CHARPTER IV

Results and Discussions

In this study, the experiments are conducted in a fixed bed reactor. Commercial hydrotreating catalysts, $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts are used. Mercuric chloride and diphenylmercury are used as model compounds for inorganic and organic mercury, respectively. Toluene is used as a liquid carrier because of its high boiling point and good solubility for metal compounds. Initial concentration of mercuric chloride in each experiment is 10 ppm and that of diphenylmercury is 7 ppm (maximum solubility). The operating conditions used for hydrodemetallation reaction test are summarized in Table 4.1. The details of types of mercury compounds, catalysts, and operating temperatures of each experiment are presented in Table 4.2.

Table 4.1 Experimental Operating Conditions.

Operating conditions:	
Temperature	: 35°C, 150°C, 200°C and 250°C
Pressure	: 400 psig
LHSV	: 5 hr^{-1}
Hydrogen flow rate	: 30 cm^3/min
Catalyst weight	: 5 grams
Duration of experiments	: 24 hours for experiments 1 to 4 and experiments 12 to 15
	: 60 hours for experiments 5 to 11 and experiments 16 to 25
Sampling	: every 12 hours

Table 4.2 Details of Types of Mercury Compounds, Catalysts, and Operating Temperatures of Each Experiment.

Experimental numbers	Mercury compound	Catalyst	Temperature °C
1	Mercuric chloride	-	35
2	Mercuric chloride	-	150
3	Mercuric chloride	-	200
4	Mercuric chloride	-	250
5	Mercuric chloride	$CoMo/Al_2O_3$	150
6	Mercuric chloride	$CoMo/Al_2O_3$	200
7	Mercuric chloride	$CoMo/Al_2O_3$	200
8	Mercuric chloride	$CoMo/Al_2O_3$	250
9	Mercuric chloride	$NiMo/Al_2O_3$	150
10	Mercuric chloride	$NiMo/Al_2O_3$	200
11	Mercuric chloride	$NiMo/Al_2O_3$	250
12	Diphenylmercury	-	35
13	Diphenylmercury	-	150
14	Diphenylmercury	-	200
15	Diphenylmercury	-	250
16	Diphenylmercury	$CoMo/Al_2O_3$	150
17	Diphenylmercury	$CoMo/Al_2O_3$	200
18	Diphenylmercury	$CoMo/Al_2O_3$	250
19	Diphenylmercury	$CoMo/Al_2O_3$	250
20	Diphenylmercury	$NiMo/Al_2O_3$	150
21	Diphenylmercury	$NiMo/Al_2O_3$	200
22	Diphenylmercury	$NiMo/Al_2O_3$	200
23	Diphenylmercury	$NiMo/Al_2O_3$	250
24	-	$CoMo/Al_2O_3$	200
25	-	$NiMo/Al_2O_3$	200

The experiments are classified into three parts. The first part is the blank test experiment, experiments 1-4 and 12-15, which is conducted to study the adsorption of mercury on the reactor tube. The second part is experiments 6-7, 18-19, and 21-22, which is conducted to study the repeatability of the experiments at the conditions chosen. In the third part, hydrodemetallation reaction, experiments 5-11 and 16-25, is conducted to study the effect of the catalyst, temperature and type of mercury on removal of mercury compounds. The results of these experiments are presented in Appendix A. From the results of the experiments, the discussion can be classified into four sections:

Section 1. Analytical errors

Section 2. Blank test

Section 3. Experimental errors

Section 4. Removal of mercury by catalyst

4.1 Analytical Errors

In this study, mercury compounds are dissolved in liquid hydrocarbon. Therefore, the concentration of mercury in the sample can not be measured directly. It's necessary to digest and transfer the mercury compound in the sample to aqueous phase. In the process of digestion, there might be some errors occur in the experiments. Therefore, this section focuses on possible errors from digestion process. ASTM D 3223, which is a standard test method for determining the total of mercury in water, is applied to determine the concentration of mercury in liquid samples and spent catalysts. The flow injection analysis mercury hydride system of atomic absorption spectrometer from Perkin-Elmer is used to measure the mercury containing in aqueous phase. Each sample is analyzed twice in order to repeat the results. The reported concentration is the average concentration. The analysis of the calibration standard is conducted during and at the end of the experiment in order to checks the derivation of instruments. Thus, the errors of instruments can be neglected.

The errors associated with digestion procedure can be found by dividing the same solution into five samples. Each sample is digested and analyzed for mercury content. The errors are found in both mercuric chloride and diphenylmercury solutions.

$$\% \text{ Maximum error} = \frac{\text{maximum value} \left| \text{sample conc.} - \text{average conc.} \right|}{\text{average conc.}} * 100$$

The average value and maximum percentage of errors are calculated and listed in Table 4.3.

Table 4.3 Average Value and Maximum Percentage of Error.

Mercury type	Sample conc. (ppb)	Average conc. (ppb)	Maximum percentage of deviation
Mercuric chloride (1,000 ppb)	924, 955, 935, 932, 895	928	3.56
Diphenylmercury (1,000 ppb)	893, 855, 868, 814, 852	856	4.95

The average value of mercury concentrations that are analyzed in study of mercuric chloride is 928 ppb and that in the study of diphenylmercury is 856 ppb. The maximum percentage of error is 3.56% in the study of mercuric chloride and 4.95% in the study of diphenylmercury.

4.2 Blank Test

From the experiments, the material balance of mercury in the process is calculated from the quantity of mercury in the liquid feed, quantity of mercury in liquid product, and quantity of mercury deposited on catalysts. The material balance of mercury is calculated as following equation:

Quantity of mercury in feed = Quantity of mercury in the liquid product
+ Quantity of mercury deposited on the catalyst

The results of material balance calculation for each experiment are shown in Appendix B. It indicates that certain quantity of mercury does not either deposit on the catalyst or is present in liquid product. Careful investigation of the reactor system leads to the suspicious that mercury compound may deposit on the reactor tube wall.

Accordingly, the reactor tube operated with mercuric chloride and another tube operated with diphenylmercury were cut in various positions illustrated in Figure 4.1. They are analyzed to determine the quantity of deposited mercury on the reactor wall.

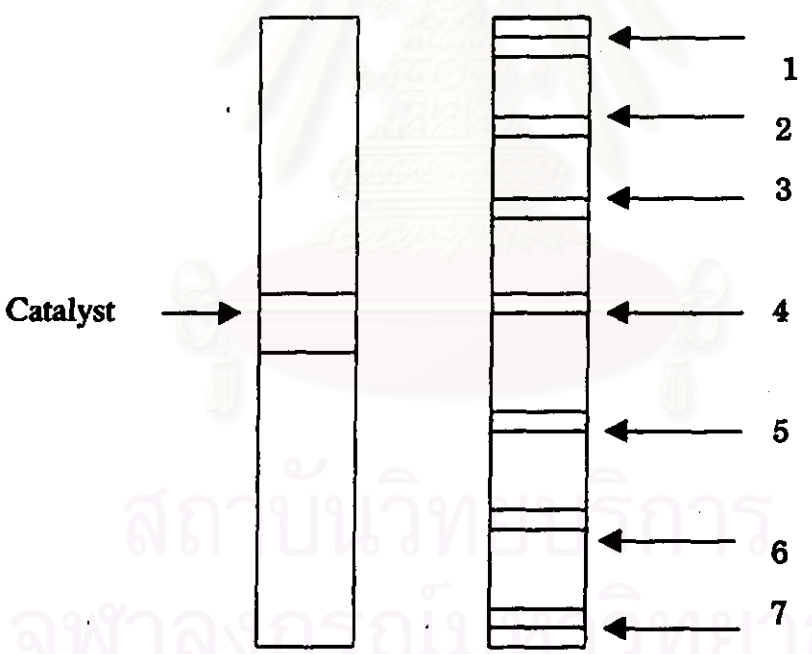


Figure 4.1 Positions analyzed in the reactor tube.

The results are shown in Appendix C. Figure 4.2 shows the distribution of deposited mercury on the reactor wall of mercuric chloride and diphenylmercury.

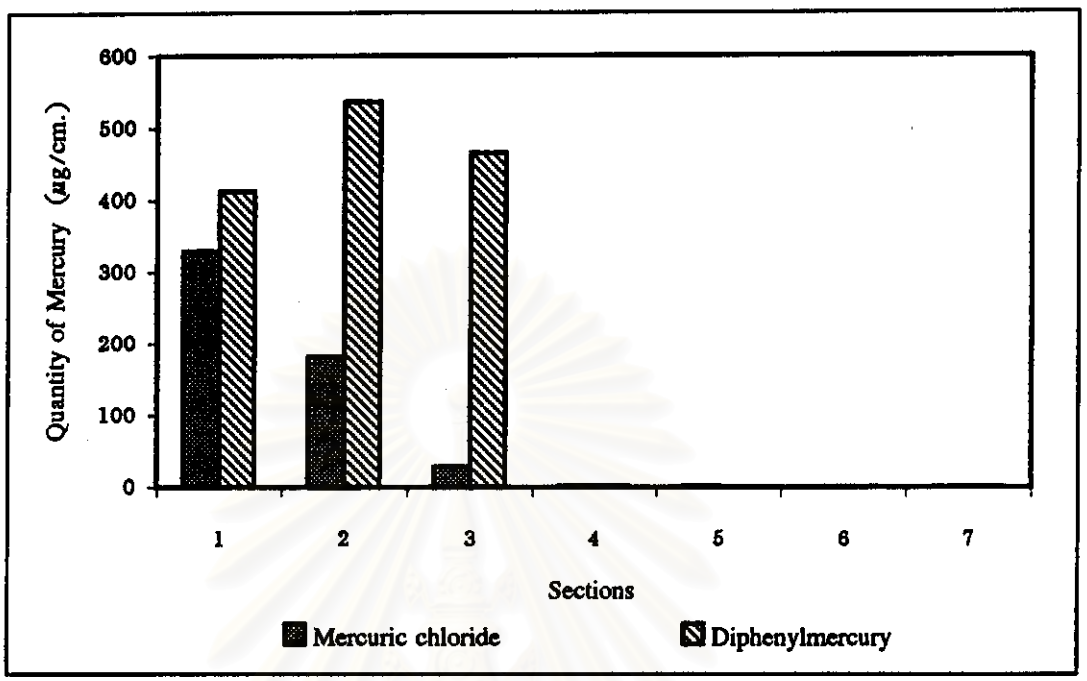


Figure 4.2 Distribution of deposited mercury on the reactor wall of mercuric chloride and diphenylmercury.

The results indicate that mercury does deposit on the reactor wall. Quantity of mercuric chloride adsorbed at the inlet of the reactor tube very high and gradually decreases along the tube length, while diphenylmercury shows its highest quantity at the position next to the reactor tube inlet.

As a result of the observation, the blank tests are conducted to study the deposition of mercury on the surface of the reactor tube. The blank tests of mercuric chloride are assigned to experiments 1 to 4 and the blank tests of diphenylmercury are assigned to experiments 12 to 15. The empty reactor is used to carry out the blank tests at the temperature of 35°C, 150°C, 200°C, and 250°C. The results are shown in the Table 4.4 and 4.5.

Table 4.4 Result of Blank Tests in Study of Mercuric Chloride.

Temperature (°C)	Feed (ppm)	Product (ppb)
35	10	560
150	10	329
200	10	214
250	10	127

Table 4.5 Result of Blank Tests in Study of Diphenylmercury.

Temperature (°C)	Feed (ppm)	Product (ppm)
35	7	6.460
150	7	3.420
200	7	1.050
250	7	0.496

The results show that the quantity of mercury compounds remaining in liquid at the reactor tube outlet are less than those in the feed stream. Considering the conditions of the experiment in with there are no catalyst packed inside the reactor tube, it indicates that mercury compounds adsorb on reactor wall. As indicate in Table 4.4 and 4.5, the quantity of mercury compounds remaining in liquid at the reactor tube outlet varies with temperature. It decreases as the temperature increases. In addition, the quantity of mercuric chloride remaining in liquid at reactor tube outlet is less than that of diphenylmercury even at room temperature. The material balance of the blank tests is shown in Appendix B. Figure 4.3 shows the comparison of percentages of the decrement of the quantity of mercury in the liquid product in study of the blank test between mercuric chloride and diphenylmercury at the temperature of 35°C, 150°C, 200°C, and 250°C.

