

CHAPTER V

DISCUSSION

5.1 Preliminary Experiment

A preliminary study was conducted to find suitable operating conditions for other experiments. The suitable operating conditions are the ones that thiophene conversion is approximately 50 %. For hydrodesulfurization reaction, operating temperature normally plays a major role in conversion of each compound. Therefore the pressure in this experiment was maintained at 3.45 MPa (500 psig) and the temperature was varied from 100 to 300°C (212 to 572°F) with a step size of 100°C (180°F).

As shown in Table 4.6, at operating temperature of 100°C (212°F), there was no conversions of thiophene and toluene.

At the operating temperature of 200°C (392°F), the products of thiophene hydrodesulfurization reaction shown on the chromatogram were suspected to be hydrocarbons containing 4 carbon atoms (C4s). The actual compounds could not be identified because the standard C4s were not available in our laboratory. Conversion of thiophene at this operating temperature was 31.98 %.

At the operating temperature of 300°C (572°F), the major products shown on the chromatogram were still the same as the products of the experiment conducted at the operating

temperature of 200°C (392°F) with addition of a small quantity of methylcyclohexane. Methylcyclohexane forms from hydrogenation reaction of toluene. Conversion of thiophene increased from 31.98 % to 100 %.

From thiophene conversion in preliminary study, the operating temperature chosen for other experiments was approximately 200°C (392°F).

5.2 Deactivation Experiments

5.2.1 Hydrodesulfurization of Thiophene

Experiment 1 is a reference experiment. The data on the amount of coke form on the catalyst and the hydrodesulfurization activity were used as a basis of comparison with the other experiments.

Experiment 1 was operated at the pressure of 3.45 MPa (500 psig) and at the temperature of 220°C (428°F). At the temperature of 200°C (392°F), thiophene conversion of 31.98 % was rather low, effects of the addition of organometallic compounds would not be clearly observed. A higher temperature of 220°C (428°F) was more suitable than 200°C (392°F) because the effects of organometallic compounds would be easily identified. Another experiment, experiment 3, was conducted at the same condition as experiment 1 in order to study the repeatability of the experiments.

At the operating temperature of 220°C (428°F), the products of thiophene hydrodesulfurization reaction shown on the chromatogram were still a mixture of C4s. The results of experiment 1 and 3, shown in Figure 5.1, showed that there was an unsteady state period during the start-up of

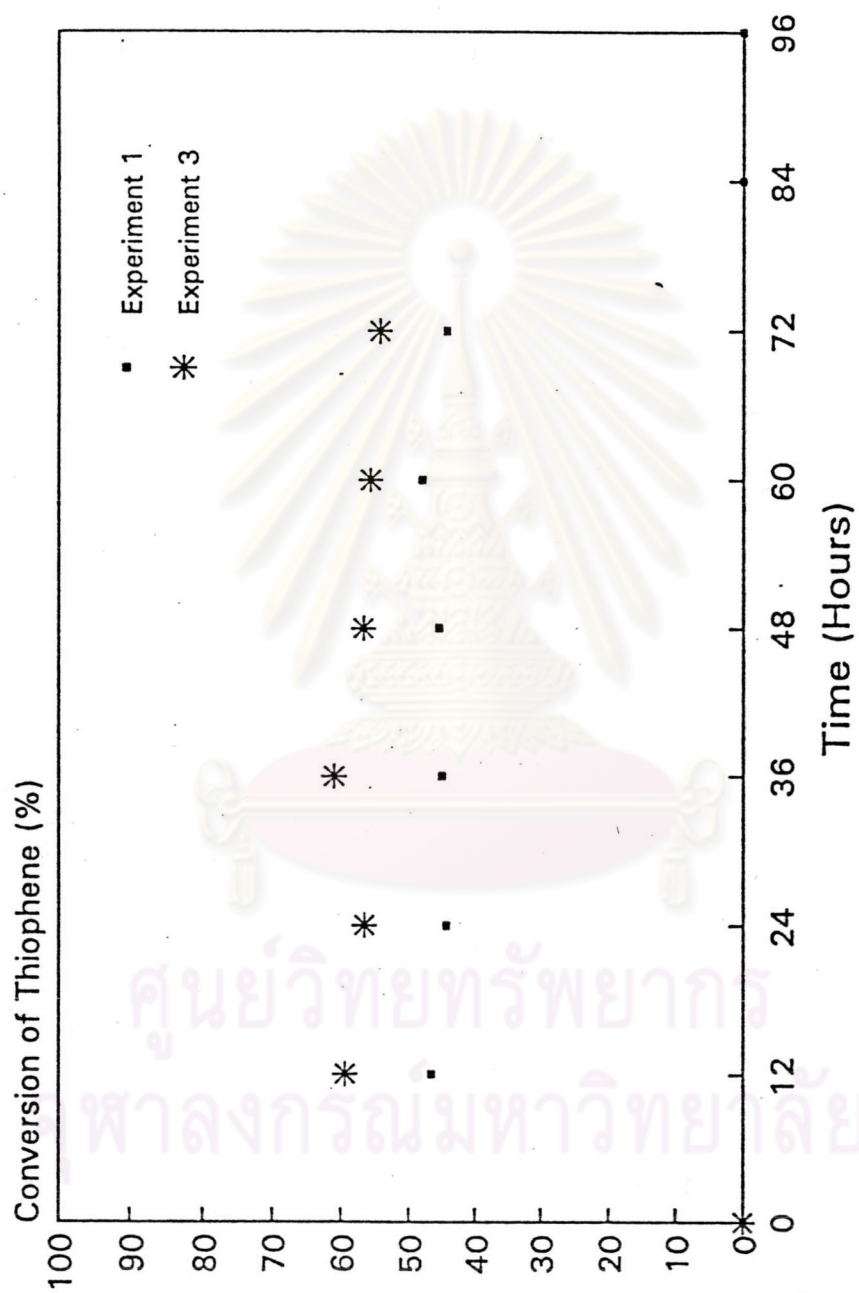


Figure 5.1 Conversion of Thiophene for Experiments 1 and 3

the experiment. This period was identified by the change in thiophene conversion during the first 36 hours. A steady-state operation was reached after 36 hours from start-up and the average of thiophene conversion of the samples during this period were used for comparison. Thiophene conversion of experiment 1 was approximately 47.29 % and of experiment 3 was approximately 55.49 %. These numbers were used as the lower and upper limits of thiophene conversion.

