# CHAPTER IV

# RESULTS AND DISCUSSIONS

## 4.1 Procedures

In this study, the experiments were classified into three sections. First, preliminary experiment was conducted to find suitable operating condition. Second, reference experiments 1 through 3 were conducted in order to study the repeatibility of the experiments. And third, deactivated experiments, 4 through 8 were conducted to study influence of nitrogen compounds on hydrodesulfurization of thiophene.

Before start-up of each experiment, the reactor was packed in the middle part with 3 grams of catalyst. The top part of the reactor was left empty and was used as vaporizing zone. The bottom part was packed with glass bead and was used as cooling zone. The reactor was then connected to a gas feed line and a liquid feed line at the top of the reactor, and was connected to a sample bomb at the bottom. The system was checked for leak by gradually pressurizing the system with nitrogen gas. The leak test was conducted at 3.45 MPa (500 psig) which was 0.69 MPa (100 psig) higher than the reaction operating pressure. A pressure drop of 68.95 kPa (10 psig) in one hour was the maximum acceptable leak. Every experiment was started with fresh $CoMo/Al_2O_3$ and the catalyst was sulfided in situ to increase catalyst activity for HDS reaction. Catalyst preparation in each experiment was conducted by using identical sulfiding procedure.

Toluene and n-hexane, non-polar sovents, were used as liquid carriers. These liquid carriers were chosen because they had good solubility for sulfur and nitrogen model compounds at the reaction conditions and conversion of these liquid carriers were negligible at our operating conditions. Thiophene was chosen as sulfur model compound because its HDS reaction is known to be strongly poisoned by nitrogen compounds (La Vopa and Satterfield, 1988). The high reactivity of thiophene allows the inhibition to be measured at sufficiently high space velocities that limits reaction of most added nitrogen compounds to occur (La Vopa and Satterfield, 1988). Nitrogen compounds used to doctor the feedstock in each deactivated experiment were pyridine, quinoline, 1,2,3,4-tetrahydroquinoline (1,2,3,4-THQ), 2,6-lutidine, and pyrrole. All sulfur and nitrogen model compounds were analyzed grade from suppliers. The catalyst used in this study was 1/8 inch extrudate CoMo/$Al_2O_3$. Properties of each reactants are shown in the appendix. Details of feedstock and operating condition of each experiment are given in Tables 4.1 through 4.3.

During each experiment, liquid samples were taken every 6 hours. The 12-hours samples were analyzed for amounts of thiophene by using gas chromatograph. Conversion of thiophene was then calculated by

$$\%\ \text{Conversion of thiophene} = (1-C_t/C_{to}) * 100$$

TABLE 4.1 Procedure of Preliminary Experiment

| | | |
|---|---|---|
| Feedstock : | | |
| | Feed I - | Toluene + 5 wt% n-Hexane +<br>3 wt% sulfur (as Thiophene) |
| Operating Conditions : | | |
| | Pressure - | 400 psig, H flow rate - 400 cc/min |
| | WSHV - | 3.0 /hr , H /oil ratio - 2,400 $m^3$ H /$m^3$ oil |
| | Catalyst - | 3 grams 1/8" extrudate of Co-Mo/$Al_2O_3$ |
| | Sampling - | every 6 hours |
| Run variable : | | |
| | Temperature - | 200 °C, Time - 24 hours |
| | Temperature - | 210 °C, Time - 24 hours |
| | Temperature - | 220 °C, Time - 24 hours |
| | Temperature - | 230 °C, Time - 24 hours |

TABLE 4.2 Procedure of Reference Experiment *

| | | |
|---|---|---|
| Feedstock : | | |
| | Feed I - | Toluene + 5 wt% n-Hexane +<br>3 wt% sulfur (as Thiophene) |
| Operating Conditions : | | |
| | Temperature - | 210°C |
| | Pressure - | 400 psig, H flow rate - 400 cc/min |
| | WSHV - | 3.0 /hr , H /oil ratio - 2,400 $m^3$H /$m^3$ oil |
| | Catalyst - | 3 grams 1/8" extrudate of Co-Mo/$Al_2O_3$ |
| | Sampling - | every 6 hours |
| | Duration of Run - | 120 hours |

* Runs for three times called 1-Ref. Exp., 2-Ref. Exp., and 3-Ref. Exp.

TABLE 4.3 Procedure of Deactivated Experiments

| | | |
|---|---|---|
| Feedstock : | | |
| | Feed I - | Toluene + 5 wt% n-Hexane +<br>3 wt% sulfur (as Thiophene) |
| | Feed II - | Toluene + 5 wt% n-Hexane +<br>3 wt% sulfur (as Thiophene) +<br>0.5 wt% nitrogen (as N*) |
| Operating Condition : | | |
| | Temperature - | 210 °C |
| | Pressure - | 400 psig, H flow rate - 400 cc/min |
| | WSHV - | 3.0 /hr , H /oil ratio - 2,400 $m^3$H /$m^3$oil |
| | Catalyst - | 3 grams 1/8" extrudate of Co-Mo/$Al_2O_3$ |
| | Sampling - | every 6 hours |
| Switching Feedstock : | | |
| | Feed I - | Duration of run 48 hours |
| | Feed II - | Duration of run 48 hours |
| | Feed I - | Duration of run 24 hours |

where

$C_{to}$ = weight % of thiophene in feed.

$C_t$ = weight % of thiophene in product sample.

After each experiment, Spent catalyst sample was extracted with tetrahydrofuran to remove organic compounds on the catalyst surface and was dried in the air at room temperature for 2 weeks. Catalyst samples were divided in two groups. One group was burnt to find coke content in high temperature furnace and was called burned catalysts, while the other group was not burned in high temperature furnace and was called unburned cataltyst. Both burned and unburned catalysts were analyzed for pore characteristic and total surface area by using Micromeritics poresizer 9300 and Micromeritics AZAP 2000, respectively.

The results from liquid samples and catalyst samples are showed in Tables 4.4 through 4.11. The results are interpreted to find suitable operating condition, repeatibility and influence of nitrogen compounds.

## 4.2 Results and Discussions

### 4.2.1 Suitable Operating Condition

Preliminary experiment was conducted to find a suitable operating temperature for hydrodesulfurization of thiophene in toluene and n-hexane solution. In this experiment, temperature was varied in the range of 200-230°C (392-446°F) at a step increment of 10°C. In order to observe the influence of nitrogen compounds on HDS of

TABLE 4.4 Thiophene Conversion with Time of Preliminary Experiment

| Time (hr.) | Temperature (°C) | Thiophene Conversion ( % ) |
|---|---|---|
| 12 | 200 | 31 |
| 24 | | 35 |
| 12 | 210* | 54 |
| 24 | | 56 |
| 12 | 220 | 87 |
| 24 | | 90 |
| 12 | 230 | 100 |
| 24 | | 100 |

* Suitable Operating Condition

TABLE 4.5 Thiophene Conversion with Time of Reference Experiments

| Time (hr.) | Thiophene Conversion ( % ) | | | | Deviation (%) | |
|---|---|---|---|---|---|---|
| | 1-Ref Exp. | 2-Ref Exp. | 3-Ref Exp. | AVG. Exp. | Max. | Min. |
| 12 | 36.80 | 53.57 | 48.83 | 46.40 | 15.45 | 20.68 |
| 24 | 52.84 | 56.95 | 52.00 | 53.93 | 5.60 | 2.02 |
| 36 | 52.30 | 58.02 | 53.10 | 54.47 | 6.52 | 2.17 |
| 48 | 51.00 | 58.14 | 54.24 | 54.46 | 6.76 | 6.35 |
| 60 | 56.34 | 58.23 | 55.00 | 56.52 | 3.02 | 2.69 |
| 72 | 55.30 | 59.19 | 55.60 | 56.70 | 4.39 | 2.47 |
| 84 | 53.25 | 58.02 | 54.12 | 55.13 | 5.24 | 3.41 |
| 96 | 55.65 | 54.95 | 53.00 | 54.53 | 2.05 | 2.80 |
| 108 | 51.30 | 57.86 | 55.50 | 54.86 | 5.43 | 6.52 |
| 120 | 52.50 | 55.37 | 55.00 | 54.29 | 1.99 | 3.09 |
| Average Deviation | | | | | 4.41 | 3.71 |