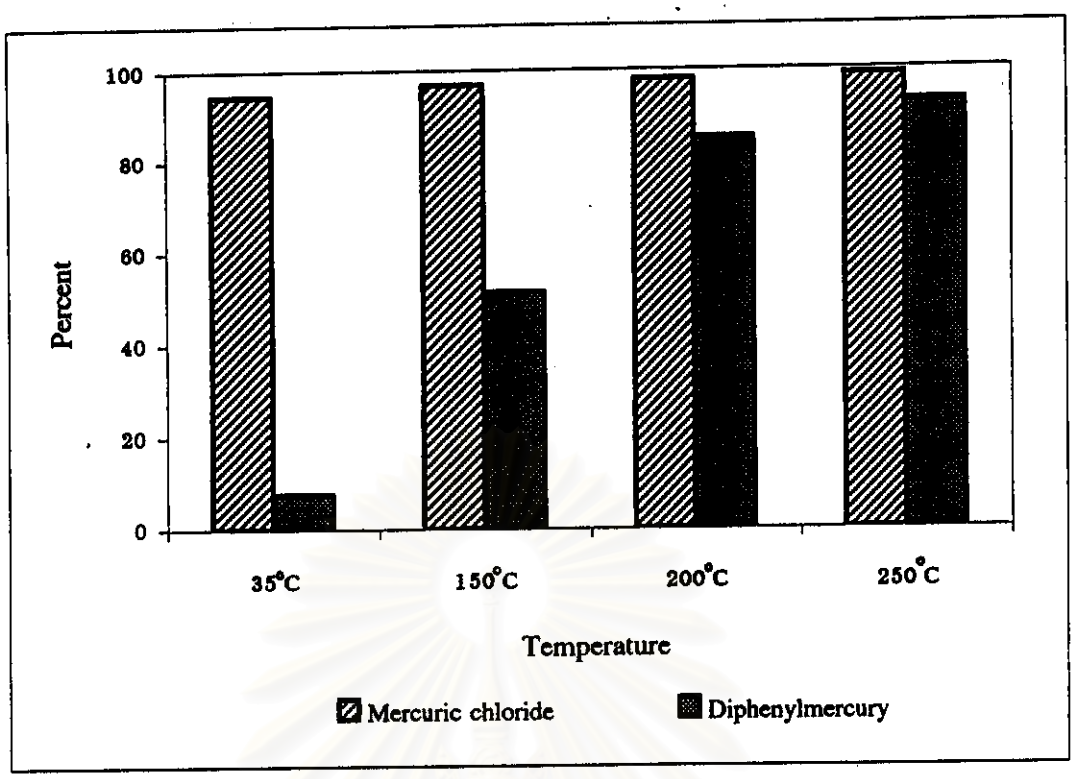


Figure 4.3 Comparison of percentages of the decrement of quantity of mercury in the liquid product in study of the blank tests between mercuric chloride and diphenylmercury at various temperatures.

It shows that the percentages of the decrement of quantity of mercuric chloride in the liquid at the reactor tube outlet are higher than of the diphenylmercury's, especially at room temperature. Since mercuric chloride can lose on the reactor tube wall very well even at room temperature, mercuric chloride may lose in the other parts of the feed system before reaching the reactor tube. Thus, the concentration of mercury in feed toluene containing mercuric chloride which flows through the high-pressure pump before reaching the reactor tube is measured. It is found that the remaining mercury concentration in toluene is only 1.45 ppm. It indicates that mercuric chloride lose easily on the surface of stainless steel. The electrochemistry and polarity can explain these results. In aqueous solution, the greater part of mercuric chloride ($HgCl_2$) is found to be undissociated into ionic form (Hg^{2+} and Cl^-) (Remy, 1995). It exists in the $HgCl_2$ or $(HgCl_2)_2$ forms (Biscarini et al.

1971). Therefore, in toluene, mercuric chloride also exists in $HgCl_2$ or $(HgCl_2)_2$ forms because toluene has less polarity than water. In addition, the stainless steel consists of nickel, chromium and iron. Thus, its surface is covered by chromium oxide film. The free electrons of oxide film are created by the imperfections and impurities in the lattice of the oxide film (Clark, 1970). The imperfections may due to nonstoichiometric composition or the presence of actual foreign-ion impurities. Therefore, the nonstoichiometric oxide film can give free electrons. The $HgCl_2$ which has high polarity can adsorb on the surface of the chromium oxide film by sharing the electron. Leeper (1980) studied the corrosion of mercury on stainless steel. He concluded that metallic mercury would disturb the oxide film and form an amalgam with chromium, iron, or nickel. Yan (1991) studied the reaction of trace mercury in natural gas with dilute polysulfide solutions in packed column. He presumed that stainless steel packing probably adsorbed and reacted with the mercury itself.

However, in case of diphenylmercury, the quantity of deposited mercury in the reactor depends on the temperature. Diphenylmercury have two aromatic rings, which are stable, because it has high resonance energy of π electron. As a result, the mercury is well adsorbed on the surface of stainless steel when it is dissociated into mercury atom. Yamada (1995) has been studied the removal of mercury compound. He found that when the temperature increases, mercury compounds could be decomposed and converted into elementary mercury at higher temperature. Diethylmercury, which has higher heat-resistance than the other mercury compounds, can be decomposed and converted to elementary mercury about 90% at temperature of 200°C. Diphenylmercury is organomercury like diethylmercury. Thus, when the temperature increases the bonds between mercury and carbons of diphenylmercury are broken to mercuric ion and organic compound. Then mercuric ion is adsorbed on the reactor wall. These reasons indicate that the deposition of diphenylmercury in the empty reactor tube depend on the temperature.

In addition, mercury may deposit on the reactor wall because the toluene may vaporize and the remained mercury compound deposit on surface of reactor tube at high temperature.

4.3 Experimental Errors

This section is conducted to verify repeatability of the experiments and to find error limits of the experiments. Experiment 6, 18, and 21 are repeated at the same condition to determine the percentage of deviation of the experiments. The results of these experiments are shown in Appendix A. The concentration of mercury remaining in liquid product, the average values, and the percentages of the deviation are calculated and listed in Table 4.6. The quantity of deposited mercury on catalyst per weight of the catalyst in each experiment, the average values, and percentage of the deviation are calculated and listed in Table 4.7. In addition, the surface area and the pore volume of the catalysts are measured by the BET method. The surface area and the pore volume of the catalyst in each experiment, the average values and percentages of the deviations are calculated and listed in Table 4.8 and 4.9.

$$\text{Percentage of the deviation} = \left| \frac{\text{value of sample 1} - \text{value of sample 2}}{\text{average value.}} \right| * 100$$

Table 4.6 Concentration of Mercury Remaining in Liquid Product, Average Values, and Percentage of Deviation.

Catalyst	Mercury compound	Temp. °C	Conc. of Hg in liq. product (ppb)	Average conc. (ppb)	Percentage of deviation (%)
CoMo	Mercuric chloride	200	85.1 88.5	86.8	3.92
CoMo	Diphenylmercury	250	226.7 237.9	232.3	4.82
NiMo	Diphenylmercury	200	266.7 251.8	259.2	5.75

Table 4.7 Amount of Deposited Mercury on Catalyst per Weight of Catalyst, Average Values, and Percentage of Deviation.

Catalyst	Mercury compound	Temp. °C	Quantity of Hg on catalyst (μg/g)	Average conc. (μg/g)	Percentage of deviation (%)
CoMo	Mercuric chloride	200	37.7 34.6	36.15	8.58
CoMo	Diphenylmercury	250	72.4 65.5	68.95	10.01
NiMo	Diphenylmercury	200	209.3 195.5	202.40	6.82

Table 4.8 Surface Area of Catalyst, Average Value and Percentage of Deviation.

Catalyst	Mercury compound	Temp. °C	Surface area of catalyst (sq.m/g)	Average value (sq.m/g)	Percentage of deviation (%)
CoMo	Mercuric chloride	200	85.96 87.84	86.90	2.16
CoMo	Diphenylmercury	250	83.60 88.02	85.81	5.15
NiMo	Diphenylmercury	200	133.60 137.34	135.47	2.76

Table 4.9 Pore Volume of Catalyst, Average Value and Percentage of Deviation.

Catalyst	Mercury compound	Temp. °C	Pore volume of catalyst (cc/g)	Average value (cc/g)	Percentages of deviation (%)
CoMo	Mercuric chloride	200	0.233 0.230	0.2315	1.30
CoMo	Diphenylmercury	250	0.215 0.221	0.2180	2.76
NiMo	Diphenylmercury	200	0.323 0.332	0.3275	2.75

4.4 Removal of Mercury Compounds by Hydrodemetallation

Removal of mercury compounds by hydrodemetallation is studied on the commercial catalysts, $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts. The experiments are conducted using operating conditions as indicated in Table 4.1. The efficiency of mercury compound removal is considered from the remaining mercury or concentration of mercury in liquid products and the quantity of deposited mercury on the catalysts. The liquid products and spent catalysts are analyzed to determine the quantity of mercury and the results of each experiment are shown in Appendix A.

It is concluded earlier in this chapter that mercury compounds, mercuric chloride and diphenylmercury, adsorb on the reactor wall and on other parts of the reactor system. The quantity of adsorbed mercury depends on the types of mercury compounds and temperatures, and it leads to the loss of certain quantity of the mercury compounds from the liquid hydrocarbons to the reactor system before it reaches the catalyst bed. It will be assumed in this study that concentration of mercury compounds found in liquid product of the blank tests are the concentrations of mercury compounds entering the catalyst bed at operating temperatures and is summarized in Table 4.10.

Table 4.10 Concentration of Mercury Remaining in Liquid Product of Blank Test.

Temperature ($^{\circ}C$)	Mercuric chloride (ppb)	Diphenylmercury (ppb)
35	560	6,460
150	329	3,420
200	214	1,050
250	127	496

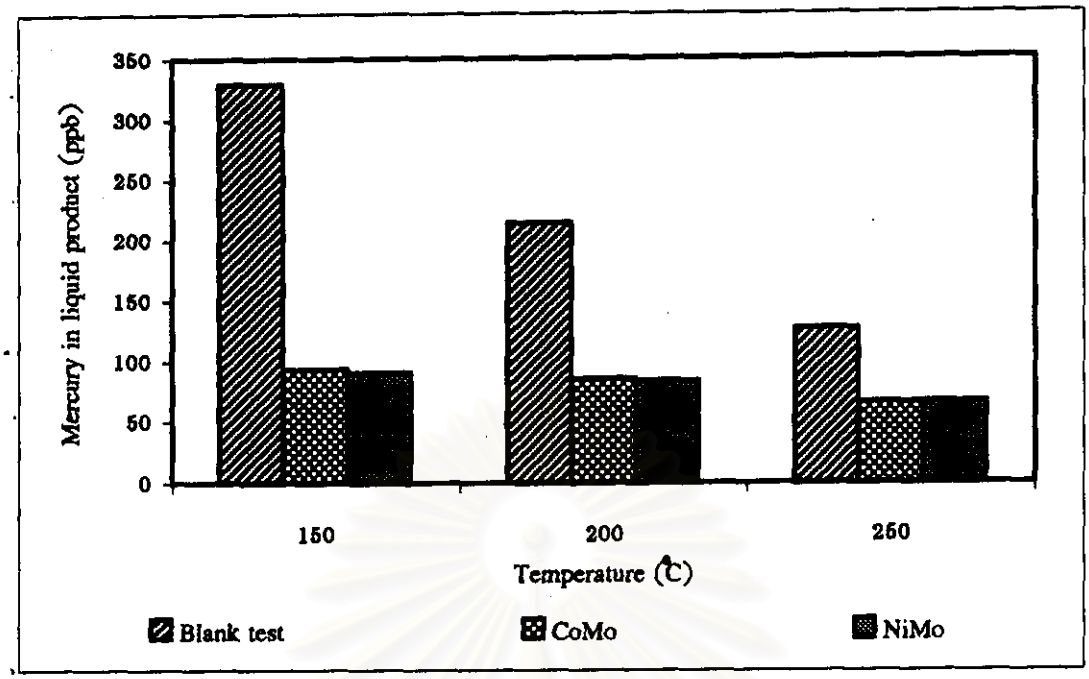


Figure 4.4 Comparison of quantity of mercury remaining in liquid product between blank tests and hydrodemetallation tests in study of mercuric chloride.