Coke content analysis in experiment 1 showed that the amount of coke on the catalyst in middle and bottom sections of the bed were approximately the same whereas the amount of coke in the top section was slightly higher. The coke results of experiment 3 also followed the same pattern as the results of experiment 1 but at slightly lower numbers. Figure 5.2 shows the results of coke content from experiments 1 and 3.

Eventhough coke can be formed from either parallel or series reactions [119]. Coke in these experiments was suspected to be parallel reactions, which was formed from the reactant, because the reaction in the top section involved higher reactant concentration than the other sections.

5.2.2 Effect of Ferrocene

In experiment 2, 100 ppm of iron as ferrocene was added to thiophene solution. The feedstock was hydrodesulfurized at the same operating conditions as in the reference experiment.

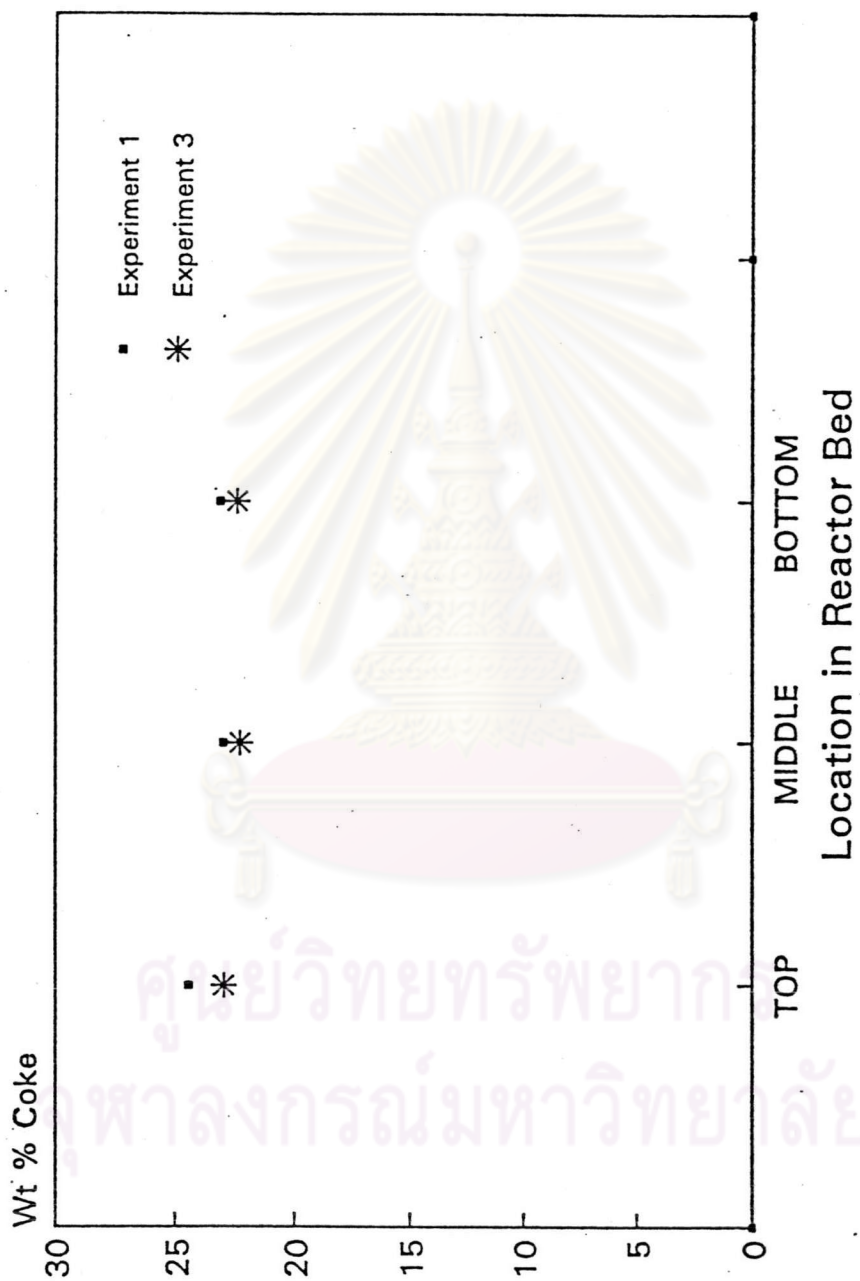


Figure 5.2 Coke Content of Experiments 1 and 3

The conversion of thiophene in experiment 2 was approximately 44.85 %, as shown in Figure 5.3. It slightly decreased from the reference experiment.

In Figure 5.4, the amount of coke in experiment 2 was low in the top section, whereas the coke contents in middle and bottom sections were higher than the top section and almost equal to the coke content of the reference experiment.

Figure 5.5 shows iron distributions in the catalyst pellets for all three sections. It showed that iron deposited mostly on the edge of the pellet and gradually decreased at other positions till the center of the pellet. Iron also deposited on the catalyst at higher amount in the top section of the catalyst bed than the lower sections.

Earlier studies [45-47] showed that iron was successively used as a catalyst promoter for hydrogenation and hydrodesulfurization reactions. In this study, a high conversion of thiophene at the initial period was suspected to be a promotion behavior of iron which could be used as a promoter on hydrodesulfurization catalyst. Adsorption of iron compound continued until the active surface was totally covered in the top section which caused the deactivation of top section catalyst. Coke was decreased in this section because catalyst surface was fully adsorbed by iron compound. Eventhough the catalyst in the top section was deactivated, total conversion of thiophene decreased slightly because the catalyst in middle and bottom sections were promoted by small amount of iron on the catalyst surface.

