# CHAPTER IV

## EXPERIMENTAL RESULTS AND DISCUSSIONS

In this study, the experiments can be categorized into three parts. The first part is preliminary experiment, which is performed to test the reaction of toluene at four different temperatures (Experiment 1) and determine the suitable operating condition for quinoline hydrodenitrogenation reaction (Experiment 2). The second part is Experiments 3 and 4 which are conducted to study the repeatability of the experiments and determine product distributions at a operating condition. The third part is Experiments 5 to 9 which are carried out to study effects of sulfur compounds on catalyst and hydrodenitrogenation of quinoline.

The experiments are carried out in a fixed-bed reactor employing a commercial $NiMo/Al_2O_3$ hydrotreating catalyst. The operating conditions used for hydrodenitrogenation reaction test are summarized in Table 4.1. For Experiments 5 to 9, after the reaction reaches a steady-state, the solution is replaced by another solution containing both original liquid feed and a sulfur compound to determine effects of sulfur compounds on hydrodenitrogenation reaction for 48 hours. Subsequently, the solution is switched to original liquid feed to determine the change in catalyst activity by the presence or absence of sulfur compound during reaction. Experimental numbers and the liquid feed compositions of each experiment are presented in Table 4.2. The liquid feed contains 0.05% by weight of $CS_2$ for experiments with sulfided catalyst to keep the catalyst in sulfided form. Toluene is used as a feed carrier and has a good solubility for used compounds.

Table 4.1 Experimental Operating Conditions

| Operating Conditions: | | |
|---|---|---|
| Temperature | : | 300, 350, 370 and 390°C for Experiment 1 and 2 |
| | : | 370°C for Experiments 3 to 9 |
| Pressure | : | 400 psig |
| Feed flow rate | : | 10 $cm^3/hr$ |
| Hydrogen flow rate | : | 400 $cm^3/min$ |
| Reaction period | : | 96 hours for Experiment 1 and 2 |
| Sampling | : | every 6 hours until the end of experiment |
| Reaction period | : | 144 hours for Experiments 3 to 9 |
| Sampling | : | every 12 hours for first 48 hours and every 6 hours until the end of experiment |
| Catalyst | : | 1/16" Extruded of NiMo/$Al_2O_3$ |
| Catalyst weight | : | 1 gram |
| Space time based on quinoline feed rate only | : | 160 (hr)(g of cat.)/(g-mol of quinoline) |
| $H_2$/oil ratio | : | 2,400 $m^3$ of $H_2/m^3$ of oil |

Table 4.2 Experiment Numbers and the Liquid Feed Compositions of Each Experiment

| | | |
|---|---|---|
| Experiment 1 | : | Toluene, 0.05 wt% Carbon Disulfide (preliminary experiment 1) |
| Experiment 2 | : | Original liquid feed* (preliminary experiment 2) |
| Experiment 3 | : | Original liquid feed (reference experiment) |
| Experiment 4 | : | Original liquid feed (duplication of reference experiment) |
| Experiment 5 | : | Original liquid feed/ Toluene, 0.5 wt% Nitrogen as Quinoline, 0.05 wt% Carbon Disulfide, and 0.4 wt% Sulfur as Ethyl Sulfide** |
| Experiment 6 | : | Original liquid feed/ Toluene, 0.5 wt% Nitrogen as Quinoline, 0.05 wt% Carbon Disulfide, and 0.4 wt% Sulfur as Thiophene |
| Experiment 7 | : | Original liquid feed/ Toluene, 0.5 wt% Nitrogen as Quinoline, 0.05 wt% Carbon Disulfide, and 0.4 wt% Sulfur as Methyl Sulfide |
| Experiment 8 | : | Original liquid feed/ Toluene, 0.5 wt% Nitrogen as Quinoline, 0.05 wt% Carbon Disulfide, and 0.4 wt% Sulfur as Methyl Disulfide |

| | | |
|---|---|---|
| Experiment 9 | : | Original liquid feed/ Toluene, 0.5 wt% Nitrogen as Quinoline, 0.05 wt% Carbon Disulfide, and 0.4 wt% Sulfur as Carbon Disulfide |