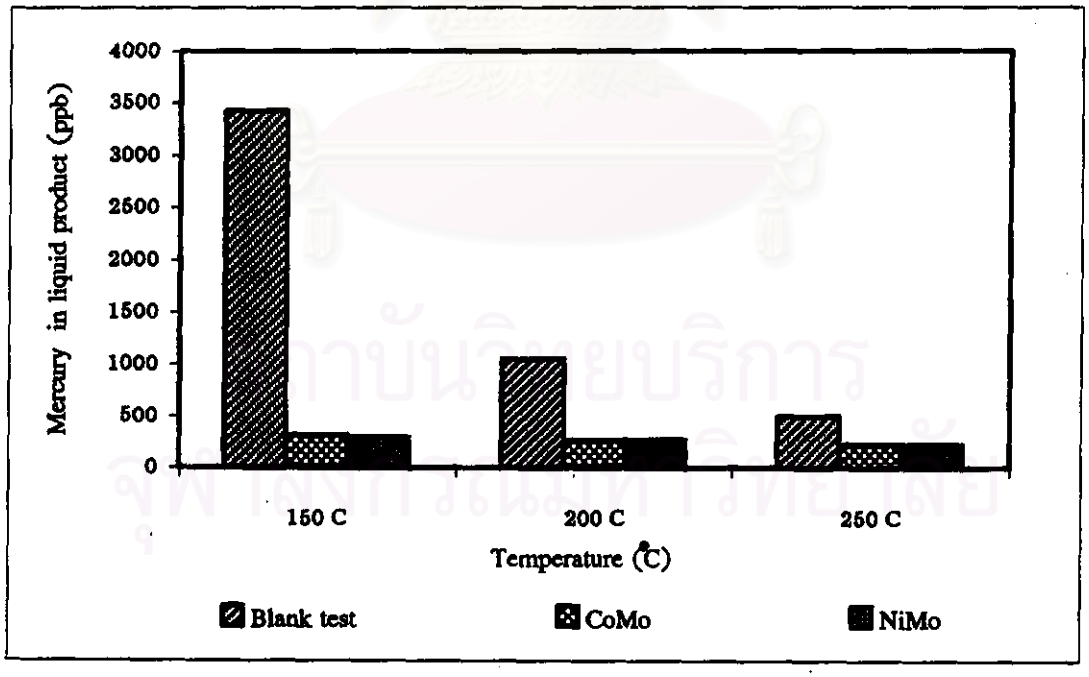


Figure 4.5 Comparison of quantity of mercury remaining in liquid product between blank tests and hydrodemetallation tests in study of diphenylmercury.

Figures 4.4 and 4.5 show the comparisons of the quantity of mercury remaining in liquid products between the blank tests and hydrodemetallation reaction tests. It can be observed that the remaining mercury in liquid products of hydrodemetallation reaction is less than that of the blank test at every temperature. Analysis of the catalyst samples also show certain quantity of mercury on the catalysts. It indicates that the catalysts can effectively be used to remove mercury compounds from liquid hydrocarbon. The mechanisms of hydrodemetallation of mercuric chloride and diphenylmercury by use of sulfided $CoMo/Al_2O_3$ and sulfided $NiMo/Al_2O_3$ catalysts are not well known. However, from the literature, it was found that mercury could easily react with sulfur to form HgS

$$Hg + S \longrightarrow HgS$$

Therefore, we can postulate the hydrodemetallation reaction, according to

In case of mercuric chloride

$$HgCl_2 + H_2 + S\text{-Catalyst} \longrightarrow HgS\text{-Catalyst} + 2HCl$$

In case of diphenylmercury

$$(C_6H_5)_2Hg + H_2 + S\text{-Catalyst} \longrightarrow HgS\text{-Catalyst} + 2C_6H_6$$

Figures 4.6 and 4.7 show comparisons of quantity of deposited mercury on the catalysts per weight of the catalyst between the $CoMo/Al_2O_3$ and the $NiMo/Al_2O_3$ catalysts. Since, the surface area of $CoMo/Al_2O_3$ is different from $NiMo/Al_2O_3$ catalyst, the quantity of deposited mercury on the catalyst per surface area of catalyst is considered. Figures 4.8 and 4.9 show the comparisons of the quantity of deposited mercury on the catalyst per surface area of the catalyst between $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts. It indicates that the quantity of deposited mercury on the catalyst per surface area of the catalyst of $CoMo/Al_2O_3$ catalyst is similar to that of $NiMo/Al_2O_3$ catalyst. Therefore, it is suspected that the efficiency of $CoMo/Al_2O_3$ and of $NiMo/Al_2O_3$ catalysts on mercury compounds removal are similar.

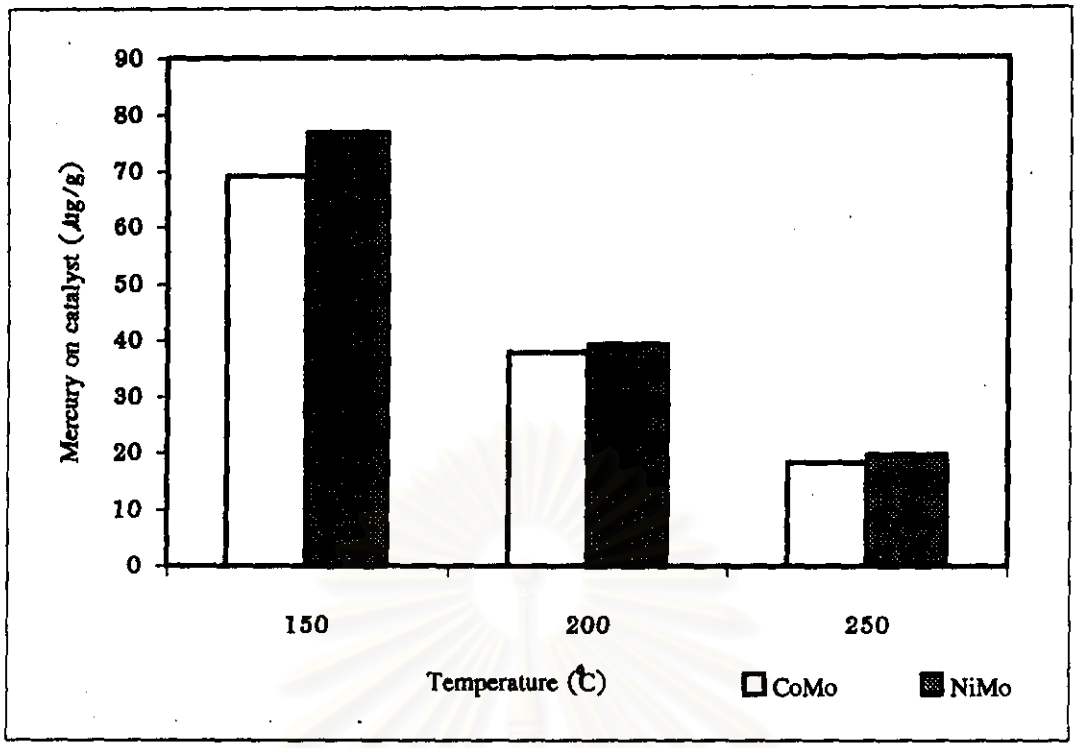


Figure 4.6 Comparison of quantity of deposited mercury on catalysts per weight of catalyst between $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts in study of mercuric chloride.

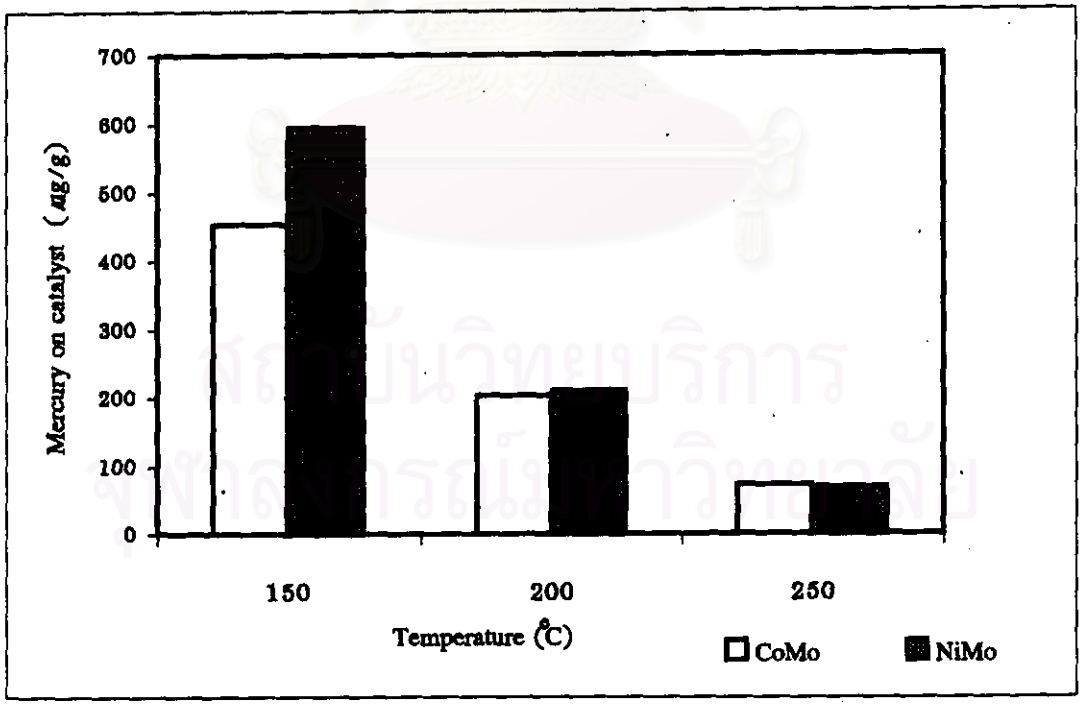


Figure 4.7 Comparison of quantity of deposited mercury on the catalysts per weight of catalyst between $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts in study of diphenylmercury.

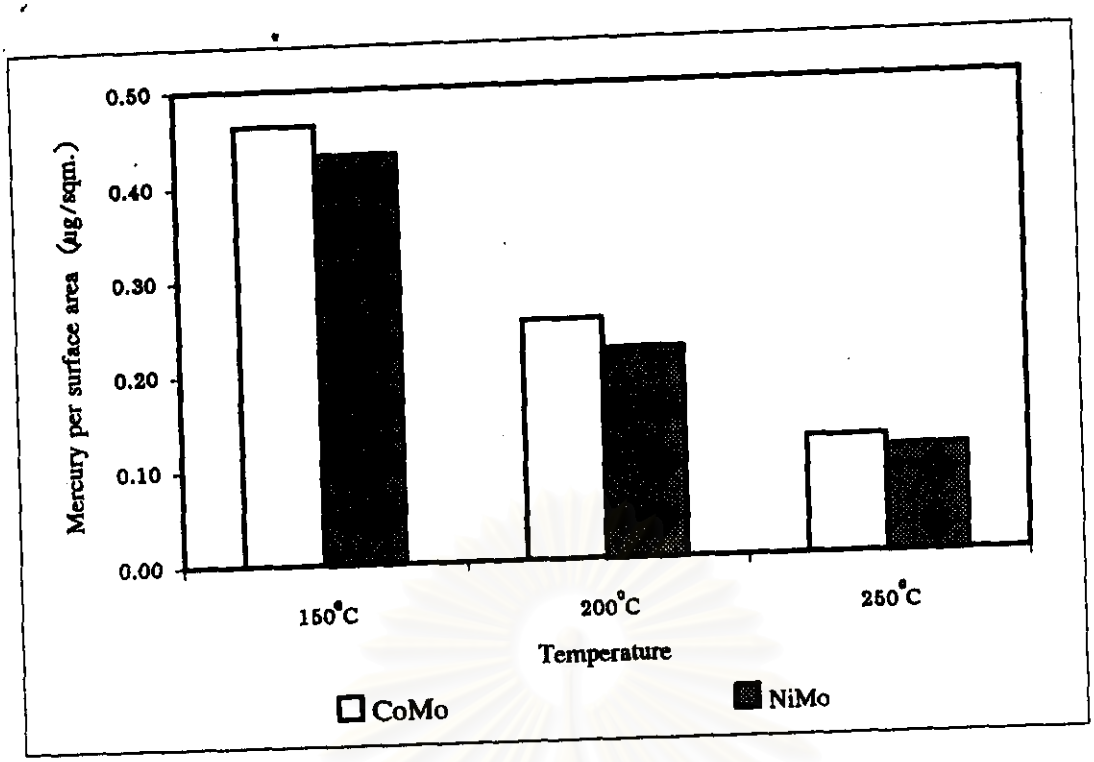


Figure 4.8 Comparison of the quantity of deposited mercury on the catalyst per surface area of the catalyst between $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalyst in study of mercuric chloride.

