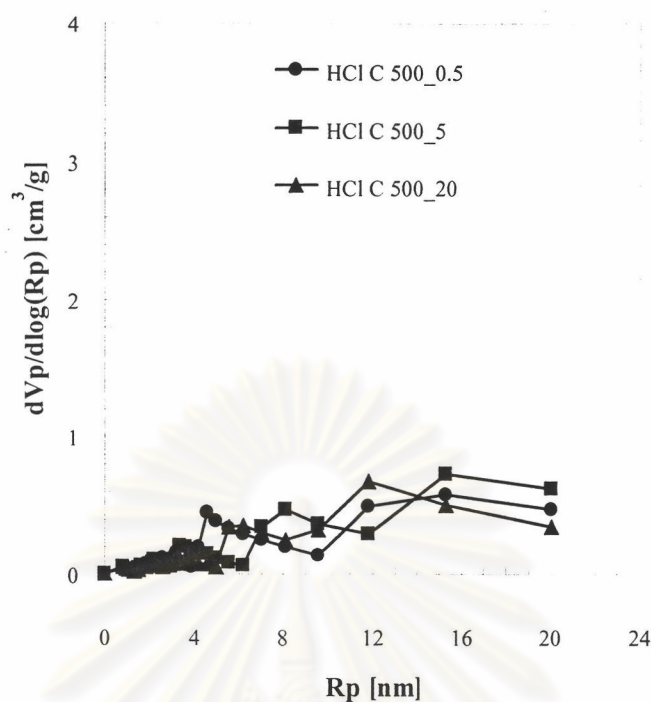


Figure 5.3.2 Pore size distribution of HCl-treated chars from waste tires carbonized at 500°C at the heating rate of 0.5, 5, and 20°C/min

In Table 5.3.1, it was found that during the acid treatment, some of inorganic compounds in char are eliminated, as a result, the ash content of HCl-treated chars were around 6.5 %. Table 5.3.1 also shows the porous properties of the HCl-treated chars carbonized at 500°C at varied heating rates.

Table 5.3.1 Porous properties of HCl-treated chars from waste tires carbonized at 500°C at the heating rate of 0.5, 5, and 20°C/min

Sample	Carbonization yield (%)	Ash content (%)	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
HCl C 500_0.5	35.07	6.2	0.32	N.D.	82
HCl C 500_5	35.10	6.5	0.34	N.D.	80
HCl C 500_20	35.08	6.2	0.31	N.D.	85

Comparing Table 5.1.1 and Table 5.3.1, the  $V_{meso}$  and  $S_{BET}$  values of HCl-treated chars were essentially the same as those of non-treated chars. However, after the acid treatment by HCl, the  $V_{micro}$  value still could not be characterized by  $N_2$  adsorption.

In the case of chars obtained at different carbonization temperatures, after HCl treatment, their  $N_2$  adsorption-desorption isotherms are provided in Figure 5.3.3. It was also indicated that the shape of isotherms and  $N_2$  adsorption capacity of HCl-treated chars carbonized at varied temperatures are almost the same as those of non-treated chars.

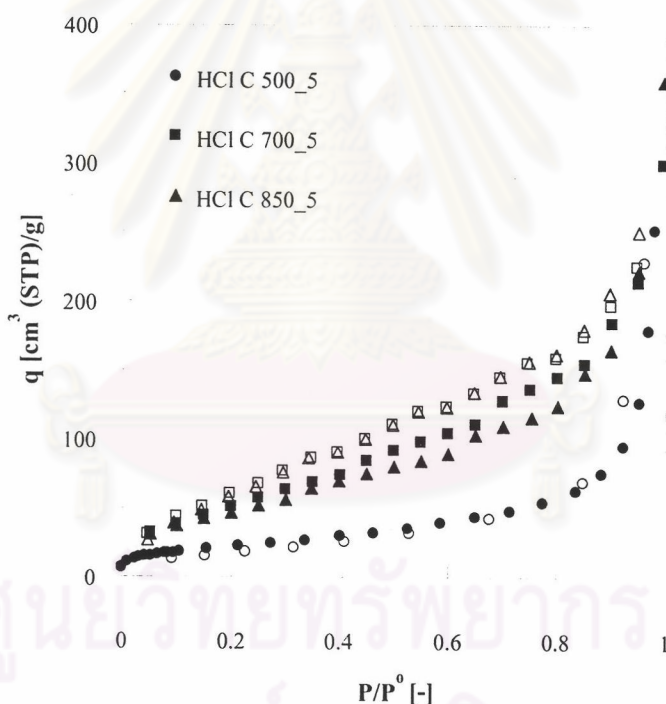


Figure 5.3.3  $N_2$  adsorption-desorption isotherms on HCl-treated chars from waste tires carbonized at 500, 700, and 850°C at the heating rate of 5°C/min;

closed symbols: adsorption, open symbols: desorption

Figure 5.3.4 shows the pore size distribution of chars after the HCl treatment carbonized at varied temperatures. It was found that HCl-treated char obtained at 500°C shows more large mesopores but less small mesopores

than that carbonized at 700 and 850°C as also can be found in case of non-treated chars.

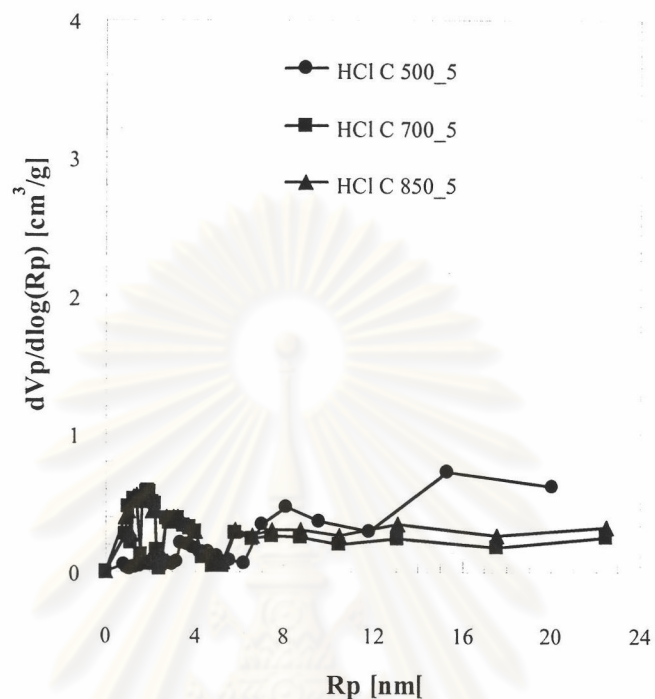


Figure 5.3.4 Pore size distribution of HCl-treated chars from waste tires carbonized at 500, 700, and 850°C at the heating rate of 5°C/min

By the HCl treatment, the ash content in acid-treated chars carbonized at varied temperatures were less than 7.0 %. Table 5.3.2 summarizes the porous properties of HCl-treated chars prepared at varied carbonization temperatures.

Table 5.3.2 Porous properties of HCl-treated chars from waste tires carbonized at 500, 700, and 850°C at the heating rate of 5°C/min

Sample	Carbonization yield (%)	Ash content (%)	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
HCl C 500_5	35.10	6.5	0.34	N.D.	80
HCl C 700_5	33.95	6.9	0.34	N.D.	208
HCl C 850_5	33.56	6.7	0.37	N.D.	182

Both the  $V_{meso}$  and  $S_{BET}$  values of HCl-treated chars presented in Table 5.3.2 did not significantly differ from those of non-treated chars shown in Table 5.1.2, while the  $V_{micro}$  value could not be calculated by using the t-plot method as the chars before the acid treatment.

### Conclusion for Section 5.3

- Some inorganic contents in the prepared char are removed in HCl treatment.
- The  $V_{meso}$  values of the HCl-treated chars prepared at different carbonization temperatures and heating rates are nearly the same.
- The  $V_{micro}$  values of all HCl-treated chars are essentially zero.
- Heating rate during carbonization does not affect the  $S_{BET}$  value of HCl-treated chars.
- Raising the carbonization temperature increases the  $S_{BET}$  value of HCl-treated chars but over 700°C the  $S_{BET}$  value seems to be constant.



#### 5.4 Porous properties of activated carbons from acid-treated chars

The higher % burn-off could be achieved at longer activation time as shown in Table 5.4.1. However, the HCl treatment did not significantly influence on the activation rate by comparing Table 5.4.1 with Table 5.2.1.

**Table 5.4.1** Porous properties of activated carbons prepared at 850°C from HCl-treated chars from waste tires carbonized at 500°C at the heating rate of 0.5, 5, and 20°C/min

Sample	Burn-off (%)	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
AC HCl 850_1 500_0.5	31.4	0.48	0.22	609
AC HCl 850_3 500_0.5	60.5	0.99	0.48	1045
AC HCl 850_4 500_0.5	71.0	1.27	0.56	1116
AC HCl 850_1 500_5	33.1	0.49	0.22	664
AC HCl 850_3 500_5	68.0	1.18	0.51	1107
AC HCl 850_4 500_5	77.5	1.62	0.57	1119
AC HCl 850_1 500_20	30.7	0.53	0.20	585
AC HCl 850_3 500_20	68.6	1.22	0.54	1177
AC HCl 850_4 500_20	78.6	1.52	0.54	1166

Activated carbons obtained from HCl-treated chars carbonized at different heating rates are characterized and their N<sub>2</sub> adsorption-desorption results are presented in Figures 5.4.1-5.4.3. Interestingly, activated carbons prepared with the HCl treatment prior to steam activation of chars carbonized at different heating rates showed obviously higher N<sub>2</sub> adsorption capacity when compared with those obtained through the conventional activation method as shown in Figures 5.2.1-5.2.3.

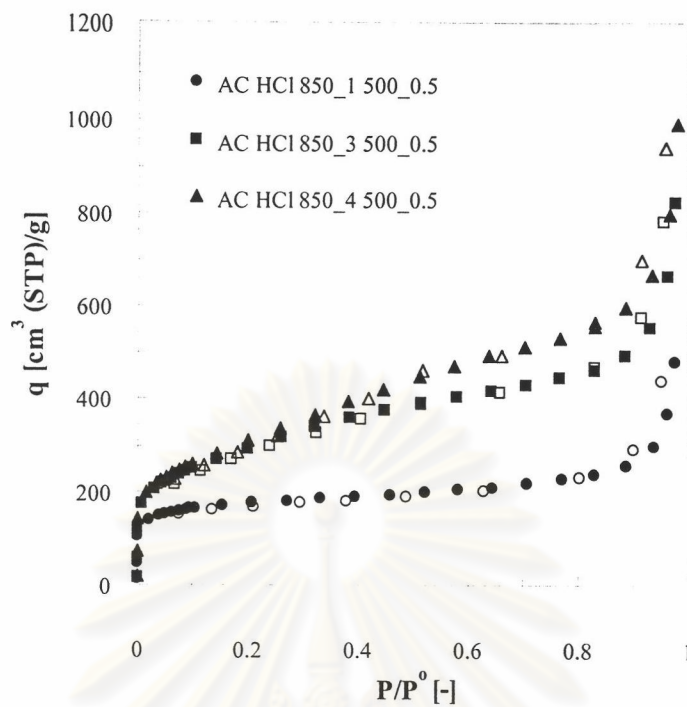


Figure 5.4.1  $N_2$  adsorption-desorption isotherms on activated carbons prepared at  $850^\circ\text{C}$  from HCl-treated chars from waste tires carbonized at  $500^\circ\text{C}$  at the heating rate of  $0.5^\circ\text{C}/\text{min}$ ; closed symbols: adsorption, open symbols: desorption

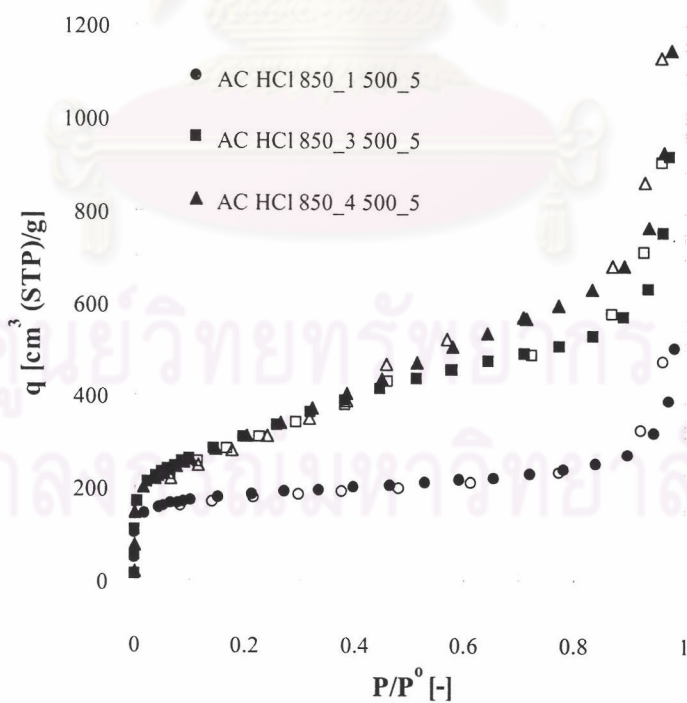


Figure 5.4.2  $N_2$  adsorption-desorption isotherms on activated carbons prepared at  $850^\circ\text{C}$  from HCl-treated chars from waste tires carbonized at  $500^\circ\text{C}$  at the heating rate  $5^\circ\text{C}/\text{min}$ ; closed symbols: adsorption, open symbols: desorption

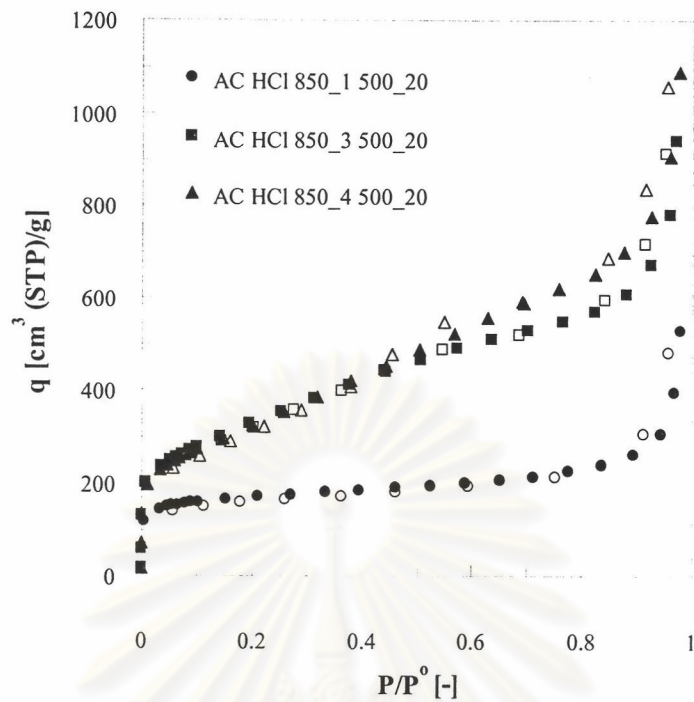


Figure 5.4.3  $N_2$  adsorption-desorption isotherms on activated carbons prepared at  $850^\circ\text{C}$  from HCl-treated chars from waste tires carbonized at  $500^\circ\text{C}$  at the heating rate of  $20^\circ\text{C}/\text{min}$ ; closed symbols: adsorption, open symbols: desorption

