CHAPTER V

RESULTS AND DISCUSSION

In the preparation and characterization of activated carbon from anthracite powder by hydrothermal (supercritical water) process, the steam activated anthracite, i.e. activated carbon prepared from anthracite powder without carbonization step, is used as reference for comparison with the activated anthracite prepared with supercritical water treatment.

This research consists of 3 main parts:

1. To study the effect of the preparation condition on the porous properties of steam activated anthracite in section 5.1 and 5.2.
2. To prepare activated carbon by supercritical water treatment either directly from anthracite powder or steam activated anthracite in section 5.3 and studies the effect of the supercritical water treatment on the porous properties of two types of carbons in section 5.4.
3. To study the feasibility of regenerating exhausted activated carbon by batch supercritical water reaction in section 5.5.

In the hydrothermal treatment of low rank coal, elevating the temperature in the presence of water vapor is known to help eliminate curtain volatile mater and tar.

In this work activated carbon is prepared by assuming that a similar hydrothermal treatment but under supercritical water condition will be effective for making enhancing the porous properties of anthracite powder.

So far, it has been found that there is no literature on the preparation of activated carbon by supercritical water treatment. In first batch of experiments, we attempt to prepare activated carbon from anthracite powder by supercritical water treatment by using distilled water or hydrogen peroxide solution as liquid medium; the results are summarized in section 5.3. In addition, we attempt to improve the porous properties of steam activated carbons (activated anthracite, a commercial activated carbon and activated carbon from waste tire) by the same supercritical water treatment; the results were summarized in topic 5.4. Finally, we study the adsorption characteristics of activated anthracite and compare with the commercial activated carbon (CAL carbon, Calgon, U.S.A.) and study the efficiency of regenerating the exhausted activated carbon by batch supercritical water reaction; the results are summarized in section 5.5.

5.1 Porous properties of activated carbon from anthracite powder and activated anthracite

This topic described the porous properties of activated carbon from anthracite powder compared with activated anthracite. As described in chapter 4, the process of making activated anthracite is similar to conventional process of making activated carbon by steam activation except carbonization step was skipped.

Table 5.1.1 Porous properties of activated anthracite and activated carbon prepared at 850°C from anthracite powder and char-carbonized at 500°C for 2 hr., respectively activated with steam flow rate 0.25 g/min

Sample	Burn-off (%)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)	S_{BET} (m^2/g)
A850_1C500_2	35.88	0.037	0.124	262.00
A850_3C500_2	55.82	0.081	0.434	686.00
A850_1	32.00	0.011	0.184	325.00
A850_2.30	52.01	0.040	0.302	719.72

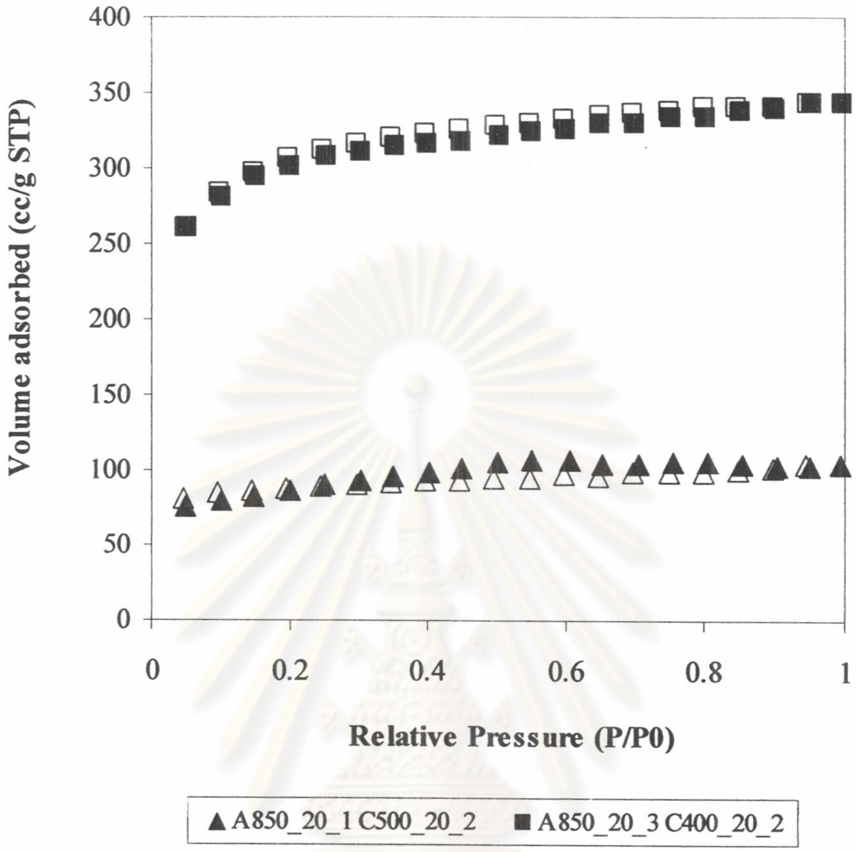
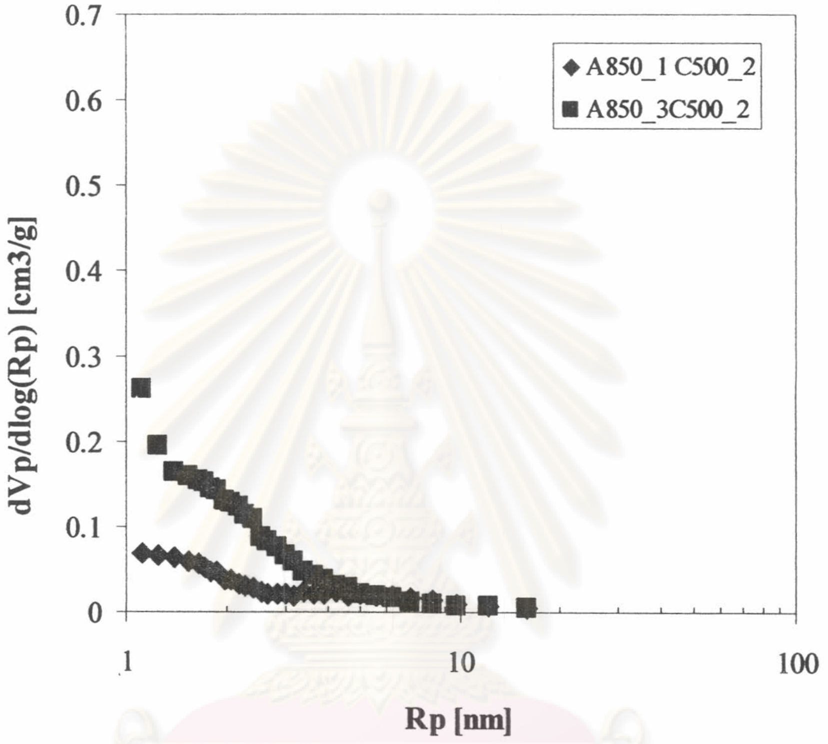


Figure 5.1.1 N_2 adsorption-desorption isotherm on activated carbon prepared at 850°C from chars from anthracite powder carbonized at 500°C for 2 hours at the steam flow rate 0.5g/min

closed symbols: adsorption, open symbols: desoprtion



5.1.2 Pore size distribution of activated carbon prepared at 850°C from chars from anthracite powder carbonized at 500°C at the steam flow rate 0.5 g/min

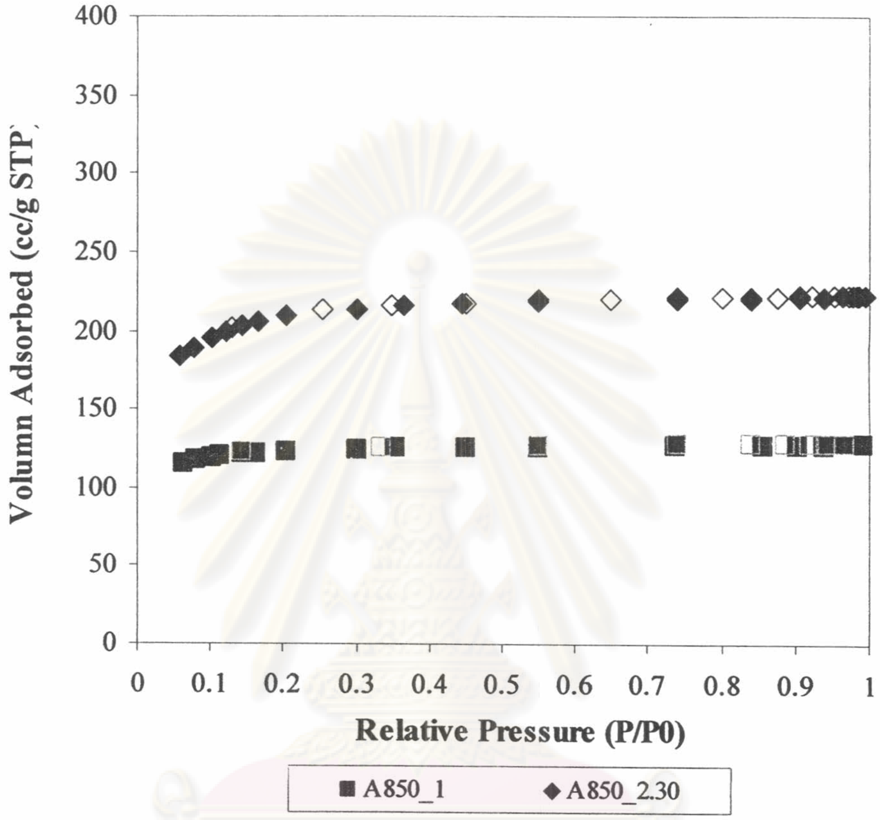
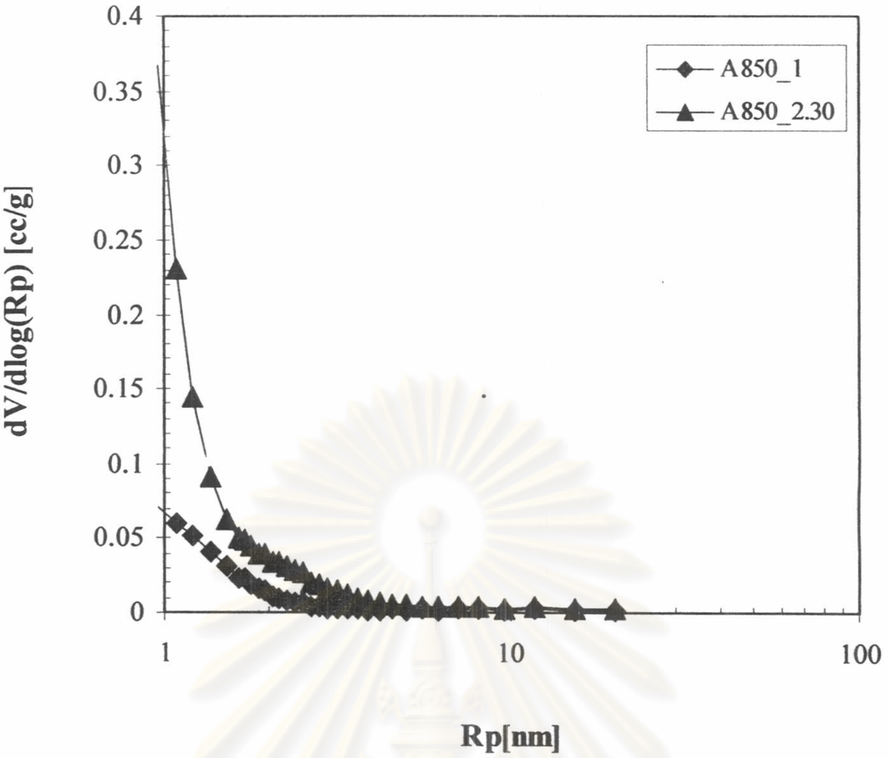


Figure 5.1.3 N_2 adsorption-desorption isotherm on activated anthracite prepared at 850°C from anthracite powder at steam flow rate 0.5g/min closed symbols: adsorption, open symbols: desoprtion



5.1.4 Pore size distribution of activated anthracite prepared at 850°C from anthracite powder with steam flow rate 0.5 g/min.

Figures 5.1.1 and 5.1.3 show the N_2 adsorption-desorption isotherms on activated anthracite obtained through the steam activation at steam flow rate 0.5g/min at the activation temperature 850°C and activated carbon prepared at 850°C from chars from anthracite powder carbonized at 500°C for 2 hours, respectively. Considering the shape of isotherm and the N_2 adsorption capacity, the development of micropores and mesopores during activation could be clearly observed.

From the isotherms, the pore size distributions of obtained activated anthracite from anthracite powder and activated carbon prepared at 850°C from chars from anthracite powder carbonized at 500°C for 2 hours are shown in Figures 5.1.2 – 5.1.4.

From figures 5.1.1-5.1.3, they can be easy to observe that every isotherm almost have no hysteresis loop and exhibit Type I isotherm, with larger uptake indicating that they have a large degree of microporosity. The shape of isotherms or both activated anthracite and activated carbon were almost same, so carbonization of anthracite powder did not play an importance role on porous properties of activated carbon. Additional reason is the volatile matter content of raw anthracite powder is only 8.5 %by mass, which is quite low when compare with another source material such as waste tires, GG bituminous coal(31.6 %by mass) and MT bituminous coal (33.1%by mass) [Hsisheng Teng, et al, 1996]. From these two reasons, activated carbon can be obtained from direct activation of anthracite powder without carbonization step and this activated carbon was named "activated anthracite".

Table 5.1.1 also provides the porous properties of obtained activated anthracite and activated carbon calculated from isotherms. The S_{BET} value of activated carbon at 30 and 50%burn-off are 262 and 686 m^2/g, which is similar to S_{BET} value of activated anthracite at the same order of the %burn-off- 325 and 719.2 m^2/g, respectively.

5.2 Porous properties of prepared activated anthracite from anthracite powder

As expected, in table 5.2.1, the % burn-off during activation increased with the increase of the activation time as well as V_{micro}, V_{meso} and S_{BET} values. However, there is no obvious trend for the variation in surface area and pore volume with respect to activation temperature even it plays an importance role in activation rate.