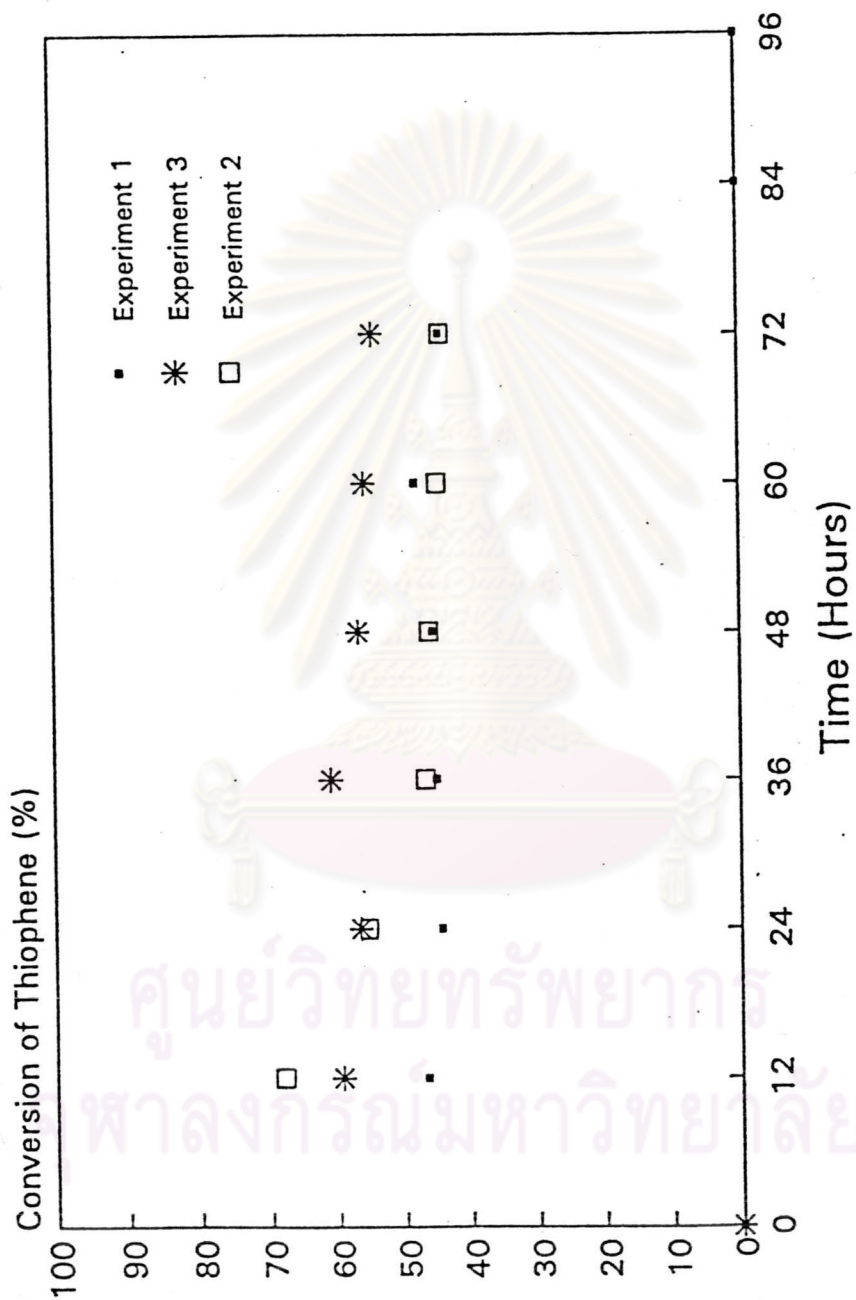


Figure 5.3 Conversion of Thiophene for Experiments 1, 3 and 2

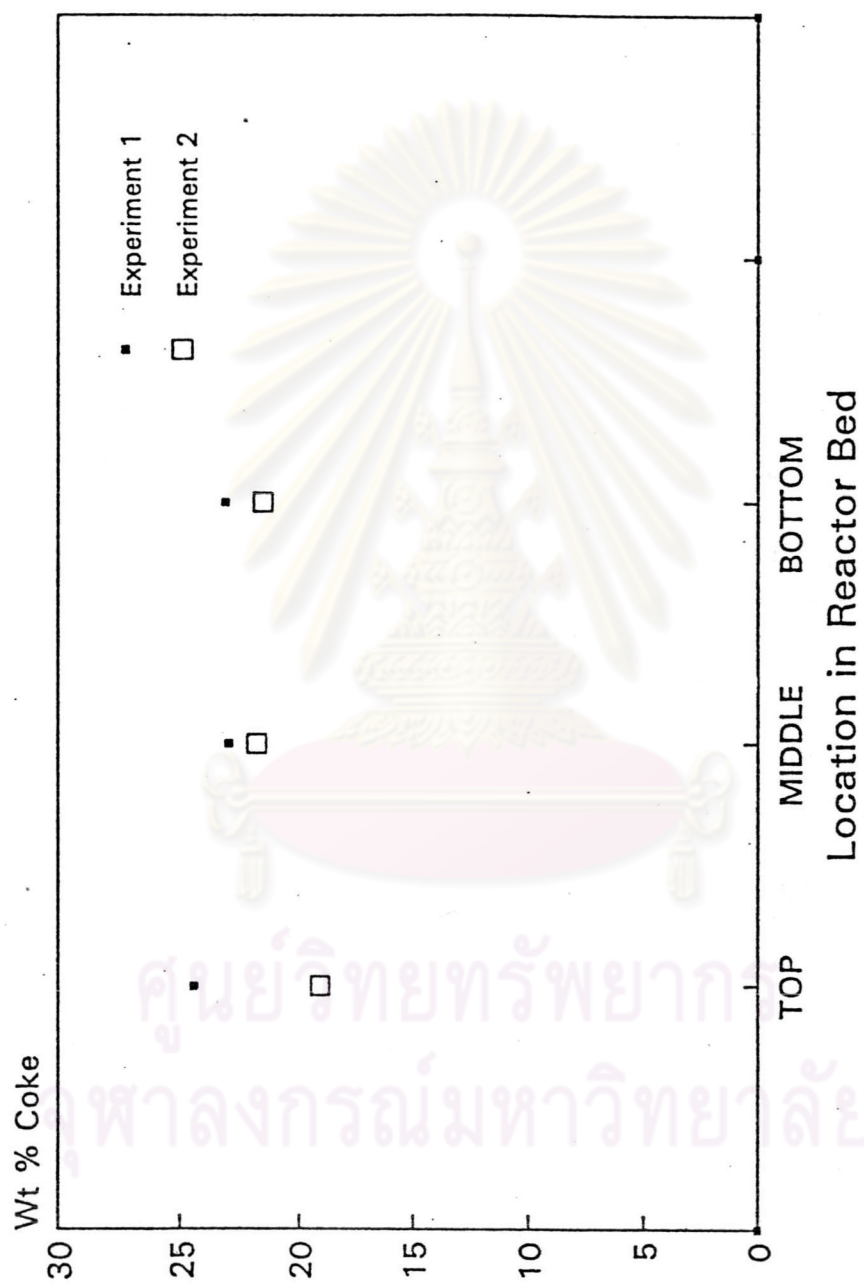


Figure 5.4 Coke Content of Experiments 1 and 2

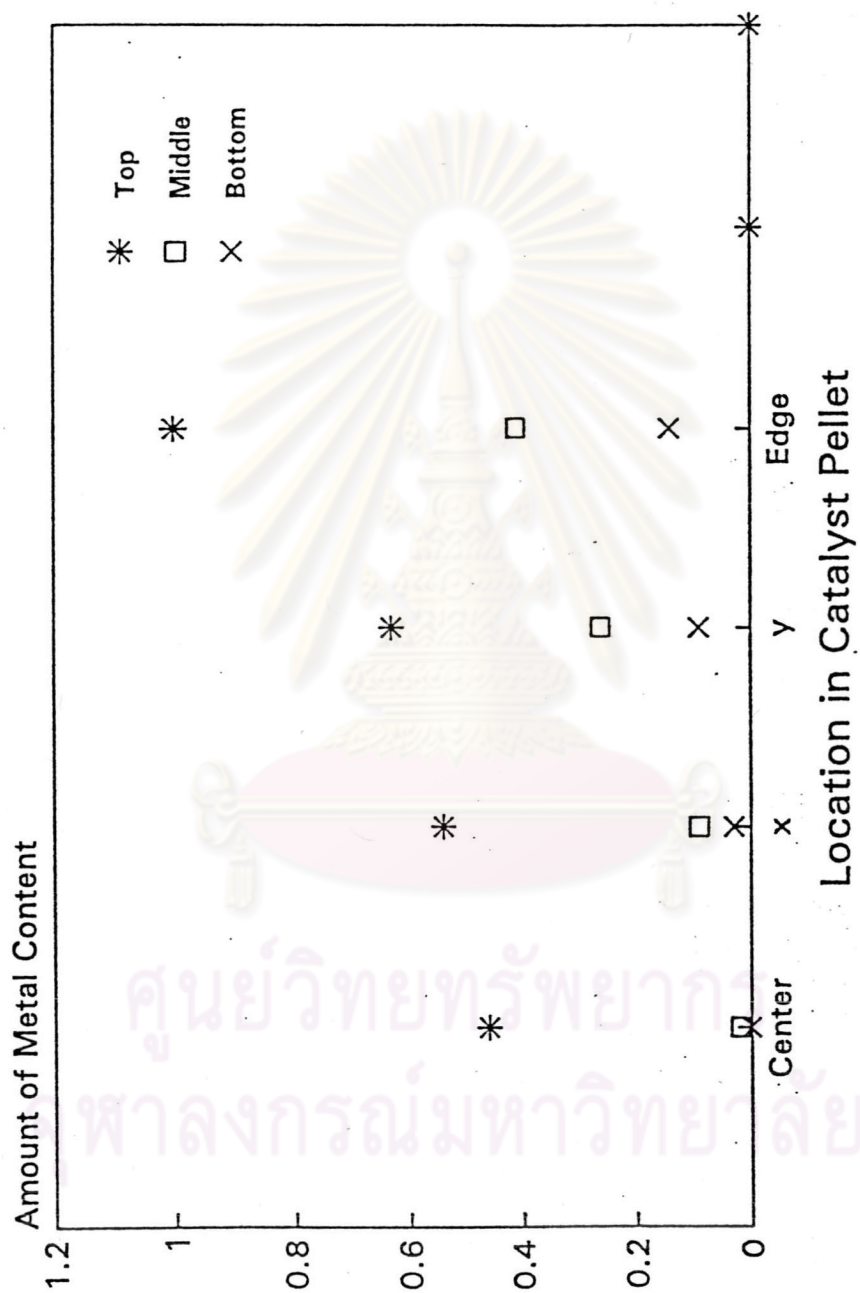


Figure 5.5 Distribution of Iron in Catalyst Pellet

5.2.3 Effect of Titanocene Dichloride

In experiment 4, 100 ppm of titanium as titanocene dichloride was added to thiophene solution. The feedstock was hydrodesulfurized at the same operating condition as in the reference experiment.

Conversion results from Figure 5.6 showed that the conversion of thiophene in experiment 4 was approximately 30.53 %. The conversion obviously decreased when it was compared with the reference experiment.

Figure 5.7 shows that the amount of coke in experiment 4. Coke contents in this experiment were lower than the ones in the reference experiment. The coke content in each section of experiment 4 was nearly the same.

From Figure 5.8, titanium was found to be deposited mainly on the edge and the position adjacent to the edge of the catalyst pellet. Only small amount of titanium was found at the center of the pellet. The amounts of titanium deposited on the catalyst also decreased from the top section to the bottom section of the bed. Most of titanium was found on the outer surface of catalyst pellet in top and middle sections.