TABLE 4.6 Thiophene conversion with Time of Deactivated Experiments and of Average Reference Experiment

| | Time (hr.) | Thiophene Conversion ( % ) Deactivated Experiment | | | | | Average Ref. Exp. |
|---|---|---|---|---|---|---|---|
| | | Pyridine | Quinoline | 1,2,3,4-THQ | 2,6-Lutidine | Pyrrole | |
| Undoctored Feedstock | 12 | 53.94 | 55.31 | 60.40 | 55.75 | 48.76 | 46.40 |
| | 24 | 57.70 | 58.05 | 60.66 | 57.21 | 53.55 | 53.93 |
| | 36 | 58.31 | 62.04 | 64.66 | 59.41 | 56.19 | 54.47 |
| | 48 | 59.37 | 62.34 | 64.78 | 60.12 | 56.00 | 54.46 |
| Doctored Feedstock | 60 | 20.48 | 28.47 | 29.61 | 51.16 | 37.18 | 56.52 |
| | 72 | 18.94 | 17.80 | 23.75 | 51.51 | 18.61 | 56.70 |
| | 84 | 19.83 | 17.85 | 23.60 | 49.73 | 33.55 | 55.13 |
| | 96 | 17.46 | 18.73 | 18.73 | 52.52 | 33.60 | 54.53 |
| Undoctored Feedstock | 108 | 61.55 | 21.83 | 30.52 | 67.33 | 57.48 | 54.88 |
| | 120 | 72.57 | 25.04 | 36.54 | 67.05 | 61.33 | 54.29 |

thiophene, the range of thiophene conversion required was 50-60 %. Table 4.4 showed conversion of thiophene for preliminary experiment. The data showed that the temperature of 210°C was a suitable operating temperature and was used in other experiments.

### 4.2.2 Repeatibility

Reference experiment was conducted to find suitable time to reach steady state of thiophene HDS reaction and to find total time to cover the whole range of the experiment. Two additional experiments were also conducted to verify their repeatibility and to find their average results. Average results of reference experiments were used as basis results. These basis results consisted of results from both liquid products and catalysts samples, which depend only on the reaction of thiophene and liquid carriers at the same operating condition and at the same duration of time as of each deactivated experiment. So, influence of each nitrogen compound on conversion of thiophene and on catalyst characteristic was carried out by comparision of the average results of reference experiment with results of each deactivated experiment.

Thiophene conversion at any time of reference experiments were shown in Table 4.5. From the data, the steady-state operation was reached after 24 hours from start-up. Total time to cover the whole range of experiment was 120 hours and the average conversion of thiophene at any time was in the range of 54-57%. The results of three experimental runs (1 through 3) were reproducible within an accuracy of 5%. Coke content of reference experiments were shown in Table 4.7. Average coke content of reference experiments was 12.65 wt% within an accuracy of 3%. Average reduction of pore volume and reduction total surface area of reference experiment with respect to the fresh catalyst were shown in Table 4.8 and 4.9. Thiophene HDS in liquid carriers caused reduction of pore volume and surface area as 64.43% and 77.77% within and accuracy of 7 and 2%, respectively. This result indicated that HDS of thiophene in liquid carriers caused coke formation on $CoMo/Al_2O_3$. The deposition of coke on the catalyst covered the outer surface of the catalyst and blocked the pores of the catalyst, which were observed by the reduction of both total surface area and pore volume. After regeneration, the catalysts recovered their physical properties which was observed by regeneration characteristics with respect to fresh catalyst, as shown in Table 4.8, 4.9, were nearly 1. These results indicated that coke was physical adsorption on the catalyst. Similar results was obtained by Thomas (1979) who reported that aromatic S-, N-, and O- containing heterocyclic compounds caused coke deposition on catalyst.

### 4.2.3 Influence of Nitrogen Compounds

Deactivated experiments, were designed to varify influence of each nitrogen compound on thiophene conversion and on catalyst by comparison with average results of reference experiment.

During the first 48 hours of the experiment; a mixture of thiophene and liquid carriers was used as feedstock. Then the feedstock was switched to a mixture containing nitrogen compound. The feedstock was altered back to non-nitrogen compound again at 96 hours.

Nitrogen compound (aprroximately 0.5 wt% nitrogen) was added to pure feedstock in each deactivated experiment. Amount of nitrogen compound added was calculated by assuming that nitrogen atom poisoned Co and Mo atom as 1:1 monolayer adsorption. From our calculation, approximately 0.0006 wt% of nitrogen was obtained. In practice, this amount was not enough to observe the influence of each nitrogen compound on HDS of thiophene, clearly.

Figure 4.1 showed the comparision of thiophene conversion with time of each experiment. During the first 48 hours, the feedstock contained no nitrogen compound. Thiophene conversion of each experiment was steady and was in the range of 55-65%. At 48 hour, after the feedstock was switched from pure feedstock to a mixed feedstock containing nitrogen compound, thiophene conversion decreased. It was caused by competitve adsorption of nitrogen compounds on the active sites. Similar results was obtained by Krish et al.(1959). The degree of decreasing in conversion depended upon the type and structure of nitrogen compounds. After 96 hours, the feedstock was changed back to pure feedstock. Removal of pyridine, 2,6-lutidine and pyrrole from the feedstock caused thiophene conversion to increase to 55-65%. These results indicated that pyridine, 2,6-lutidine and pyrrole