Table5.2.1 Porous properties of activated anthracite prepared from anthracite powder at 750, 850 and 950°C with steam flow rate of 0.5 g/min

Sample	Burn-off (%)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)	S_{BET} (m^2/g)
A750_15	34.39	0.074	0.311	645.12
A750_20	52.76	0.071	0.238	536.202
A750_25	62.30	0.101	0.439	965.28
A850_1	32.00	0.011	0.184	413.72
A850_2	40.74	0.025	0.277	632.70
A850_2.30	52.01	0.040	0.302	719.72
A850_4	70.03	0.072	0.406	1038.09
A950_0.15	35.47	0.068	0.179	405.53
A950_0.30	50.99	0.131	0.346	817.75
A950_0.45	66.53	0.823	0.589	1666.64

Figures 5.2.1-5.2.3 show the N_2 adsorption-desorption isotherms on activated anthracite obtained through the steam activation at steam flow rate 0.5g/min at the activation temperature 750, 850 and 950°C, respectively. Considering the shape of isotherm and the N_2 adsorption capacity, the development of micropores and mesopores during activation could be clearly observed.

From the isotherms, the pore size distributions of obtained activated anthracite from anthracite powder are shown in Figures 5.2.4 – 5.2.6.

From figures 5.2.1-5.2.3, they are clearly seen that every isotherm almost have no hysteresis loop and exhibit Type I isotherm, with larger uptake indicating that they have a large degree of microporosity. The shape of every isotherms are similar to each others, so it can be concluded that activation temperature has no effect on type of porosity but plays an importance role in activation rate.

Table 5.2.1 also provides the porous properties of obtained activated anthracite calculated from isotherms. The prepared activated anthracite has the V_{micro} and V_{meso} values up to 0.346 and 0.131, respectively, and posses the S_{BET} value up to1666.64 m^2/g. It is found that the higher V_{micro}, V_{meso} and S_{BET} values of prepared activated anthracite can be obtained at higher %burn-off or longer activation time. Similar behavior has been observed by other researchers (Hsisheng Teng et al, 1996) in the preparation of activated carbon from bituminous coals by conventional carbon dioxide activation.

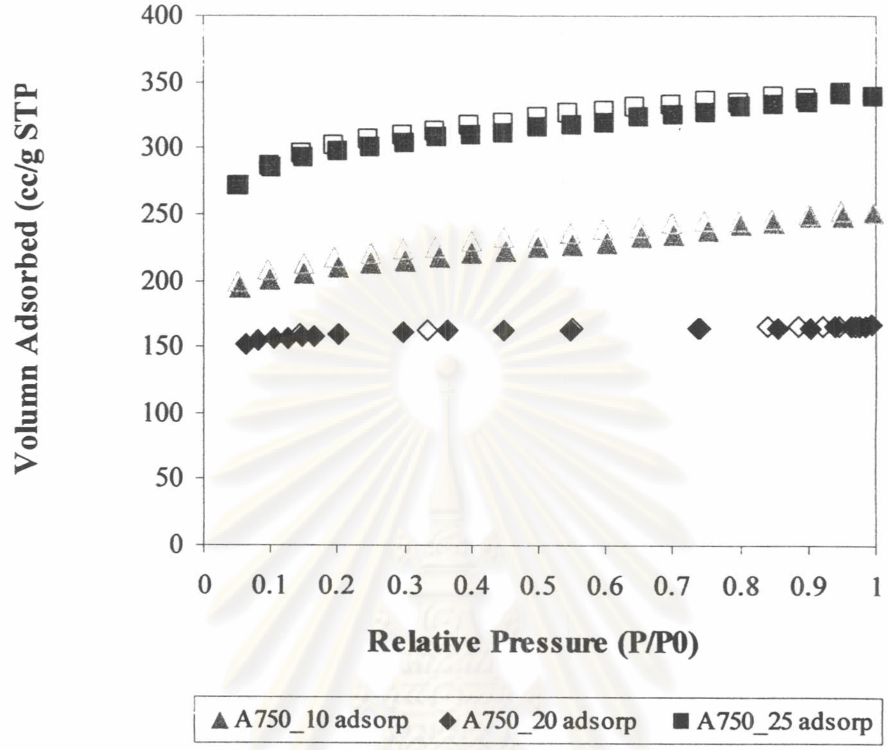


Figure 5.2.1 N_2 adsorption-desorption isotherm on activated anthracite prepared at 750°C from anthracite powder with steam flow rate 0.5g/min closed symbols: adsorption, open symbols: desoprtion

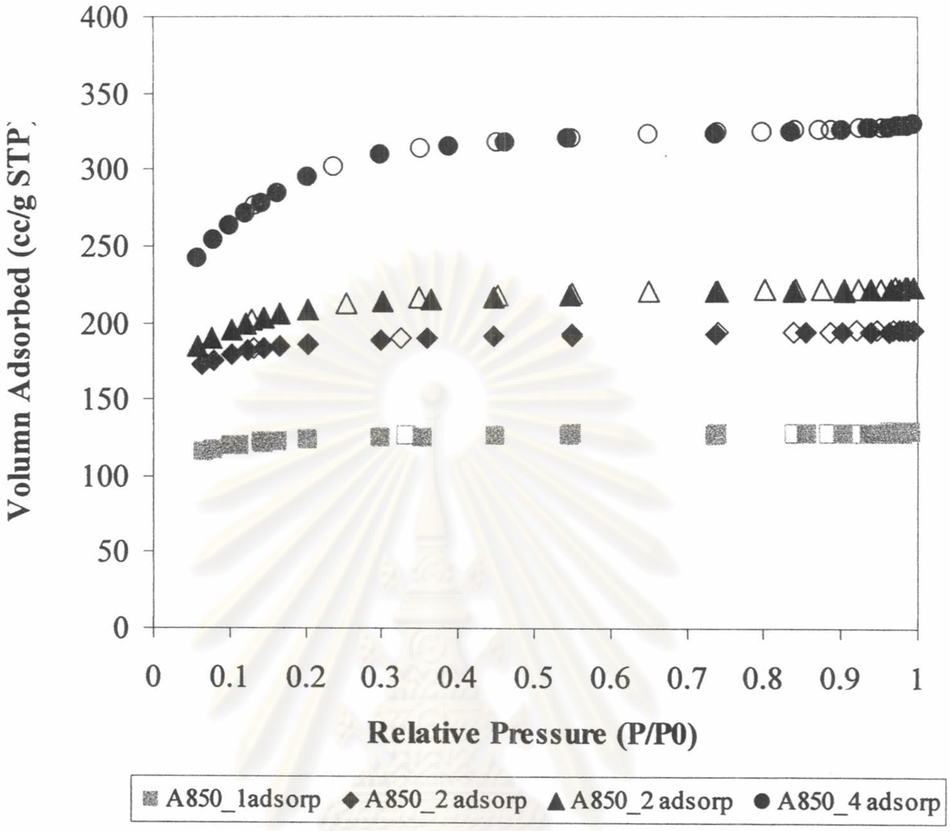


Figure 5.2.2 N_2 adsorption-desorption isotherm on activated anthracite prepared at 850°C from anthracite powder with steam flow rate 0.5g/min closed symbols: adsorption, open symbols: desoprtion

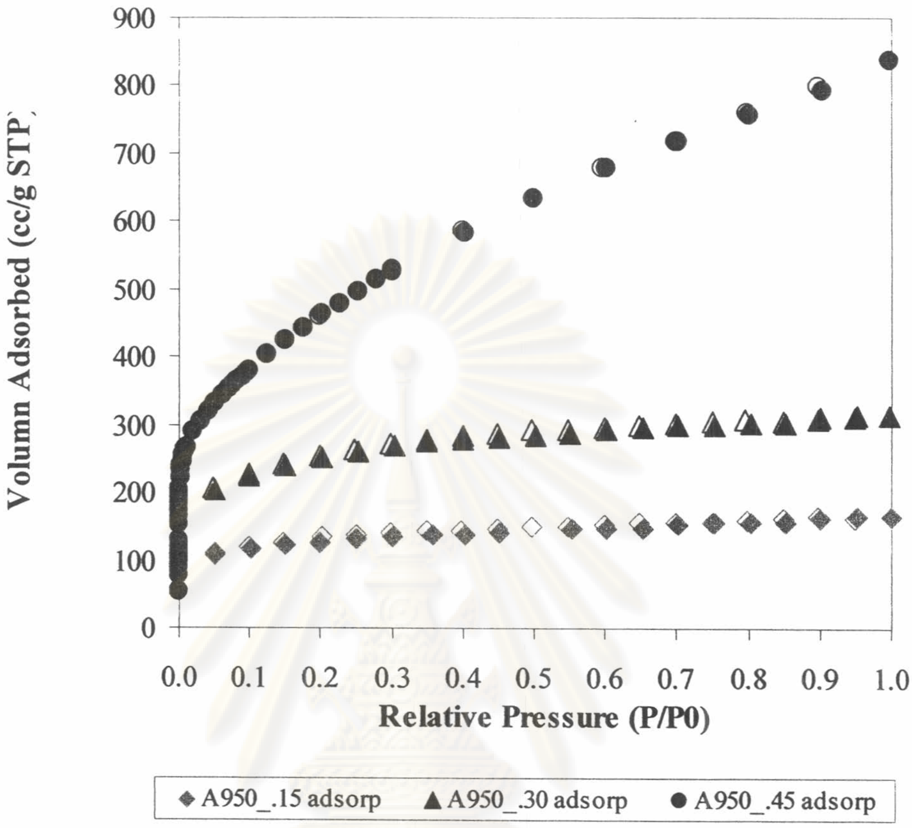


Figure 5.2.3 N_2 adsorption-desorption isotherm on activated anthracite prepared at 950°C from anthracite powder with steam flow rate 0.5g/min closed symbols: adsorption, open symbols: desoprtion

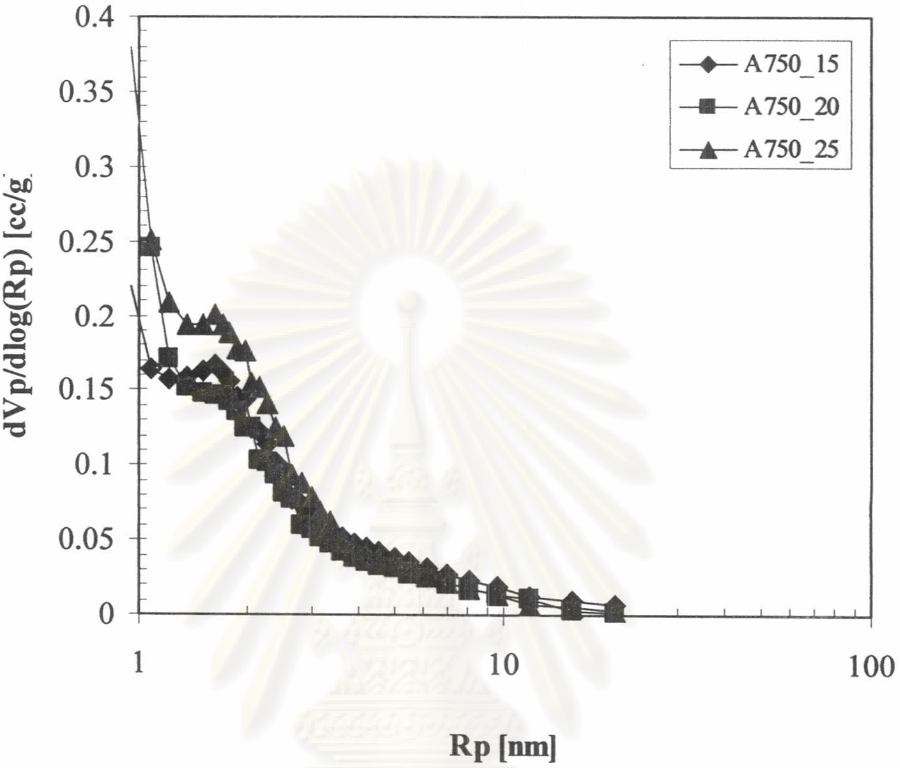


Figure 5.2.4 Pore size distribution of activated anthracite prepared at 750°C from anthracite powder with steam flow rate 0.5 g/min.

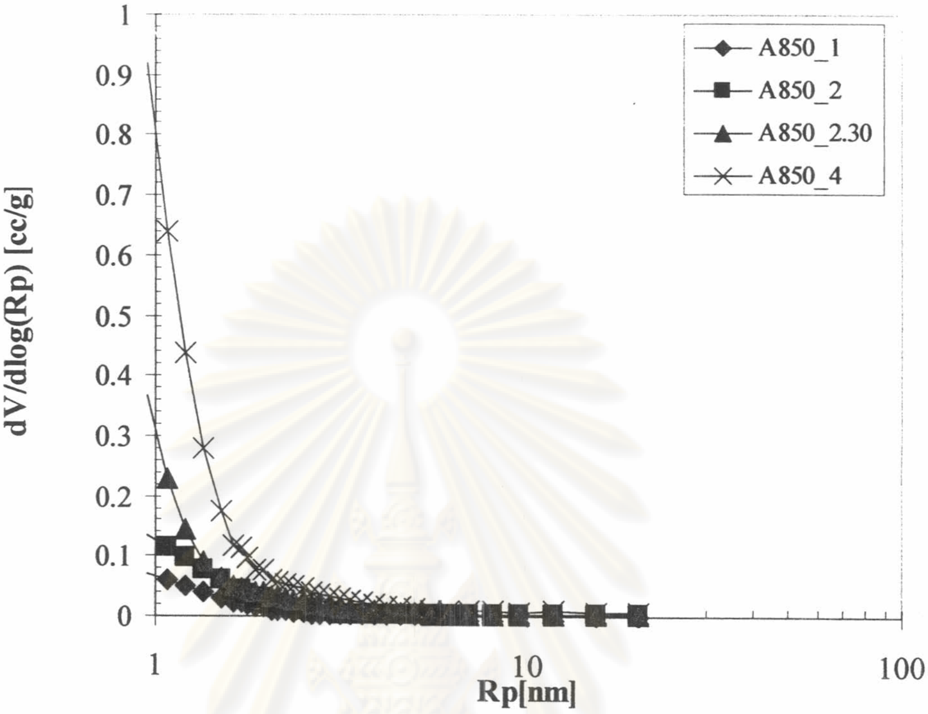


Figure 5.2.5 Pore size distribution of activated anthracite prepared at 850°C from anthracite powder with steam flow rate 0.5 g/min.