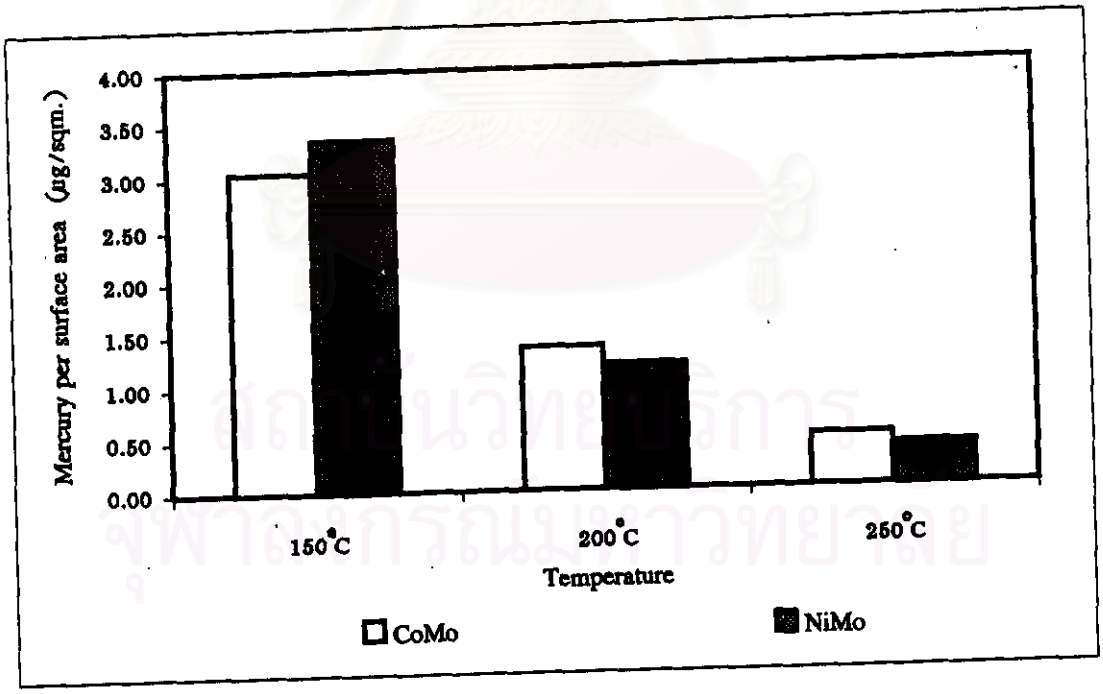


Figure 4.9 Comparison of the quantity of deposited mercury on the catalyst per surface area of the catalyst between $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalyst in study of diphenylmercury.

Table 4.11 Material Balance of Mercuric chloride.

Catalyst	Temp °C	Feed (ppb)	quantity of Mercury in Feed 60 hr. (µg)	Product (ppb)	quantity of Mercury in Product 60 hr. (µg)	quantity of Mercury Removed	Mercury in Cat (µg/g)	quantity of Mercury in Cat.(µg)
CoMo	150	329	598.3	93.2	169.5	428.8	69.1	345.5
	200	214	389.2	85.1	154.8	234.4	37.7	188.5
	250	127	231.0	65.5	119.1	111.8	18.2	91.0
NiMo	150	329	598.3	90.7	164.9	433.4	76.7	383.5
	200	214	389.2	83.5	151.9	237.3	39.1	195.5
	250	127	231.0	66.2	120.4	110.6	19.6	98.0

Table 4.12 Material Balance of Diphenylmercury.

Catalyst	Temp °C	Feed (ppb)	quantity of Mercury in Feed 60 hr. (µg)	Product (ppb)	quantity of Mercury in Product 60 hr. (µg)	quantity of Mercury Removed	Mercury in Cat (µg/g)	quantity of Mercury in Cat.(µg)
CoMo	150	3420	6219.6	311.8	567.0	5652.6	453.4	2267.0
	200	1050	1909.5	263.1	478.5	1431.1	202.6	1013.0
	250	496	902.0	226.7	412.3	489.7	72.4	362.0
NiMo	150	3420	6219.6	293.3	533.4	5686.2	594.5	2972.5
	200	1050	1909.5	266.7	485.0	1424.5	209.3	1046.5
	250	496	902.0	225.3	409.7	492.3	68.4	342.0

Furthermore, these results indicate that the quantity of mercury remaining in liquid products and deposited on catalysts in each experiment depends on the temperatures. However, in this study, the relationship between the quantities of mercury compound removal and the temperatures can not be clearly defined because the concentration of mercury compound in liquid hydrocarbons, which flow through the catalyst bed at various temperatures, are different. Material balances of mercury are calculated for each experiment and are presented in Tables 4.11 and 4.12. The results show that the quantity of mercury remaining in liquid products in study of mercuric chloride is less than of diphenylmercury's. However, the quantity of deposited mercury in liquid products in study of mercuric chloride is less than of diphenylmercury's. Thus, the capability of each catalyst to remove each type of mercury compounds can not be clearly distinguished because the concentration of mercury compound in liquid hydrocarbons, which flow through the catalyst bed at various temperatures, are different.

The fresh and spent catalysts are characterized by BET method to determine the surface area, pore volume, and pore size distribution. The results are shown in Appendix D.

Hydrodemetallation is one of the reactions in hydrotreating process, such as hydrogenation and hydrogenolysis reaction can occur simultaneously at the same time of hydrodemetallation reaction and lead to formation of carbonaceous compound, called coke, on the surface of the catalyst resulting in reduction of surface area and pore volume of catalyst. Therefore, the non-mercury experiments in which $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts are used and conducted by using toluene without adding mercury at the temperature of 200°C. The catalysts of the non-mercury experiments are used as reference catalysts to be compared with spent catalysts of mercury removal experiments in order to investigate the effect of mercury deposition on the surface area and pore volume of catalysts.

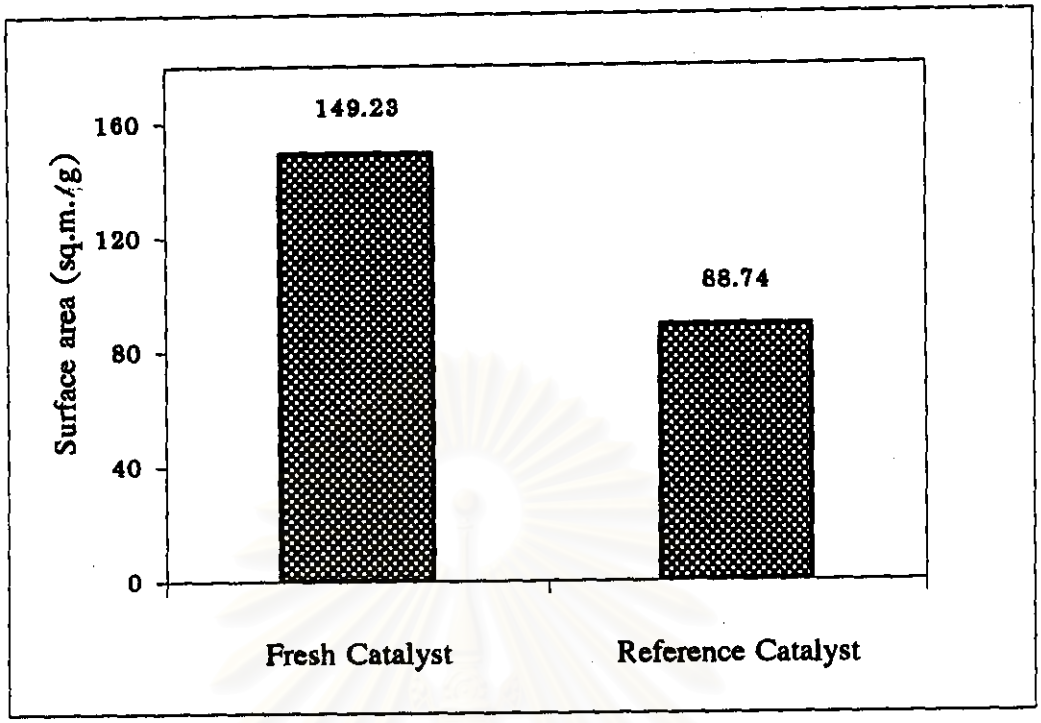


Figure 4.10 Comparison of surface area between fresh and reference $CoMo/Al_2O_3$ catalysts.

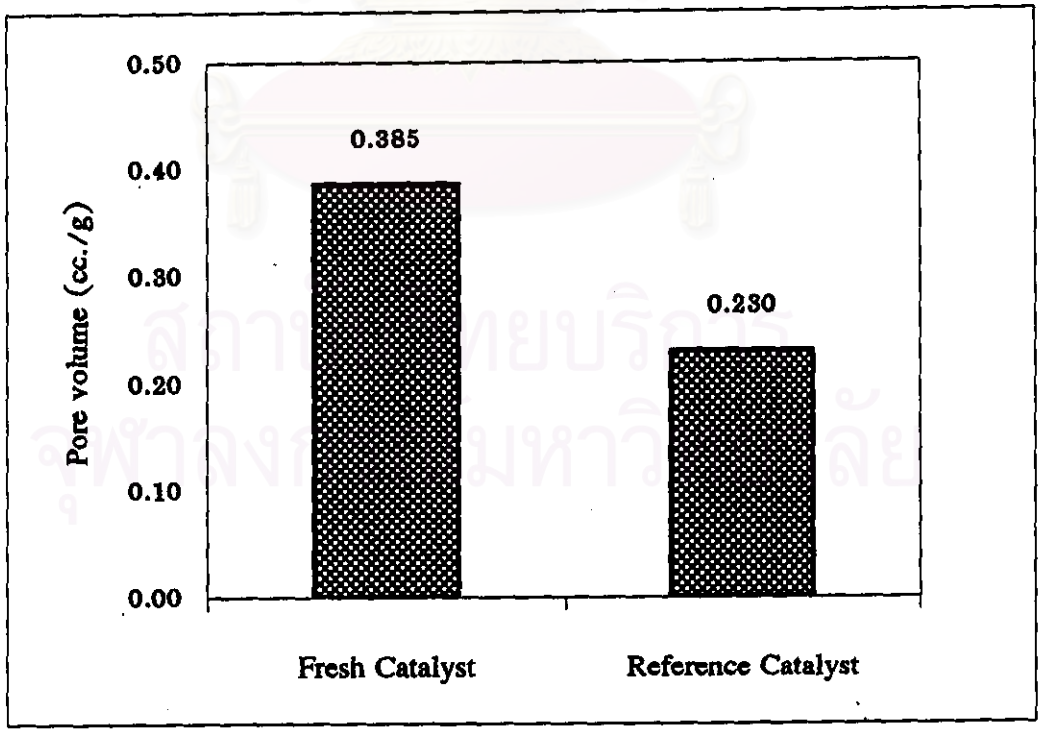


Figure 4.11 Comparison of pore volume between fresh and reference $CoMo/Al_2O_3$ catalysts.

Figures 4.10 and 4.11 show the comparisons of the surface area and pore volume between fresh and reference $CoMo/Al_2O_3$ catalysts. It is found that the surface area of reference $CoMo/Al_2O_3$ catalyst decreases from 149.23 m^2/g to 88.74 m^2/g comparing with fresh catalyst. This corresponds to a decrease of 40.23% in surface area. The pore volumes of reference $CoMo/Al_2O_3$ catalysts decreases from 0.385 cm^3/g to 0.230 cm^3/g with respect to fresh catalyst. This corresponds to a decrease of 40.40% in pore volume.

Figures 4.12 and 4.13 show the comparisons of the surface area and the pore volume between fresh and reference $NiMo/Al_2O_3$ catalysts. It indicates that the surface area of reference $NiMo/Al_2O_3$ catalyst decreases from 177.43 m^2/g to 160.49 m^2/g with respect to fresh catalyst, corresponding to 9.55% of decreasing of surface area. Furthermore, the pore volume of reference $NiMo/Al_2O_3$ decreases from 0.462 cm^3/g to 0.350 cm^3/g comparing with fresh catalyst. This corresponds to 24.37% of decreasing of pore volume. It can be concluded that the formation of carbonaceous compound reduces both surface area and pore volume of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts.