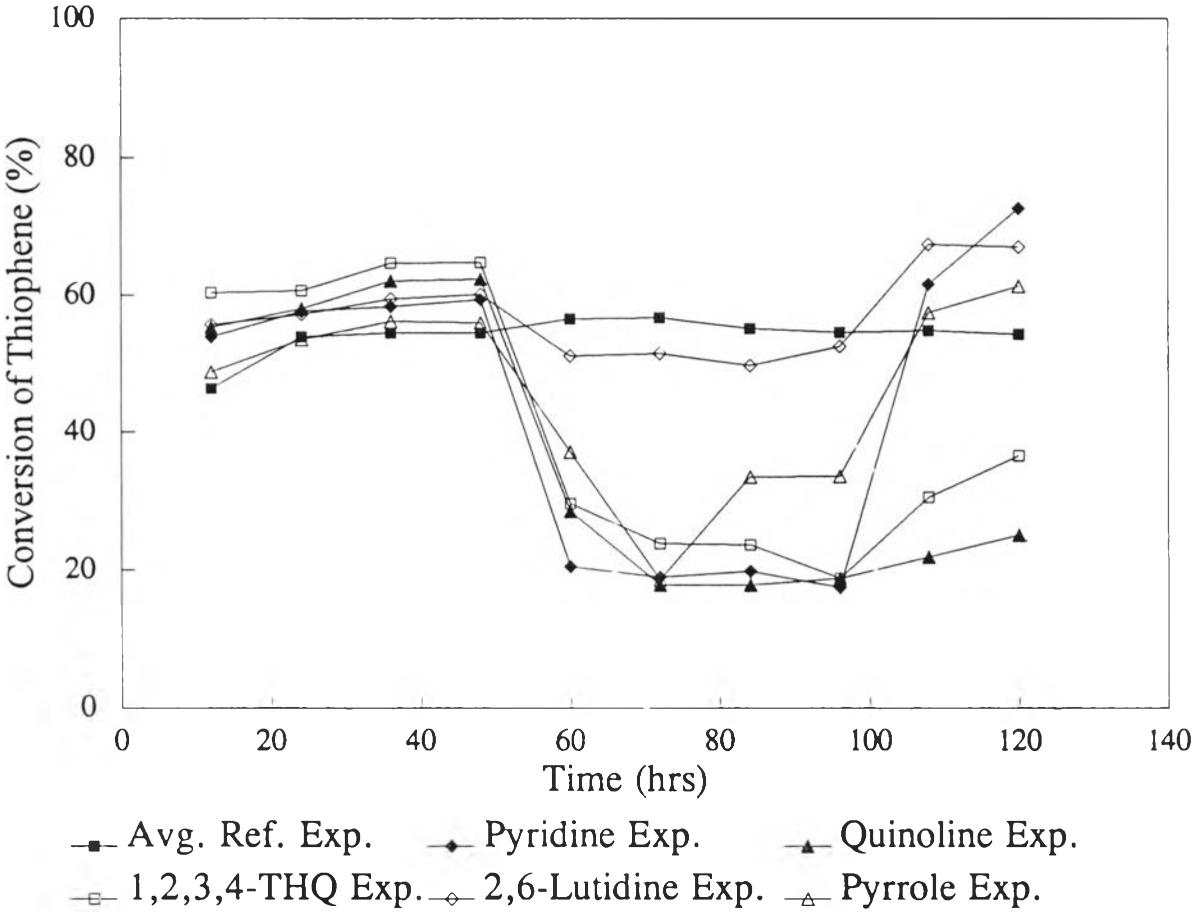

Figure 4.1 Conversion of Thiophene with Time of Average Reference Experiment and Deactivated Experiments

desorbed from the catalyst surface and the catalyst recovered its active surface area. Although thiophene conversion did not increase to 55-65% after removal of quinoline and 1,2,3,4-THQ, but it increased slightly. These results also indicated that quinoline and 1,2,3,4-THQ desorbed from the catalyst surface, but at a slower rate. Degree of desorption from catalyst surface depended on the type, structure and phase of each nitrogen compound in the reactor. Similar results was observed by Massoth and Miciukiewicz (1986) who observed that the effect of nitrogen compounds poison on catalytic activity is generally site specific and may be reversible or irreversible. Removal of the poison from the feed regenerated the catalytic activity in the former case, whereas a permanent loss in activity remained in the latter case. For a truly reversible poison, the amount adsorbed and the (lower) catalytic activity reached steady state values depended upon the concentration of poison in the feed. Changes in the feed concentration reversibly altered the amount adsorbed and the catalytic activity.

In the deactivated experiments, the effects of nitrogen compounds on HDS of thiophene were categorized to study the influence of their types and structures as follows;

-The effects of basicity.

-The effects of number of ring.

-The effects of saturated ring nitrogen compounds.

-The stearic hindrance effects.

Basicity Effect

The influence of basicity effect of nitrogen compounds was observed by comparing experiments using a feedstock containing pyridine and a feedstock containing pyrrole. Pyridine is a basic nitrogen compound, while pyrrole is a nonbasic nitrogen compound. Figure 4.2 showed the comparison of thiophene conversion for the feedstocks containing pyridine and pyrrole. It showed that pyridine decreased thiophene conversion from 55% to 19% while pyrrole decreased thiophene conversion from 55% to 33%. These results indicated that basic nitrogen compound increased the inhibition of hydrodesulfurization. This result can also be explained by the acidity of the catalyst. Catalyst used in this study has two types of acidic sites, Bronsted acid site is able to donate a proton to a base, and Lewis acid site is able to accept unpaired electrons from a base (Fu and Schaffer, 1985). Both acid sites were believed to be poisoned by basic compound. Increasing basicity also increased the inhibition of thiophene conversion. Similar results was obtained by many researchers (Nagai and Kabe, 1983; Nagai and Aiba, 1986, etc.). Although observations were made on different kinds of catalysts and conditions but the same trend was obtained. The comparison in thiophene converson of each experiment, shown in Figure 4.1, showed that increasing basicity of the nitrogen compound, especially gas-phase basicity (Proton Affinity) as shown in Table 2.4, reduced thiophene conversion. In the absence of stearic effect, inhibition strength is in the order of quinoline > pyridine > 1,2,3,4-THQ > pyrrole.

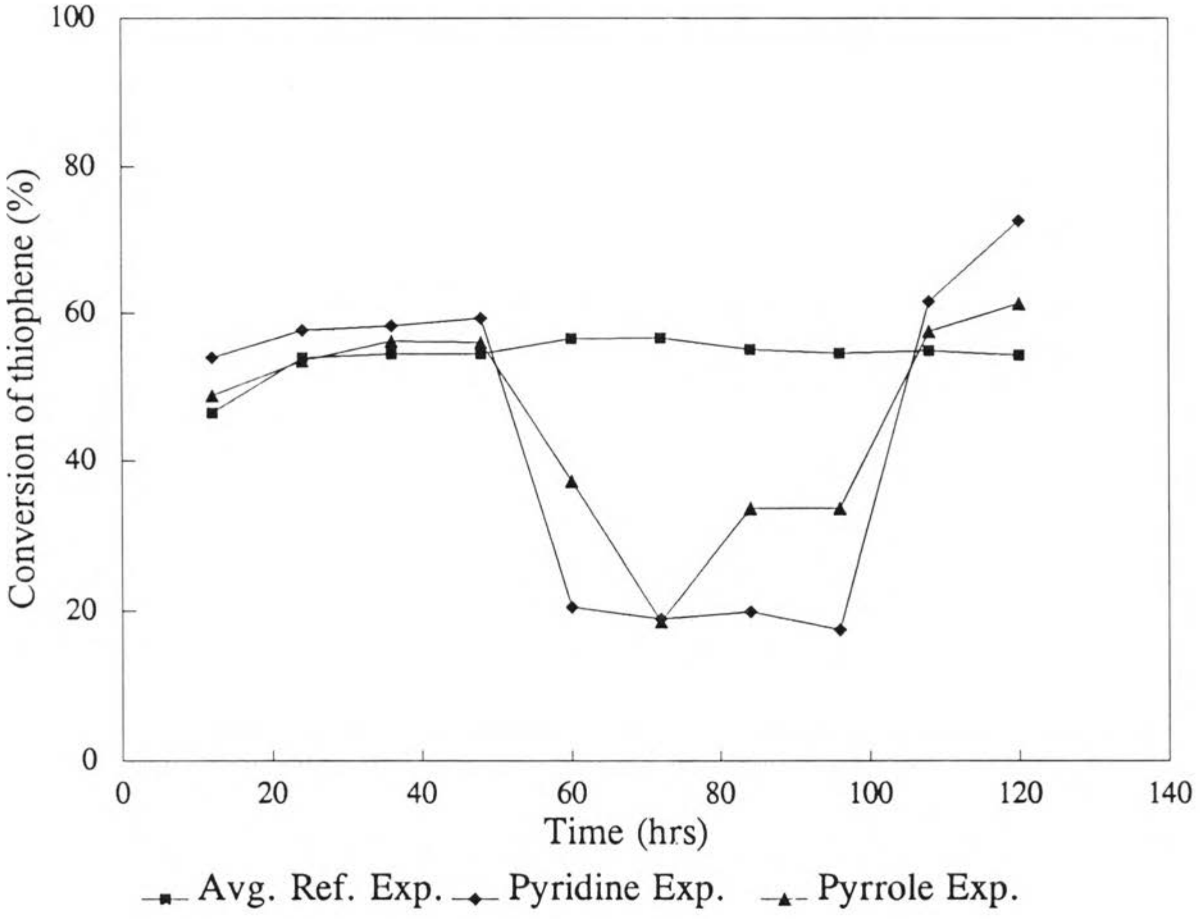

Figure 4.2 Conversion of Thiophene with Time Basicity Effect

These results also corresponded to those of La Vopa, and Satterfield, (1988) who studied poisoning effect of various nitrogen compounds on HDS of thiophene over NiMo/$Al_2O_3$ at higher pressure (7 MPa) and reported that the poisoning effect of nonstearically hindered nitrogen compounds correlated well with the proton affinities.