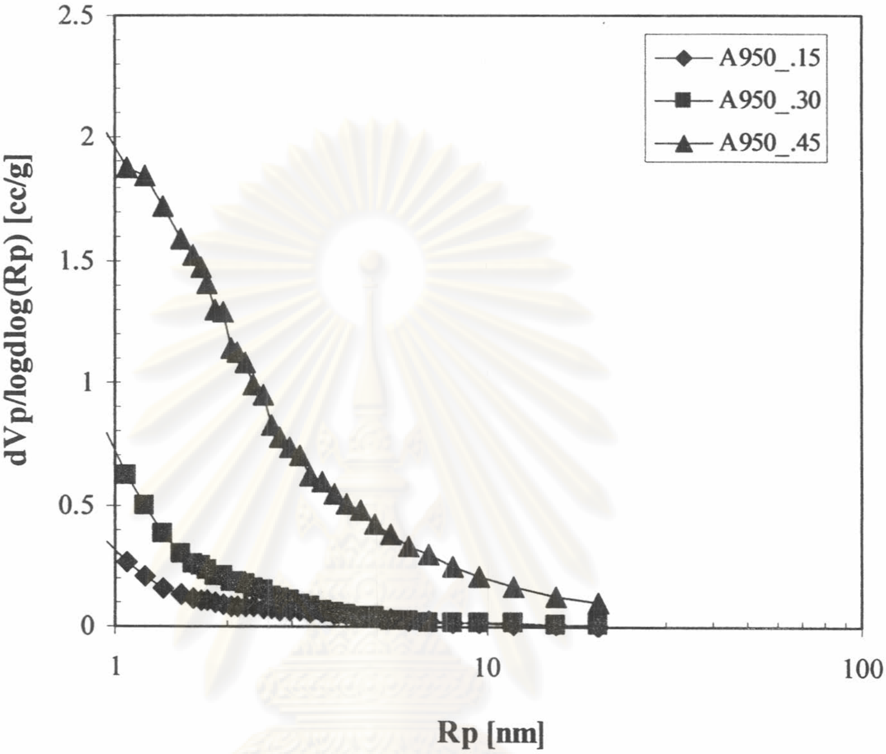


Figure 5.2.6 Pore size distribution of activated anthracite prepared at 950°C from anthracite powder with steam flow rate 0.5 g/min.

Furthermore from Figures 5.2.1-5.2.3, it is noticed that shape of isotherms in range of *P/Po* = 0.1-1 is a bit shift when activation time is increase at the same activation temperature, which presents a higher V_{meso} value. This behavior is assured by V_{meso} value in table 5.1.1 and pore size distribution graph in figures 5.2.4-5.2.6 and it is clearly observed in case of activation temperature of 950°C. This behavior was similarly observed by others researches (Konvacik et al. 1995) in the preparation of activate carbon from bituminous coals with conventional steam activation. Since pore diffusion resistance increases its importance with and increase in activation temperature, the results suggest that pore widening is the predominant mechanism at high temperature whereas pore deepening is favored by low temperature.

The effect of steam flow rate in the activation step is also studied. The porous properties of activated anthracite from anthracite powder prepared at steam flow rate 0.25 g/min at activation temperature 750°C, 850°C and 950°C are summarized in table 5.1.2

Figures 5.2.7-5.2.9 show the N_2 adsorption-desorption isotherms on activated anthracite obtained through the steam activation at steam flow rate 0.25g/min at the activation temperature 750, 850 and 950°C, respectively. Considering the shape of isotherm and the N_2 adsorption capacity, the development of micropores and mesopores during activation can be clearly observed.

From the isotherms, the pore size distributions of obtained activated anthracite from anthracite powder are shown in Figures 5.2.10 – 5.2.12.

From figures 5.2.1-5.2.3, they can be easy to observe that every isotherm almost have no hysteresis loop and exhibit Type I isotherm, with larger uptake indicating that they have a large degree of microporosity. Since, the shape of the isotherms was quite similar to the ones that prepared at steam flow rate 0.5 g/min, so it can be concluded that steam flow rate has no obvious effect upon porous properties of obtained activated anthracite. However, when compare with activated anthracite prepared at steam flow rate 0.5 g/min a pore widening mechanism was noticed easier. As a result, it can be concluded that pore diffusion resistance increases its role when the steam flow rate is lower. On the others hand, it can be said that at the same activation temperature the pore diffusion resistance was higher when the activation rate was lower which influenced in V_{meso} value of prepared activated anthracite

Table 5.2.2 also provides the porous properties of obtained activated anthracite calculated from isotherms. The prepared activated anthracite had the V_{micro} and V_{meso} values up to 0.635 and 0.287, respectively, and possessed the S_{BET} value up to 1589.75 m^2/g. It is found that the higher V_{micro}, V_{meso} and S_{BET} values of prepared activated anthracite can be obtained at higher %burn-off or longer activation time as same as ones prepared at steam flow rate 0.5 g/min.

Table 5.2.2 Porous properties of activated anthracite prepared from anthracite powder at 750, 850 and 950°C with steam flow rate of 0.25 g/min

Sample	Burn-off (%)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)	S_{BET} (m^2/g)
A750_10 (0.25)	30.12	0.078	0.145	312.58
A750_15 (0.25)	52.77	0.062	0.312	644.65
A750_25 (0.25)	60.01	0.240	0.422	941.39
A850_3 (0.25)	37.81	0.047	0.311	694.72
A850_4 (0.25)	44.46	0.027	0.289	655.13
A850_6 (0.25)	72.41	0.287	0.635	1589.75
A950_0.20(0.25)	30.126	0.119	0.284	628.90
A950_0.40(0.25)	52.49	0.119	0.247	578.58
A950_1 (0.250	60.40	0.169	0.418	1001.76

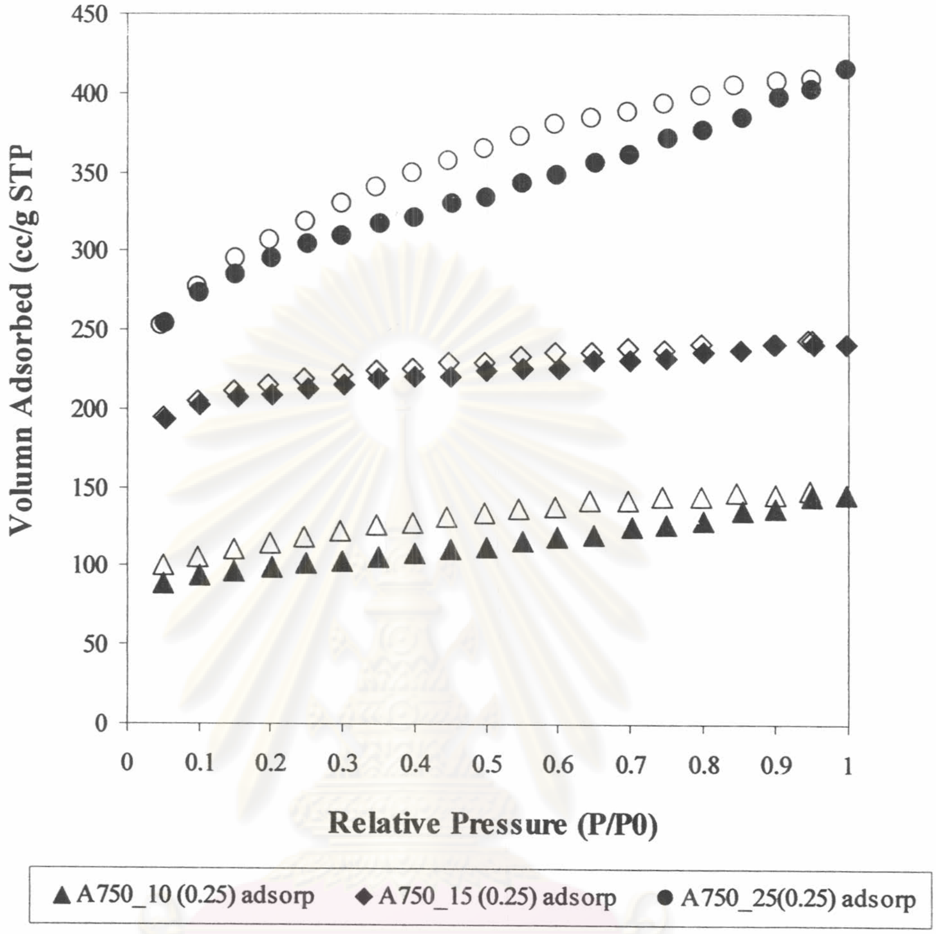


Figure 5.2.7 N_2 adsorption-desorption isotherm on activated anthracite prepared at 750˚C from anthracite powder with steam flow rate 0.25g/min closed symbols: adsorption, open symbols: desoprtion

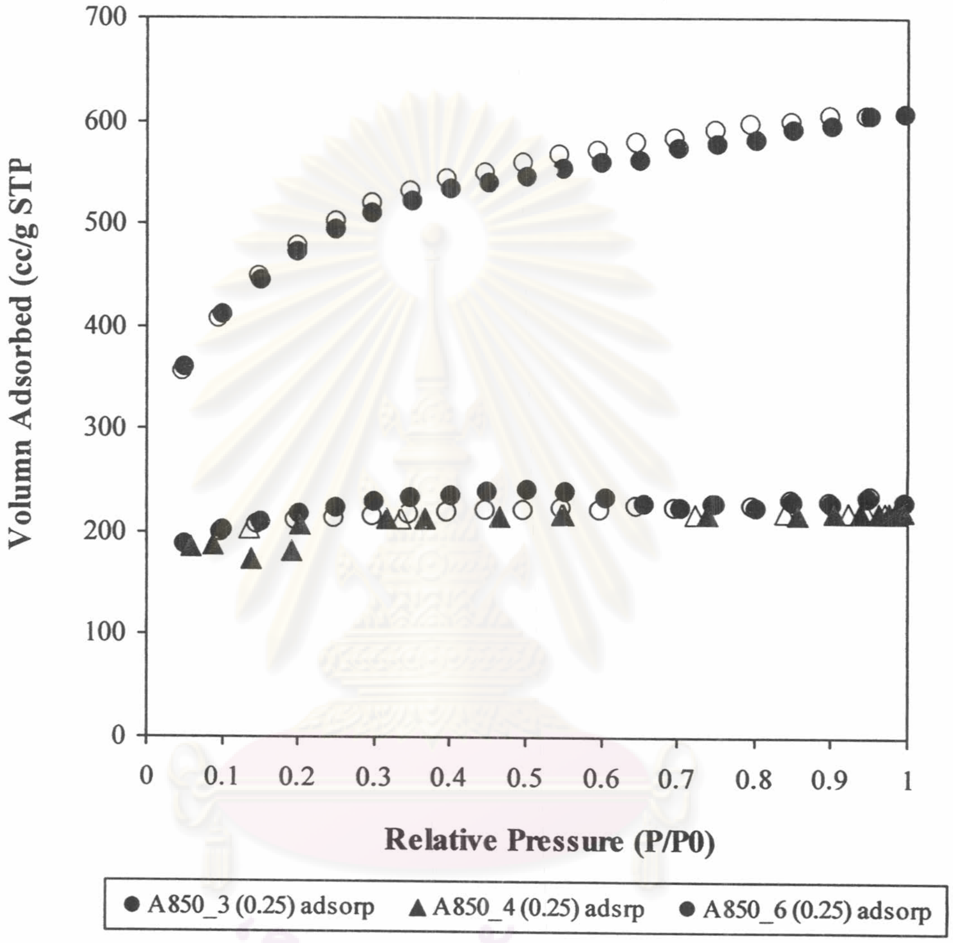


Figure 5.2.8 N_2 adsorption-desorption isotherm on activated anthracite prepared at 850°C from anthracite powder with steam flow rate 0.25g/min