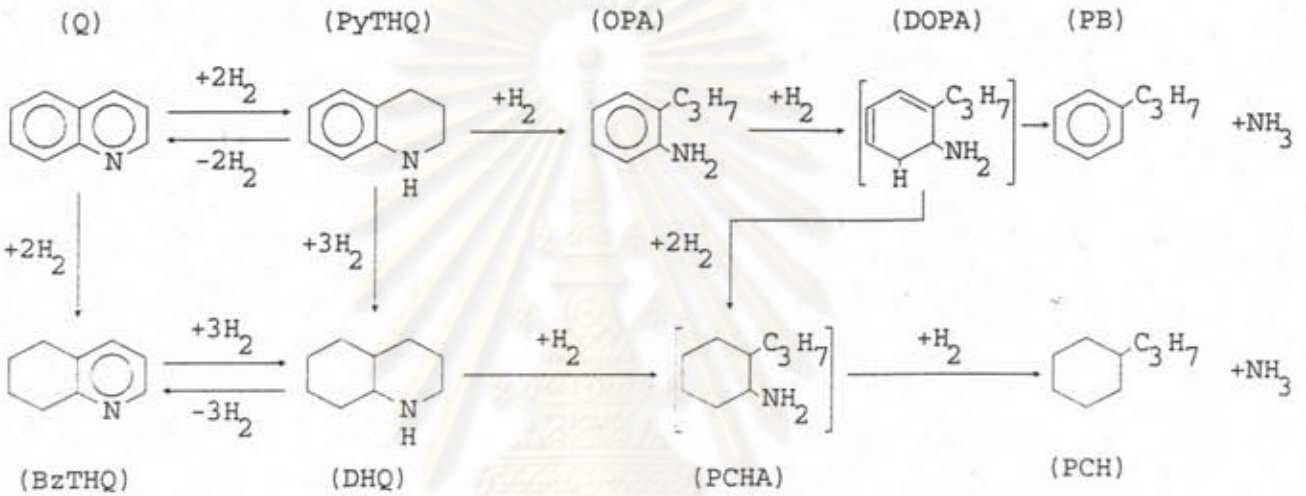
---

* Toluene, 0.5 wt% Nitrogen as Quinoline, 0.05 wt% Carbon Disulfide

** Solution containing both original liquid feed and an additive compound

The major reaction products detected by the gas chromatographic technique are quinoline, 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, decahydroquinoline, o-propylaniline, propylcyclohexane and propylbenzene. Propylcyclohexylamine and dihydro o-propylaniline are plausible reaction intermediates which presumably denitrogenated very rapidly, and therefore are not specifically identified in the hydrodenitrogenation products.

The proposed reaction network for hydrodenitrogenation of quinoline is shown in Figure 4.1. This proposed reaction network is similar to that used previously (Shih et al., 1977; Satterfield et al., 1978; Satterfield and Gultekin, 1981; Satterfield and Yang, 1984). There are two pathways in this reaction network: one involves the successive formation from quinoline (Q) hydrogenation of 1,2,3,4-tetrahydroquinoline (PyTHQ) and subsequently 1,2,3,4-tetrahydroquinoline is hydrogenolyzed to o-propylaniline (OPA), dihydro o-propylaniline (DOPA) and propylbenzene (PB) with ammonia. A second pathway involves the successive formation from quinoline hydrogenation of 5,6,7,8-tetrahydroquinoline (BzTHQ) and subsequently 5,6,7,8-tetrahydroquinoline is hydrogenated to




| | | | |
|---|---|---|---|
| Q | quinoline | PCHA | propylcyclohexylamine |
| PyTHQ | Py(or 1,2,3,4)-tetrahydroquinoline | PB | propylbenzene |
| BzTHQ | Bz(or 5,6,7,8)-tetrahydroquinoline | PCH | propylcyclohexane |
| DHQ | decahydroquinoline(cis and trans isomers) | DOPA | dihydro o-propylaniline |
| OPA | o-propylaniline | | |





Figure 4.1 Proposed Reaction Network for Hydrodenitrogenation of Quinoline

decahydroquinoline (DHQ). After that, decahydroquinoline is hydrogenolyzed to propylcyclohexylamine (PCHA). Then, propylcyclohexylamine is hydrogenolyzed to propylcyclohexane (PCH) and ammonia.