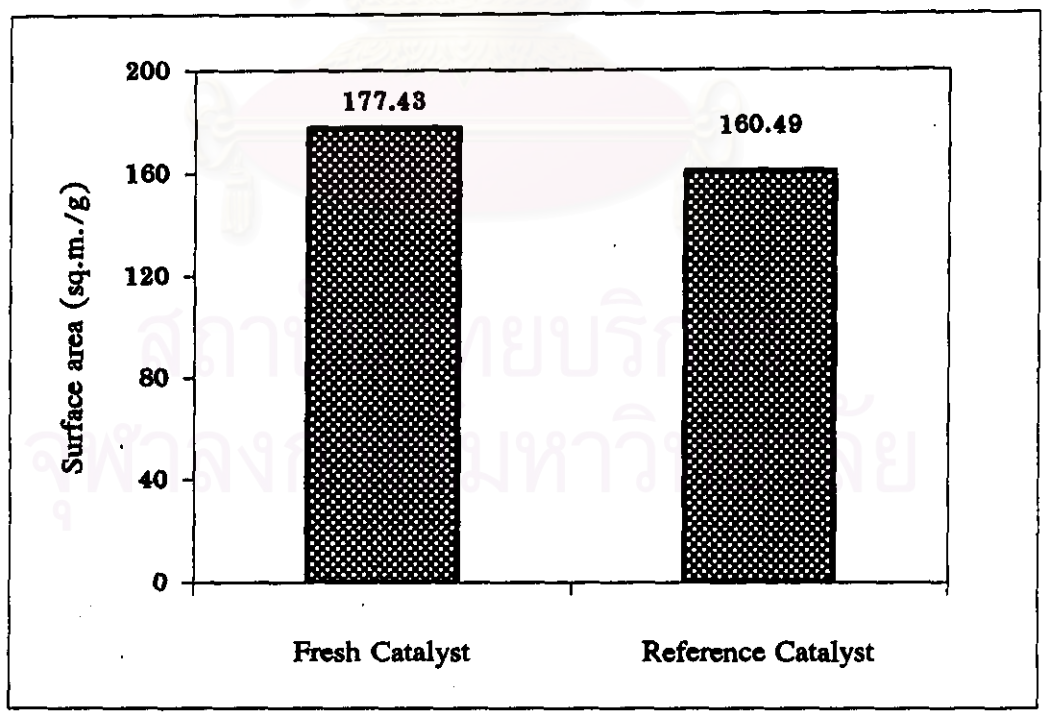


Figure 4.12 Comparison of surface area between fresh and reference $NiMo/Al_2O_3$ catalysts.

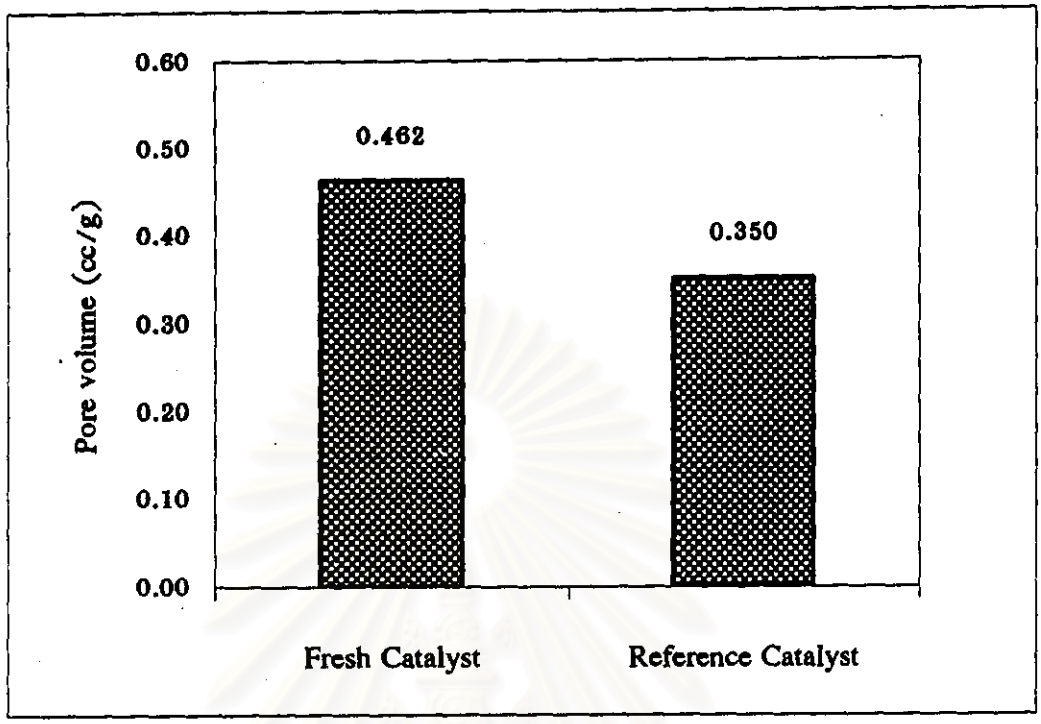
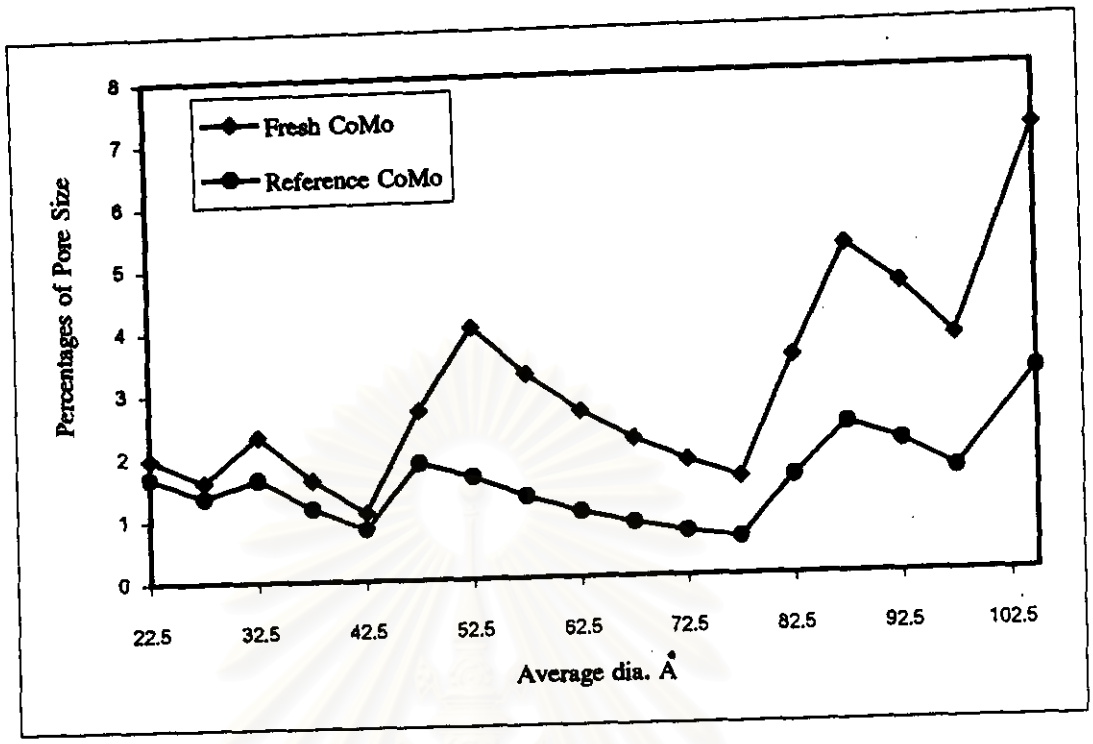


Figure 4.13 Comparison of the pore volume between fresh and reference $NiMo/Al_2O_3$ catalysts.

The pore size distribution between fresh and reference $CoMo/Al_2O_3$ is shown in Figure 4.14. It shows that the pore size between 22.5 A° and 330 A° decrease while the pore size which larger than of 330 A° do not change. In addition, the comparison of the pore size distribution between fresh and reference $NiMo/Al_2O_3$ catalyst is shown in Figure 4.15. It can be observed that some pore sizes ranging from 30 A° to 230 A° is decreased and the pore size which are smaller than of 30 A° increase significantly. This reason can be explained to the reduction of large pore size to small pore size. Additionally, the pore sizes which are larger than of 205 A° do not change.



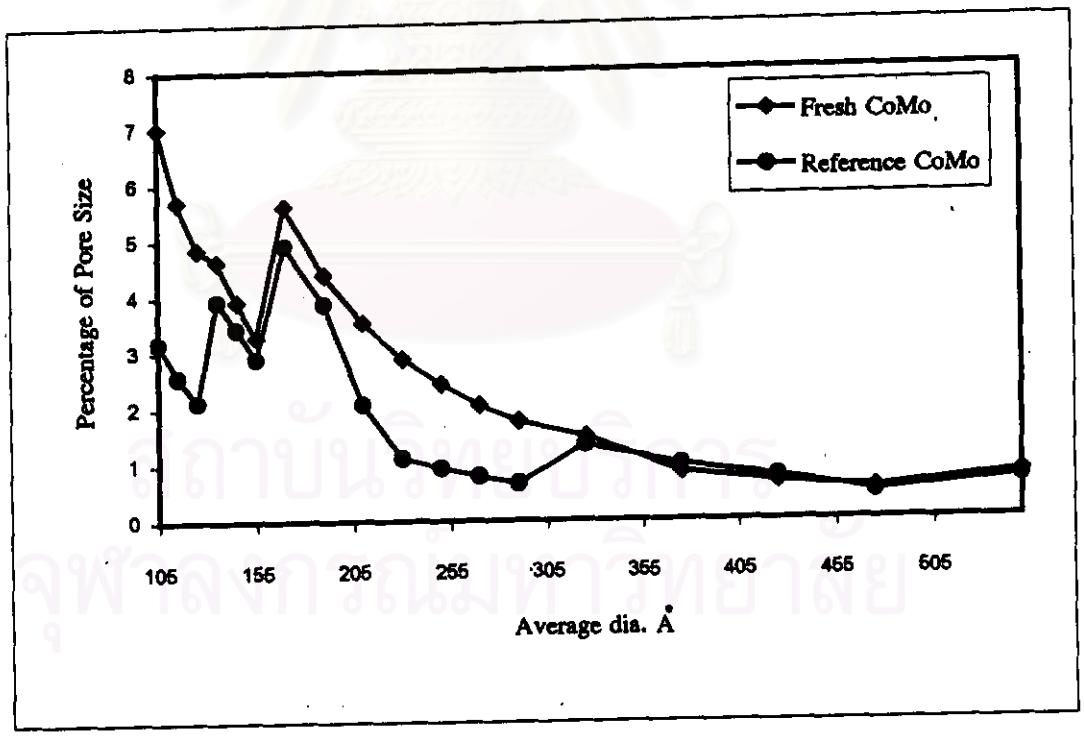
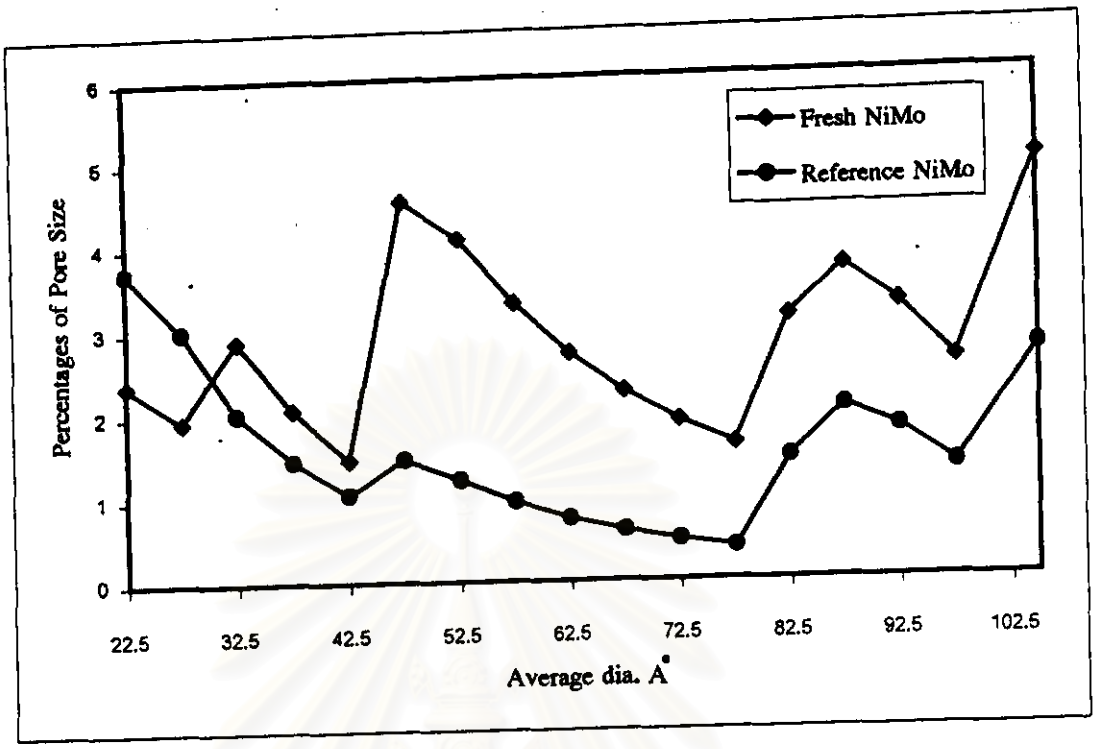


Figure 4.14 Comparison of the pore size distribution between fresh and reference $CoMo/Al_2O_3$ catalyst.