closed symbols: adsorption, open symbols: desoprtion

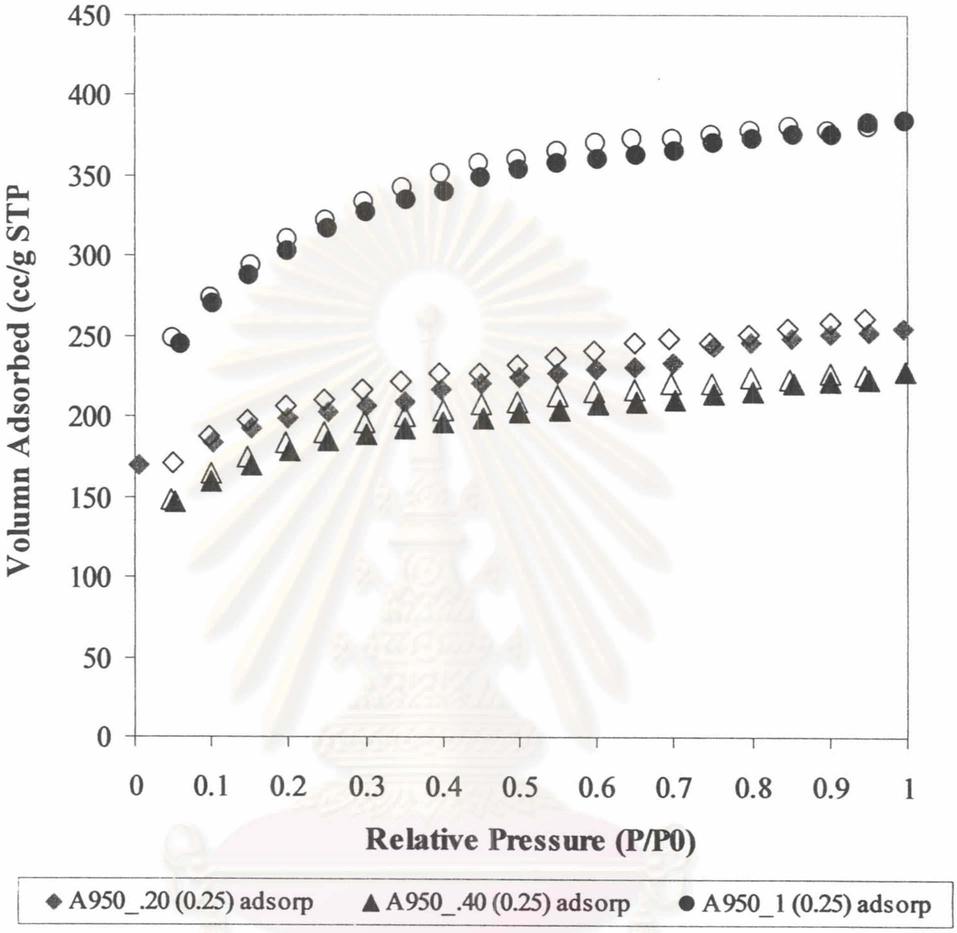
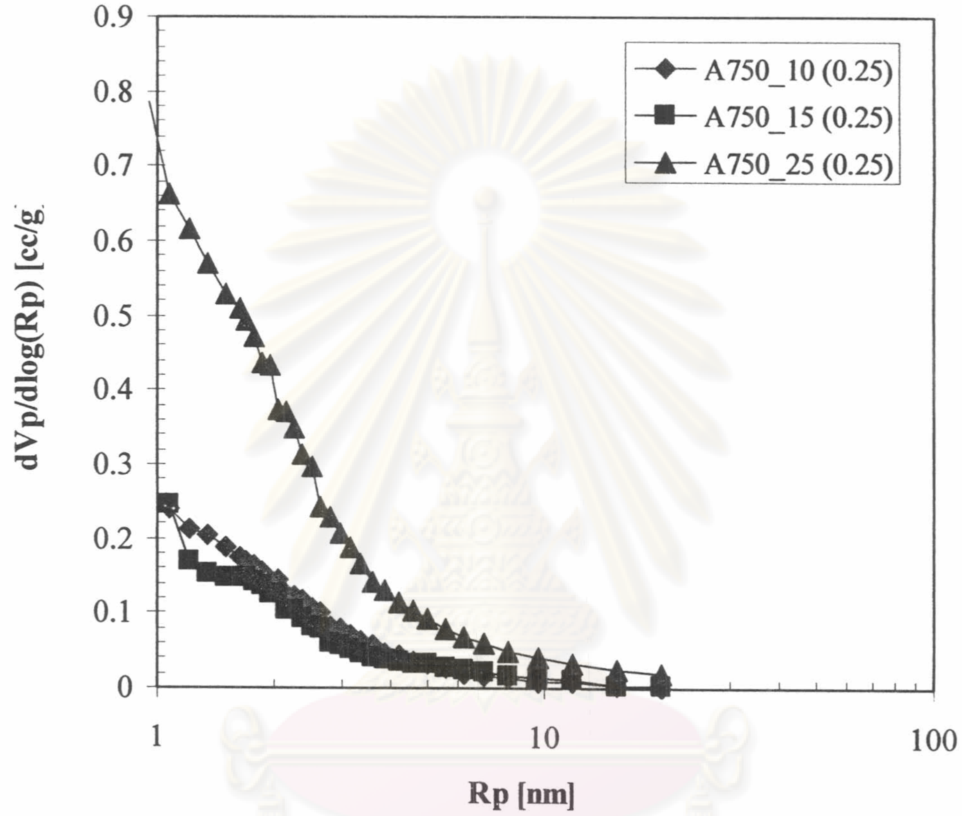
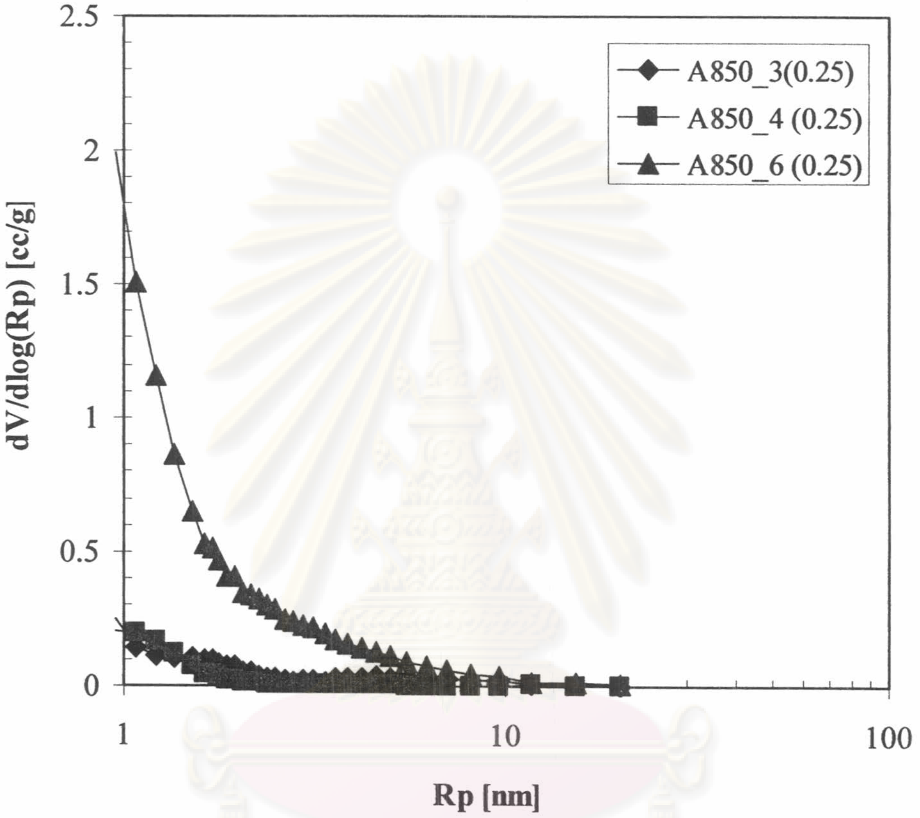


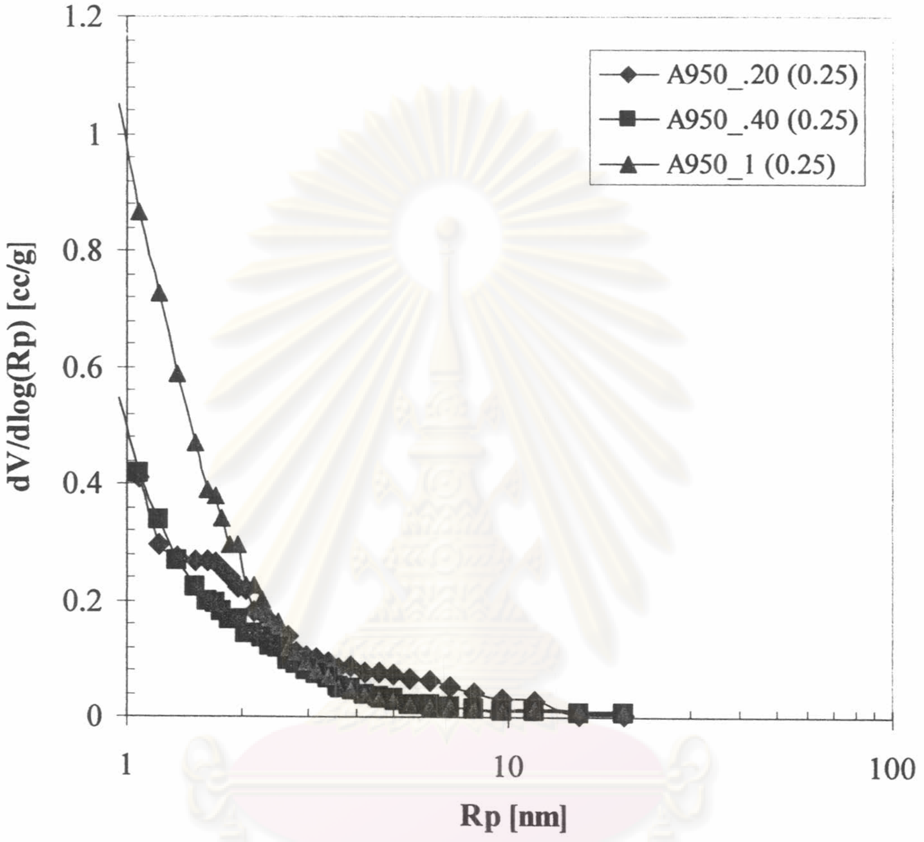
Figure 5.2.9 **N_2 adsorption-desorption isotherm on activated anthracite prepared at 950˚C from anthracite powder with steam flow rate 0.25g/min closed symbols: adsorption, open symbols: desoprtion**



5.2.10 Pore size distribution of activated anthracite prepared at 750°C from anthracite powder with steam flow rate 0.25 g/min.



5.2.11 Pore size distribution of activated anthracite prepared at 850°C from anthracite powder with steam flow rate 0.25 g/min.



5.2.12 Pore size distribution of activated anthracite prepared at 950°C from anthracite powder with steam flow rate 0.25 g/min.

5.3 Porous properties of activated anthracite after treated by supercritical water treatment

In this topic, anthracite powder is used as a starting material in supercritical water treatment to find the possibility to produce activated carbon and to study the effect of the treatment on porous properties of anthracite powder.

5.3.1 Effect of treatment time

By observing the weight of remaining sample or treatment yield, ratio between remaining weight and weight input, of the treatment, it can predict the degree of the treatment at different treatment time. As the critical conditions of pure water are 374.5°C and 220.2 bar, so the treatment conditions are set at 400°C and 360 bar with different treatment time.

Table 5.3.1 Treatment yield of anthracite powder treated under supercritical water conditions with different treatment time

Treatment time	Treatment yield (%)
5 min.	96.76
15 min.	95.82
2 hrs.	94.92
3 hrs.	96.45
20 hrs.	96.64

*Treatment yield is a ration between weight of remaining sample and input sample

As shows in table 5.3.1, treatment yield of every samples are around 95 % yield, so we it can be assumed that treatment time has no effect on the porous properties of samples

In addition, figures 5.3.1 shows N_2 adsorption-desorption of anthracite powder and sample prepared at 400°C and 360 bar for 20hrs. From the shape of both isotherms, indicate Type III isotherm, with a weak interaction between adsorbate and adsorbent and there is no change observed between both isotherms. Thus treatment time have no effect on porous properties of samples due to very fast reaction of supercritical water.

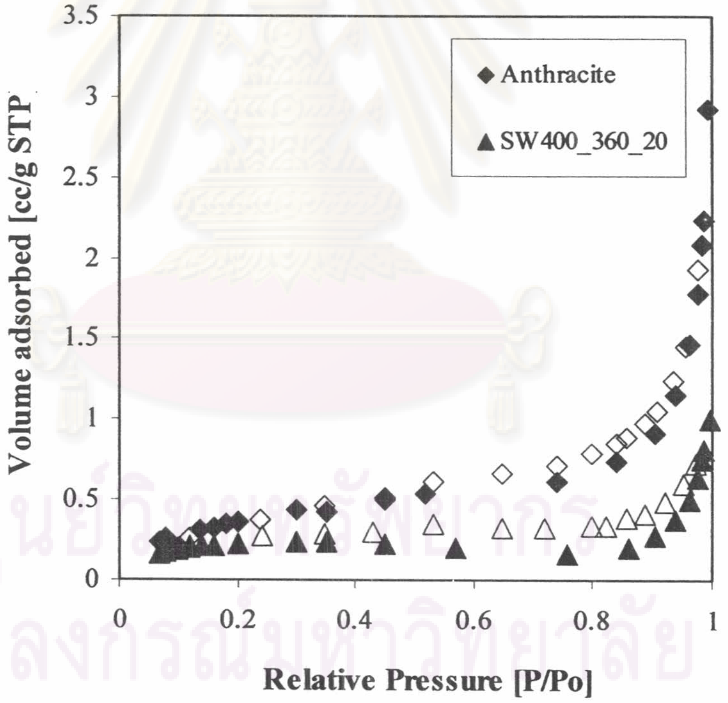


Figure 5.3.1 N_2 adsorption – desorption isotherm of anthracite powder and anthracite powder treated with supercritical water treatment for 20 hours

5.3.2 Pre-treatment with sodium hydroxide and potassium hydroxide

Anthracite powder is impregnated with NaOH or KOH before supercritical water treatment. Our hypotheis is to use great solubility and extraction power of supercritical water to dissolve organic compounds and NaOH / KOH-carbon compounds that obstructed the pores of anthracite powder.

Two grams of anthracite powder are mixed by stirring with a solution that contained 10 ml of water and 4 g of KOH or NaOH for 2 hr at 60°C. The resulting slurry is dried at 110°C overnight in an oven. The resulting mixture is used for supercritical water treatment. Then one gram of mixture is treated in stainless steel tube reactor at 400°C and 360 bar, which is in supercritical water region.

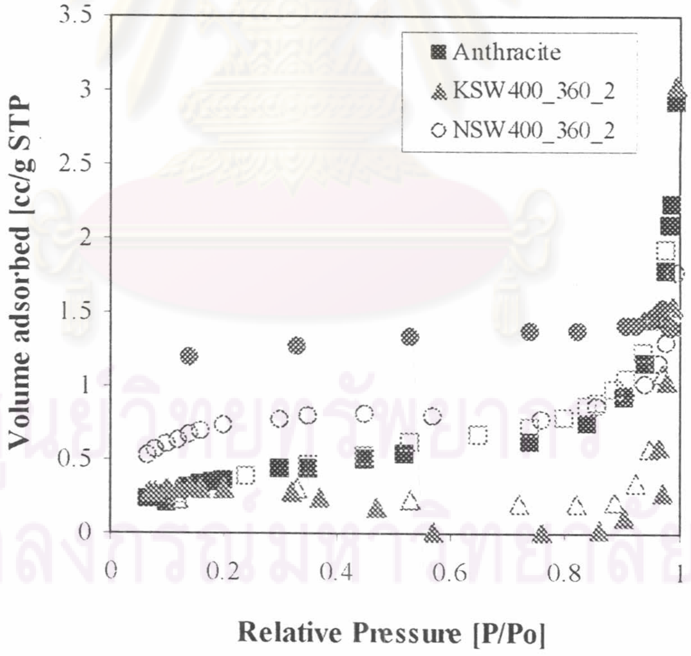


Figure 5.3.2 N_2 **adsorption-desorption isotherm on anthracite powder and samples with NaOH/KOH pre-treatment treated with supercritical water treatment.**

Figure 5.3.2 shows, N_2 adsorption-desorption isotherm of anthracite powder and samples with NaOH / KOH pre-treatment treated with supercritical water treatment. Porous properties of samples calculated from isotherms are summarized in table 5.3.2

Table 5.3.2 Porous properties of anthracite powder and samples with NaOH / KOH pre-treatment treated with supercritical water treatment

Sample	S_{BET} **(m^2/g)**	V_{MICRO} **(cm^3/g)**	V_{MESO} **(cm^3/g)**
Anthracite	1.45	0.0003	N.D.
NSW400_360_2	2.77	0.0009	N.D.
KSW400_360_2	1.08	0.0005	N.D.