## The Influence of Number of Ring

The influence of number of ring in nitrogen compounds was observed by comparing experiments using feedstock containing quinoline and feedstock containing pyridine. Quinoline is the nitrogen compound with structure consists one aromatic ring attached to a pyridine parent compound. Figure 4.3 showed the comparison of thiophene conversion for feedstock containing quinoline and pyridine, respectively. It showed that quinoline decreased thiophene conversion from 55% to 17%, while pyridine decreased thiophene conversion from 55% to 19%. From our repeatibility experiments, the accuracy of each experiment is within 5%. The difference in thiophene in this section is 2% which falls in the accuracy range. So, it is difficult to conclude that the addition of aromatic ring to pyridine has any effect on HDS of thiophene. In contrast, Fu and Schaffer (1985), reported that the addition of one or two fused rings to pyridine parent compound substantially increased the poisoning effect on cracking catalysts.

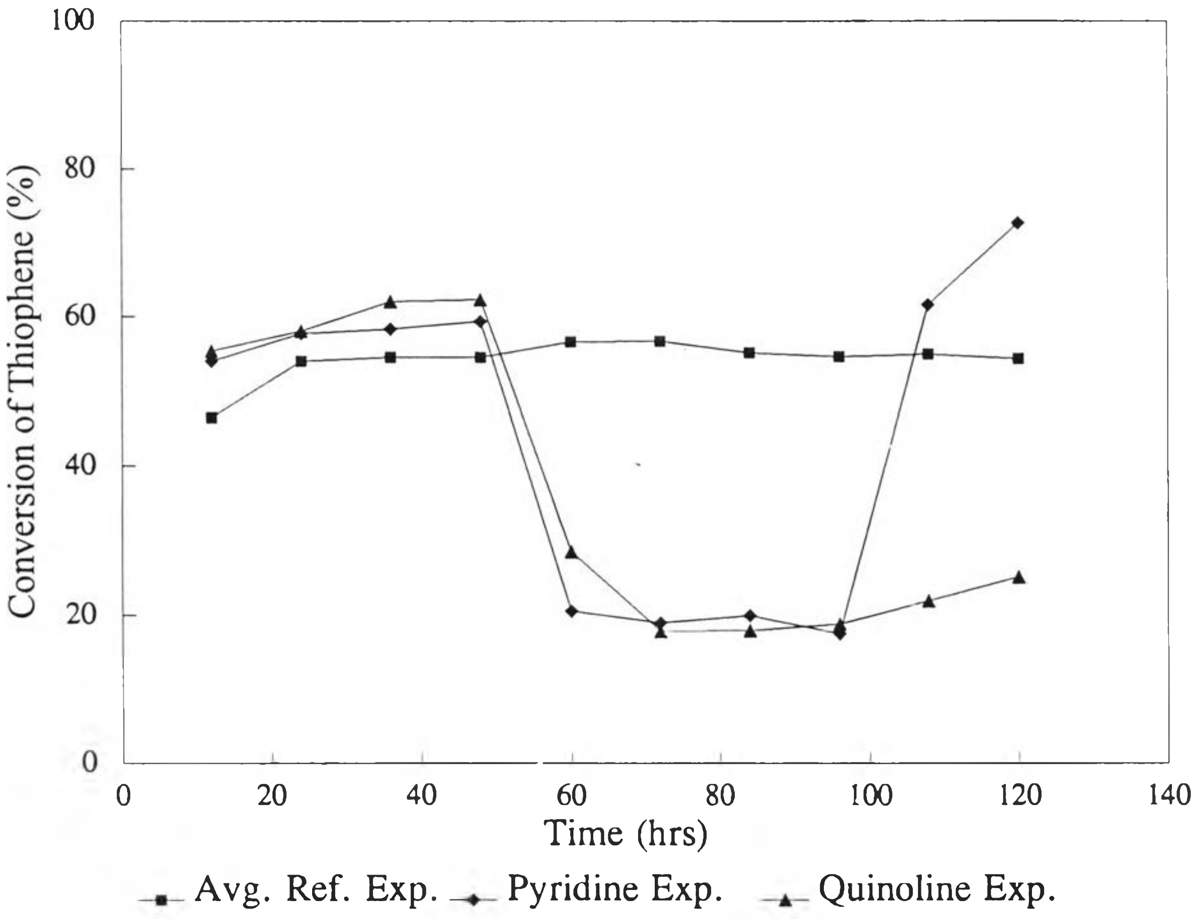

Figure 4.3 Conversion of Thiophene with Time
Number of Ring Effect

### The Influence of the Saturated Ring.

The influence of the saturated ring in nitrogen compounds was observed by comparing experiments using feedstock containing quinoline and 1,2,3,4-tetrahydroquinoline (1,2,3,4-THQ), respectively. Figure 4.4 showed the comparison of thiophene conversion when feedstock containing quinoline and 1,2,3,4-THQ. It showed that quinoline decreased thiophene conversion from 55% to 17%, while 1,2,3,4-THQ decreased thiophene conversion from 55% to 23%. These results indicated that the saturated nitrogen compound inhibited HDS of thiophene less than the unsaturated nitrogen compound. It was observed that the decreasing of thiophene conversion by 1,2,3,4-THQ was less than that of quinoline. This results can be described by lower adsorption activity of saturated ring which caused less inhibition to active sites of catalyst. In contrast, Sivasubramanian (1980) who studied the effect of saturated ring by comparison of pyrrole and pyrrolidine and reported that saturated ring nitrogen compound inhibited HDS reaction than unsaturated nitrogen compound because it has higher basicity which caused higher poisoned to acid catalyst.

### Stearic Effects

The influence of stearic effect in nitrogen compounds was observed by comparing experiments using feedstock containing pyridine and 2,6-lutidine, respectively. Pyridine is nonstearic hindrance in structure while 2,6-lutidine is stearic hindrance in structure. Figure 4.5 showed the comparison of thiophene conversion