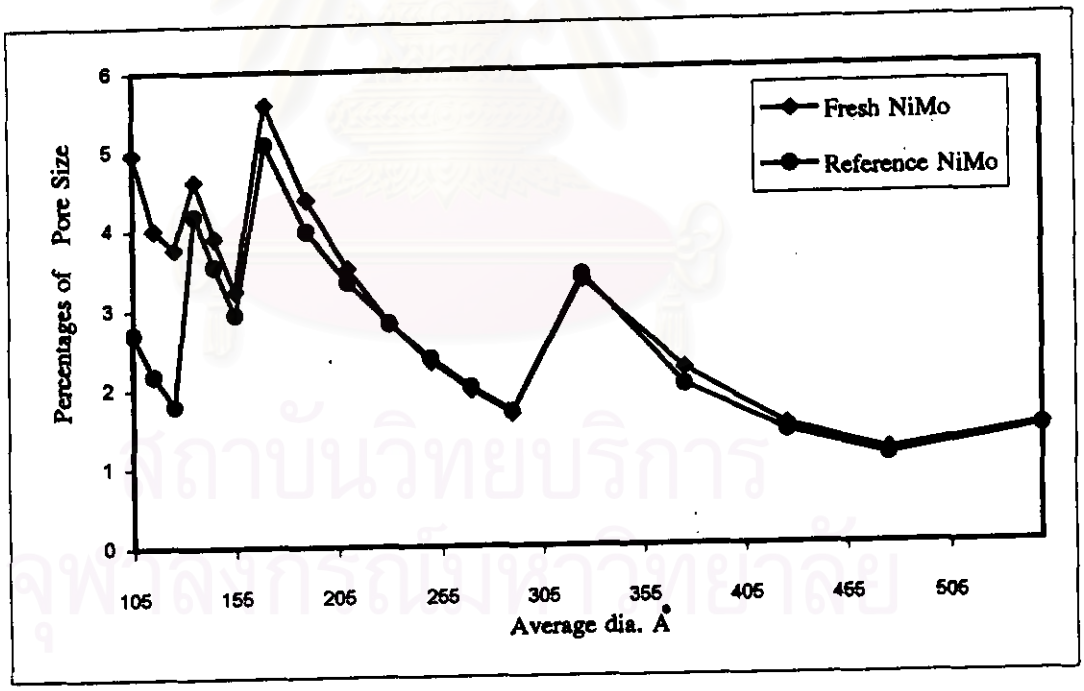


Figure 4.15 Comparison of the pore size distribution between fresh and reference NiMo/Al_2O_3 catalyst.

The comparisons of the surface area and the pore volume between fresh and spent $CoMo/Al_2O_3$ catalysts which are used to remove mercury compounds by hydrodemetallation at various temperatures are shown in Figures 4.16 and 4.17. The comparisons of the surface area and the pore volume between fresh and spent $NiMo/Al_2O_3$ catalysts which are used to remove mercury compounds by hydrodemetallation at various temperatures are shown in Figures 4.18 and 4.19. It is found that both surface area and pore volume of spent $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts which are used to remove mercury compounds at various temperatures decrease with respect to fresh $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts for all temperatures and mercury compounds. However, the decrease of the surface area and the pore volume of spent catalysts are almost similar to the reference catalysts, which are conducted with toluene without mercury at the temperature of 200°C. It can be explained that the quantity of mercury deposited on spent catalysts at various temperatures is not sufficiency high.

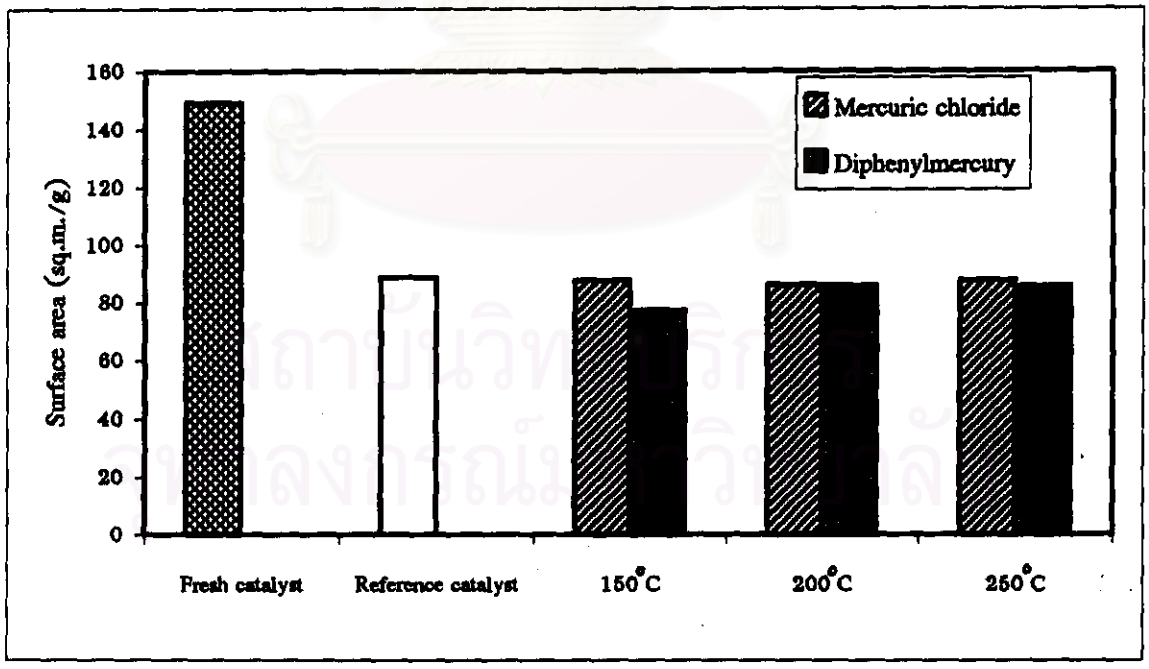


Figure 4.16 Comparison of the surface area between fresh and spent $CoMo/Al_2O_3$ catalysts in study of mercuric chloride and diphenylmercury at various temperatures.

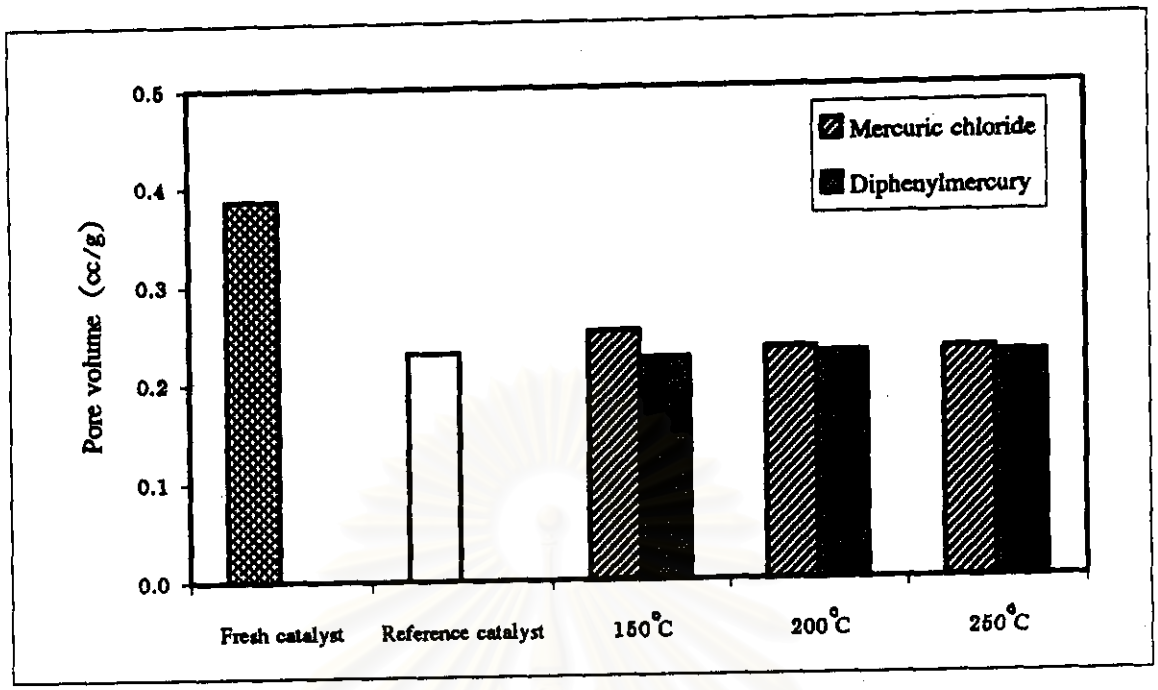


Figure 4.17 Comparison of pore volume between fresh and spent $CoMo/Al_2O_3$ catalysts in study of mercuric chloride and diphenylmercury at various temperatures.

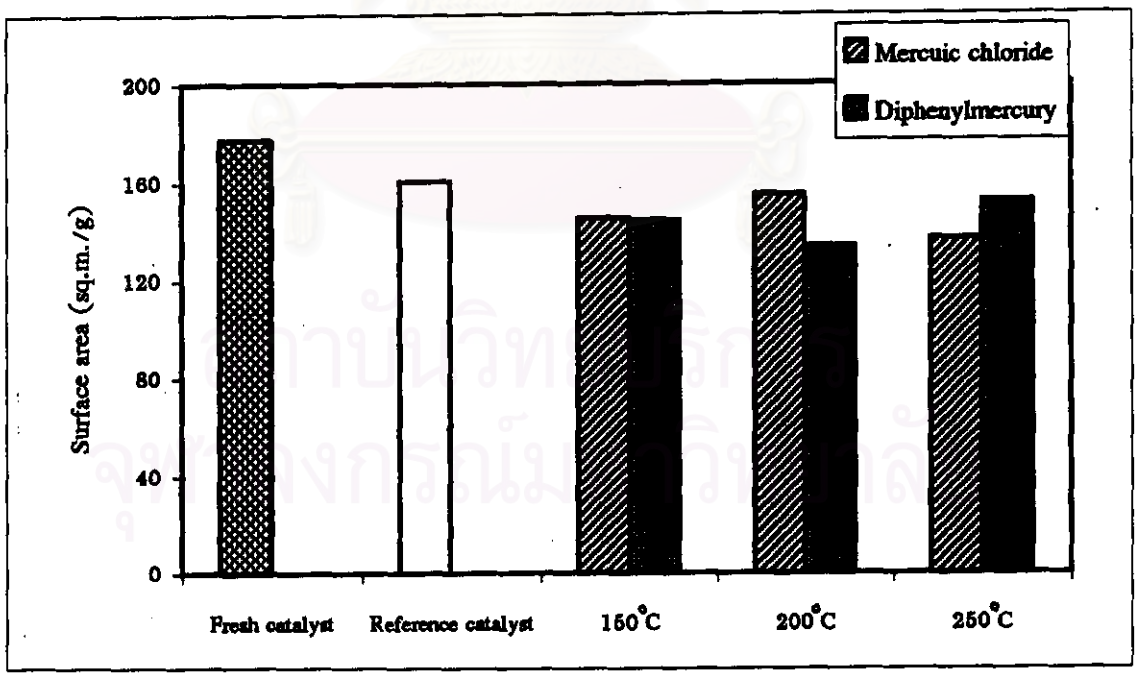


Figure 4.18 Comparison of the surface area between fresh and spent $NiMo/Al_2O_3$ catalyst in study of mercuric chloride and diphenylmercury at various temperatures.