- NSW400_360_2: anthracite powder impregnated with NaOH before treated under supercritical water conditions at 400°C and 360bar for 2 hrs
- KSW400_360_2: anthracite powder impregnated with KOH before treated under supercritical water conditions at 400°C and 360bar for 2 hrs
- N.D.: non-detectable
-

From figure 5.3.2 and S_{BET} values of anthracite powder, sample with NaOH and KOH pre-treatment are 2.77 and 1.08 m^2/g, respectively. The different between raw anthracite powder and samples with pre-treatment is not observed. Hence, it is clearly that pre-treatment with NaOH or KOH before treated under supercritical water conditions does not enhance the porous properties of anthracite powder.

5.3.3 Supercritical water treatment using carbon dioxide solution as liquid medium

Carbon dioxide solution or drinking soda water is used as a liquid medium in this treatment. By using carbon dioxide solution, supercritical water oxidation occurred as it can be observed by the lower yield of treatment (68.77% yield) compare with one treated by distilled water (96% yield).

Figure 5.3.2 shows N_2 adsorption-desorption isotherm of anthracite powder and sample obtained from supercritical water treatment using carbon dioxide solution as liquid medium. The porous properties calculated from the isotherms are summarized in table 5.3.3.

Table 5.3.3 Porous properties of anthracite powder and sample treated with supercritical water treatment by using drinking soda as liquid medium

Sample	S_{BET} (m^2/g)	V_{MICRO} (cm^3/g)	V_{MESO} (cm^3/g)
Anthracite	1.45	0.0003	-
COSW400_360_2	1.05	0.0004	

- COSW400_360_2: anthracite powder treated under supercritical water conditions at 400°C and 360bar for 2 hrs using drinking soda as liquid medium

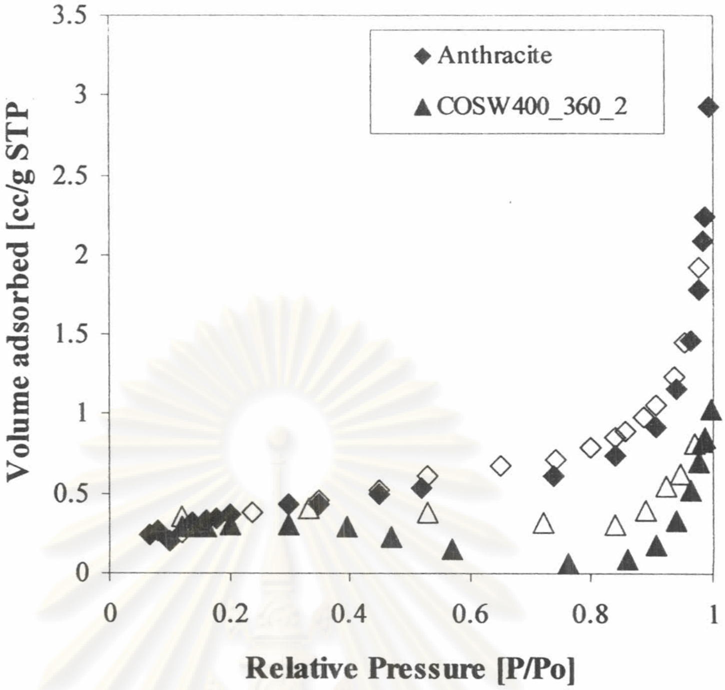


Figure 5.3.3 N_2 adsorption-desorption isotherm on anthracite powder and sample obtain from supercritical water treatment using drinking soda as liquid medium

From shape of both isotherms, they are indicating as Type III isotherm with a weak adsorbate-adsorbent interaction. S_{BET} and V_{micro} values of treated sample are similar to raw anthracite powder. Thus, it is clearly that supercritical water treatment using drinking soda water as liquid medium can not improve the porous properties of anthracite powder even oxidation reaction occurred.

5.4 Porous properties of activated carbons after treated by supercritical water treatment

In this topic, various kind of activated carbons; activated anthracite, commercial activated carbon (CAL carbon) and activated carbon from waste tired are treated with supercritical water treatment by using distilled water or hydrogen peroxide solution as liquid medium to observe to porous properties change after treatment. The objective of this topic is to find the possibility of porous properties improvement especially for S_{BET} and V_{MESO} of activated carbons after treated by supercritical water treatment. The advantages of supercritical treatment are high yield of obtained activated carbon and short treatment time.

In case of using hydrogen peroxide solution as liquid medium, supercritical water oxidation reaction was occurred and the results are discussed below.

Figures 5.4.1-5.2.3 show the N_2 adsorption-desorption isotherms on original various kind of activated carbons, activated carbons treated with supercritical water treatment using distilled water and activated carbons treated with supercritical water treatment using hydrogen peroxide solution. Considering the shape of isotherm and the N_2 adsorption capacity, the development of micropores and mesopores could be clearly observed.

From the isotherms, the pore size distributions of original various kinds of activated carbons, activated carbons treated with supercritical water treatment using distilled water and activated carbons treated with supercritical water treatment using hydrogen peroxide solution are shown in Figures 5.4.4 – 5.2.6.

Table 5.4.1 Porous properties of original activated carbons, activated carbon treated with supercritical water using distilled water and activated carbons treated with supercritical water using hydrogen peroxide solution. Treatment conditions are 400°C, 360 bar and 15 minutes.

AC.	CAL			AA			WT		
Properties	**CAL**	**WCAL**	**HCAL**	**AA**	**WAA**	**HAA**	**WT**	**WWT**	**HWT**
S_{BET} (m^2/g)	820	778	792	679	691	321	641	669	51
V_{MESO} (cm^3/g)	0.19	0.20	0.28	0.08	0.12	0.14	0.45	0.49	0.09
V_{MICRO} (cm^3/g)	0.38	0.35	0.35	0.30	0.32	0.13	0.25	0.27	0.001
V_{TOTAL} (cm^3/g)	0.58	0.55	0.63	0.38	0.44	0.27	0.70	0.76	0.1
V_{MESO}/V_{TOTAL}	0.33	0.36	0.44	0.21	0.27	0.52	0.64	0.64	-
Yield (%)	-	85.90	28.62	-	95.89	45.73	-	91.20	16.74

AC. =Activated carbon CAL = Commercial activated carbon (CAL carbon)

AA= Activated anthracite WT= Activated carbon from waste tires

Prefix "W" = Supercritical water treatment by distilled water

Prefix "H" = Supercritical water treatment by Hydrogen peroxide solution (H_2O:H_2O_2; 1:1)

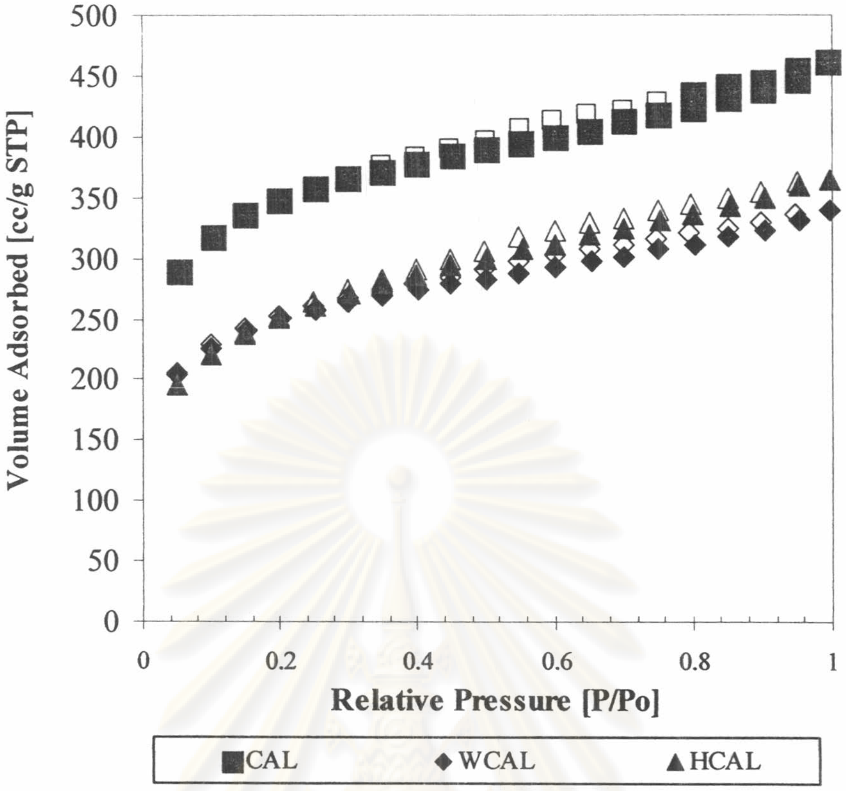


Figure 5.4.1 N_2 adsorption-desorption isotherm on original CAL carbon, CAL carbon treated with supercritical water using distilled water and CAL carbon treated with supercritical water using hydrogen peroxide solution. Treatment conditions are 400°C, 360 bar and 15 minutes.

closed symbols: adsorption, open symbols: desoprtion

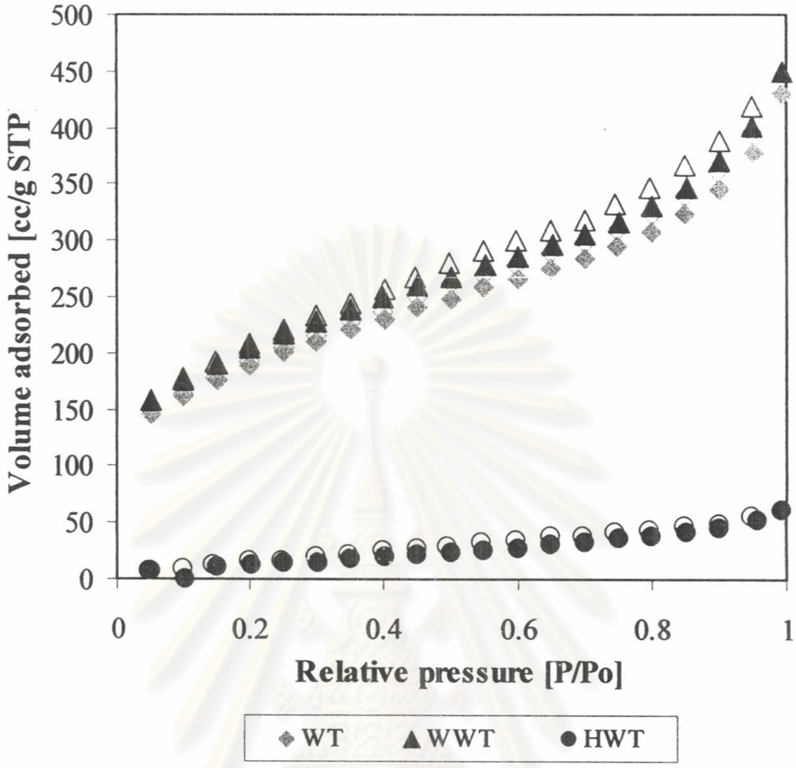


Figure 5.4.2 N_2 adsorption-desorption isotherm on activated carbon from waste tires, activated carbon from waste tires treated with supercritical water using distilled water and activated carbon from waste tires treated with supercritical water using hydrogen peroxide solution. Treatment conditions are 400°C, 360 bar and 15 minutes.