These observations showed that deposition of titanium compound on the edge of the catalyst pellet would result in blocking of catalyst pores. This pore blocking inhibited the diffusion of thiophene into the inner active surface. Both hydrodesulfurization activity and coke formation were decreased because the catalyst lost the inner surface area for hydrodesulfurization reaction.

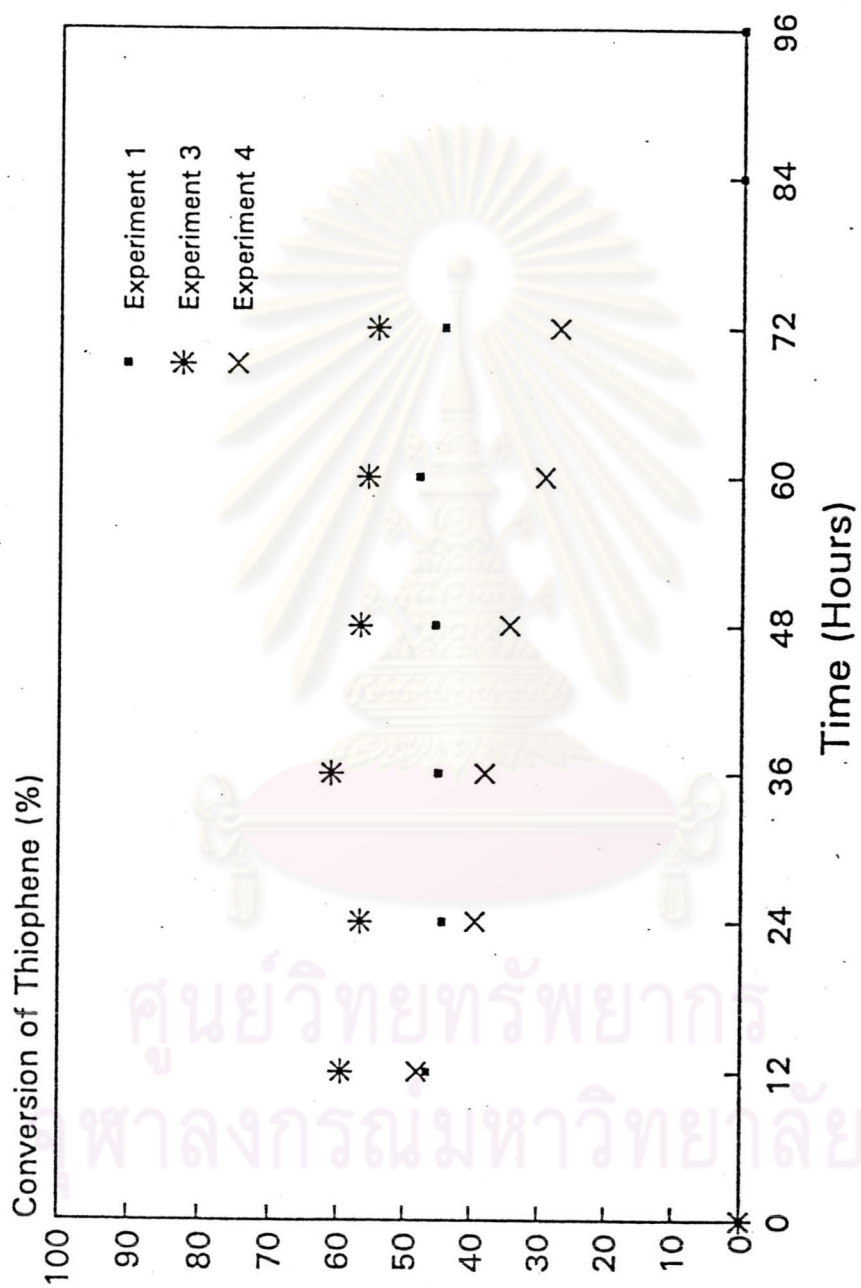


Figure 5.6 Conversion of Thiophene for Experiments 1, 3 and 4

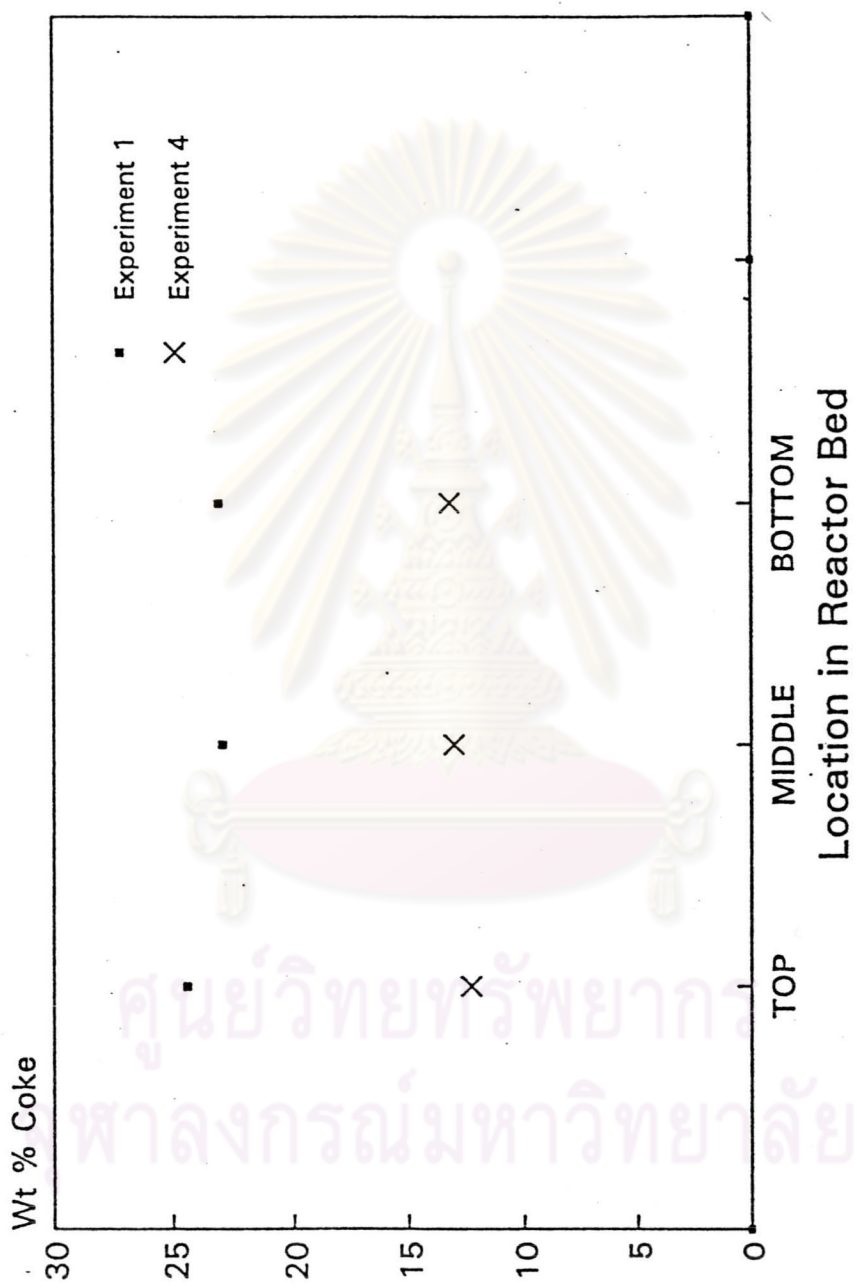


Figure 5.7 Coke Content of Experiments 1 and 4

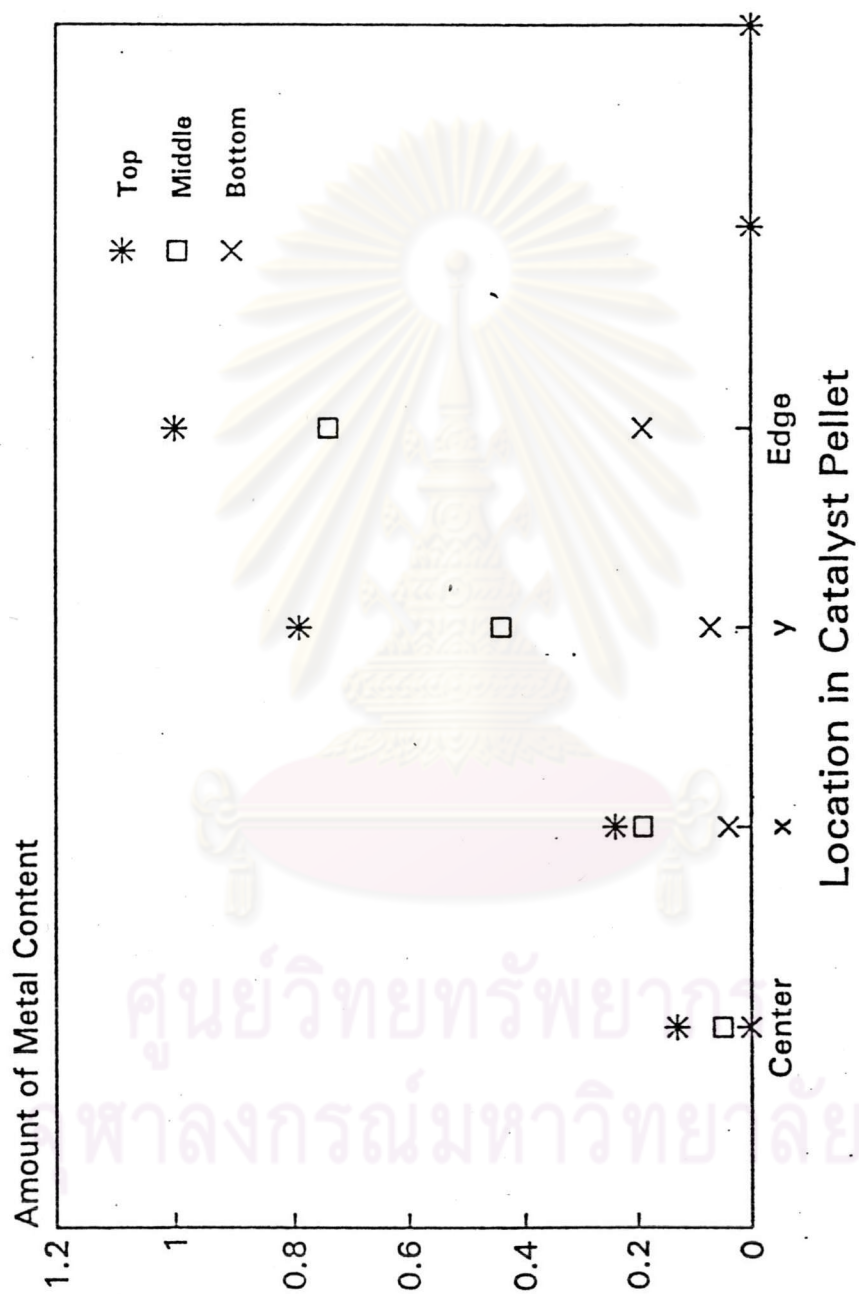


Figure 5.8 Distribution of Titanium in Catalyst Pellet

5.2.4 Effect of Vanadyl Acetylacetonate

In experiment 5, 100 ppm of vanadium as vanadyl acetylacetonate was added to thiophene solution. The feedstock was hydrodesulfurized at the same operating condition as in the reference experiment.

Conversion result from Figure 5.9 shows that the conversion in experiment 5 was approximately 47.72 %, which was nearly the same as the conversion from the reference experiment.

The result of coke analysis in Figure 5.10 shows that the amount of coke formed on the catalyst was low and almost the same in all three section.