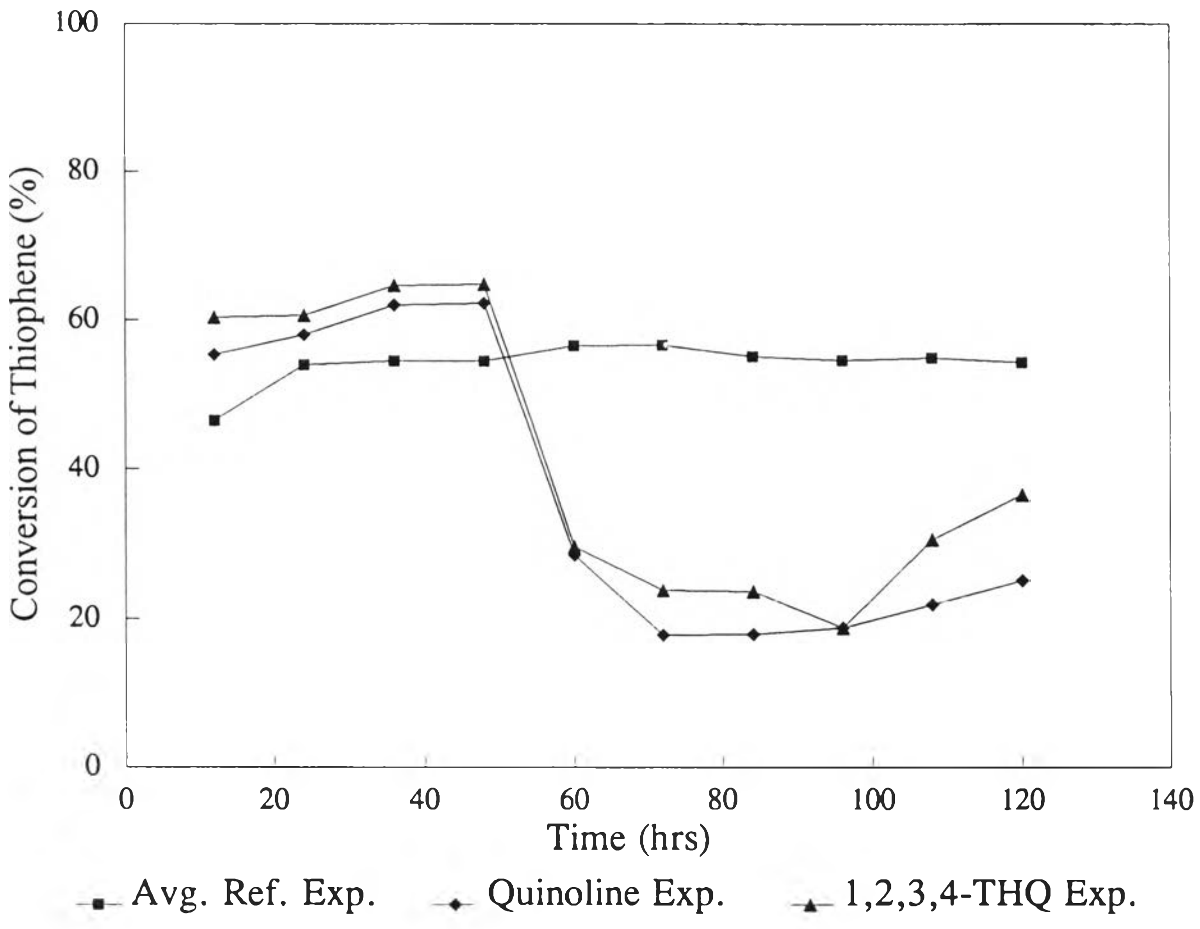

Figure 4.4 Conversion of Thiophene with Time Saturated of Ring Effect

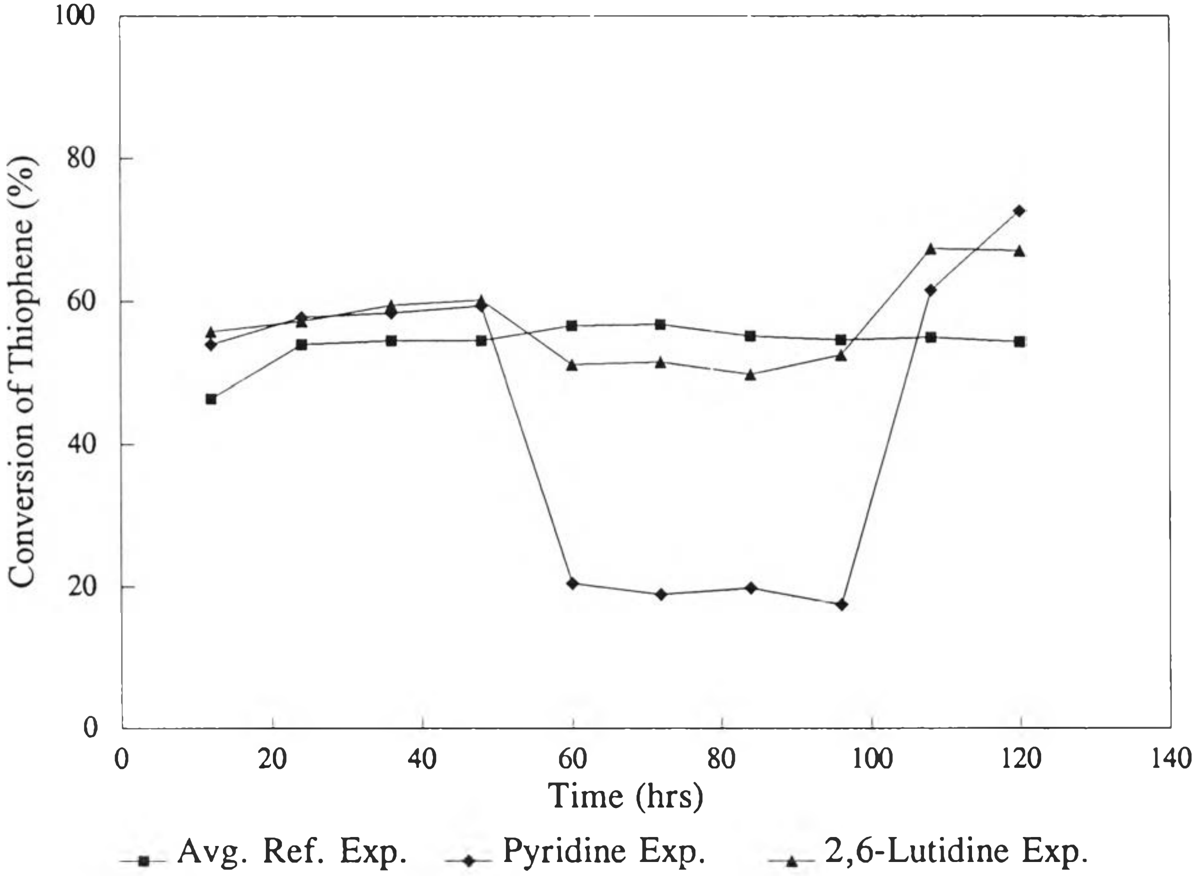

Figure 4.5 Conversion of Thiophene with Time
Stearic Hindrance Effect

for feedstock containing pyridine and 2,6-lutidine. It showed that pyridine decreased thiophene conversion from 55% to 19% while 2,6-lutidine decrease thiophene conversion from 55% to 49%. Although, the basicity (based upon pKa and proton affinity as shown in Table 2.4) of 2,6-lutidine was higher than that of pyridine, but 2,6-lutidine decreased thiophene conversion less than that of pyridine. These results can be explained by the adsorption of nitrogen compound on the catalyst which occured through nitrogen atom rather than $\pi$-bonding of the ring. In addition, nitrogen atom of pyridine was not hindered by the methyl groups as that of 2,6-lutidine, adsorption on catalyst through nitrogen atom of pyridine was easier than that of 2,6-lutidine. So, it indicated that increasing stearic hindrance to structure caused decreasing inhibition effect. Similar results were obtained by Knosinger (1976) and Gutberlet and Bertolacini (1983) who studied many nitrogen compounds on HDS of naptha and reported that the lack of inhibition when methyl groups were attached to ring carbons adjacent to the nitrogen atom and suggested that adsorption of pyridine molecule on the active desulfurization sites through the nitrogen atom.