closed symbols: adsorption, open symbols: desoprtion

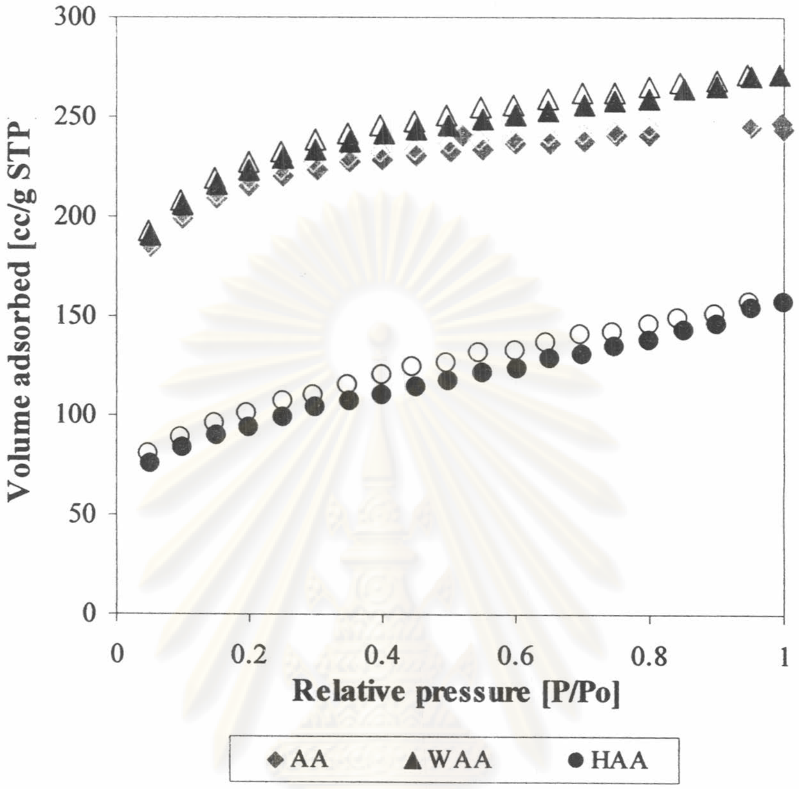


Figure 5.4.3 N_2 **adsorption-desorption isotherm on activated anthracite, activated anthracite treated with supercritical water using distilled water and activated anthracite treated with supercritical water using hydrogen peroxide solution. Treatment conditions are 400°C, 360 bar and 15 minutes.**

closed symbols: adsorption, open symbols: desoprtion

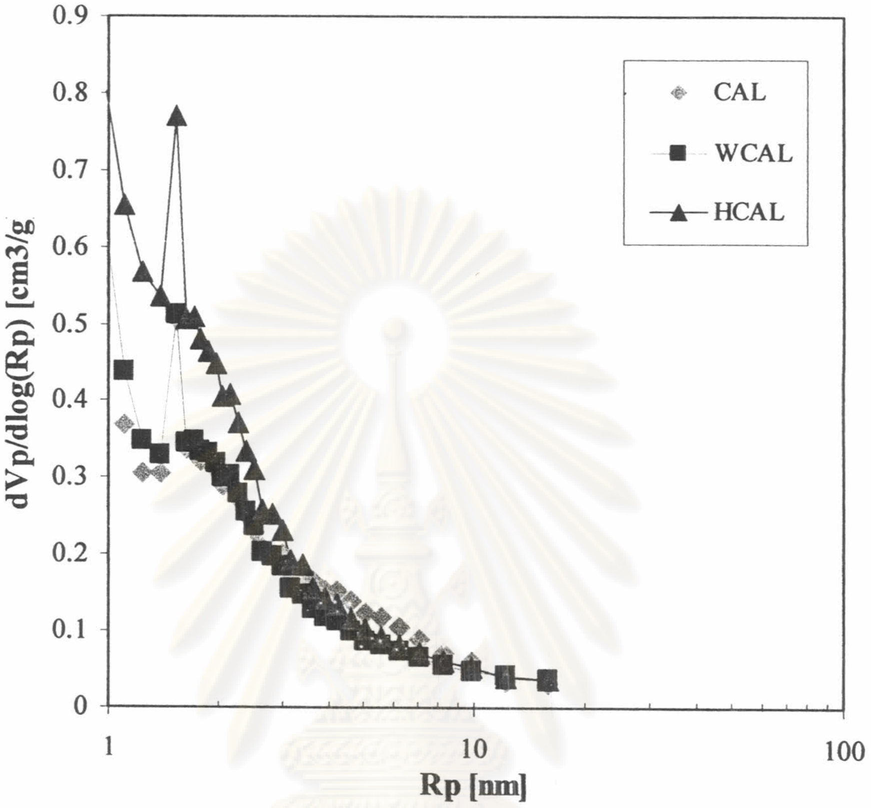


Figure 5.4.4 Pore size distribution of CAL carbon, CAL carbon treated with supercritical water using distilled water and CAL carbon treated with supercritical water using hydrogen peroxide solution. Treatment conditions are 400°C, 360 bar and 15 minutes.

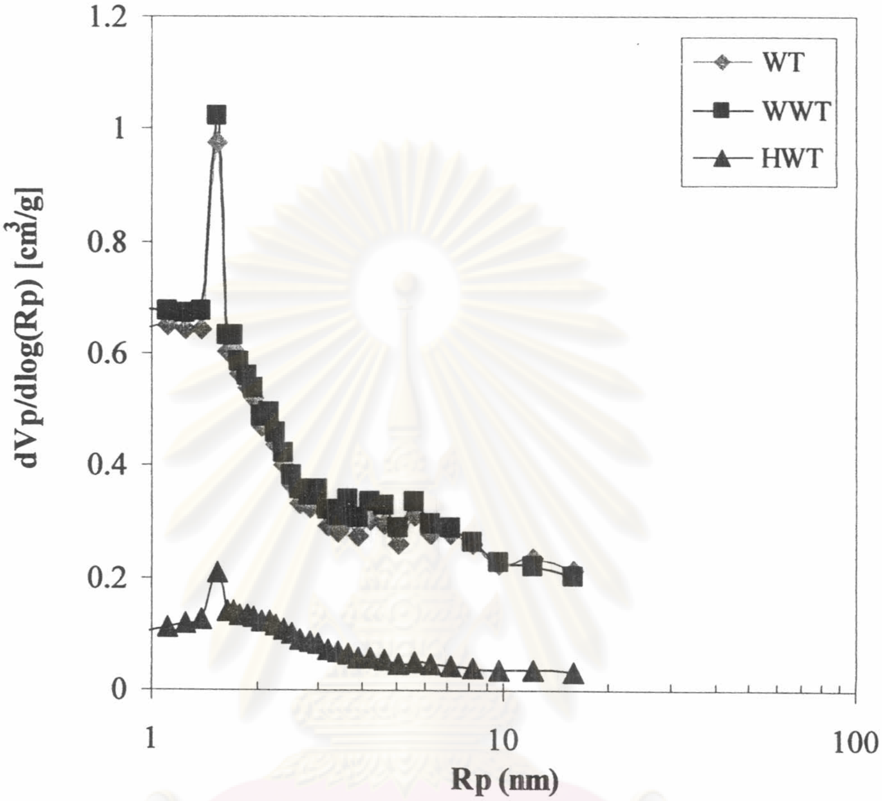


Figure 5.4.5 Pore size distribution of activated carbon from waste tires, activated carbon from waste tires treated with supercritical water using distilled water and activated carbon from waste tires treated with supercritical water using hydrogen peroxide solution. Treatment conditions are 400°C, 360 bar and 15 minutes.

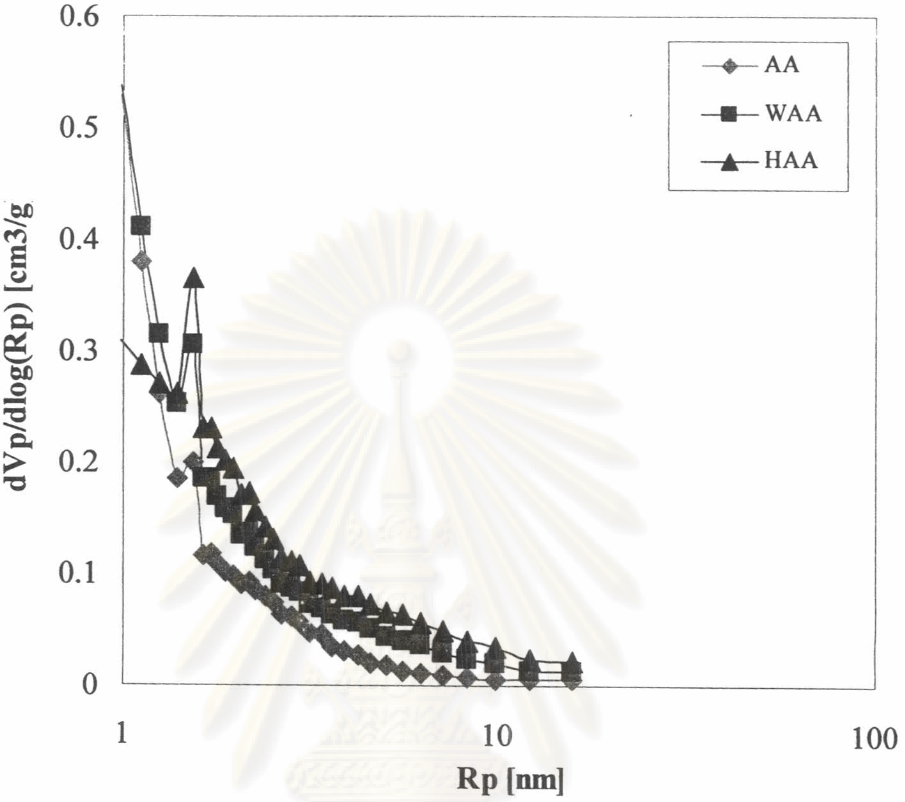


Figure 5.4.6 Pore size distribution of activated anthracite, activated anthracite treated with supercritical water using distilled water and activated anthracite treated with supercritical water using hydrogen peroxide solution. Treatment conditions are 400°C, 360 bar and 15 minutes.

From figures 5.4.1 and 5.4.3, show the isotherms of CAL carbons and activated anthracites, respectively, it can be easy to observe that every isotherm almost have no hysteresis loop and exhibit Type I isotherm, with larger uptake indicating that they have a large degree of microporosity. Unlike figure 5.4.2 which shows the isotherms of activated carbon from waste tires, the shape of the isotherms is exhibit Type IV isotherm, with a large degree of mesoporosity. From the shape of the isotherm, it can be concluded that CAL carbons and activated anthracite are microporous activated carbon, while activated carbon from waste tries is mesoporous activated carbon.

Table 5.2.1 also provides the porous properties of original activated carbons, activated carbons treated with supercritical water treatment using distilled water and activated carbons treated with supercritical water treatment using hydrogen peroxide solution.

From table 5.2.1, we can observed that S_{BET}, V_{micro} and V_{meso} values of activated anthracite and activated carbon from waste tires become 2 – 5 % higher after treated with supercritical water treatment using distilled water. Since, water at 400°C and 360 bar has grate extraction and solubilizing capacity such that a cleaning effect of obstructed pores would be expected. Under these conditions, the water might dissolve some of the compound which obstructed the pores, thus facilitating the adsorption capacity. Another, possibility is pressure during the treatment might give rise to microfissures which would facilitate access to closed pores (F. Salvador, C. Sanchez Jimenez, 1999). However, there is no obvious change occurred via this treatment so it can be said that supercritical water treatment using distilled water can not use for improve porous properties of activated carbons.

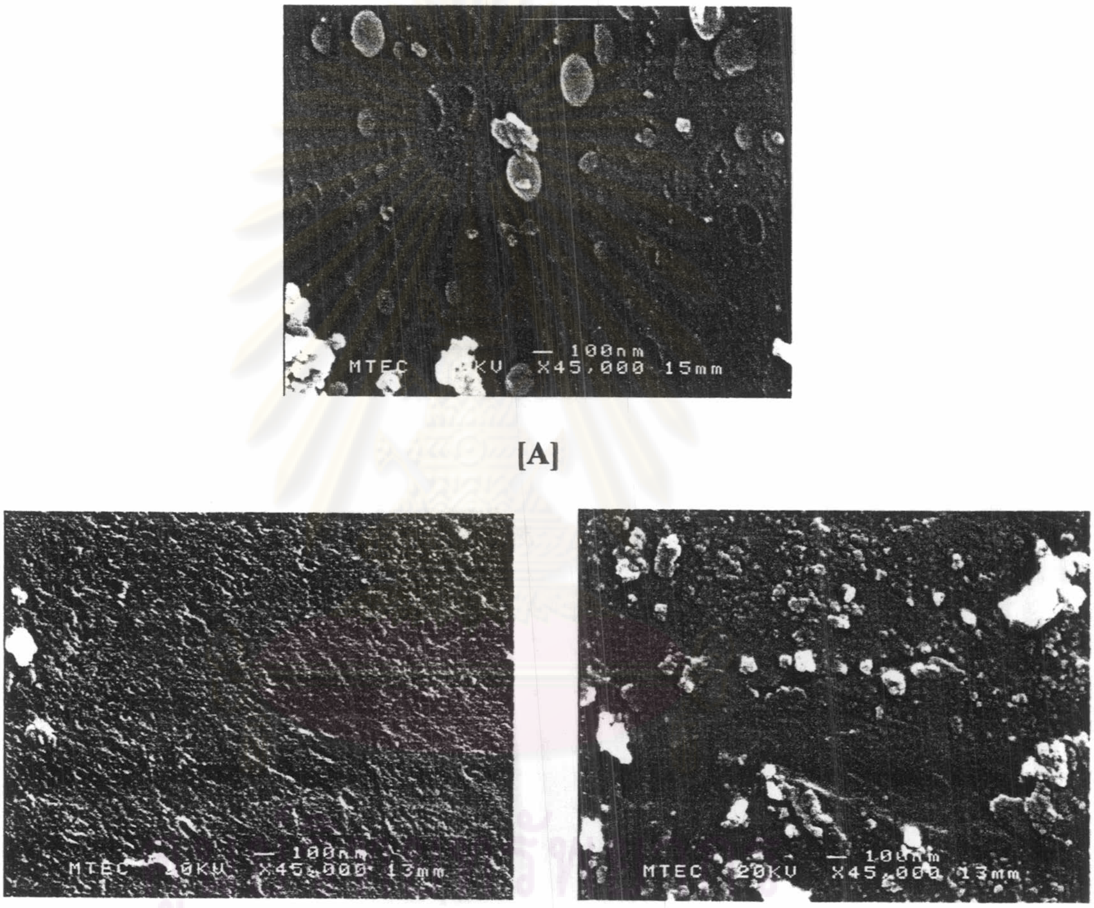
Figures 5.4.7 and 5.4.8 show SEM images of activated anthracite, supercritical water treated activated anthracite by distilled water and supercritical water treated activated anthracite by hydrogen peroxide solution. From figures 5.4.7 [A] and [B], it can be observed that there are fragments on activated anthracite surface which possibly be organic compounds and they are not showed on supercritical water treated activated anthracite by distilled water. As a result, it can be said that supercritical water might dissolve some of the compound which obstructed the pores, thus facilitating the adsorption capacity and raising the mesopores values.

Additional, from pore size distribution curves of supercritical water treated activated carbon by using distilled water in figures 5.4.4-5.4.6, can be noticed that the shape of the curves still represent a microporous activated carbon for WCAL and WAA and represent a mesoporous activated carbon from WWT, but every curve show a few increase in pore volume.

In case of using hydrogen peroxide as liquid medium the activated carbons are oxidized which can be observed by the treatment yield. Firstly, we intend to use hydrogen peroxide as oxidizing agent to oxidize the activated carbon and expect that the porous properties will be improved like steam activation.