**4.1 Preliminary Experiment**

Experiment 1 is performed to test the reaction of toluene at four different temperatures. The percent weight of toluene in samples at 300, 350, 370 and 390°C is presented in Figure 4.2 which shows that the percent weight of toluene is approximately 100 at all temperatures, so toluene does not react at these temperatures. It can be concluded that toluene can be used as a feed carrier for this study.

Earlier investigating (Satterfield et al., 1978; Cocchetto and Satterfield, 1981; Gultekin et al., 1989) suggested that quinoline hydrodenitrogenation reaction varied greatly with temperature. Thus Experiment 2 is performed to determine the suitable operating condition for quinoline hydrodenitrogenation reaction by varying the temperatures. Figures 4.3 and 4.4 show the effect of temperature on product composition. The figures show that weight of quinoline, o-propylaniline, propylbenzene, propylcyclohexane and area of 5,6,7,8-tetrahydroquinoline are directly proportional to the temperature, whereas weight of 1,2,3,4-tetrahydroquinoline is inversely proportional to the temperature. Decahydroquinoline has a maximum weight at 350°C. The effect agreed with the results of Satterfield et al. (1978) who studied intermediate reactions in the catalytic hydrodenitrogenation of quinoline. They found that at the lower temperatures the concentration of quinoline was much less than that of 1,2,3,4-tetrahydroquinoline and the latter was then converted either to o-propylaniline or to decahydroquinoline. At higher temperatures the equilibrium concentration of 1,2,3,4-tetrahydroquinoline