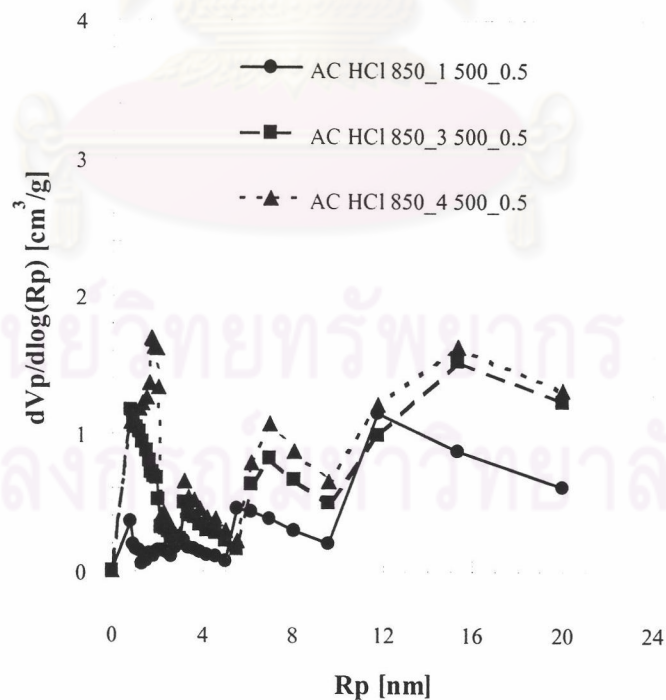


Figure 5.4.4 Pore size distribution of activated carbons prepared at  $850^\circ\text{C}$  from HCl-treated chars from waste tires carbonized at  $500^\circ\text{C}$  at the heating rate of  $0.5^\circ\text{C}/\text{min}$

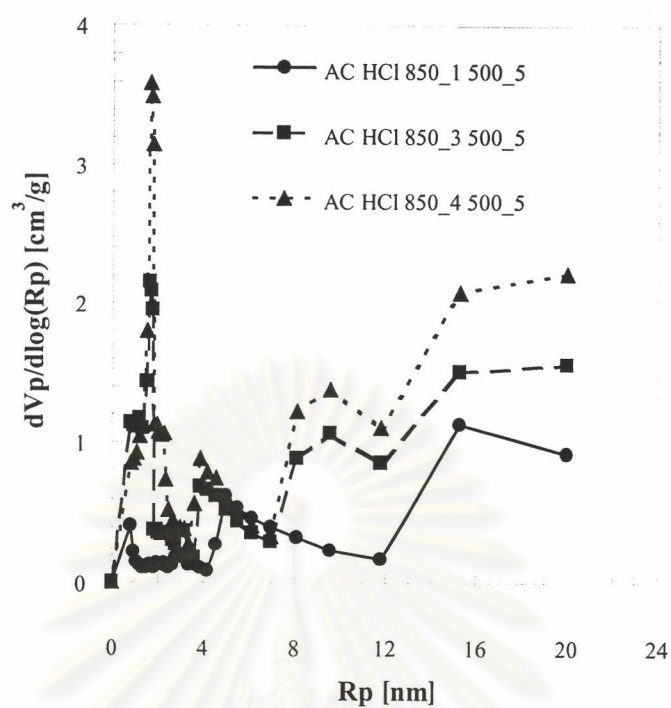


Figure 5.4.5 Pore size distribution of activated carbons prepared at 850°C from HCl-treated chars from waste tires carbonized at 500°C at the heating rate of 5°C/min

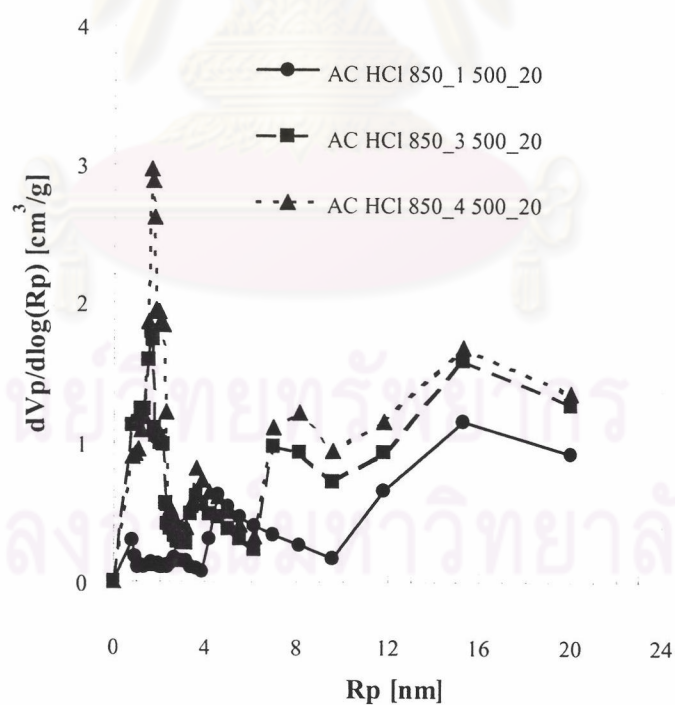


Figure 5.4.6 Pore size distribution of activated carbons prepared at 850°C from HCl-treated chars from waste tires carbonized at 500°C at the heating rate of 20°C/min

Then the pore size distributions calculated from the isotherms in Figures 5.4.1-5.4.3 on activated carbons prepared from HCl-treated chars are given in Figures 5.4.4-5.4.6, respectively. It was suggested that activated carbons prepared with the HCl treatment prior to steam activation show the peak of pore size distribution at the radius around 2 nm. However, they also have the large size of mesopores, pore radius > 4 nm, which is similar to the activated carbons obtained by the conventional activation method.

The porous properties of activated carbons prepared with the HCl treatment prior to steam activation are determined and also given in Table 5.4.1. Typical activated carbons prepared from the HCl-treated chars possessed the  $V_{meso}$  and  $V_{micro}$  values up to 1.62 and 0.57 cm<sup>3</sup>/g, respectively, and the  $S_{BET}$  value up to 1177 m<sup>2</sup>/g. It was clear that the HCl treatment prior to steam activation can improve not only mesoporosity but also microporosity. In addition, the heating rate in carbonization step did not show any significant effect on both the  $V_{meso}$  and  $V_{micro}$  values as well as the  $S_{BET}$  one.

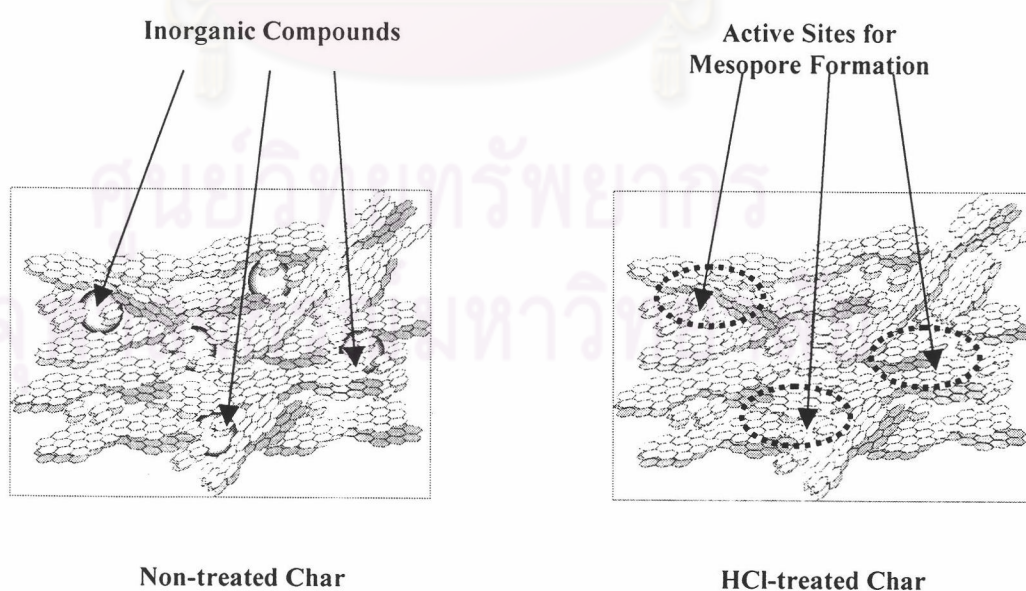


Figure 5.4.7 Model of char structure

It was suggested that according to the model of char structure shown in Figure 5.4.7 the inorganic compounds are removed from the chars during the acid treatment, thus creating the active sites for mesopore formation.

As shown in Table 5.4.2, the activation rate of HCl-treated char prepared at higher carbonization temperature slightly decreased when compared with the HCl-treated char carbonized at lower temperature, which is the same trend as the non-treated chars. It was indicated that after acid treatment the char carbonized at higher temperature is more stable.

**Table 5.4.2** Porous properties of activated carbons prepared at 850°C from HCl-treated chars from waste tires carbonized at 500, 700, 850°C at the heating rate of 5°C/min

Sample	Burn-off (%)	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
AC HCl 850_1 500_5	33.1	0.49	0.22	664
AC HCl 850_3 500_5	68.0	1.18	0.51	1107
AC HCl 850_4 500_5	77.5	1.62	0.57	1119
AC HCl 850_1 700_5	27.2	0.34	0.14	425
AC HCl 850_3 700_5	62.3	0.70	0.41	1041
AC HCl 850_4 700_5	71.6	0.69	0.34	732
AC HCl 850_1 850_5	22.0	0.31	0.09	314
AC HCl 850_3 850_5	57.6	0.93	0.36	1077
AC HCl 850_4 850_5	66.9	1.07	0.38	1125

Figures 5.4.8-5.4.9 show the N<sub>2</sub> adsorption-desorption isotherms on activated carbons from HCl-treated chars carbonized at 700 and 850°C, respectively. Comparing with Figures 5.2.7-5.2.8, it was found that the HCl treatment can enhance the N<sub>2</sub> adsorption capacity of activated carbons at

investigated carbonization temperatures. The pore size distributions of these activated carbons are provided in Figures 5.4.10-5.4.11. It was observed that, in the case of activated carbons from char carbonized at 500°C, the HCl treatment prior to steam activation develops mainly the small size of mesopores. On the contrary, during steam activation the activated carbons from the HCl-treated chars carbonized at 700 and 850°C were developed in the large size of mesopores by widening the existing small mesopores in chars.

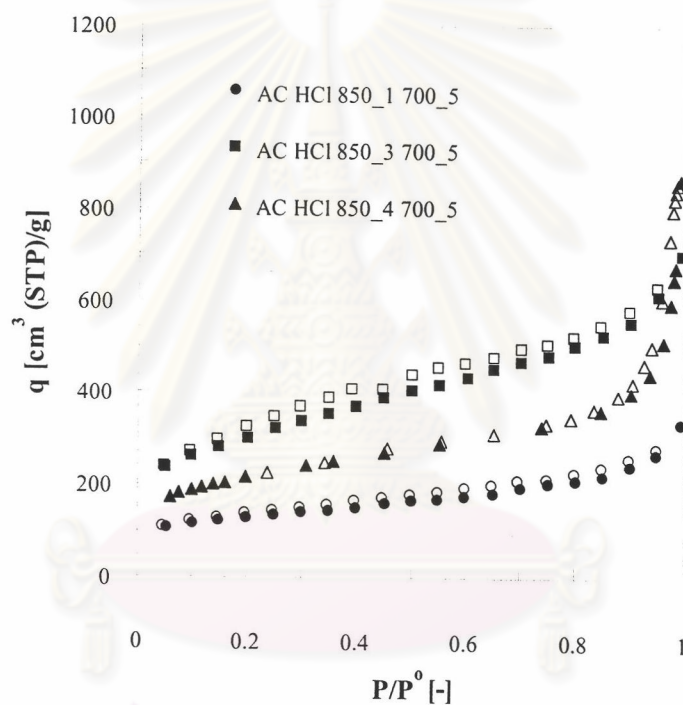


Figure 5.4.8  $N_2$  adsorption-desorption isotherms on activated carbons prepared at 850°C from HCl-treated chars from waste tires carbonized at 700°C at the heating rate of 5°C/min; closed symbols: adsorption, open symbols: desorption

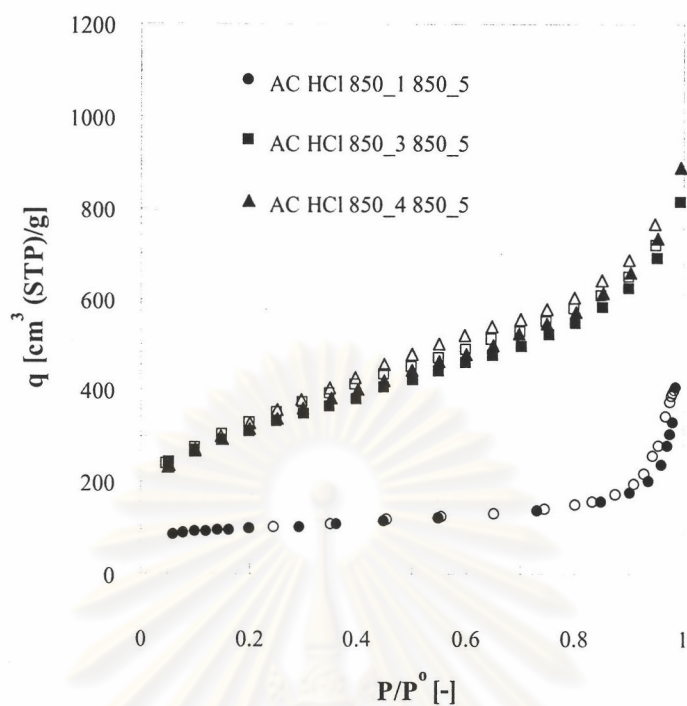


Figure 5.4.9  $N_2$  adsorption-desorption isotherms on activated carbons prepared at  $850^\circ\text{C}$  from HCl-treated chars from waste tires carbonized at  $850^\circ\text{C}$  at the heating rate of  $5^\circ\text{C}/\text{min}$ ; closed symbols: adsorption, open symbols: desorption