S_{BET} value of CAL carbon treated with supercritical water treatment using hydrogen peroxide (HCAL), activated anthracite treated with supercritical water treatment using hydrogen peroxide solution (HAA) and activated carbon from waste tires treated with hydrogen peroxide solution (HWT) in table 5.4.1 are decrease after treatment except HCAL. This phenomenon can be described by very fast oxidation rate or surface of activated carbon was oxidized in layers which different from steam activation that some carbons on activate carbon surface were oxidized. However, HCAL still have S_{BET} value similar to original carbon due to orderly structure of CAL carbon.

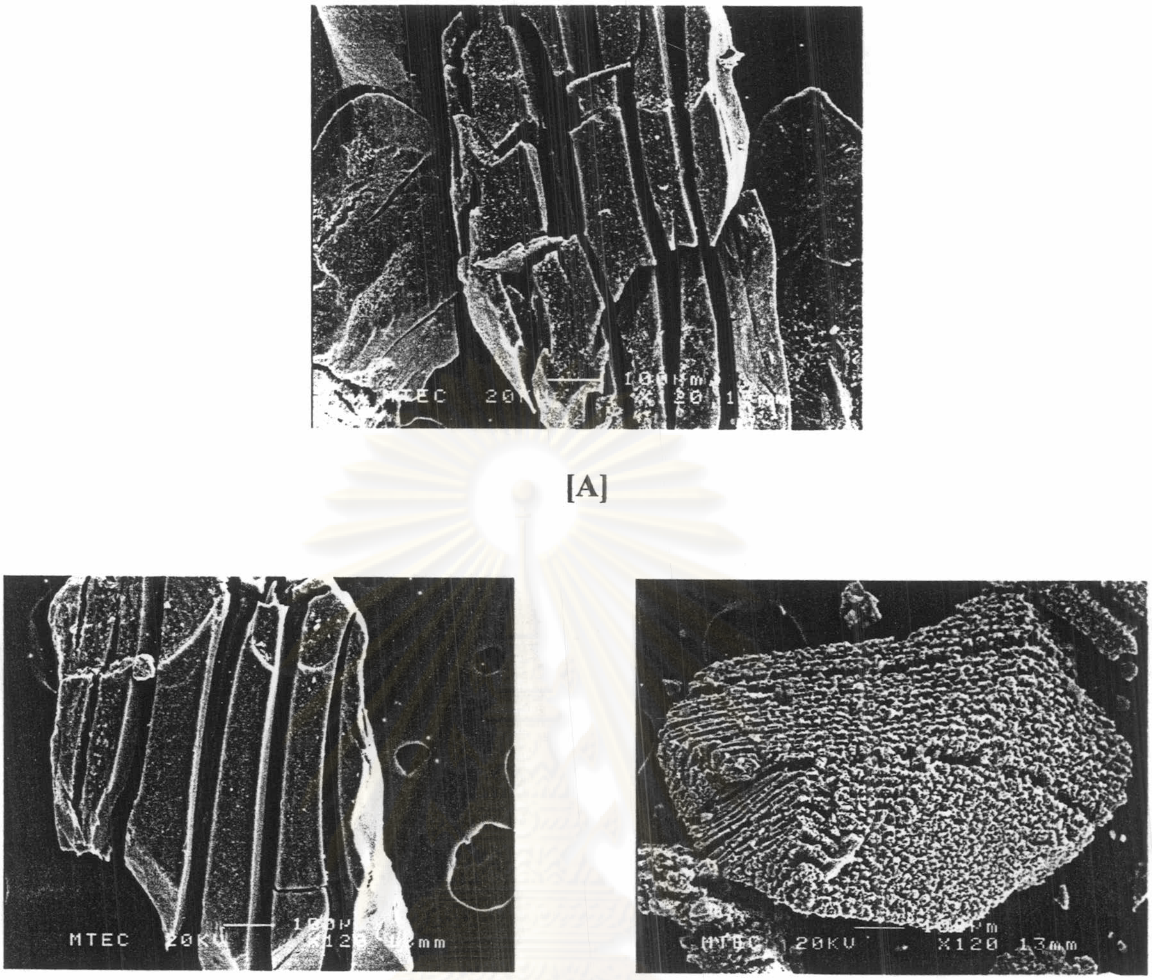
Therefore, it can be concluded that porous properties of activated carbon are decrease as treatment yield decrease and supercritical water treatment using distilled water does no effect on porous structure of activated carbons.



[A]

[B] **[C]**

Figure 5.4.7 SEM images of activated anthracite [A], supercritical water treated activated anthracite by distilled water [B] and supercritical water treated activated anthracite by hydrogen peroxide solution [C] at power of 45,000



[A]

[B]

[C]

Figure 5.4.8 SEM images of activated anthracite [A], supercritical water treated activated anthracite by distilled water [B] and supercritical water treated activated anthracite by hydrogen peroxide solution [C] at power of 120

Table 5.4.2 Porous properties of original activated carbons, activated carbon treated with supercritical water using different concentration of hydrogen peroxide solution. Treatment conditions are 400°C, 360 bar and 15 minutes.

Activated carbon	AA	HAA(1:1)	HAA(3:2)	HAA(6:2)
S_{BET} (m^2/g)	679	321	612	702
V_{MESO} (cm^3/g)	0.082	0.138	0.119	0.178
V_{MICRO} (cm^3/g)	0.307	0.129	0.270	0.319
Yield (%)	-	45.73	55.68	77.01

AA= original activated anthracite
HAA(1:1) = 15 % hydrogen peroxide solution
HAA (3:2) = 12 % hydrogen peroxide solution
HAA (6:2) = 7.5 % hydrogen peroxide solution

In this part effect of concentration of hydrogen peroxide solution was studied. The samples with treatment yield are 45 – 77% was prepared by varying the concentration of hydrogen peroxide solution used in supercritical water treatment. Fig.5.3.9 shows the N_2 adsorption-desorption isotherms of original activated anthracite and activated anthracite treated with supercritical water using hydrogen peroxide solution with different treatment yield.

From the isotherms, the pore size distributions are shown in Figures 5.4.8 and we can notice that the shape of isotherms of supercritical water treated samples present an increase in V_{MESO} value. The porous properties calculated from the isotherms were summarized in table 5.4.2.

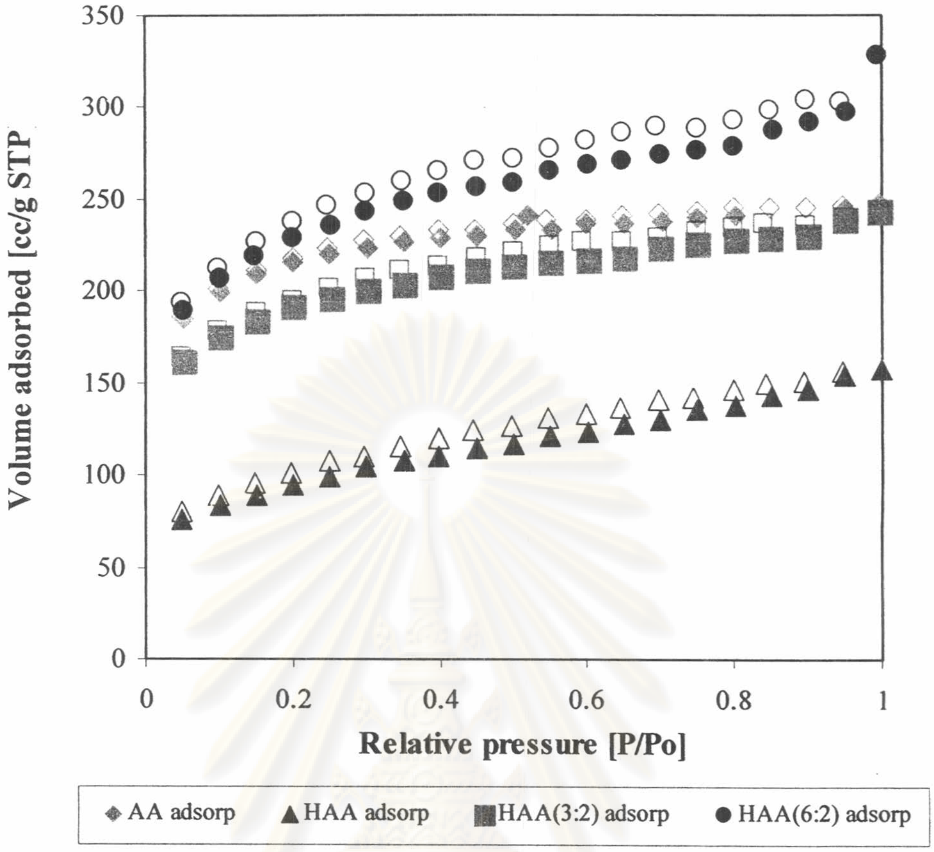


Figure 5.4.9 N_2 adsorption-desorption isotherm on activated anthracite, activated anthracite treated with supercritical water using various concentration of hydrogen peroxide solution. Treatment conditions are 400°C, 360 bar and 15 minutes. closed symbols: adsorption, open symbols: desoprtion

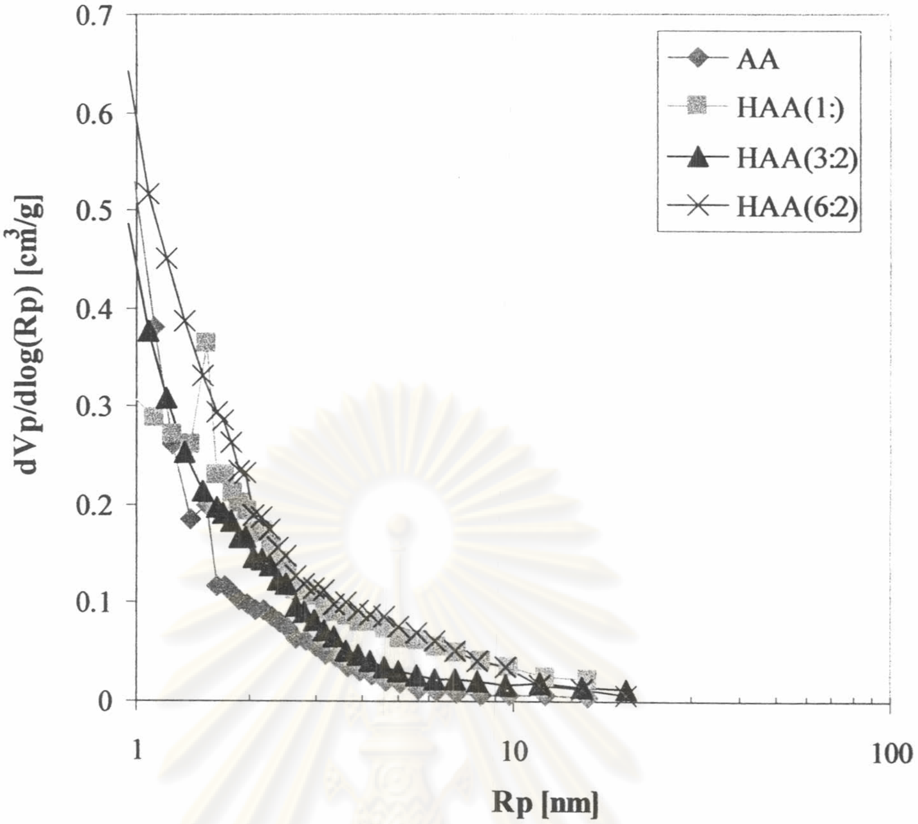


Figure 5.4.10 Pore size distribution of activated anthracite, activated anthracite treated with supercritical water using various concentration of hydrogen peroxide solution. Treatment conditions are 400°C, 360 bar and 15 minutes.

From table 5.4.2 show that S_{BET} of samples at 77% treatment yield is still similar to original activated anthracite then decrease when treatment yield is decrease. In addition, V_{MESO} value of treated activated anthracite becomes 1.5 – 2 times higher than original activated anthracite, while V_{MICRO} value becomes lower.

From the results, it is clear that the supercritical water treatment using hydrogen peroxide solution can not enhance the porous properties of activated anthracite although the V_{MESO} value is slightly increase.

5.5 Liquid-phase adsorption and regeneration characteristics

5.5.1 Porous properties of adsorbents

Both representative adsorbents, AA and CAL carbon, are characterized and their N_2 adsorption-desorption isotherms are shown in Figure 5.5.1. From the shape of both isotherms, they are indicating that both activated carbons show microporous structure. However, CAL carbon presents higher mesopore volume than AA. Owing to the N_2 adsorption capacity of CAL carbon was larger than that of AA at $P/P^0 > 0.3$.

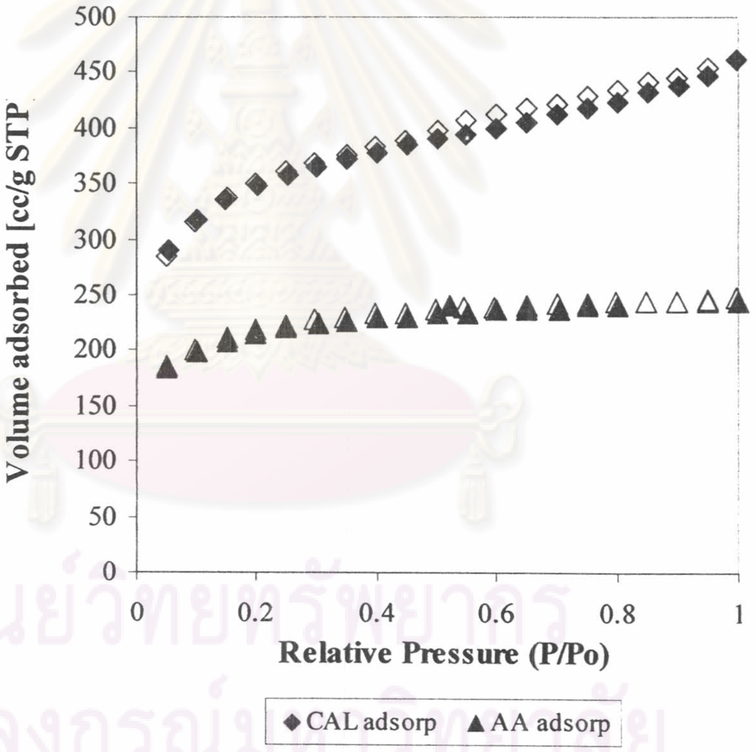


Figure 5.5.1 N_2 adsorption-desorption isotherm on CAL carbon and activated anthracite

closed symbols: adsorption, open symbols: desoprtion

By applying the Dollimore-Heal method to the isotherm, the pore size .distribution of AA and CAL carbon are presented in Figure 5.5.2.. It is clearly that CAL carbon and AA have same shape of pore size distribution. Nevertheless, CAL carbon shows greater mesoporosity than AA and higher pore volume than that of AA at *Rp* > 2 nm.