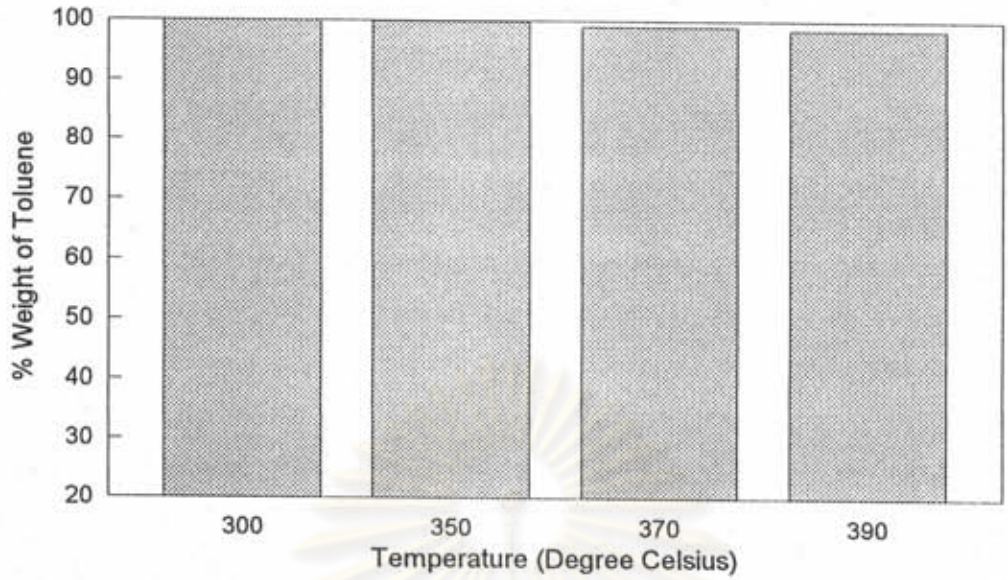



Figure 4.2 Percent Weight of Toluene in Samples with Temperature

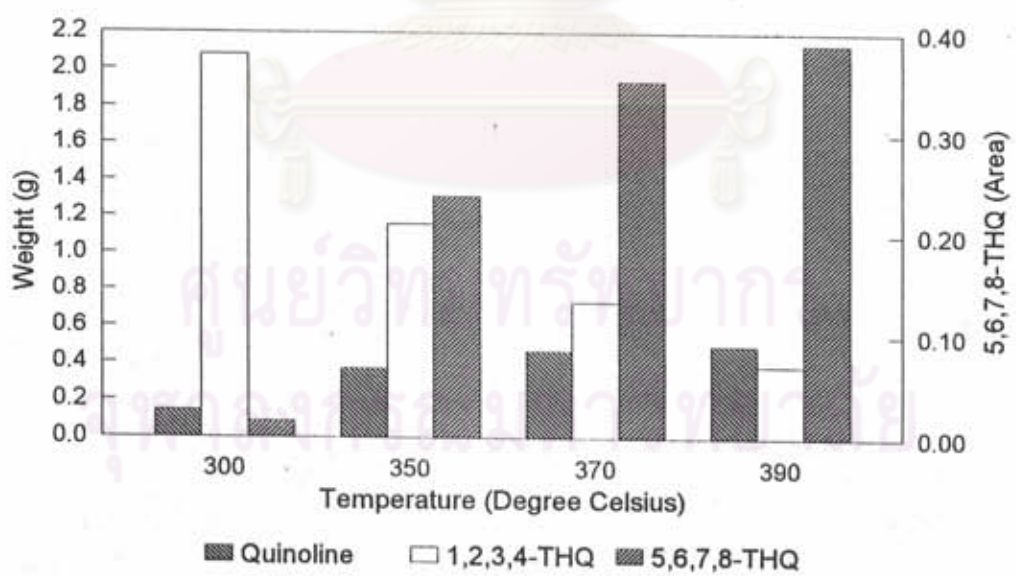



Figure 4.3 Distribution of 1,2,3,4-Tetrahydroquinoline, 5,6,7,8-Tetrahydroquinoline and Quinoline in Samples with Temperature

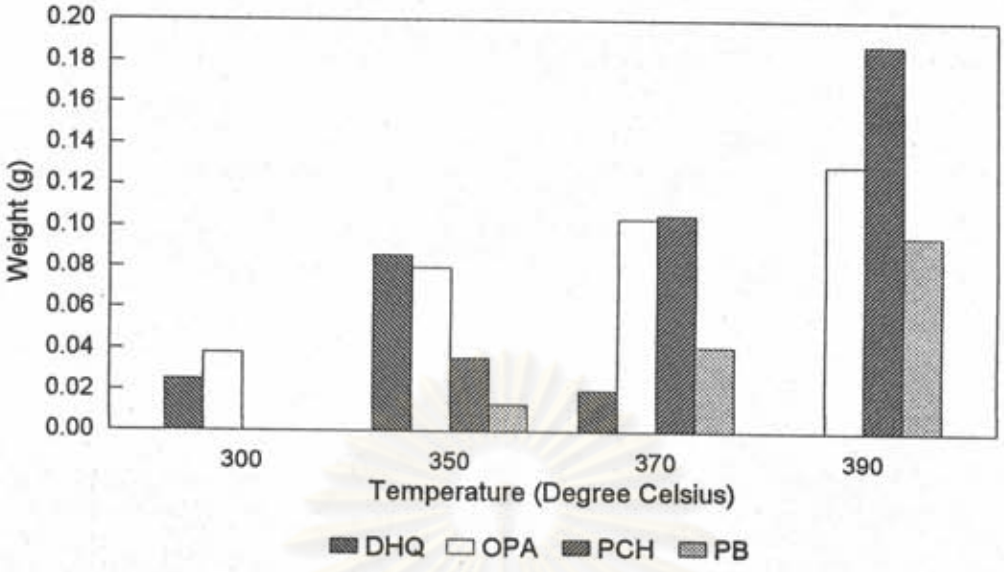



Figure 4.4 Distribution of Decahydroquinoline, o-Propylaniline, Propylcyclohexane and Propylbenzene in Samples with Temperature