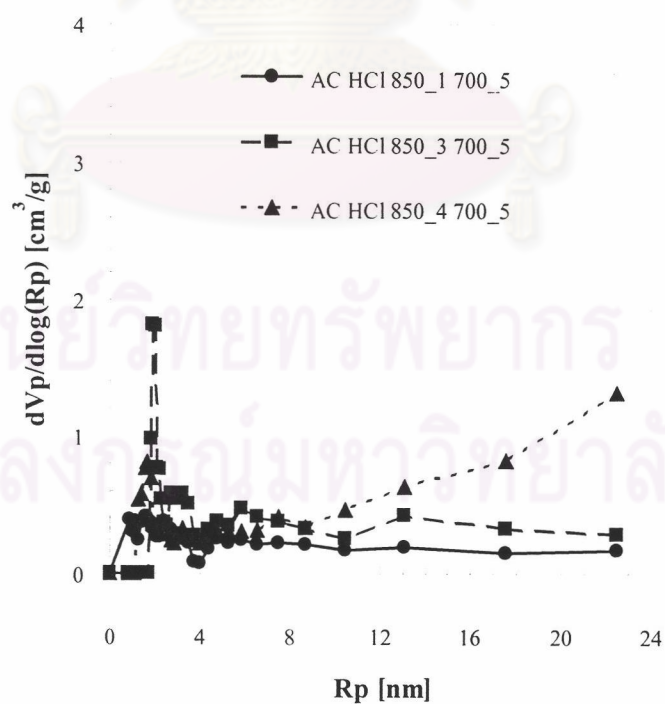


Figure 5.4.10 Pore size distribution of activated carbons prepared at  $850^\circ\text{C}$  from HCl-treated chars from waste tires carbonized at  $700^\circ\text{C}$  at the heating rate of  $5^\circ\text{C}/\text{min}$



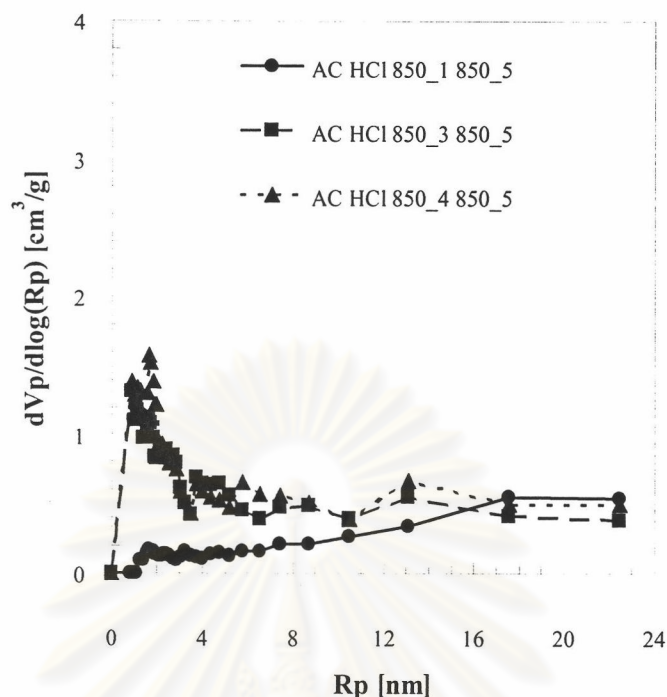


Figure 5.4.11 Pore size distribution of activated carbons prepared at 850°C from HCl-treated chars from waste tires carbonized at 850°C at the heating rate of 5°C/min

Table 5.4.2 also summarizes the porous properties of activated carbons derived from HCl-treated chars prepared at different carbonization temperatures. The  $V_{meso}$  values of carbons activated from HCl-treated chars carbonized at 700 and 850°C were not higher than those of activated carbons prepared without the treatment, while the  $V_{micro}$  values increased by the HCl treatment prior to steam activation. However, the  $S_{BET}$  values of obtained activated carbons were enhanced by HCl treatment of chars carbonized at the varied temperatures due to the increasing of microporosity.

Comparing the achieved % burn-off during activation in Table 5.4.3 and 5.2.3, the rates of activation at varied temperatures of HCl-treated char and non-treated char were almost the same.

**Table 5.4.3** Porous properties of activated carbons prepared at 750, 850, 950°C from HCl-treated chars from waste tires carbonized at 500°C at the heating rate of 5°C/min

Sample	Burn-off (%)	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
AC HCl 750_4 500_5	14.9	0.31	0.09	301
AC HCl 750_6 500_5	23.0	0.23	0.16	419
AC HCl 750_8 500_5	26.3	0.26	0.15	392
AC HCl 850_1 500_5	33.1	0.49	0.22	664
AC HCl 850_3 500_5	68.0	1.18	0.51	1107
AC HCl 850_4 500_5	77.5	1.62	0.57	1119
AC HCl 950_0.17 500_5	39.1	0.41	0.26	659
AC HCl 950_0.25 500_5	46.8	0.45	0.35	827
AC HCl 950_0.50 500_5	72.0	1.12	0.62	1307

The N<sub>2</sub> adsorption-desorption isotherms on activated carbons from HCl-treated char prepared at 750 and 950°C are shown in Figures 5.4.12-5.4.13, respectively. Figure 5.4.12 showed that the N<sub>2</sub> adsorption capacities of carbons activated at 750°C were obviously low when compared with those of carbons activated at 850 or 950°C but higher than those of activated carbons prepared without the HCl treatment. Similarly, the activated carbons shown in Figure 5.4.13 showed larger N<sub>2</sub> adsorption capacity than those presented in Figure 5.2.12, which were prepared by conventional activation method.

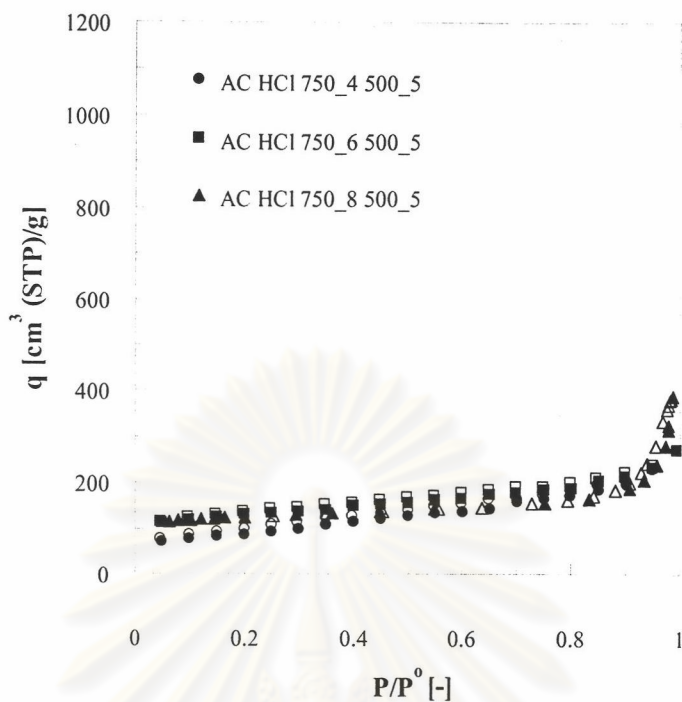


Figure 5.4.12  $N_2$  adsorption-desorption isotherms on activated carbons prepared at  $750^\circ\text{C}$  from HCl treated chars from waste tires carbonized at  $500^\circ\text{C}$  at the heating rate of  $5^\circ\text{C}/\text{min}$ ; closed symbols: adsorption, open symbols: desorption

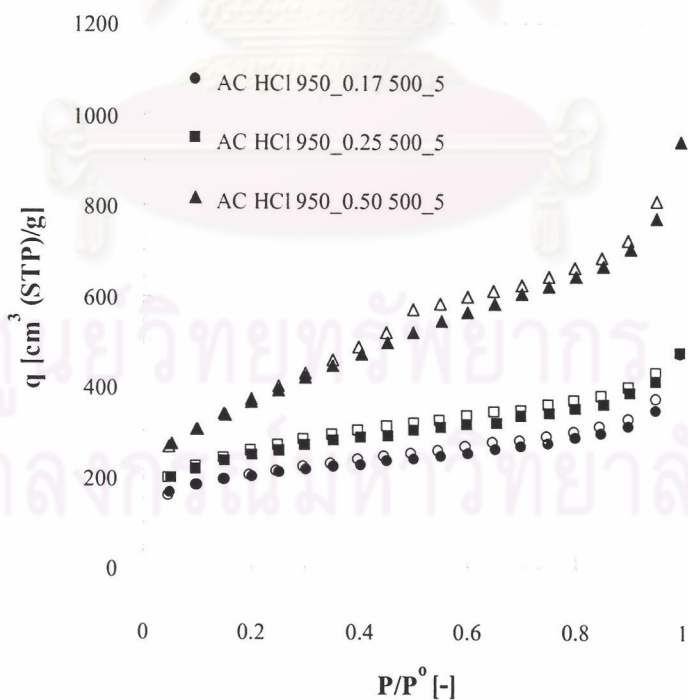


Figure 5.4.13  $N_2$  adsorption-desorption isotherms on activated carbons prepared at  $950^\circ\text{C}$  from HCl treated chars from waste tires carbonized at  $500^\circ\text{C}$  at the heating rate of  $5^\circ\text{C}/\text{min}$ ; closed symbols: adsorption, open symbols: desorption

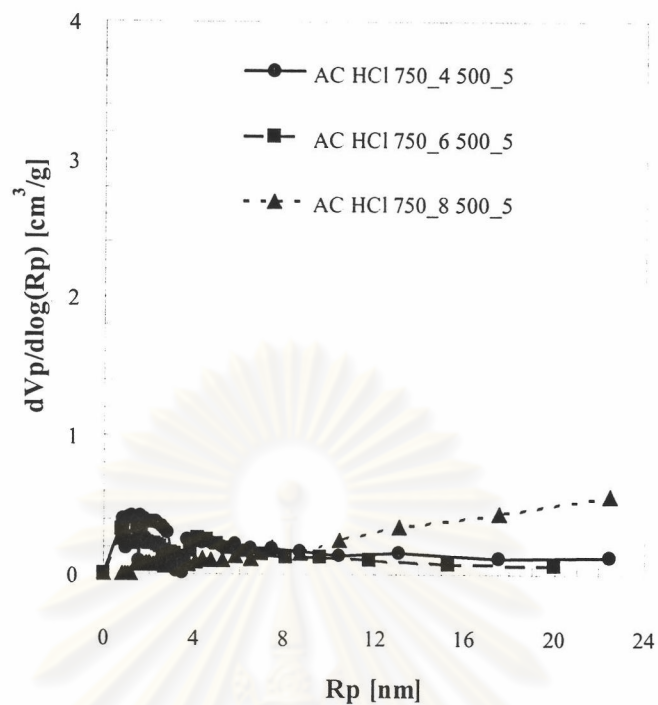


Figure 5.4.14 Pore size distribution of activated carbons prepared at 750°C from HCl treated chars from waste tires carbonized at 500°C at the heating rate of 5°C/min

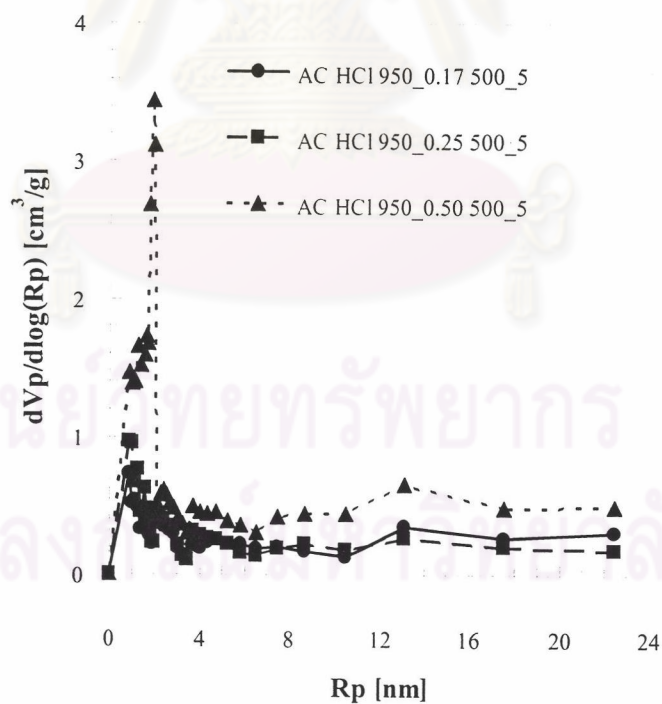


Figure 5.4.15 Pore size distribution of activated carbons prepared at 950°C from HCl treated chars from waste tires carbonized at 500°C at the heating rate of 5°C/min

Figures 5.4.14-5.4.15 present the pore size distributions calculated from these isotherms. In Figure 5.4.14, it was found that the mesoporosity has not been developed in obtained activated carbons because of very low % burn-off achieved. Although activated carbons presented in Figure 5.4.15 showed well development in mesoporosity, they possessed lower amount of large mesopores than those activated at 850°C.

Table 5.4.3 also provides the porous properties of activated carbons prepared at the investigated temperatures from HCl-treated char carbonized at 500°C at the heating rate of 5°C/min. All the  $V_{meso}$ ,  $V_{micro}$ , and  $S_{BET}$  values of activated carbons from HCl-treated char prepared at 850 and 950°C were obviously greater than those of activated carbons prepared without acid treatment prior to steam activation. Nevertheless, as for activation at 750°C, the HCl treatment improved only microporosity, while any improvement in mesoporosity could not be observed in prepared activated carbons.

For comparison, the acid treatment prior to steam activation by HNO<sub>3</sub> was also investigated. In Table 5.4.4, the ash content of HNO<sub>3</sub>-treated char was about 5.7% which is a little bit less than that of HCl-treated one. Moreover, the char treated by HNO<sub>3</sub> showed the lower rate of steam activation when compared with the HCl-treated char.