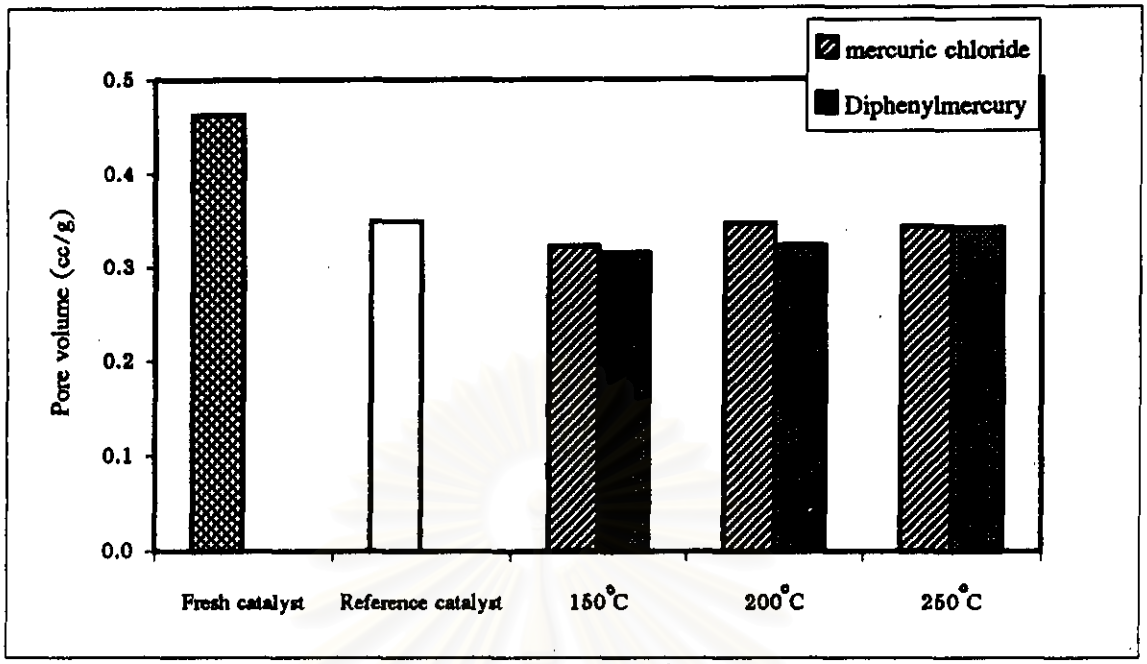
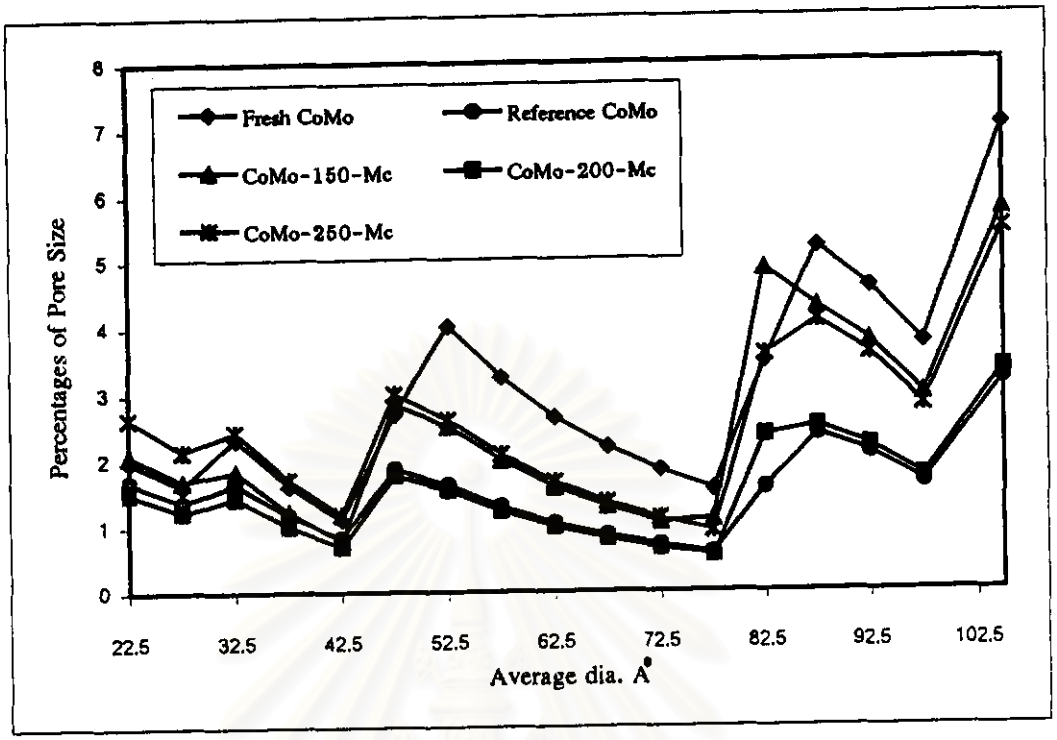


Figure 4.19 Comparison of pore volume between fresh and spent $NiMo/Al_2O_3$ catalyst in study of mercuric chloride and diphenylmercury at various temperatures.

The comparisons of pore size distribution between fresh and spent $CoMo/Al_2O_3$catalysts are shown in Figure 4.20-4.21. The comparisons of pore size distribution between fresh and spent $NiMo/Al_2O_3$ catalysts are shown in Figure 4.22-4.23. The results show that there is significant difference of the pore size distribution between them. However, the pore size distribution of reference catalysts which are conducted with the toluene without mercury compound at the temperature of 200°C are similar to the spent catalysts which are conducted in the removal of mercury compounds at the temperature of 200°C. It can be explained that the quantity of deposited mercury on catalyst, which are conducted in the removal of mercury compounds at various temperatures, are not sufficiently high to show the effect of mercury deposition on the catalysts. The spent catalysts are analyzed to investigate the form of mercury compound by X-ray Diffraction (XRD). It agrees with the above mention, XRD can not show the distinctive result of mercury forms because the quantity of mercury in the catalyst is not high enough.



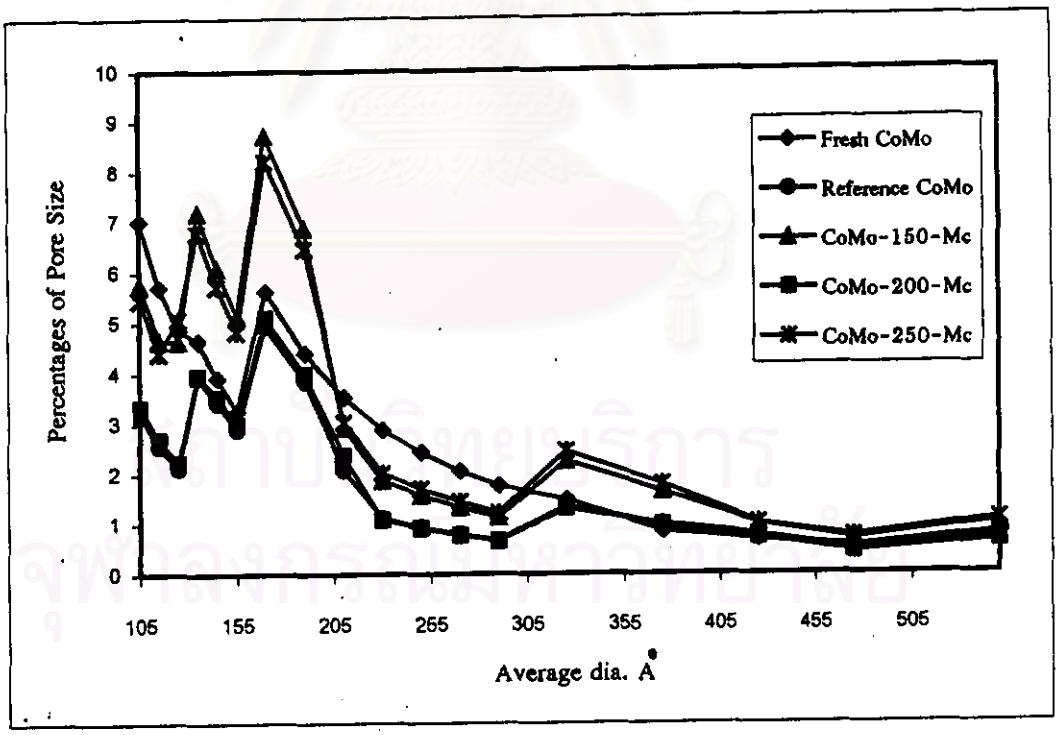
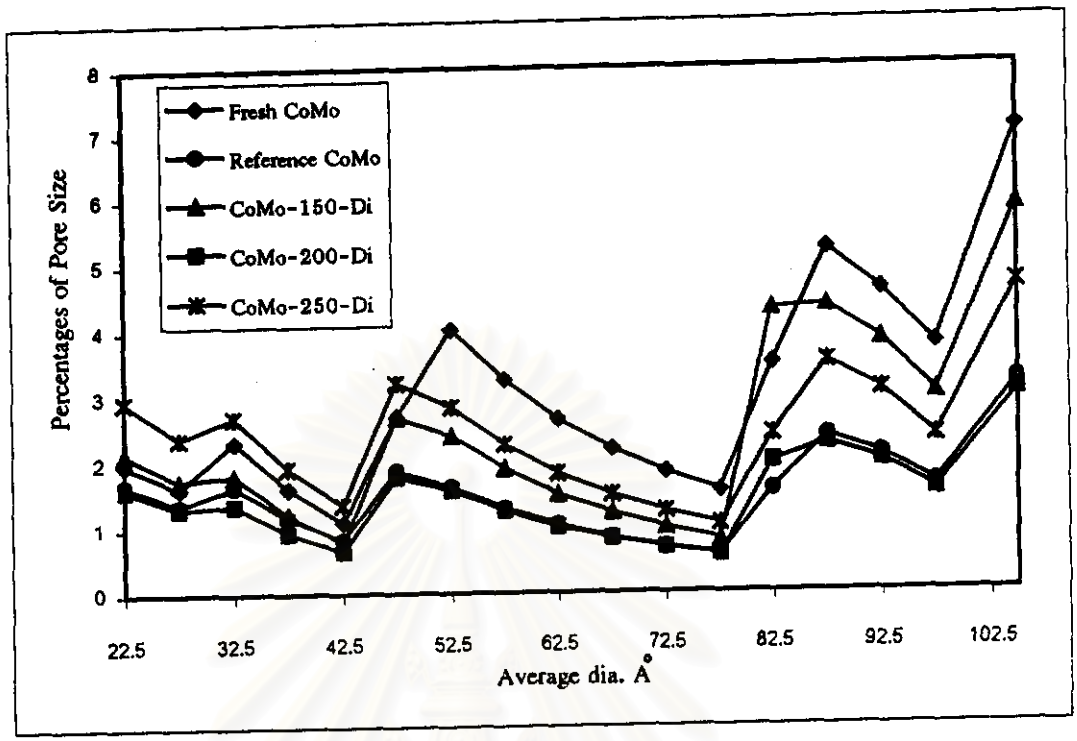


Figure 4.20 Comparisons of the pore size distribution between fresh and spent $CoMo/Al_2O_3$ catalysts in study of mercuric chloride.