was much diminished relative to quinoline and the conversion rate of the latter to 5,6,7,8-tetrahydroquinoline and subsequently to decahydroquinoline and its products became significant. The increasing quantity of quinoline found at higher temperatures suggested that a thermodynamic equilibrium between quinoline and 1,2,3,4-tetrahydroquinoline was approached, which shifted in favor of quinoline at higher temperatures. So, quinoline conversion is decreased by increasing the temperature and is shown in Figure 4.5. In addition, Cocchetto and Satterfield (1981) studied chemical equilibria among quinoline and its reaction products in hydrodenitrogenation at 515 and 1015 psig, 330 to 420$^{o}$C and also found that the heterocyclic equilibria favored decahydroquinoline at lower temperature and high hydrogen pressure, while quinoline was favored at higher temperature and lower hydrogen pressure. They reported that effects of temperatures and pressures were consistent with the fact that the ring

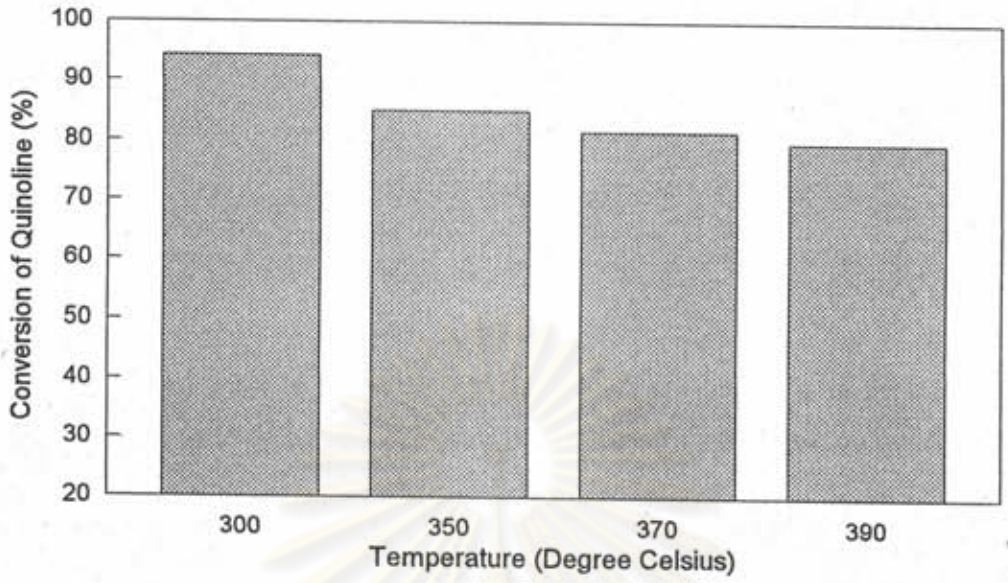



Figure 4.5 Quinoline Conversion with Temperature

saturation (hydrogenation) reactions were exothermic and consume hydrogen.

Gultekin et al. (1989) found that decahydroquinoline concentration was higher at 330°C and decreased rapidly with increasing temperature (350°C and 370°C). They postulated that at low temperature (330°C) the hydrogenolysis reaction might be rate limiting. At 300°C decahydroquinoline appeared in small concentrations because the main step which given decahydroquinoline appeared to be through 5,6,7,8-tetrahydroquinoline than via 1,2,3,4-tetrahydroquinoline. This was consistent with the observations of Satterfield et al. (1978). At low temperature the hydrogenolysis reaction might be rate limiting so that increasing the temperature caused significant increases in quantities of o-propylaniline, propylcyclohexane and propylbenzene.