**Table 5.4.4** Porous properties of HNO<sub>3</sub>-treated char and activated carbons prepared at 850°C from waste tires carbonized at 500°C at the heating rate of 5°C/min

Sample	Carbonization Yield (%)	Ash Content (%)	$V_{meso}$	$V_{micro}$	$S_{BET}$
			(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(m <sup>2</sup> /g)
HNO <sub>3</sub> C 500_5	35.1	5.7	0.28	n/a	66

Sample	Burn-off (%)	$V_{meso}$	$V_{micro}$	$S_{BET}$
		(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(m <sup>2</sup> /g)
AC HNO <sub>3</sub> 850_1 500_5	26.9	0.57	0.13	386
AC HNO <sub>3</sub> 850_3 500_5	45.2	0.67	0.42	1025
AC HNO <sub>3</sub> 850_4 500_5	61.3	0.79	0.46	1003

Respectively, Figures 5.4.16 and 5.4.17 are the N<sub>2</sub> adsorption-desorption isotherms and the pore size distributions of HNO<sub>3</sub>-treated char and the activated carbons obtained from this treated char. It was observed that the HNO<sub>3</sub>-treated char has the same N<sub>2</sub> adsorption capacity as the non-treated and HCl-treated ones. It was also found that the HNO<sub>3</sub>-treated char possesses mainly very large size of mesopores, pore radius > 8 nm.

As for the activated carbons prepared from HNO<sub>3</sub>-treated char, at the burn-off lower than 50%, they had the mesoporosity more than those obtained through conventional activation method but mostly the same as those prepared with HCl treatment. However, over 50% burn-off, the HNO<sub>3</sub> treatment prior to steam activation did not show the improvement in mesoporosity as well as the HCl one.

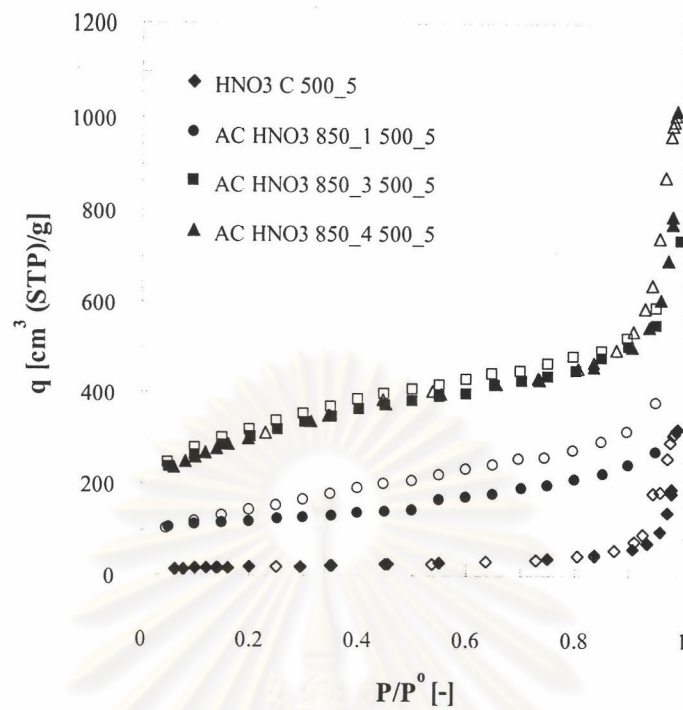


Figure 5.4.16  $N_2$  adsorption-desorption isotherms on  $HNO_3$ -treated char and activated carbons prepared at  $850^\circ C$  from waste tires carbonized at  $500^\circ C$  at the heating rate of  $5^\circ C/min$ ; closed symbols: adsorption, open symbols: desorption

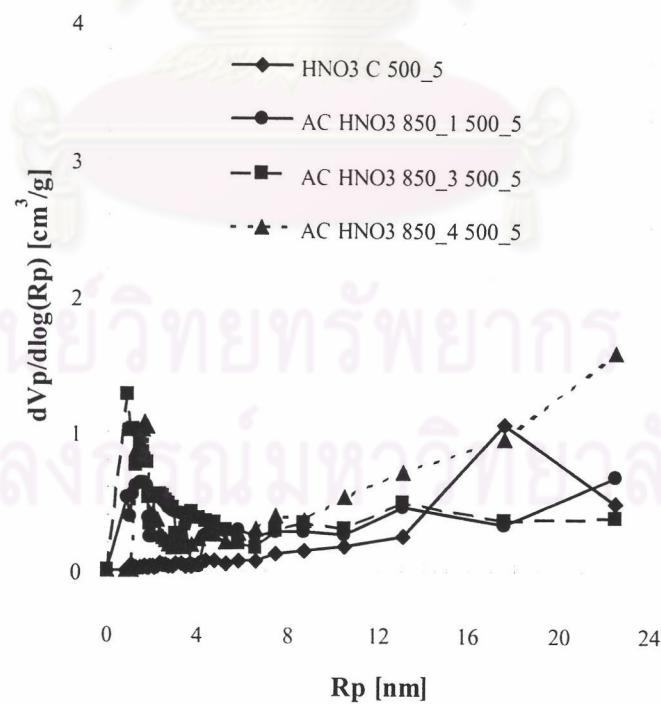


Figure 5.4.17 Pore size distribution of  $HNO_3$ -treated char and activated carbons prepared at  $850^\circ C$  from waste tires carbonized at  $500^\circ C$  at the heating rate of  $5^\circ C/min$

Table 5.4.4 also shows the porous properties of activated carbons obtained from HNO<sub>3</sub>-treated char. Both the  $V_{micro}$  and  $S_{BET}$  values were enhanced by HNO<sub>3</sub> treatment prior to activation by steam. Interestingly, it was indicated that the HNO<sub>3</sub> treatment improves the  $V_{meso}$  value at the burn-off lower than 50%, but over this value no further development is observed.

Therefore, it was suggested that the kind of acid used for treatment prior to steam activation also affects the porous properties of prepared activated carbons.

**Table 5.4.5 Comparison of the best porous properties of activated carbons achieved in the present study and reported in the literature**

<b>Raw Material : Preparation Method</b>	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
Waste tires : Conventional steam activation	1.09	0.26	737
Waste tires : HCl treatment prior to steam activation	1.62	0.57	1119
Plum stones : Calcium catalyst reaction	1.15	0.18	1000
Pitch : Iron catalyst reaction	1.07	0.08	410
Coconut shell : ZnCl <sub>2</sub> -chemical activation	1.36	0.55	2200
Refuse Derived Fuel (RDF) : HNO <sub>3</sub> treatment prior to steam activation	0.46	0.11	530
PET waste : Pre-treatment by metal compound	0.90	0.81	2200

For comparison, the maximum  $V_{meso}$ ,  $V_{micro}$ , and  $S_{BET}$  values of activated carbons obtained from vulcanized waste tires without and with HCl treatment prior to steam activation and those of activated carbons from various raw materials and methods in the literature are summarized in Table 5.4.5. It is



obvious that the HCl-treated activated carbon obtained in the present study has higher mesoporosity than and with some exceptions higher microporosity than other reported activated carbons.

#### Conclusion for Section 5.4

- Activation rates of HCl-treated chars are not different from those of non-treated chars at the same investigated heating rates, carbonization temperatures, and activation temperatures.
- HCl-treatment prior to steam activation of chars carbonized at 500°C and all investigated heating rates can obviously enhance the  $V_{meso}$  values of the activated carbons prepared at 850 and 950°C activation temperatures.
- The  $V_{micro}$  and  $S_{BET}$  values of activated carbons are always improved by HCl treatment prior to steam activation.
- HNO<sub>3</sub>-treated char shows lower activation rate than HCl-treated char at the same investigated condition.
- Porous properties of acid-treated activated carbons depend on the kind of acid.

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## 5.5 Porous properties of chars and activated carbons prepared with pre-treatment method

### 5.5.1 Pre-treatment by Ca[OH]<sub>2</sub>

From Table 5.5.1, the carbonization yield of the mixture of waste tires and 5%wt of Ca[OH]<sub>2</sub> was approximately 38.1% which is higher than that obtained through carbonization of waste tires, and the ash contents of obtained char and HCl-treated one were 30.3 and 5.6%, respectively. It was found that the rate of activation of this HCl-treated char does not obviously differ from the char prepared with and without HCl treatment shown in Tables 5.4.1 and 5.2.1, respectively.

**Table 5.5.1** Porous properties of char, HCl-treated char, and activated carbons prepared with pre-treatment by Ca[OH]<sub>2</sub>

Sample	Carbonization Yield (%)	Ash Content (%)	<i>V</i> <sub>meso</sub>	<i>V</i> <sub>micro</sub>	<i>S</i> <sub>BET</sub>
			(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(m <sup>2</sup> /g)
C Ca 500_5	38.1	30.3	0.32	N.D.	80
HCl C Ca 500_5	38.1	5.6	0.32	N.D.	75
Sample	Burn-off (%)	<i>V</i> <sub>meso</sub> (cm <sup>3</sup> /g)	<i>V</i> <sub>micro</sub> (cm <sup>3</sup> /g)	<i>S</i> <sub>BET</sub> (m <sup>2</sup> /g)	
AC Ca 850_1 500_5	30.1	0.25	0.19	498	
AC Ca 850_3 500_5	73.1	0.94	0.53	1178	
AC Ca 850_4 500_5	81.2	1.25	0.48	1103	

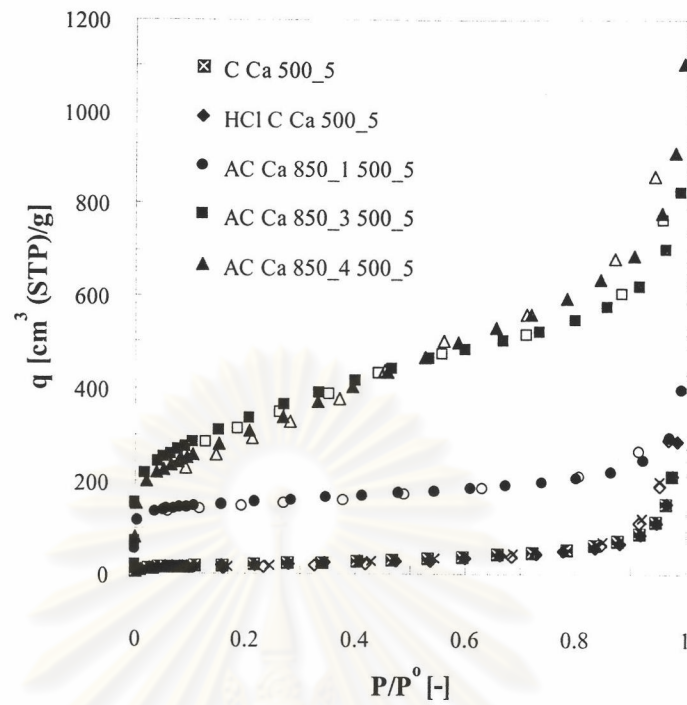


Figure 5.5.1.1  $N_2$  adsorption-desorption isotherms on char, HCl-treated char, and activated carbons prepared with pre-treatment by  $Ca(OH)_2$ ; closed symbols: adsorption, open symbols: desorption

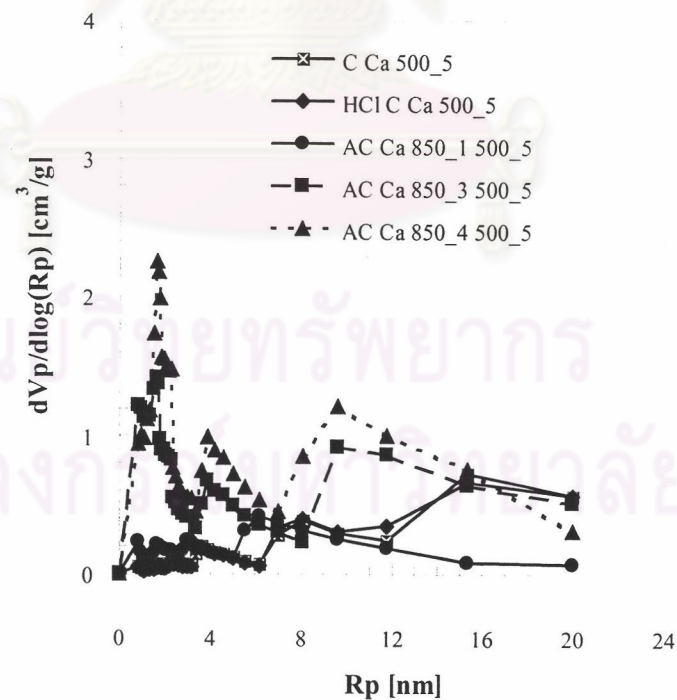


Figure 5.5.1.2 Pore size distribution of char, HCl-treated char, and activated carbons prepared with pre-treatment by  $Ca(OH)_2$

Figure 5.5.1.1 shows the N<sub>2</sub> adsorption-desorption isotherms on char and activated carbons prepared with pre-treatment by Ca[OH]<sub>2</sub>. It was found that the N<sub>2</sub> adsorption capacities of activated carbons obtained are apparently higher than those of activated carbons prepared by the conventional activation method as shown in Figure 5.2.2. From these isotherms, their calculated pore size distributions are shown in Figure 5.5.1.2. It was clear that the mesoporosity is developed during steam activation which also can be confirmed from the shape and hysteresis of the isotherms in Figure 5.5.1.1.

The porous properties of prepared chars and activated carbons are also summarized in Table 5.5.1. The  $V_{meso}$  and  $S_{BET}$  values of both char and HCl-treated one through the pre-treatment by Ca[OH]<sub>2</sub> were almost the same as those of chars obtained without the pre-treatment. However, the  $V_{micro}$  value of both chars also could not be detected by the t-plot method. The enhancement in the  $V_{micro}$  values was clearly observed in the activated carbons prepared with the pre-treatment by Ca[OH]<sub>2</sub>, while the  $V_{meso}$  values were similar to those of activated carbons obtained by the conventional activation process. As a result, the greater  $S_{BET}$  values were obtained because of the larger  $V_{micro}$  values.

### 5.5.2 Pre-treatment by ZnO

The obtained yield through carbonization of waste tires mixed with 5%wt of ZnO was around 38.4%. The ash content of prepared char was around 29.1%, but after the HCl treatment it decreased to 5.7%. Furthermore, the achieved % burn-off at varied activation times was mostly the same as that of char carbonized without pre-treatment and HCl-treated one.

**Table 5.5.2** Porous properties of char, HCl-treated char, and activated carbons prepared with pre-treatment by ZnO

Sample	Carbonization Yield (%)	Ash Content (%)	$V_{meso}$	$V_{micro}$	$S_{BET}$
			( $\text{cm}^3/\text{g}$ )	( $\text{cm}^3/\text{g}$ )	( $\text{m}^2/\text{g}$ )
C Zn 500_5	38.4	29.1	0.19	N.D.	77
HCl C Zn 500_5	38.4	5.7	0.18	N.D.	80

Sample	Burn-off (%)	$V_{meso}$	$V_{micro}$	$S_{BET}$
		( $\text{cm}^3/\text{g}$ )	( $\text{cm}^3/\text{g}$ )	( $\text{m}^2/\text{g}$ )
AC Zn 850_1 500_5	30.2	0.31	0.20	514
AC Zn 850_3 500_5	65.6	1.06	0.52	1089
AC Zn 850_4 500_5	73.8	1.41	0.59	1148

The  $\text{N}_2$  adsorption-desorption isotherms on char obtained from the mixture of waste tires and ZnO, HCl-treated char, and activated carbons from this treated char are given in Figure 5.5.2.1. The pre-treatment by ZnO enhanced the  $\text{N}_2$  adsorption capacities of prepared activated carbons when compared with the conventional activation method.