## Results from Catalyst Characterisitc

Table 4.7 and Figure 4.6 showed coke content in spent catalysts of each experiment. Difference in coke content of each deactivated experiment with respect to that of reference experiment means that coke formation is caused by each nitrogen compound. The data showed that

TABLE 4.7 Coke Content of Fresh and Spent Catalysts in Each Experiment

| Experiment | Coke Content wt (%) | | | Coke Content Average wt (%) | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | | |
| Reference Experiment | | | | | average |
| 1-Ref. Exp. | 13.39 | 11.54 | 12.19 | 12.37 | 12.65 |
| 2-Ref. Exp. | 12.56 | 12.93 | 13.27 | 12.92 | accuracy |
| 3-Ref. Exp. | 12.66 | 12.66 | 12.70 | 12.67 | 2.13% |
| Deactivated Experiment | | | | | |
| Pyridine Exp. | 11.433 | 11.43 | 12.15 | 11.67 | |
| Quinoline Exp. | 10.39 | 10.39 | 10.27 | 10.35 | |
| 1,2,3,4-THQ Exp. | 11.09 | 11.09 | 11.10 | 11.09 | |
| 2,6-Lutidine Exp. | 14.26 | 14.26 | 14.16 | 14.23 | |
| Pyrrole Exp. | 11.76 | 11.76 | 11.10 | 11.54 | |

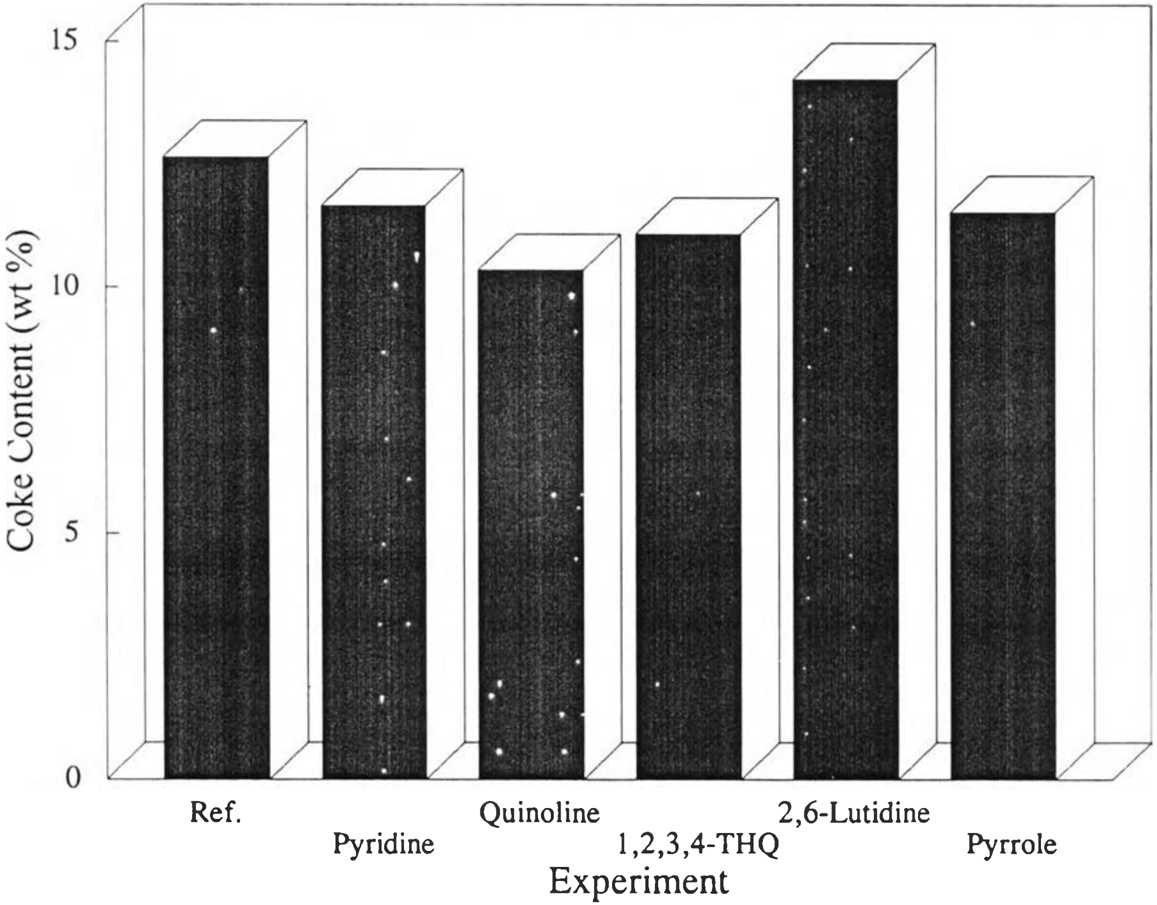

Figure 4.6 Coke Content of Spent Catalysts in Each Experiment

nonstearic nitrogen compounds (pyridine, quinoline, 1,2,3,4-tetrahydroquinoline and pyrrole) decreased coke formation while stearic nitrogen compounds caused coke formation. Coke formation was believed to occur by polymerization and dehydrogenation on hydrogen elimination reactions of the adsorbed hydrocarbon molecules on the catalyst. HDS catalyst was observed by many investigators that there were two types of active sites, one is active for hydrodesulfurization and is called HDS sites while the other is active for hydrogenation and is called HYD sites. The former was stearic hindered effect while the latter was not stearic hindered effect (Miciukiewicz et al., 1986). Nonstearic hindered nitrogen compounds poisoned HDS sites, as reversible poisoning, rather than HYD sites. When HDS site was blocked by nonstearic nitrogen compounds, it appeared that there was an increasing in amount of unreacted-thiophene and a decreasing in coke formation due to less reactant at active sites. In contrast, 2,6-lutidine caused coke formation due to its poisoning effect at HYD sites. HDS sites were less inhibited by 2,6-lutidine so reaction of thiophene HDS was increase. So selective poisoning of 2,6-lutidine caused coke formation. Similar results were obtained by Thomas (1979) who reported that N-containing heterocyclic compounds caused coke formation.

Table 4.8 and Figure 4.7 showed pore volume of fresh and spent catalysts in each experiment. Table 4.9 and Figure 4.9 showed total surface area of spent catalysts in each experiment. Comparison of pore volume and total surface area of deactivated experiments with

TABLE 4.8 Pore Volume of Fresh and Spent Catalysts in Each Experiment

| Experiment | Unburned (ml/g) | Burned (ml/g) | Regeneration Characteristic w.r.t Fresh Cat. | Reduction of Pore Volume (%) | |
|---|---|---|---|---|---|
| Fresh Catalyst | 0.2823 | 0.3734 | - | - | |
| Reference Experiment | | | | | average |
| 1-Ref. Exp. | 0.2081 | 0.4152 | 1.11 | 26.28 | 26.16 |
| 2-Ref. Exp. | 0.2166 | 0.3849 | 1.03 | 23.27 | accuracy |
| 3-Ref. Exp. | 0.2006 | 0.3239 | 0.86 | 28.94 | 2.78 |
| Average | 0.2084 | 0.3747 | 1.00 | | |
| Deactivated Experiment | | | | | |
| Pyridine Exp. | 0.2347 | 0.3791 | 1.01 | 16.86 | |
| Quinoline Exp. | 0.1951 | 0.4249 | 1.14 | 30.89 | |
| 1,2,3,4-THQ Exp. | 0.2376 | 0.3778 | 1.01 | 15.83 | |
| 2,6-Lutidine Exp. | 0.2214 | 0.3899 | 1.04 | 21.57 | |
| Pyrrole Exp. | 0.2587 | 0.3673 | 0.98 | 8.36 | |