The results of experiment can be concluded that the suitable operating condition for quinoline hydrodenitrogenation reaction is 370°C because this temperature gives suitable quantities of products. The

reason for choosing suitable quantities of products is that effects of sulfur compounds on hydrodenitrogenation of quinoline are easily identified. Under this condition, conversion of quinoline is approximately 80% (gives a moderate rate of reaction).

Conversion of quinoline is calculated by

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

Where

$C_{to}$ = weight of quinoline in feed (g)

$C_t$ = weight of quinoline in product sample (g)

## 4.2 Study the Repeatability of the Experiments and Determine Product Distributions at a Operating Condition

Experiments 3 and 4 are conducted at a operating condition in order to study the repeatability of the experiments and determine product distributions. Experiments 3 and 4 are called Reference 1 and Reference 2, respectively. The repeatability of various compounds in samples is given in Appendix (Table 2A to 8A). Maximum, minimum and average deviation are used as basis deviation. Therefore, effects of sulfur compounds on catalyst and hydrodenitrogenation of quinoline are carried out by comparison of deviation of the average reference experiment with deviation of experiments which added various sulfur compounds. Table 4.3 summarizes the maximum, minimum and average deviation of average reference experiment.

Table 4.3 Summary of the Maximum, Minimum and Average Deviation of Average Reference Experiment

| Compounds | Deviation (%) | | |
|---|---|---|---|
| | Maximum | Minimum | Average |
| Quinoline | 3.99 | 0.12 | 1.37 |
| 1,2,3,4-THQ | 3.01 | 0.23 | 1.25 |
| 5,6,7,8-THQ | 3.80 | 0.28 | 1.73 |
| DHQ | 3.784 | 0.176 | 1.218 |
| OPA | 4.63 | 0.10 | 1.80 |
| PCH | 4.14 | 0.10 | 1.44 |
| PB | 4.348 | 0.442 | 2.184 |

In Figures 4.6 to 4.12, the weight of various products is plotted against time on stream. These plot show that the reaction reaches its steady-state after approximately 48 hours. Therefore, effects of sulfur compounds on catalyst and hydrodenitrogenation of quinoline are studied after 48 hours.