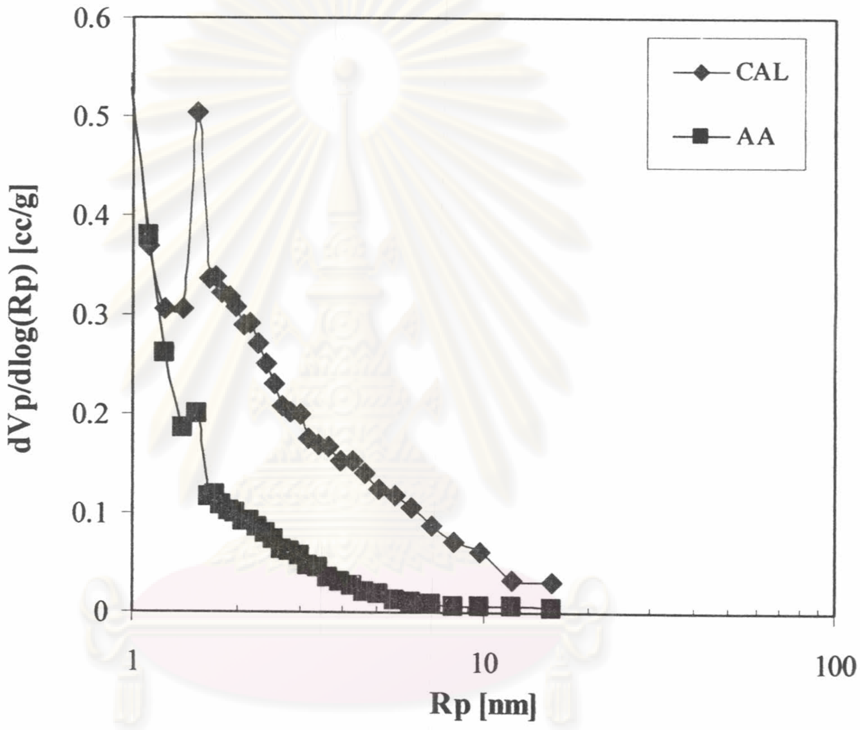


Figure 5.5.2 Pore size distribution of CAL carbon and activated anthracite

The porous properties of CAL carbon and AA determined from the isotherm in figures 5.5.1.1are given in table 5.5.1. It can be concluded that CAL carbon has larger V_{MESO} and S_{BET} values and possesses the V_{MICRO} value in the same order as the activated anthracite.

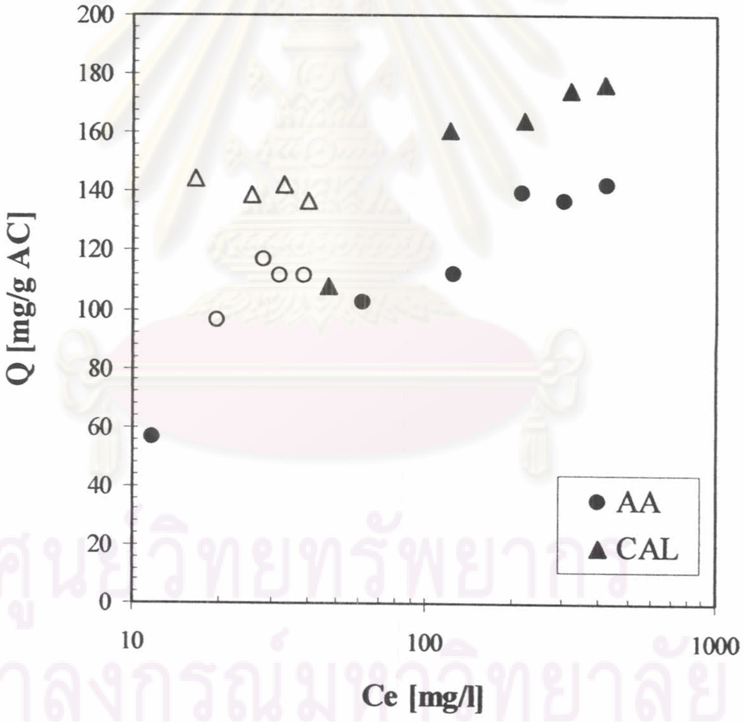
Table 5.5.1 The porous properties and physico-chemical properties of AA and CAL carbon

Sample	S_{BET} (m^2/g)	V_{MICRO} (cm^3/g)	V_{MESO} (cm^3/g)	Volatile Content (%)	Ash Content (%)	Moisture Content (%)
CAL	820	0.38	0.19	7.2	8.4	7.0
AA*	679	0.30	0.08	3.4	24.5	1.5

*Activated anthracite obtained at average 60% burn-off

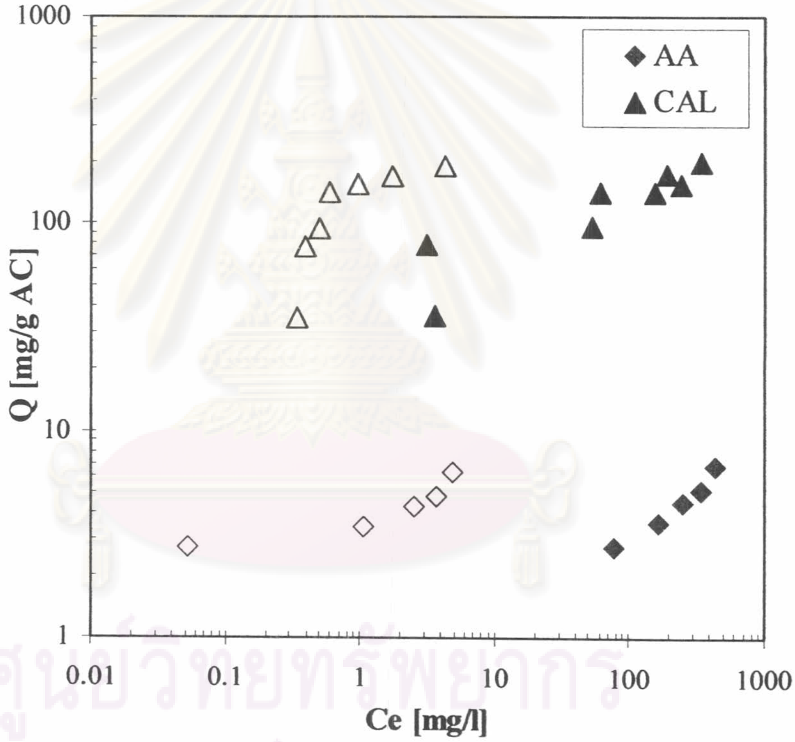
5.5.2 Adsorption-desorption isotherms

The adsorption-desorption isotherms of phenol and Red 31 on AA and CAL carbon are shown in Figures 5.5.3-5.5.4., respectively. The q and C_e are the amount of adsorbates adsorbed and equilibrium concentration, respectively. It is found that as the higher V_{MICRO} value of CAL carbon the slightly larger phenol adsorption capacity than the latter. Moreover, the existence of irreversible adsorption of phenol on both CAL carbon and AA was observed, since phenol has the electron-donating functional group, as that was investigated by Pisit *et al*, 2002 and Tamon *et al*, 1996.



Figures 5.5.3 Phenol adsorption-desorption isotherms on both adsorbents; closed symbols: adsorption, open symbols: desorption

As for the adsorption of Red 31, because of the larger V_{MESO} value, the commercial activated carbon (CAL carbon) showed obviously higher Red 31 adsorption capacity than activated anthracite prepared from anthracite powder by direct steam activation. This is because CAL carbon had more mesopores than AA as shown in figure 5.5.2 and table 5.5.1. Furthermore, the hysteresis between adsorption and desorption branches on both adsorbents suggested the appearance of irreversible adsorption, which correspond to the electron-donating fuctional groups in Red 31, amino and hydroxyl groups.



Figures 5.5.4 Red 31 adsorption-desorption isotherms on both adsorbents; closed symbols: adsorption, open symbols: desorption

Therefore, because of the comparable phenol adsorption capacity but the lower adsorption capacity of organic dye; Red 31, the activated anthracite prepared from anthracite powder by direct steam activation should apply to the gas-phase adsorption or water purification, unlike CAL carbon, which can be applied to various kind of adsorption process.

5.5.3 Regenerating exhausted activated carbon by supercritical water

In this topic, activated carbons; activated anthracite and CAL carbon, exhausted with phenol and Red 31 were regenerated by supercritical water in batch process to study the adsorption capacity of regenerated activated carbon.

Regenerating activated carbon via this procedure based on thermal desorption with liquid water at high temperature and pressure, which combines thermal and chemical regeneration into one step method. In liquid phase at supercritical conditions, water displays a series of properties that make it an excellent solvent for organic compounds. As the temperature increase, the dielectric content of water decrease, enhancing its solvent properties. Other physicochemical properties of water, such as density, viscosity and surface tension, also decrease with temperature, so that it's dynamic characteristic improve, allowing a high degree of penetrability through porous solids. Thus, the adsorbate adsorbed on the surface of activated carbon will be dissolved into the water.

Regeneration efficiency is calculated from;

$$Regeneration\ efficiecy = \frac{Present\ adsorption\ capacity}{Previous\ adsorption\ capacity} \times 100\%$$

Table 5.5.2 and 5.5.3 show adsorption capacity and regeneration efficiency (%) and regeneration yield of activated carbons adsorbed with phenol and Red 31, respectively.

Table 5.5.2 Adsorption capacity, regeneration efficiency and regeneration yield of activated carbons adsorbed with phenol

Activated carbon	**Adsorption number**	**Adsorption capacity (mg/g AC)**	**Regeneration efficiency (%)**	**Regeneration yield (%)**
CAL carbon	1	173.76	-	-
	2	95.82	55.15	98.50
	3	94.74	98.87	98.48
Activated anthracite (AA)	1	178.17	-	-
	2	116.27	65.25	99.60
	3	115.64	99.45	97.34

From table 5.5.2 adsorption capacity of phenol on CAL carbon and activated anthracite in first adsorption are 173.76 and 178.17 mg/g AC, respectively. In 2nd and 3rd adsorption, adsorption capacity of CAL carbon and activated anthracite are about 96 and 117 mg/g AC, show 35 and 45% decrease in adsorption capacity. However the loss of activated carbon by this treatment can be neglected.

From table 5.5.3 adsorption capacity of Red 31 on CAL carbon and activated anthracite in the first adsorption are 140.14 and 5.91 mg/g AC, respectively. In 2nd and 3rd adsorption, adsorption capacity of CAL carbon and activated anthracite are about 110 and 19 mg/g AC, show about 22% decrease in adsorption capacity of CAL carbon, while about 300% increase of capacity in case of activated anthracite. As mentions above, loss of activated carbon from the treatment can be neglected.

Table 5.5.3 Adsorption capacity, regeneration efficiency and regeneration yield of activated carbons adsorbed with Red 31

Activated carbon	**Adsorption number**	**Adsorption capacity (mg/g AC)**	**Regeneration efficiency (%)**	**Regeneration yield (%)**
CAL carbon	1	140.14	-	-
	2	109.81	78.36	99.84
	3	110.46	100.59	97.32
Activated anthracite (AA)	1	5.91	-	-
	2	19.98	338.07	96.37
	3	18.71	93.64	97.58

From the results, it is clearly that both activated carbons can not be successive regeneration. Unlike, the results from J. Rivera-Utrilla, et al, 2003, which regenerated *ortho*-chlorophenol-exhausted activated carbons with supercritical water and F. Salvardor, et al, 2001, which regenerated several activated carbons exhausted with phenolic compounds, dyes and pesticides, that activated carbon was fully regenerated, even slightly improvement in the adsorption capacity was observed.

Owing to, the experiment in this study is batch process, which difference from continuous process in previous studied. (F. Solvador, et al 1999 and J. Rivera-Utrilla, et al, 2003), so the phase equilibrium of activated carbon-phenol / Red 31-supercritical water might occurred. Then, water as the solvent can not fully carry out the extraction (Phenol and Red 31) and regeneration efficiency is not reach 100% like continuous process. The adsorption capacity in adsorption cycle 2 and 3 also confirm that phase equilibrium between activated carbon - phenol / Red 31 – supercritical water is occurred.

In case of activated anthracite – Red 31 adsorption, regeneration efficiencies are about 330% in both regeneration cycles. It can be assumed that, due to few amount of Red 31 adsorbed on activated anthracite, so supercritical water can dissolve all the Red 31 and also extracted some organics compounds which obstructed the pores. Additionally, supercritical might also oxidize and enlarge some micropore to mesopore that is confirmed by the increase of mesopore volume observed in activated carbons treated by supercritical water reported in Chapter 5.4. . Hence, the adsorption capacity is about 3 times increase compare to 1st adsorption cycle.

Furthermore, it can be noticed that Red 31 can be regenerated from activated carbons easier than phenol, because phenol usually occurs chemical adsorption beside physical adsorption (J.M. Schork, et al, 1988).

However, regeneration efficiency of regenerating exhausted activated carbon by batch process supercritical water regeneration is higher than ethanol regeneration (Pisit Ariyadejwanich, et al, 2003). In regeneration of CAL carbon exhausted with phenol and Red 31 by ethanol, regeneration efficiencies are 50 – 60% and 18-23%, respectively, but regeneration efficiencies of CAL carbon exhausted with phenol and Red 31 regenerated by supercritical water are about 55% and 78%, respectively.

Therefore, regenerating exhausted activated carbon with supercritical water is preferable to conventional regeneration method, due to many advantages such as; very high regeneration efficiency, adsorption capacity remains constant even slightly increase and little losses of activated carbon during regeneration.