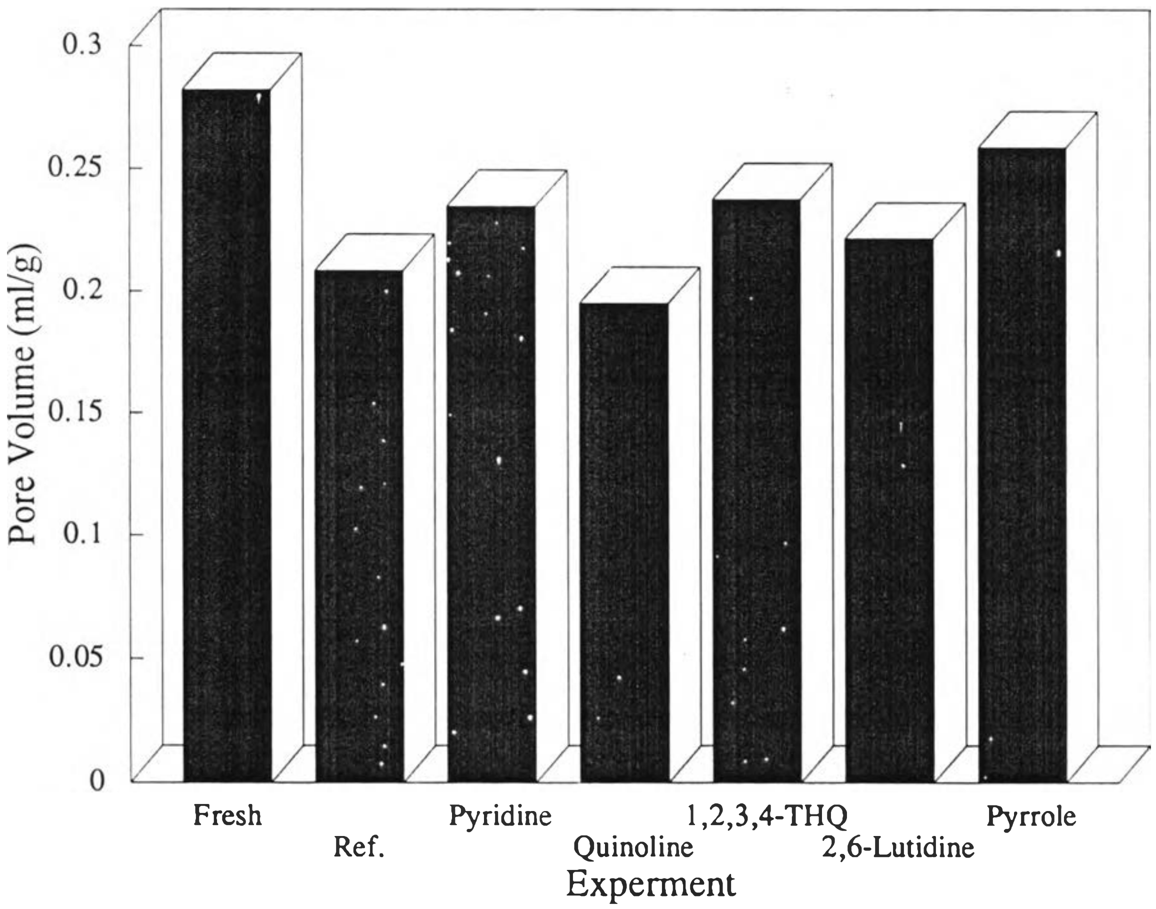

Figure 4.7 Pore Volume of Fresh and Spent Catalysts Before Burning

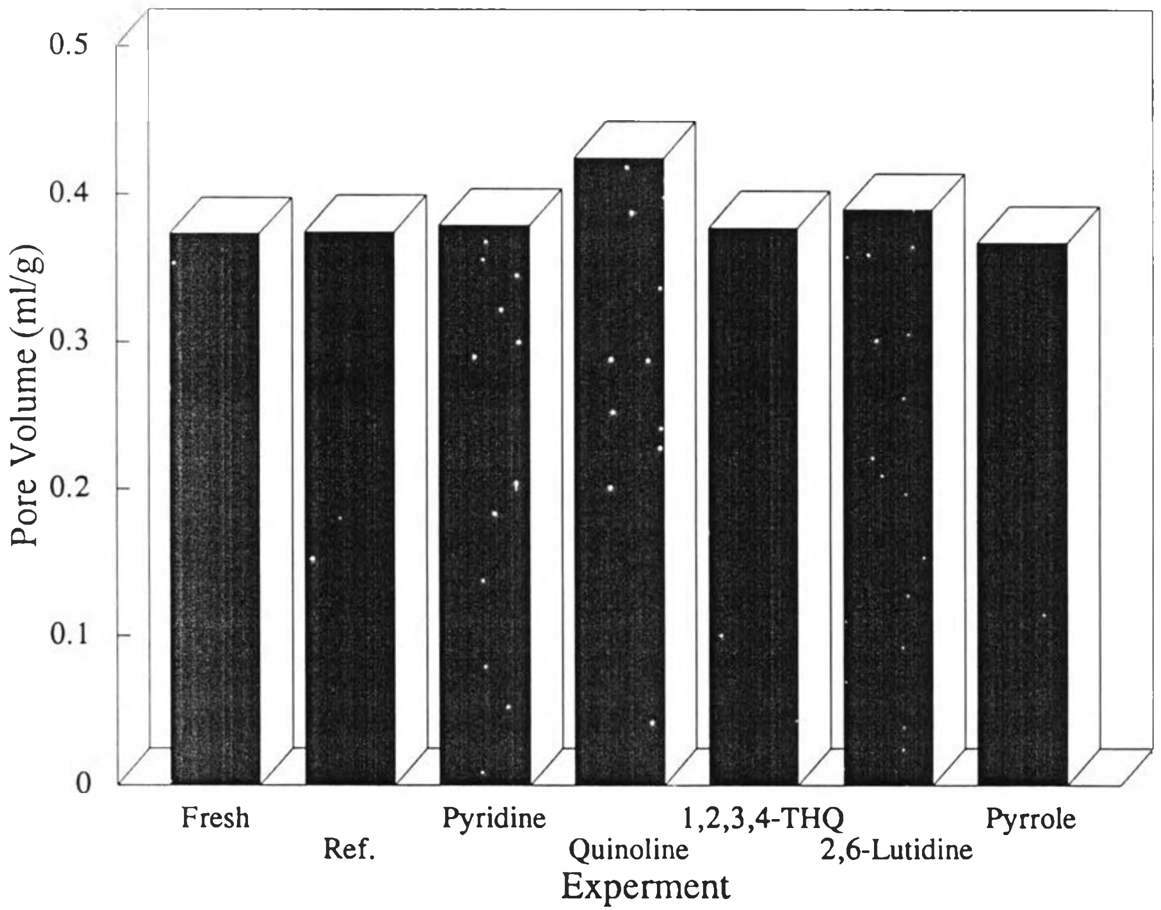

Figure 4.8 Pore Volume of Fresh and Spent Catalysts After Burning

TABLE 4.9 Total Surface Area of Fresh and Spent Catalysts in Each Experiment

| Experiment | Unburned (sq.m/g) | Burned (sq.m/g) | Regeneration Characteristic w.r.t Fresh Cat. | Reduction of Surface Area (%) | |
|---|---|---|---|---|---|
| Fresh Catalyst | 179.2938 | 220.6195 | - | - | |
| Reference Experiment | | | | | average |
| 1-Ref. Exp. | 148.4975 | 169.8863 | 0.77 | 17.17 | 18.16 |
| 2-Ref. Exp. | 148.4644 | 172.3916 | 0.78 | 17.19 | accuracy |
| 3-Ref. Exp. | 143.2409 | 172.3370 | 0.78 | 20.11 | 1.95 |
| Average | 146.7343 | 171.5383 | 0.777 | | |
| Deactivated Experiment | | | | | |
| Pyridine Exp. | 148.0142 | 180.0297 | 0.82 | 17.45 | |
| Quinoline Exp. | 138.2484 | 186.9176 | 0.85 | 22.89 | |
| 1,2,3,4-THQ Exp. | 147.0541 | 177.8176 | 0.80 | 17.98 | |
| 2,6-Lutidine Exp. | 144.0990 | 177.2236 | 0.80 | 19.63 | |
| Pyrrole Exp. | 158.3041 | 174.5313 | 0.79 | 11.71 | |