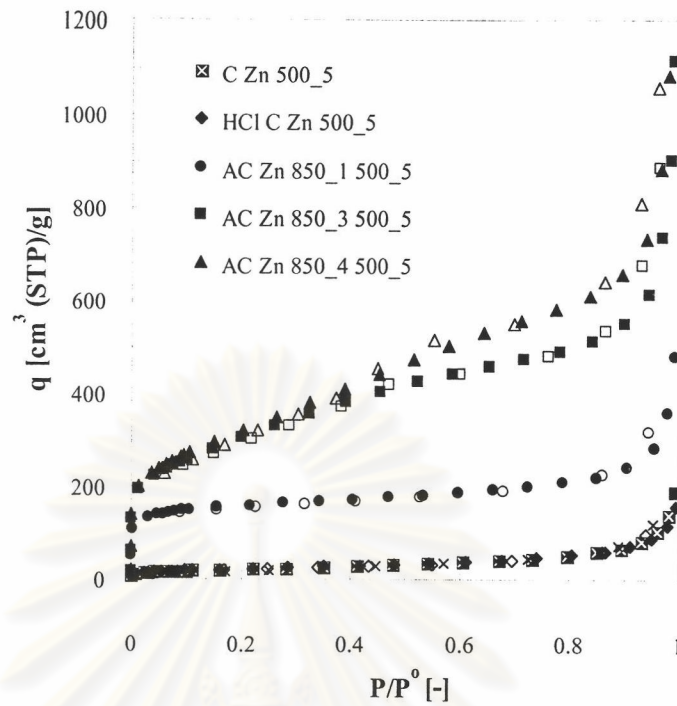


Figure 5.5.2.1  $N_2$  adsorption-desorption isotherms on char, HCl-treated char, and activated carbons prepared with pre-treatment by ZnO; closed symbols: adsorption, open symbols: desorption

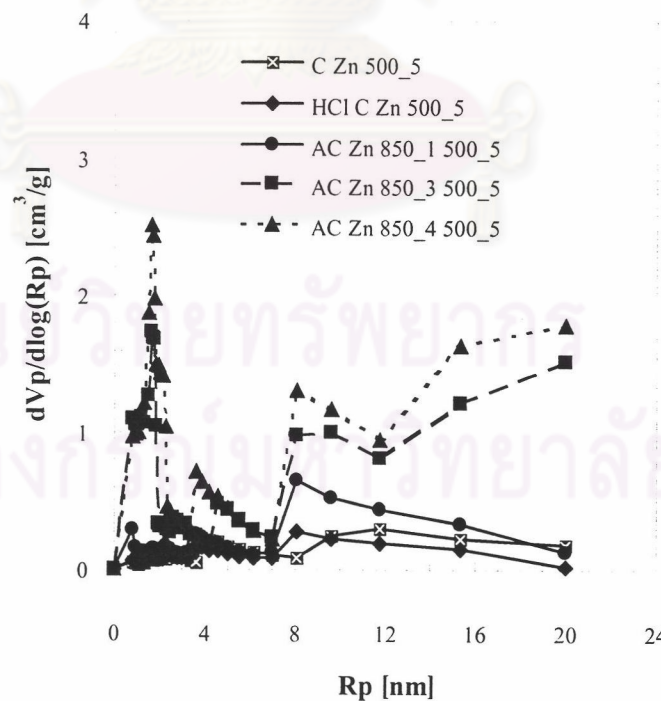


Figure 5.5.2.2 Pore size distribution of char, HCl-treated char, and activated carbons prepared with pre-treatment by ZnO

Figure 5.5.2.2 presents the pore size distribution of prepared carbons calculated from the isotherm in Figure 5.5.2.1. Using the pre-treatment by ZnO, great development in mesoporosity was observed in obtained activated carbons.

The porous properties of obtained char, HCl-treated one, and activated carbons are also shown in Table 5.5.2. Interestingly, the  $V_{meso}$  value of char carbonized from the mixture of waste tires and ZnO was lower than that of char obtained from waste tires, and the HCl treatment did not affect this value. On the other hand, chars obtained by this pre-treatment had the  $S_{BET}$  values in the same order as the chars carbonized from waste tires, while the  $V_{micro}$  values are found to be zero. Although the  $V_{meso}$ ,  $V_{micro}$ , and  $S_{BET}$  values of activated carbons prepared with the pre-treatment by ZnO were obviously larger than those of activated carbons obtained through the conventional activation process, they did not higher than those of activated carbons prepared with only HCl treatment prior to steam activation.

### 5.5.3 Pre-treatment by Fe<sub>2</sub>O<sub>3</sub>

As shown in Table 5.5.3, the yield for carbonization of the mixture of waste tires and 5%wt of Fe<sub>2</sub>O<sub>3</sub> was similar to those obtained when using the pre-treatment of Ca[OH]<sub>2</sub> and ZnO. The ash contents in char before and after the HCl treatment were 28.9 and 6.3%, respectively. Also, the pre-treatment by Fe<sub>2</sub>O<sub>3</sub> did not affect the activation rate.

**Table 5.5.3** Porous properties of char, HCl-treated char, and activated carbons prepared with pre-treatment by Fe<sub>2</sub>O<sub>3</sub>

Sample	Carbonization Yield (%)	Ash Content (%)	<i>V</i> <sub>meso</sub>	<i>V</i> <sub>micro</sub>	<i>S</i> <sub>BET</sub>
			(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(m <sup>2</sup> /g)
C Fe 500_5	38.8	28.9	0.25	N.D.	140
HCl C Fe 500_5	38.8	6.3	0.46	N.D.	171

Sample	Burn-off (%)	<i>V</i> <sub>meso</sub>	<i>V</i> <sub>micro</sub>	<i>S</i> <sub>BET</sub>
		(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(m <sup>2</sup> /g)
AC Fe 850_1 500_5	36.9	0.23	0.17	454
AC Fe 850_3 500_5	65.1	0.92	0.60	1170
AC Fe 850_4 500_5	72.1	1.07	0.45	1102

Figure 5.5.3.1 shows the N<sub>2</sub> adsorption-desorption isotherms on char obtained by carbonization of the mixture of waste tires and Fe<sub>2</sub>O<sub>3</sub>, HCl-treated one, and activated carbons from the treated char. It was found that the pre-treatment by Fe<sub>2</sub>O<sub>3</sub> also increased the N<sub>2</sub> adsorption capacities of prepared activated carbons when compared with the conventional steam activation.



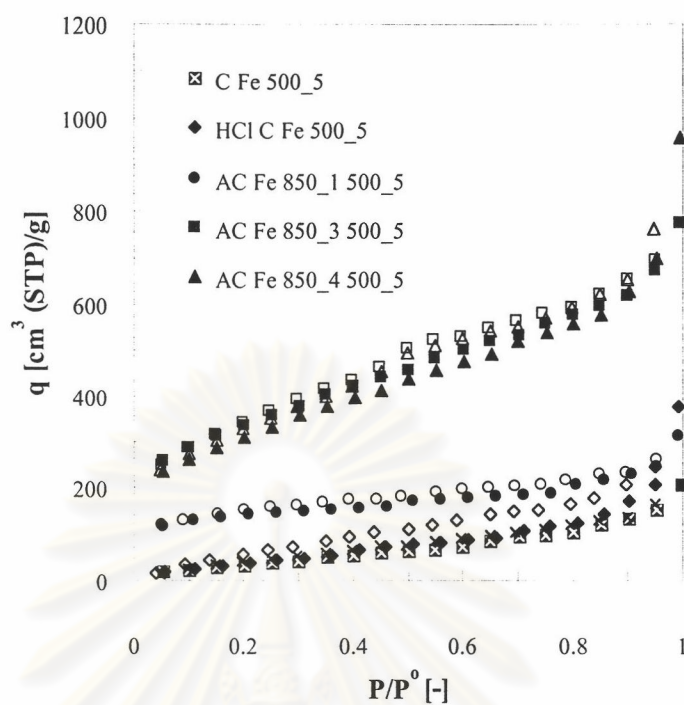


Figure 5.5.3.1  $N_2$  adsorption-desorption isotherms on char, HCl-treated char, and activated carbons prepared with pre-treatment by  $Fe_2O_3$ ; closed symbols: adsorption, open symbols: desorption

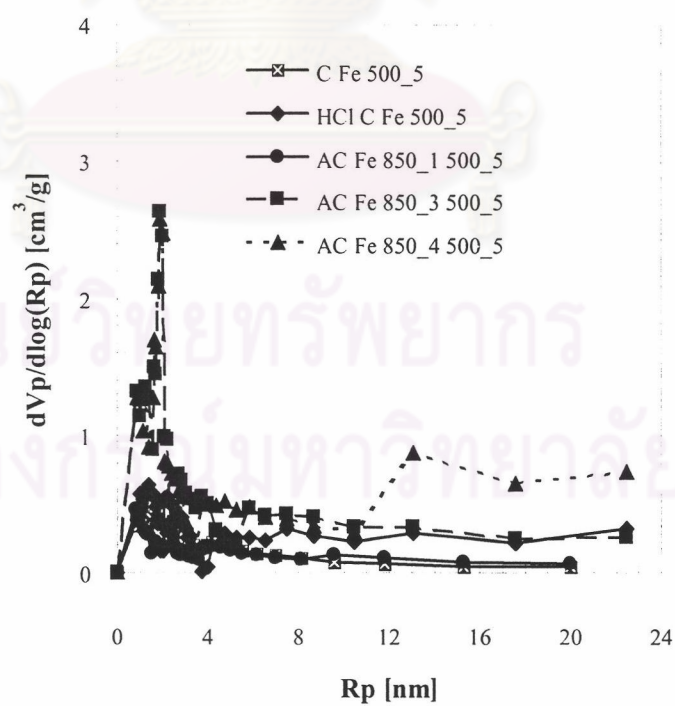


Figure 5.5.3.2 Pore size distribution of char, HCl-treated char, and activated carbons prepared with pre-treatment by  $Fe_2O_3$

The pore size distributions of carbons calculated from above isotherms are given in Figure 5.5.3.2. Using the pre-treatment by  $\text{Fe}_2\text{O}_3$ , the obvious development in mesoporosity was obtained in prepared activated carbons.

Table 5.5.3 also provides the porous properties of prepared carbons determined from their isotherms. Surprisingly, after the HCl treatment both the  $V_{meso}$  and  $S_{BET}$  values of char increased. It was assumed that before the acid treatment the iron compound blocks the pore and then it is removed during acid treatment to open the pore. Moreover, by applying t-plot method, the  $V_{micro}$  value still could not be detected.

The pre-treatment by  $\text{Fe}_2\text{O}_3$  increased only the  $V_{micro}$  values in prepared activated carbons, while the  $V_{meso}$  values were almost the same as those of activated carbons obtained via the conventional activation method.

#### 5.5.4 Pre-treatment by KNO<sub>3</sub>

The carbonization yield of the mixture of waste tires and 5%wt of KNO<sub>3</sub> was approximately 36.2 % as shown in Table 5.5.4, which is lower than the chars prepared by other metals. It was suggested that the KNO<sub>3</sub> compound is decomposed during carbonization. The ash content of obtained char decreased from 26.4 to 5.4% by the HCl treatment. Furthermore, the char treated by KNO<sub>3</sub> showed the rate of activation in the same level as that prepared without any treatment.

**Table 5.5.4** Porous properties of char, HCl-treated char, and activated carbons prepared with pre-treatment by KNO<sub>3</sub>

Sample	Carbonization Yield (%)	Ash Content (%)	$V_{meso}$	$V_{micro}$	$S_{BET}$
			(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(m <sup>2</sup> /g)
C K 500_5	36.2	26.4	0.16	N.D.	116
HCl C K 500_5	36.2	5.4	0.32	N.D.	187

Sample	Burn-off (%)	$V_{meso}$	$V_{micro}$	$S_{BET}$
		(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(m <sup>2</sup> /g)
AC K 850_1 500_5	34.7	0.32	0.20	587
AC K 850_3 500_5	66.6	0.79	0.48	1075
AC K 850_4 500_5	79.7	1.03	0.51	1156

Figure 5.5.4.1 presents the N<sub>2</sub> adsorption-desorption isotherms on char obtained by carbonization of the mixture of waste tires and KNO<sub>3</sub>, HCl-treated one, and activated carbons from the treated char. Similarly, obtained activated carbons had higher N<sub>2</sub> adsorption capacities than those prepared by the conventional activation process.