Figure 5.11 shows the distributions of vanadium in catalyst pellet for every sections in the catalyst bed. It shows that vanadium deposited mostly on the catalyst in the top section of the bed. Vanadium diffused and deposited at high concentrations at every location inside the catalyst pellet except the center of the pellet.

Based on these results, vanadyl acetylacetonate could be react with sulfur compound in the feedstock and formed vanadium sulfide which had been known as a hydrodesulfurization catalyst. Vanadium sulfide would increase the hydrogenation activity in hydrodesulfurization reaction [61]. Coke is a large hydrocarbon molecule whose hydrogen to carbon ratio is low. Coke in this experiment was decreased because hydrocarbon molecule was hydrogenated to form saturated hydrocarbon product instead of coke formation. There was no effect of vanadyl acetylacetonate to

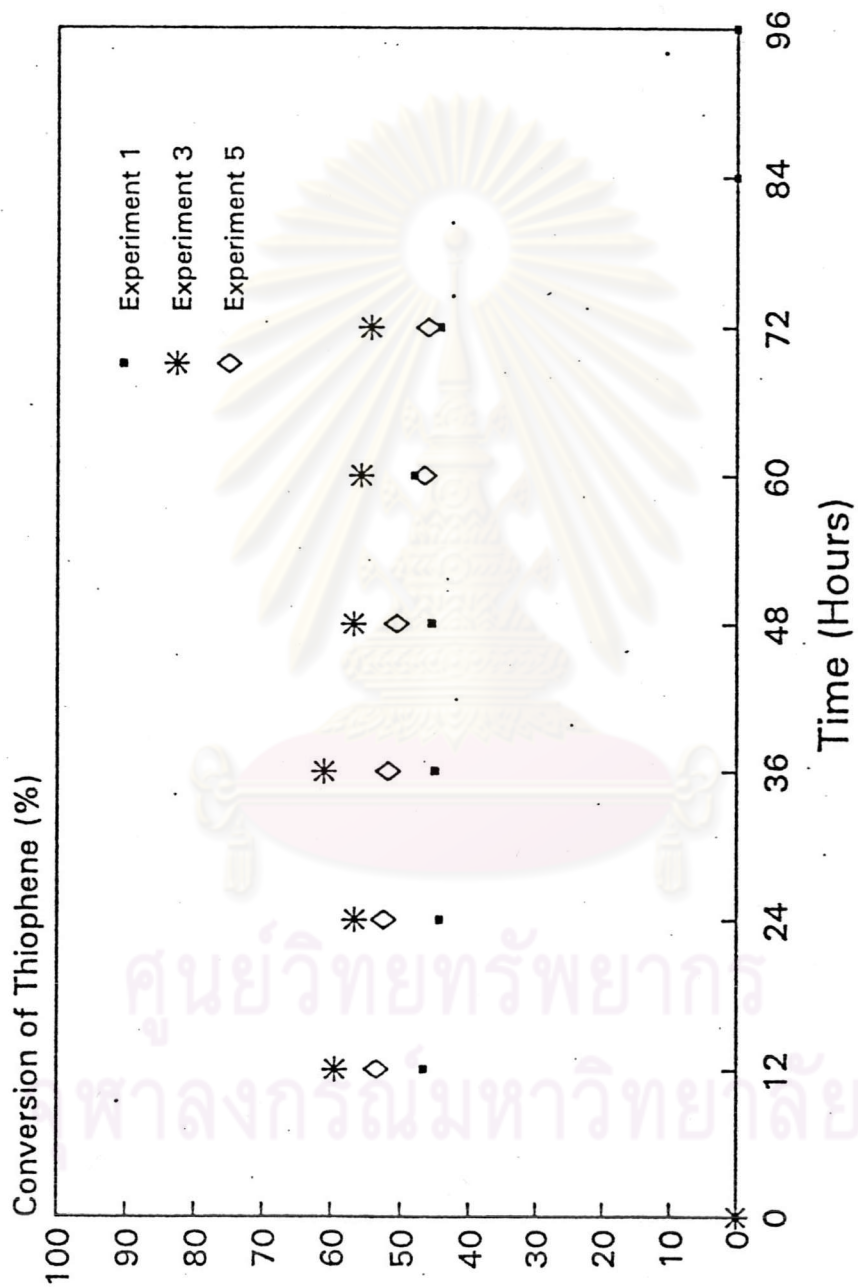


Figure 5.9 Conversion of Thiophene for Experiments 1, 3 and 5

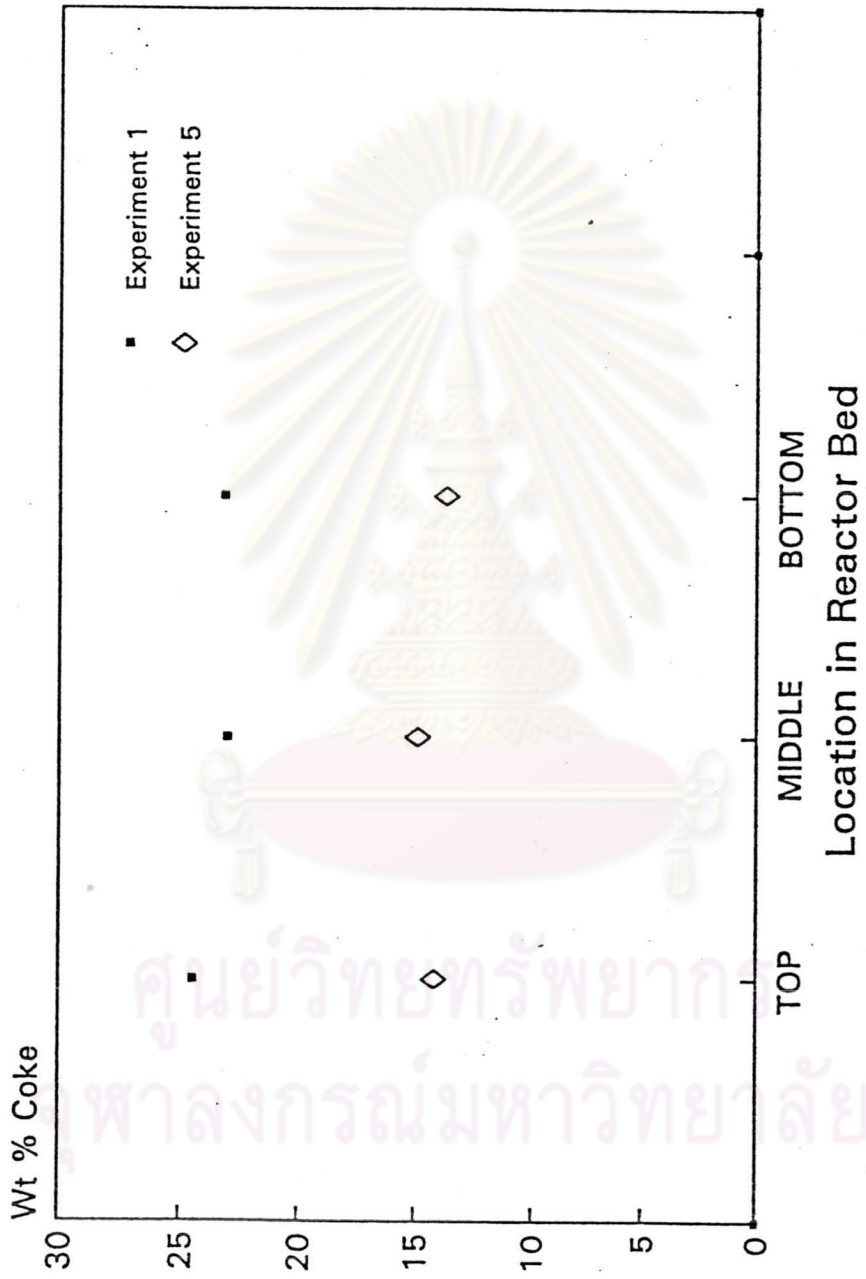


Figure 5.10 Coke Content of Experiments 1 and 5

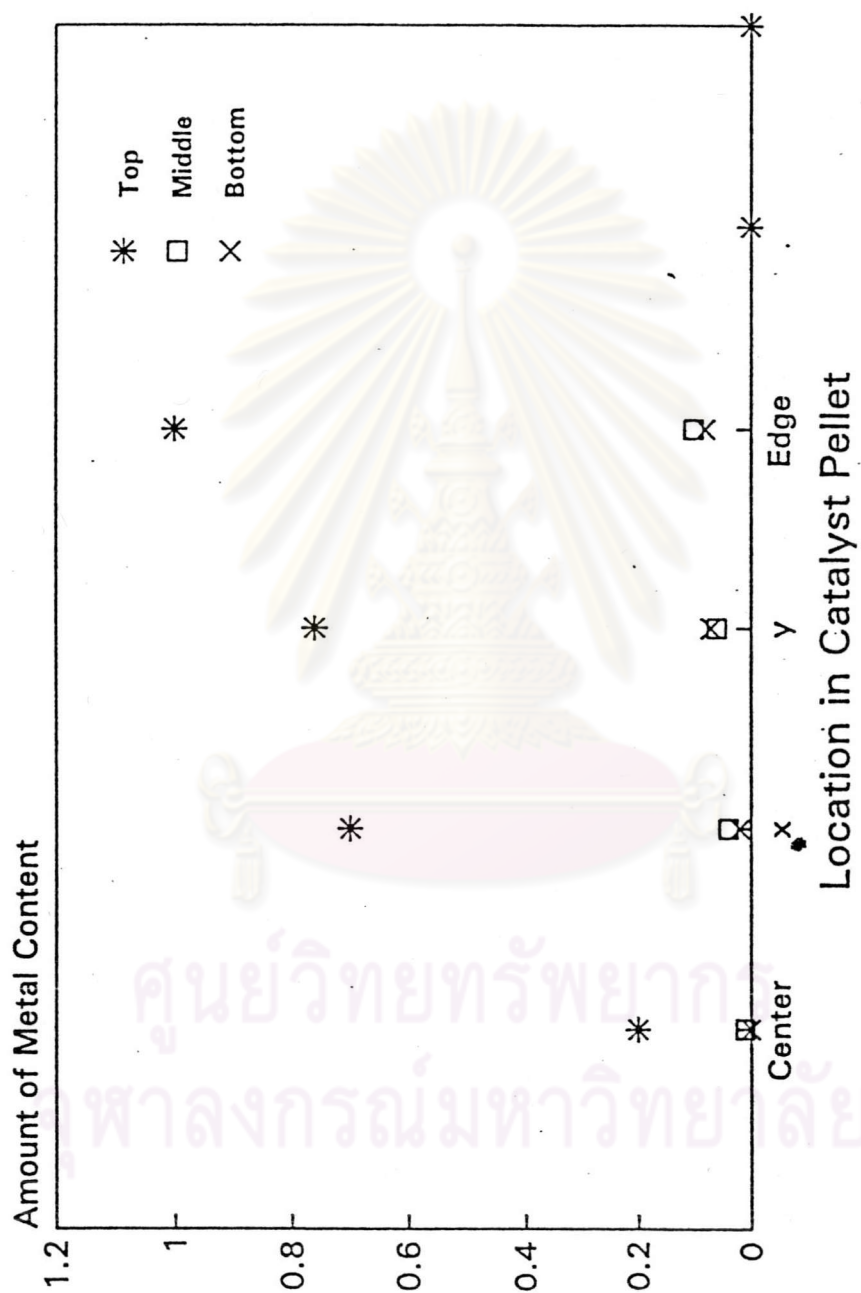


Figure 5.11 Distribution of Vanadium in Catalyst Pellet

hydrodesulfurization so that thiophene conversion was the same as the reference experiment.



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