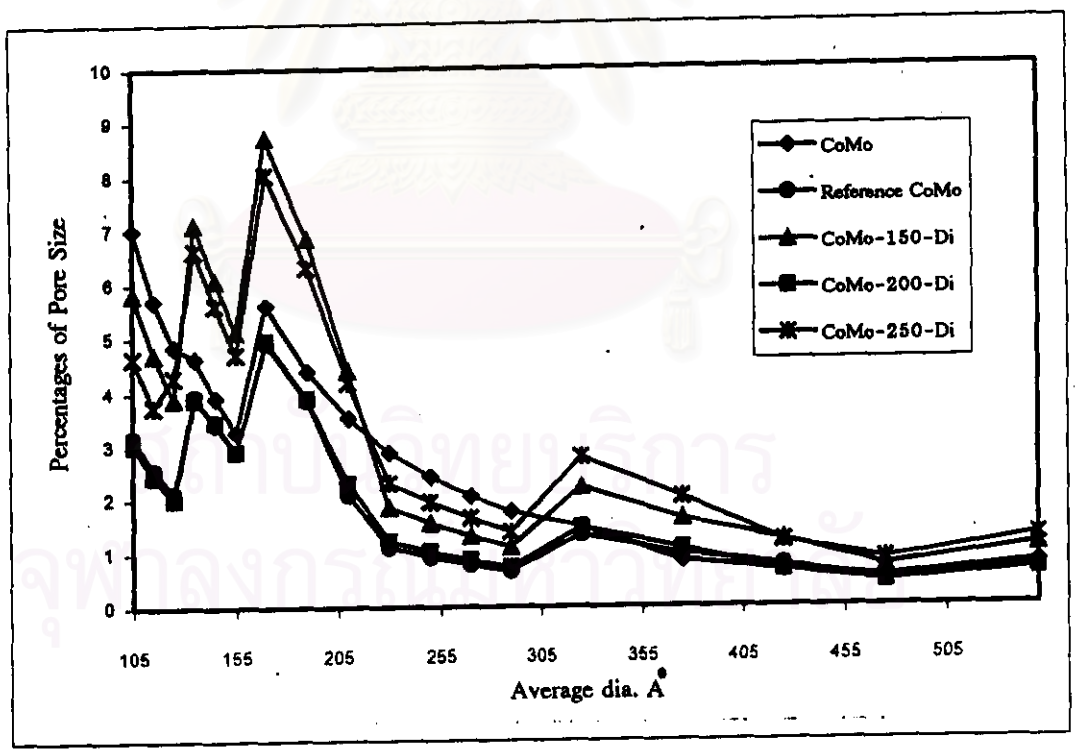
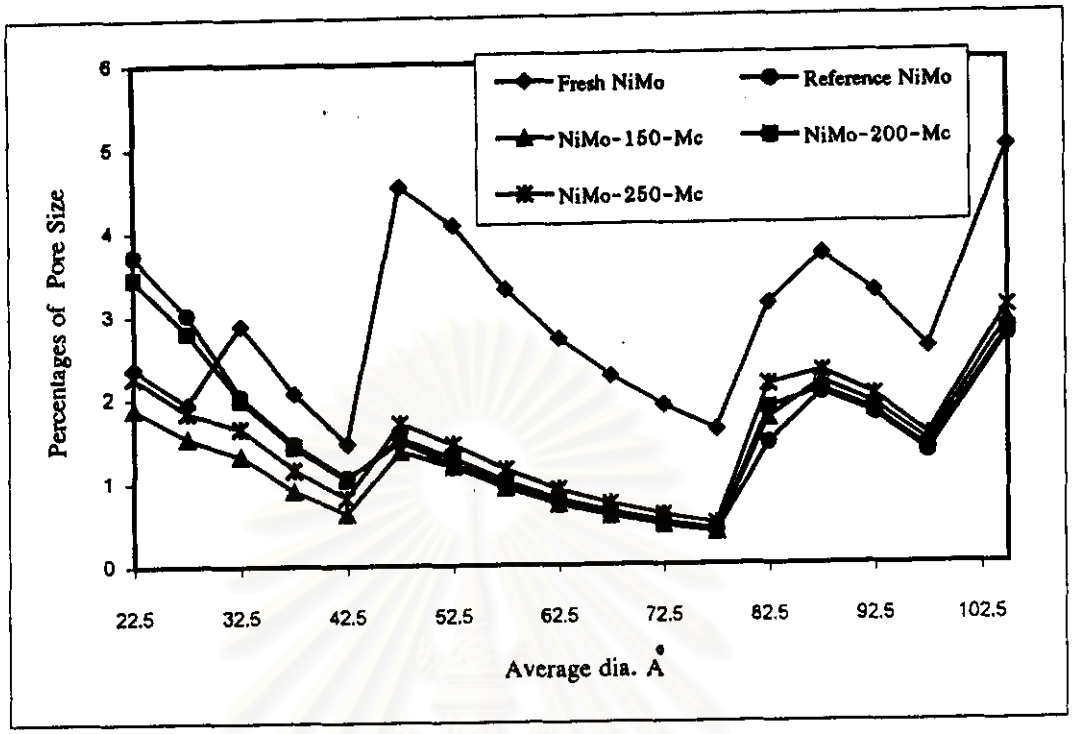


Figure 4.21 Comparisons of the pore size distribution between fresh and spent $CoMo/Al_2O_3$ catalysts in study of diphenylmercury.



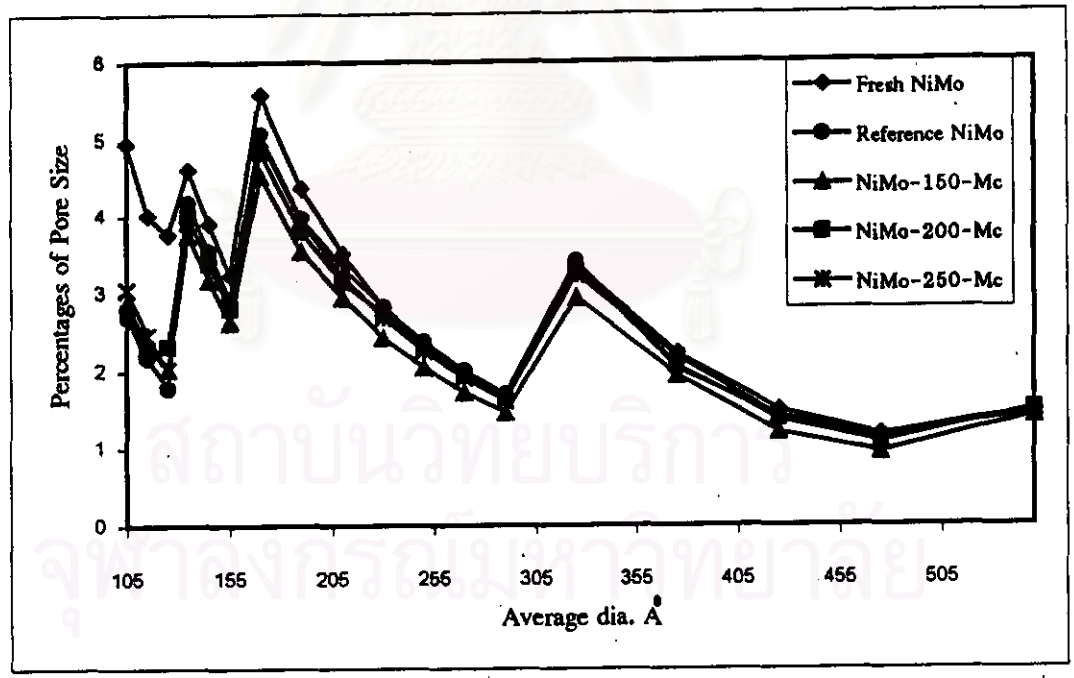
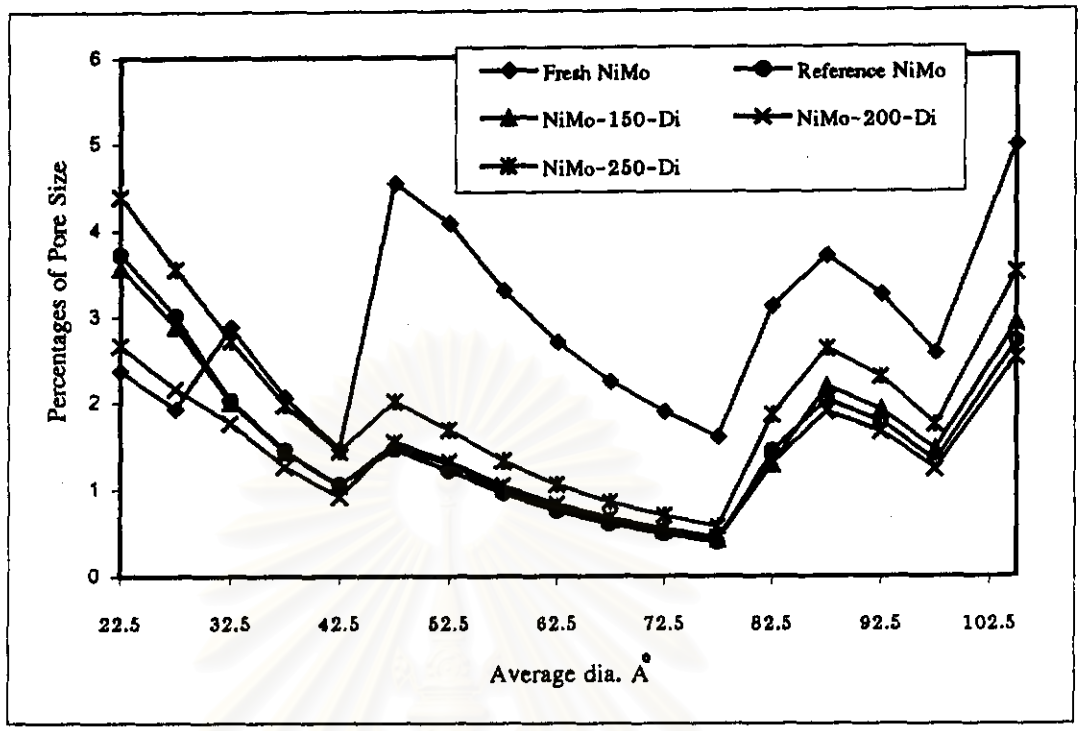


Figure 4.22 Comparisons of the pore size distribution between fresh and spent $NiMo/Al_2O_3$ catalysts in study of mercuric chloride.



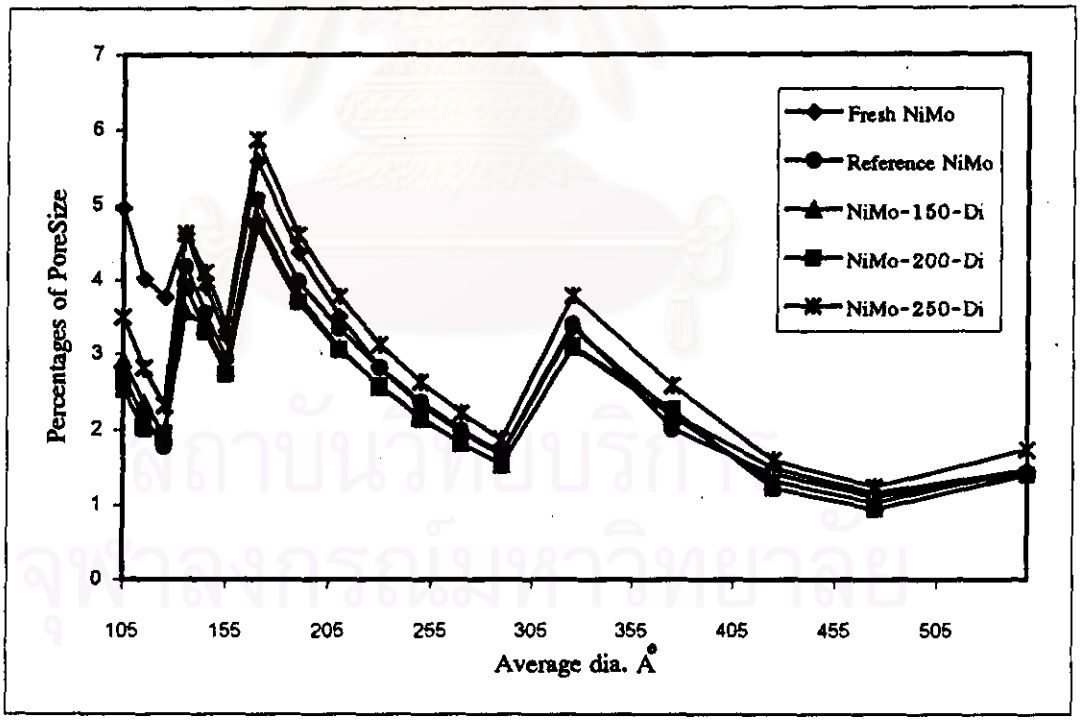


Figure 4.23 Comparisons of the pore size distribution between fresh and spent $NiMo/Al_2O_3$ catalysts in study of diphenylmercury.