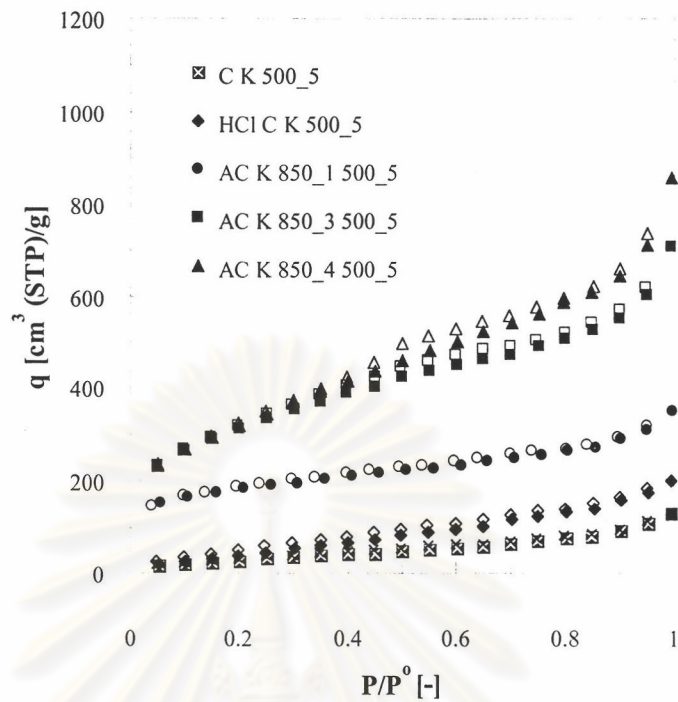


Figure 5.5.4.1 N<sub>2</sub> adsorption-desorption isotherms on char, HCl-treated char, and activated carbons prepared with pre-treatment by KNO<sub>3</sub>; closed symbols: adsorption, open symbols: desorption

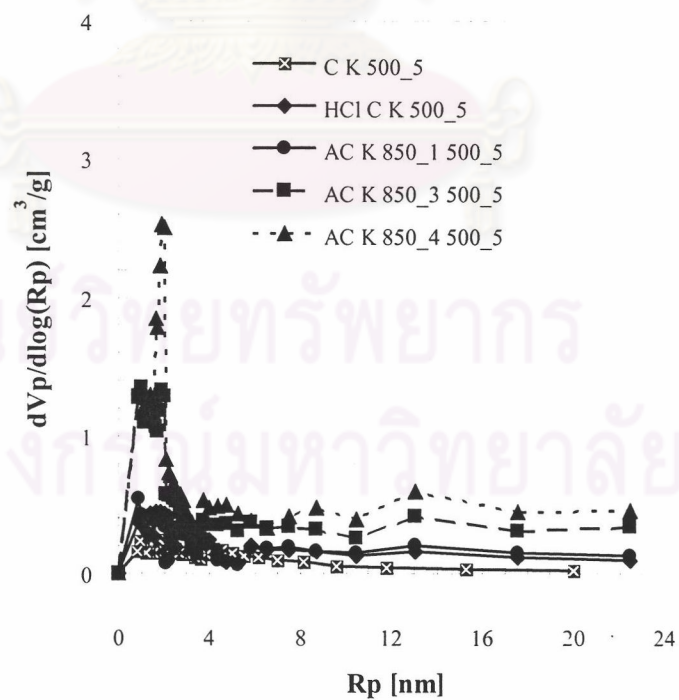


Figure 5.5.4.2 Pore size distribution of char, HCl-treated char, and activated carbons prepared with pre-treatment by KNO<sub>3</sub>

The pore size distributions of carbons calculated by applying the Dollimore-Heal method are given in Figure 5.5.4.2. It was also clear that pre-treatment by  $\text{KNO}_3$  can enhance the mesoporosity. However, it was noted that obtained activated carbons possess large size of mesopores less than those prepared by other pre-treatments.

As a result, the porous properties of prepared carbons are summarized in Table 5.5.4. After the acid treatment by  $\text{HCl}$  the  $V_{meso}$  and  $S_{BET}$  values of char increased, since the potassium metal blocked the pore was removed. Anyway, the  $V_{micro}$  values of chars were essentially zero by using the t-plot calculation.

It was found that the pre-treatment by  $\text{KNO}_3$  does not significantly improve the mesoporosity in prepared activated carbons. On the contrary, the increasing of the  $V_{micro}$  and  $S_{BET}$  values confirmed that the microporosity is improved by  $\text{KNO}_3$  pre-treatment.

### Conclusion for Section 5.5

- Chars treated by all metal compounds show essentially the same activation rates as non-treated chars.
- Pre-treatment by  $\text{ZnO}$  yields the same level of improvement in both mesoporosity and microporosity as the  $\text{HCl}$  treatment prior to steam activation.
- The pre-treatment by  $\text{Ca}[\text{OH}]_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{KNO}_3$  can enhance only microporosity.
- The development of mesoporosity by pre-treatment method depends on the kind of metal compound.

## 5.6 Porous properties of chars and activated carbons prepared from decrosslinked waste tires

### 5.6.1 Conventional steam activation

When the decrosslinked waste tires were carbonized at 500°C at the heating rate of 5°C/min, as shown in Table 5.6.1, the obtained carbonization yield was approximately 31.8%, which is lower than that of waste tires. The ash content in prepared char was around 13.8%, which is a little bit less than that of char from waste tires. From this char, the rate of activation at 850°C was slightly higher than that of char prepared from waste tires.

Table 5.6.1 Porous properties of char carbonized at 500°C at the heating rate of 5°C/min from decrosslinked waste tires and activated carbons from this char prepared at 850°C

Sample	Carbonization Yield (%)	Ash Content (%)	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
C DE 500_5	31.8	13.8	0.16	N.D.	80
Sample	Burn-off (%)		$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
AC DE 850_1 500_5	33.5		0.23	0.14	437
AC DE 850_3 500_5	76.7		0.57	0.26	690
AC DE 850_4 500_5	83.5		0.62	0.25	592

Figure 5.6.1.1 presents the N<sub>2</sub> adsorption-desorption isotherms on char and activated carbons prepared from decrosslinked waste tires. A slight hysteresis in isotherms was found which indicates the mesoporous structure in prepared carbons. It was also observed that

the  $N_2$  adsorption capacities of activated carbons obtained from decrosslinked waste tires are smaller than those of activated carbons prepared from waste tires.

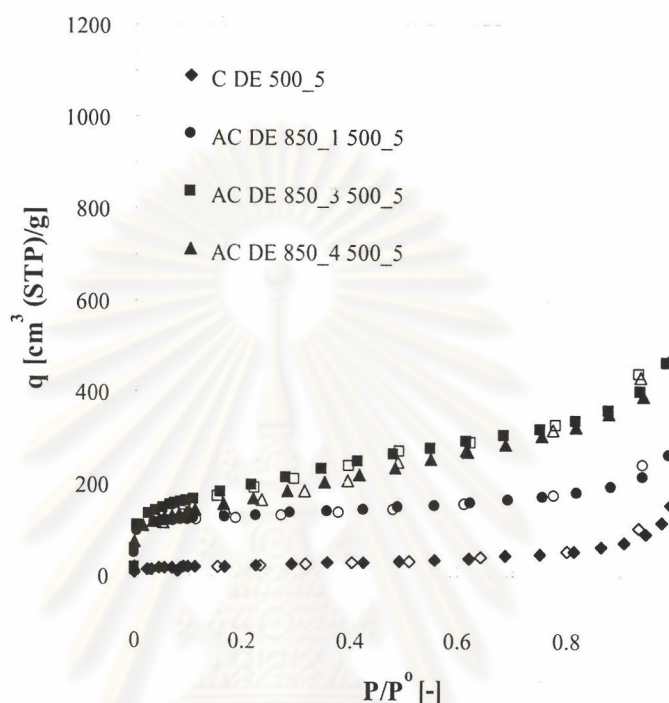


Figure 5.6.1.1  $N_2$  adsorption-desorption isotherms on char and activated carbons prepared from decrosslinked waste tires;  
closed symbols: adsorption, open symbols: desorption

From the isotherms given in Figure 5.6.1.1, the calculated pore size distributions of those carbons are provided in Figure 5.6.1.2. It was indicated that activated carbons obtained from decrosslinked waste tires possess the large size of mesopores less than those prepared from waste tires.

The porous properties of prepared carbons from decrosslinked waste tires using carbonization followed by steam activation are also shown in Table 5.6.1. It was observed that the char obtained from decrosslinked waste tires shows the  $V_{meso}$  value smaller than that

carbonized from waste tires, while the  $S_{BET}$  value is mostly the same. However, the  $V_{micro}$  value could not be detected through the t-plot calculation. It was found that the  $V_{meso}$  values of activated carbons from decrosslinked waste tires are smaller than those of carbons prepared from waste tires. On the other hand, both the  $V_{micro}$  and  $S_{BET}$  values are mainly the same as those in activated carbons obtained from waste tires. From the pore size distribution of activated carbons obtained at varied %burn-off, it was also suggested that the pore formation of activated carbons obtained from decrosslinked waste tires is also described by the general mechanism: micropore creation followed by pore enlargement into mesopore.

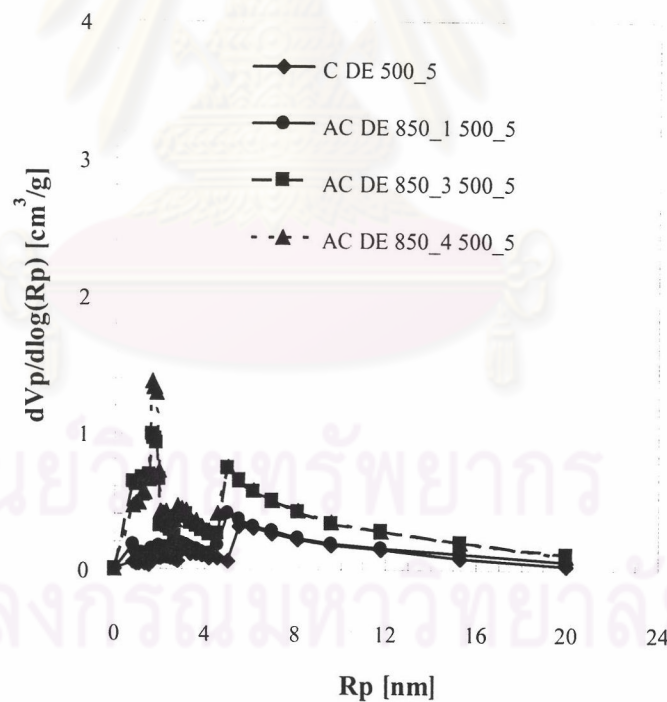


Figure 5.6.1.2 Pore size distribution of char and activated carbons prepared from decrosslinked waste tires



### 5.6.2 Process with HCl treatment prior to steam activation

After the acid treatment by HCl, the ash content in the treated char was about 5.0%. The activation rate of HCl-treated char was lower than that of non-treated char which is due to the lower inorganic content in the treated char.

**Table 5.6.2** Porous properties of HCl-treated char carbonized at 500°C at the heating rate of 5°C/min from decrosslinked waste tires and activated carbons from this char prepared at 850°C

Sample	Carbonization Yield (%)	Ash Content (%)	$V_{meso}$	$V_{micro}$	$S_{BET}$
			(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(m <sup>2</sup> /g)
HCl C DE 500_5	31.8	5.0	0.15	N.D.	76

Sample	Burn-off (%)	$V_{meso}$	$V_{micro}$	$S_{BET}$
		(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(m <sup>2</sup> /g)
AC HCl DE 850_1 500_5	31.6	0.41	0.20	556
AC HCl DE 850_3 500_5	59.3	0.78	0.44	1036
AC HCl DE 850_4 500_5	71.1	1.08	0.58	1166

The N<sub>2</sub> adsorption-desorption isotherms on the HCl-treated char and activated carbons prepared from this char are shown in Figure 5.6.2.1. Although the N<sub>2</sub> adsorption capacity of HCl-treated char was mostly the same as non-treated one, the activated carbons prepared from the former showed greatly higher N<sub>2</sub> adsorption capacities than those obtained from the latter presented in Figure 5.6.1.1.

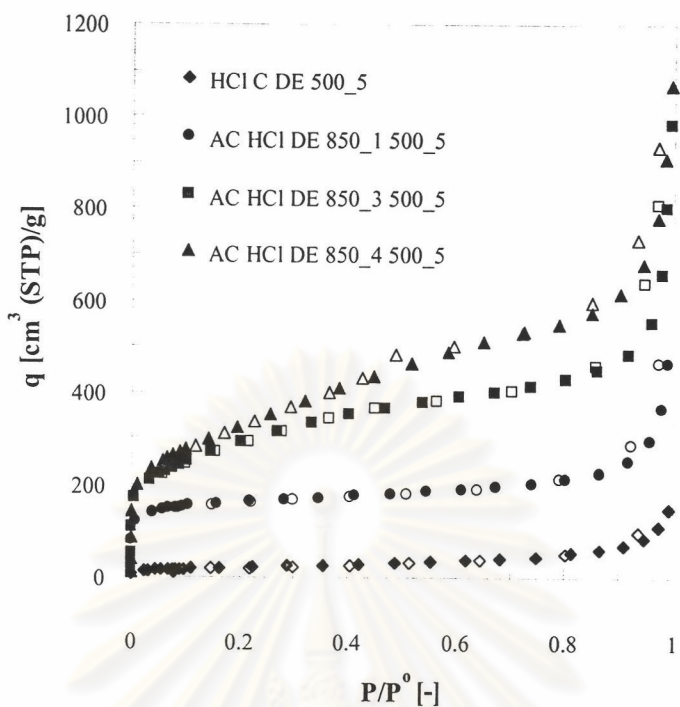


Figure 5.6.2.1 N<sub>2</sub> adsorption-desorption isotherms on HCl treated-char and activated carbons prepared from decrosslinked waste tires; closed symbols: adsorption, open symbols: desorption

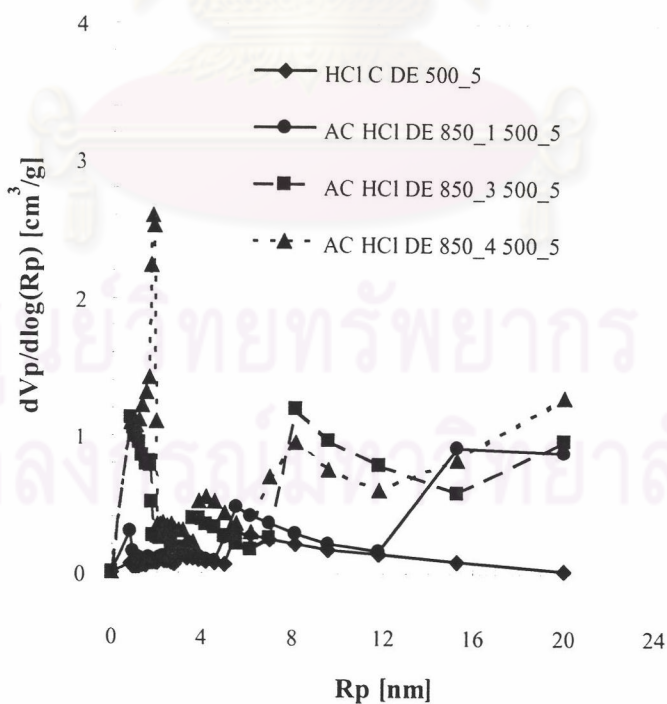


Figure 5.6.2.2 Pore size distribution of HCl-treated char and activated carbons prepared from decrosslinked waste tires

Figure 5.6.2.2 shows the pore size distributions of the carbons prepared with the HCl treatment prior to steam activation. It was clear that the obvious improvement throughout the range of mesopore size is observed in the activated carbons derived from HCl-treated char.

The porous properties of carbons calculated from above isotherms are also summarized in Table 5.6.2. Both the  $V_{meso}$  and  $S_{BET}$  values of HCl-treated char were almost the same as those of non-treated one. Anyway, by applying the t-plot method to the  $N_2$  adsorption isotherm, the  $V_{micro}$  value of HCl-treated char could not be obtained. It was obvious that the  $V_{meso}$  and  $V_{micro}$  values as well as the  $S_{BET}$  value of activated carbons are enhanced by the HCl treatment prior to steam activation as found in the case of waste tires.