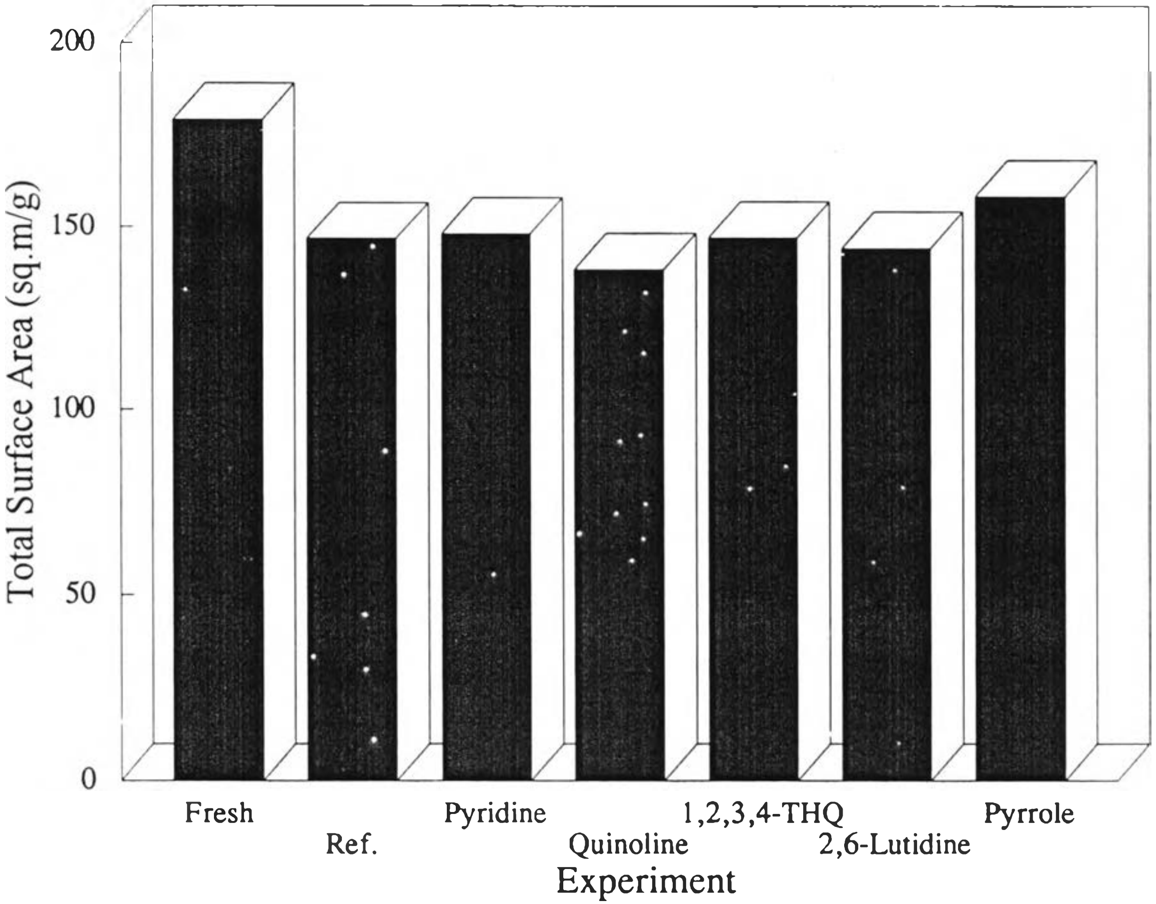

Figure 4.9 Total Surface Area of Fresh and Spent Catalysts Before Burning

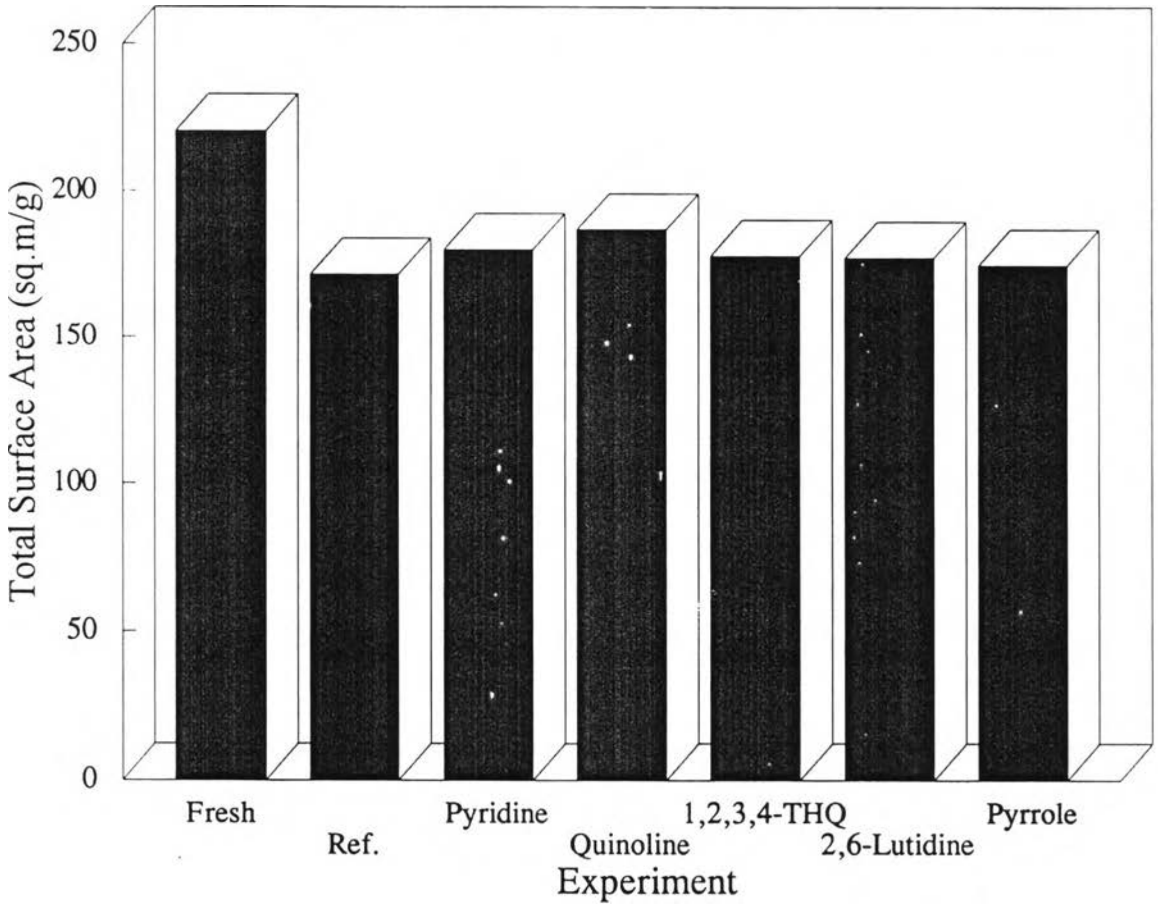

Figure 4.10 Total Surface Area of Fresh and Spent Catalysts After Burning

respect to reference experiment showed pore volume and total surface area change due to each nitrogen compound. Figure 4.8 and 4.10 showed pore volume and total surface area of spent catalysts after regeneration.

These data showed that only quinoline caused decreasing in pore volume and surface area while other nitrogen compounds increase pore volume and total surface area when compared the results with reference experiment. It can be concluded that pore volume and tatal surface area changed due to coke deposition. Nitrogen compounds as pyridine, 1,2,3,4-tetrahydroquinoline, 2,6-lutidine, and pyrrole which decreased coke formation caused pore volume and total surface area to increase with respect to reference experiment. In contrast, although quinoline caused decreasing coke formation but it still caused pore volume and total surface area to decrease also. These results indicated that the coke formed due to quinoline caused blocking the pore mouths of the catalyst. This result was explained by quick adsorption of quinoline on HYD sites caused the promotion of coke formation on HDS site. Quick aggregation of coke on the pore mouths of the catalyst caused pore mouths blocking, resulting in the reduction of pore volume and total surface area. The reduction of pore volume and total surface area caused decreasing of active sites which caused decreasing of reaction. The reaction on catalyst surface is reduced, so coke formation on the catalyst also reduced. After regeneration both pore volume and total surface area of spent catalysts returned to nearly their original values, as shown in Figure 4.8 and 4.10. This resulted indicated that all nitrogen compounds can be removed at regeneration conditions used.