### 5.6.3 Pre-treatment by ZnO

By carbonizing the mixture of decrosslinked waste tires with the 5% wt of ZnO, the obtained yield was around 36.2% as shown in Table 5.6.3. The ash contents in both before and after treated chars were approximately 25.2 and 5.6%, respectively. It was suggested that the rate of steam activation of the treated char obtained is lower than the non-treated one but mostly the same as the HCl-treated one because of the amount of inorganic content.

**Table 5.6.3** Porous properties of char, HCl-treated char, and activated carbons prepared from decrosslinked waste tires with the pre-treatment by ZnO

Sample	Carbonization Yield (%)	Ash Content (%)	$V_{meso}$	$V_{micro}$	$S_{BET}$
			( $\text{cm}^3/\text{g}$ )	( $\text{cm}^3/\text{g}$ )	( $\text{m}^2/\text{g}$ )
C Zn DE 500_5	36.2	25.2	0.13	N.D.	64
HCl C Zn DE 500_5	36.2	5.6	0.11	N.D.	66

Sample	Burn-off (%)	$V_{meso}$	$V_{micro}$	$S_{BET}$
		( $\text{cm}^3/\text{g}$ )	( $\text{cm}^3/\text{g}$ )	( $\text{m}^2/\text{g}$ )
AC Zn DE 850_1 500_5	27.4	0.22	0.18	453
AC Zn DE 850_3 500_5	63.3	0.91	0.37	972
AC Zn DE 850_4 500_5	69.9	0.93	0.63	1140

Figure 5.6.3.1 presents the  $\text{N}_2$  adsorption-desorption isotherms on chars and activated carbons prepared from decrosslinked waste tires with the pre-treatment by ZnO. It was suggested that the activated carbons prepared from the treated char show apparently higher  $\text{N}_2$  adsorption capacities than those obtained through conventional

activation process and mostly the same capacities as those prepared with the HCl treatment prior to steam activation.

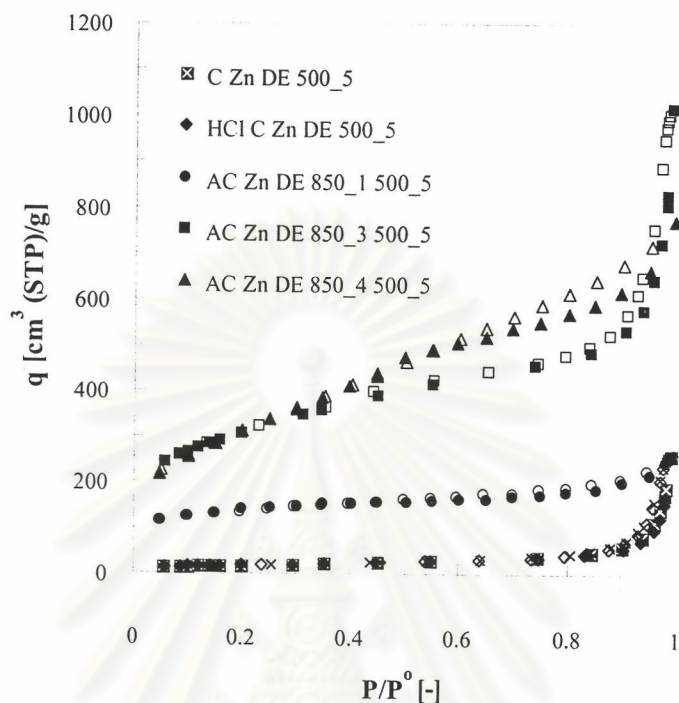


Figure 5.6.3.1  $N_2$  adsorption-desorption isotherms on char, HCl-treated char, and activated carbons prepared from decrosslinked waste tires with the pre-treatment by ZnO; closed symbols: adsorption, open symbols: desorption

The pore size distributions of carbons determined from the isotherms shown in Figure 5.6.3.1 are given in Figure 5.6.3.2. It was clear that the pre-treatment by ZnO increases the mesoporosity when compared with the conventional activation method.

Table 5.6.3 also provides the porous properties of chars and activated carbons obtained through the pre-treatment method by ZnO. The  $V_{meso}$  and  $S_{BET}$  values of chars carbonized from the mixture of decrosslinked waste tires with ZnO before and after the HCl treatment were in the same order as those of non-treated and HCl-treated ones. Nevertheless, the  $V_{micro}$  value of these chars also could not be

calculated via the t-plot method. It was indicated that the pre-treatment by ZnO improves both mesoporosity and microporosity in obtained activated carbons. Furthermore, the activated carbons obtained from the treated char by ZnO had the  $V_{meso}$ ,  $V_{micro}$ , and  $S_{BET}$  values in the same level as the activated carbons derived from HCl-treated char. However, the activated carbons prepared from vulcanized waste tires by any methods showed greater porous properties than those prepared from decrosslinked waste tires, thus it can be considered that the former is more proper to be used as a raw material of activated carbon.

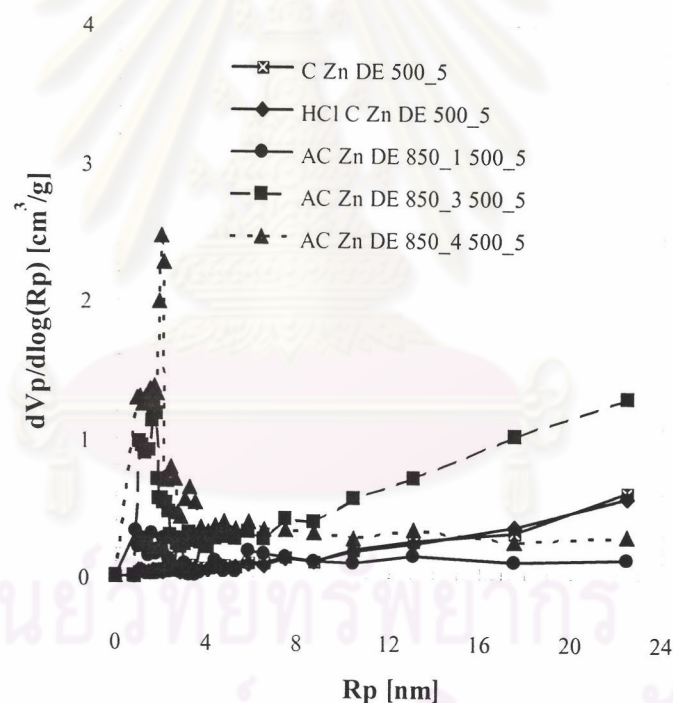
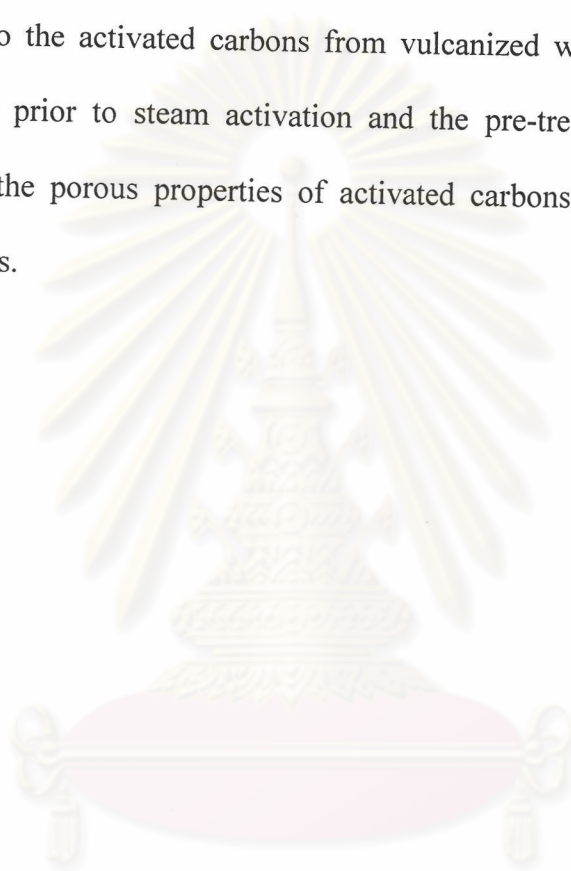


Figure 5.6.3.2 Pore size distribution of char, HCl-treated char, and activated carbons prepared from decrosslinked waste tires with the pre-treatment by ZnO

### Conclusion for Section 5.6

- Under the same condition, activation rate of char from decrosslinked waste tires is higher than that from vulcanized waste tires.

- Activated carbons from decrosslinked waste tires have lower  $V_{meso}$  values than but essentially the same  $V_{micro}$  and  $S_{BET}$  values as those from vulcanized waste tires.
- HCl-treated and ZnO-treated chars from decrosslinked waste tires show lower activation rate than their non-treated counterpart.
- Similar to the activated carbons from vulcanized waste tires, both HCl treatment prior to steam activation and the pre-treatment by ZnO can enhance the porous properties of activated carbons from decrosslinked waste tires.



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## 5.7 Liquid-phase adsorption characteristics

### 5.7.1 Porous properties of adsorbents

Both representative adsorbents, AC HCl and CAL, were characterized and their N<sub>2</sub> adsorption-desorption isotherms are shown in Figure 5.7.1.1. From the shape of isotherm, it was indicated that the AC HCl shows mesoporous structure. Obviously the N<sub>2</sub> adsorption capacity of AC HCl was larger than that of CAL at  $P/P^0 > 0.3$ .

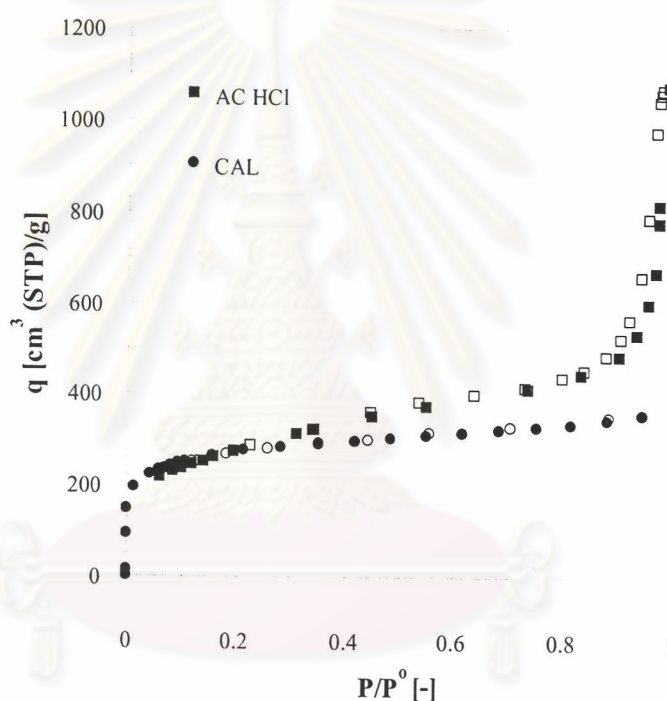


Figure 5.7.1.1 N<sub>2</sub> adsorption-desorption isotherms on AC HCl and CAL;  
closed symbols: adsorption, open symbols: desorption

By applying the Dollimore-Heal method, the pore size distribution of AC HCl and CAL are presented in Figure 5.7.1.2. It was clear that the activated carbon from waste tires prepared with HCl treatment prior to steam activation shows greater mesoporosity than CAL and has the peak in pore size distribution at the radius around 2 nm.



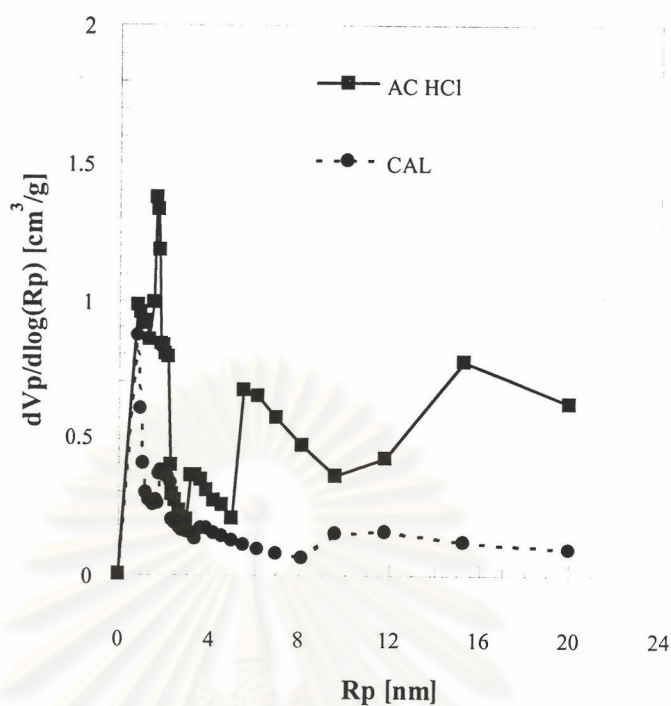


Figure 5.7.1.2 Pore size distribution of AC HCl and CAL

The porous properties of AC HCl and CAL determined from the isotherms in Figure 5.7.1.1 are given in Table 5.7.1. It was clear that the activated carbon prepared with the HCl treatment prior to steam activation has the obviously larger  $V_{meso}$  value and possesses the  $V_{micro}$  and  $S_{BET}$  values in the same order as the commercial counterpart.

Table 5.7.1 The porous properties of AC HCl and CAL

Sample	$V_{meso}$ (cm <sup>3</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)
AC HCl*	0.79	0.37	985
CAL	0.24	0.39	956

\* Activated carbon obtained at average 65% burn-off

### 5.7.2 Physico-chemical properties of adsorbents

Table 5.7.2 shows the physico-chemical properties of both AC HCl and CAL. It was found that the ash contents of prepared AC HCl is higher than that of CAL, in contrast, the former shows lower volatile content, moisture content, and bulk density than the latter. Considering the adsorption test, it was found that AC HCl has the iodine number lower than CAL, on the contrary, the methylene blue number of the former is higher than that of the latter. The iodine and methylene blue numbers suggest that AC HCl is more suitable for adsorption of large molecules than CAL.

Table 5.7.2 The physico-chemical properties of AC HCl and CAL

Sample	Volatile Content (%)	Ash Content (%)	Moisture Content (%)	Bulk Density (g/cm <sup>3</sup> )	Iodine Number (mg/g)	MB Number (mg/g)
AC HCl	4.6	18.3	2.2	0.17	659	356
CAL	7.2	8.4	7.0	0.42	746	221

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### 5.7.3 Adsorption-desorption isotherms

The adsorption-desorption isotherms of phenol, Black 5, and Red 31 on AC HCl and CAL are shown in Figures 5.7.3.1-5.7.3.3, respectively. The  $q$  and  $C_e$  are the amount of adsorbates adsorbed and equilibrium concentration, respectively. It was found that although the  $V_{micro}$  value of AC HCl is in the same order as that of CAL, the former shows a slightly lower phenol adsorption capacity than the latter. It was assumed that the chemical nature of AC HCl surface is different from that of CAL. Moreover, the existence of irreversible adsorption of phenol on both AC HCl and CAL was observed, since phenol has the electron-donating functional group, hydroxyl group, as that was investigated by Tamon *et al* [30].

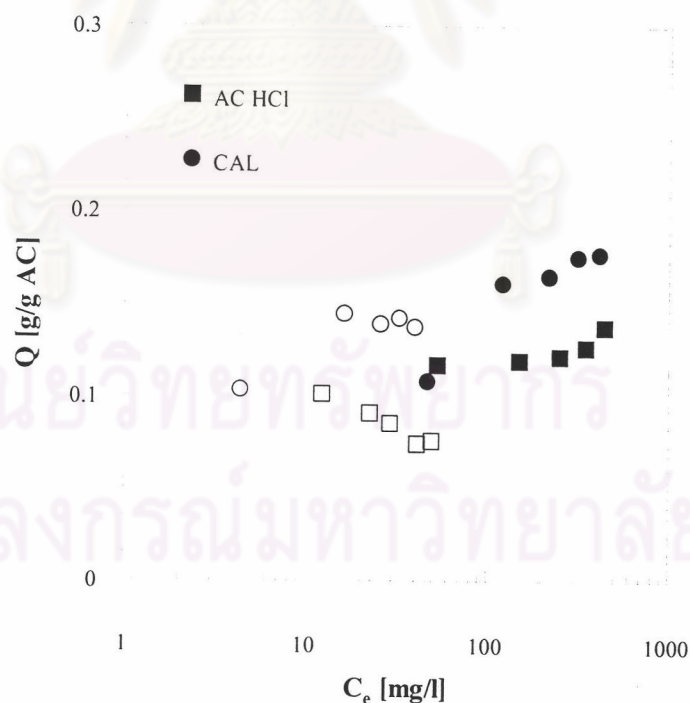


Figure 5.7.3.1 Phenol adsorption-desorption isotherms on both adsorbents;  
closed symbols: adsorption, open symbols: desorption

As for the adsorption of Black 5, because of the larger  $V_{meso}$  value, the activated carbon (AC HCl) prepared from waste tires with HCl treatment prior to steam activation showed obviously higher Black 5 adsorption capacity than the commercial one (CAL). This is because AC HCl had more mesopores than CAL as shown in Figure 5.7.1.2 and Table 5.7.1. Furthermore, the hysteresis between adsorption and desorption branches on both adsorbents suggested the appearance of irreversible adsorptions, which correspond to the electron-donating functional groups in Black 5, amino and hydroxyl groups [31]. In particular, it was indicated that the Black 5 can be desorbed from AC HCl more easily than from CAL.

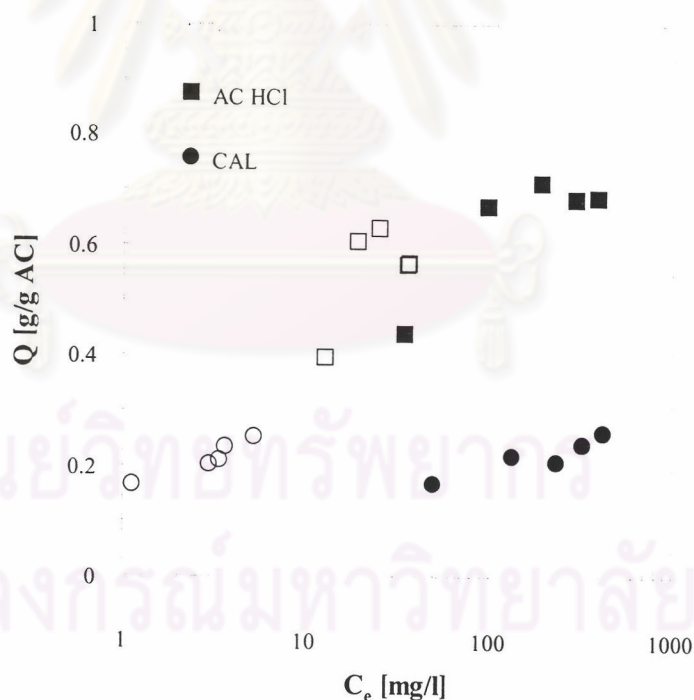


Figure 5.7.3.2 Black 5 adsorption-desorption isotherms on both adsorbents; closed symbols: adsorption, open symbols: desorption

Apparently, the adsorption capacity of Red 31 on the activated carbon obtained in present work was higher than that of the

commercial activated carbon due to the larger  $V_{meso}$  value of AC HCl. The irreversible adsorption on the commercial activated carbon was observed which can be described as Black 5, in contrast, some amount of Red 31 adsorbed could be desorbed from the activated carbon prepared in the present work.

Therefore, because of the comparable phenol adsorption capacity and the greater adsorption capacities of both organic dyes, the activated carbon prepared from waste tires with the HCl treatment prior to steam activation can be applied to the wastewater treatment system, especially the adsorption of bulky molecular adsorbates.

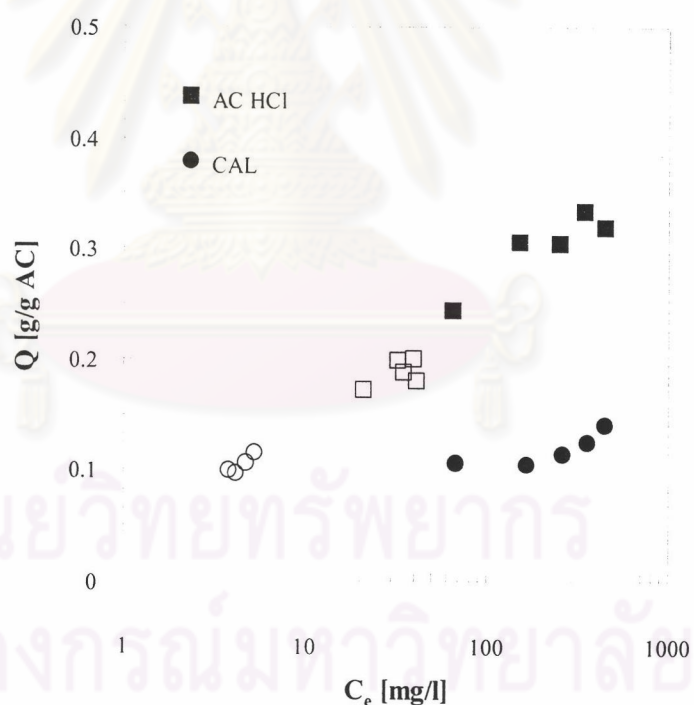


Figure 5.7.3.3 Red 31 adsorption-desorption isotherms on both adsorbents;

closed symbols: adsorption, open symbols: desorption

### 5.7.4 Solvent regeneration by ethanol

Figures 5.7.4.1-5.7.4.3 present the adsorption capacities of phenol, Black 5, and Red 31 on both the virgin and ethanol-regenerated activated carbons prepared with HCl treatment prior to steam activation as well as the commercial activated carbon, respectively.

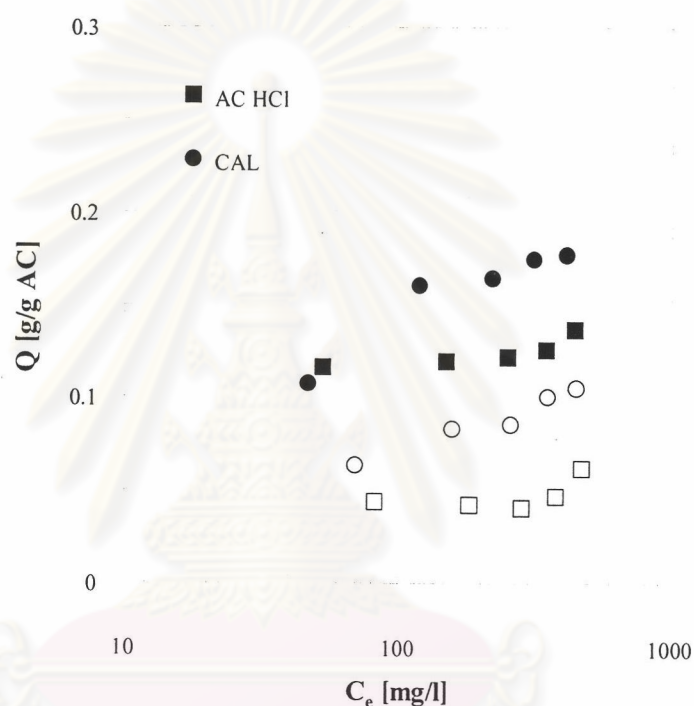


Figure 5.7.4.1 Phenol adsorption capacities on both adsorbents regenerated by ethanol; closed symbols: virgin adsorbent, open symbols: regenerated adsorbent

From Figure 5.7.4.1, it was found that the phenol adsorption capacities on AC HCl and CAL, which are regenerated by ethanol, are around 35-45 and 50-60% of that on the virgin ones, respectively. As a result, the ethanol-regenerated AC HCl showed a little lower phenol adsorption capacity than the CAL regenerated by the same solvent.

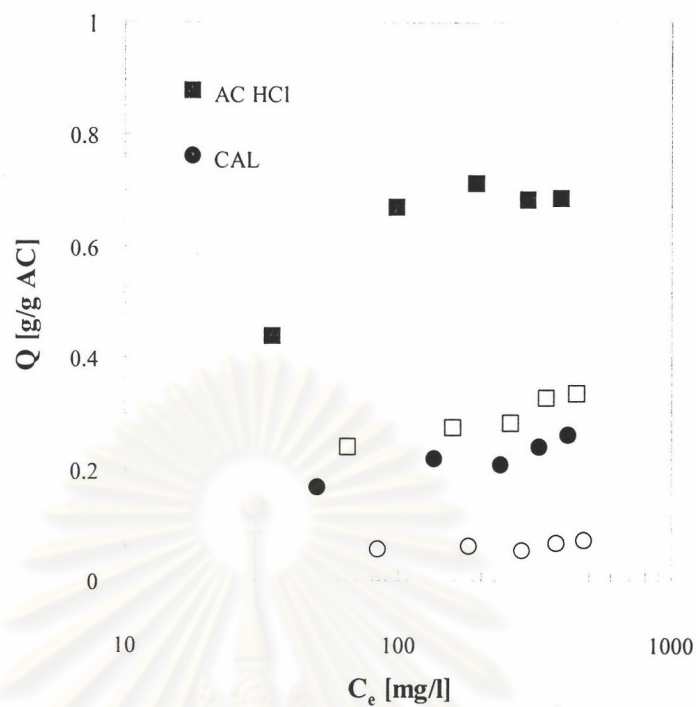


Figure 5.7.4.2 Black 5 adsorption capacities on both adsorbents regenerated by ethanol; closed symbols: virgin adsorbent, open symbols: regenerated adsorbent

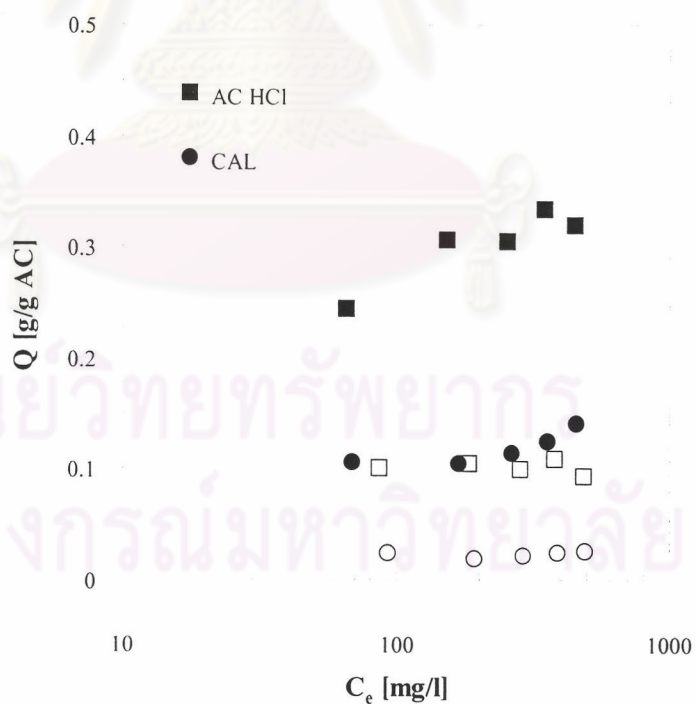


Figure 5.7.4.3 Red 31 adsorption capacities on both adsorbents regenerated by ethanol; closed symbols: virgin adsorbent, open symbols: regenerated adsorbent

After regeneration by ethanol, the activated carbon obtained from HCl-treated char had the Black 5 adsorption capacity approximately 40-55% of the capacity of the virgin one, while the ethanol-regenerated commercial carbon showed lower regeneration efficiency, about 25-35%.

As shown in Figure 5.7.4.3, it was found that the regeneration efficiencies of Red 31 on AC HCl and CAL are in the range of 30-40% and 18-23%, respectively.

It was noted that since both dyes can be desorbed from AC HCl more easily than from CAL, the ethanol regeneration efficiency of the former is higher than that of the latter. However, as for phenol adsorption, AC HCl showed lower regeneration efficiency than CAL, which is due to the chemical nature of surface of the former.

Although the efficiency of ethanol regeneration of spent AC HCl used for adsorption of organic dyes is higher than that of spent CAL, the spent carbon cannot be perfectly regenerated. Accordingly, it was indicated that the ethanol regeneration of spent activated carbons is not so effective in our study, thus the thermal regeneration should be recommended.

#### **Conclusion for Section 5.7**

- Although the activated carbon prepared in the present work has the same level of  $V_{micro}$  value as the commercial activated carbon, the former shows slightly lower phenol adsorption capacity than the latter.



- Because of its larger  $V_{meso}$  value, dyes adsorption capacities of the obtained activated carbon are obviously higher those of the commercial one.
- Activated carbon from waste tires shows less irreversible adsorption of the three investigated adsorbates than the commercial activated carbon.
- Ethanol regeneration efficiency of the obtained activated carbon with respect to the two dyes is higher than its commercial counterpart.
- Activated carbon from waste tires prepared with HCl treatment prior to steam activation is expected to adsorb large adsorbates better than commercial activated carbons.