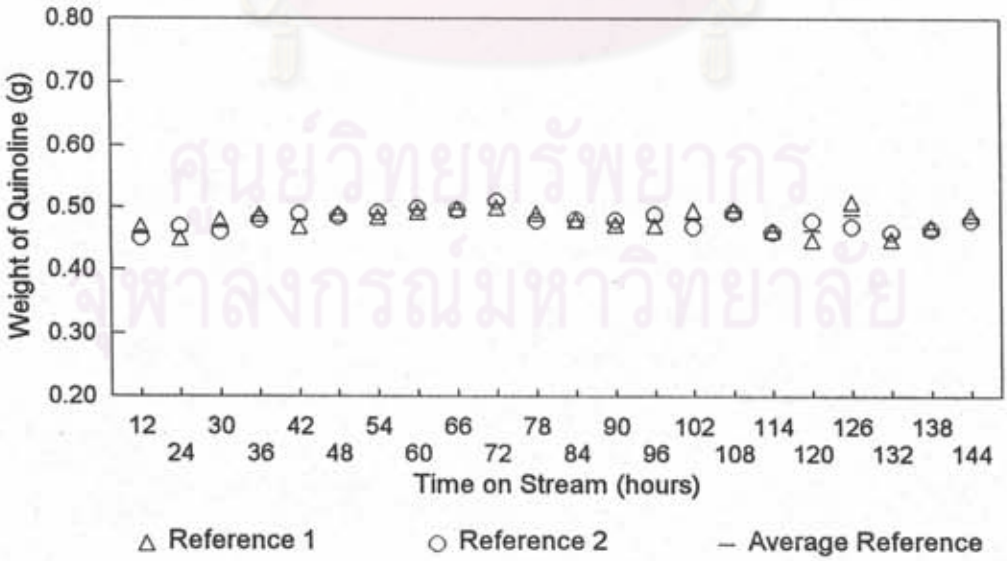



Figure 4.6 Weight of Quinoline in Samples with Time

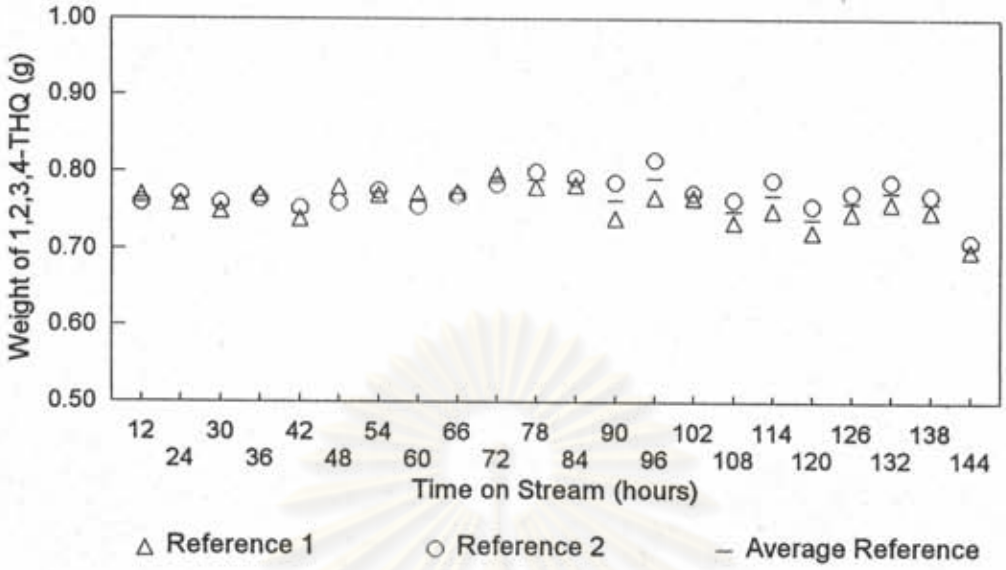



Figure 4.7 Weight of 1,2,3,4-Tetrahydroquinoline in Samples with Time

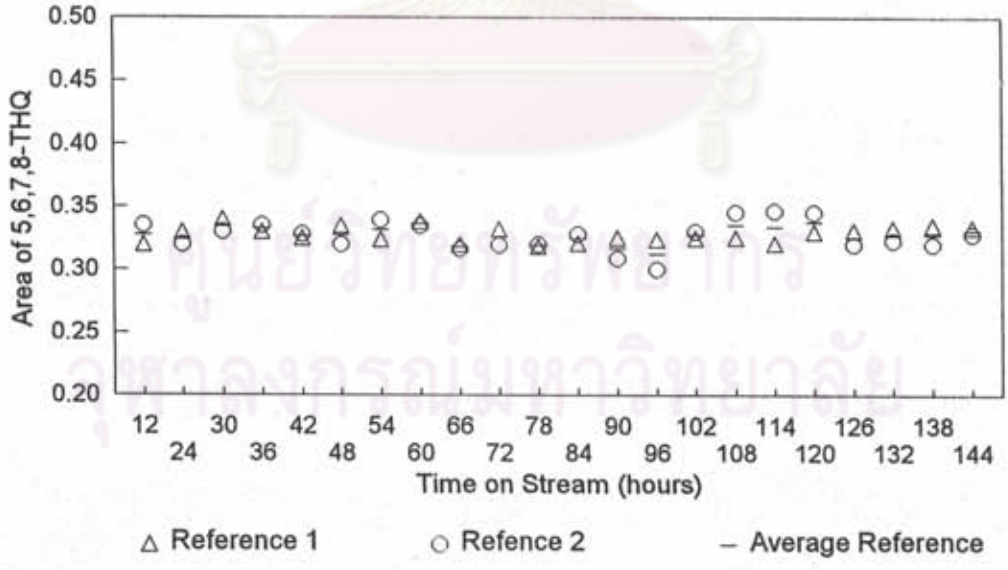



Figure 4.8 Area of 5,6,7,8-Tetrahydroquinoline in Samples with Time

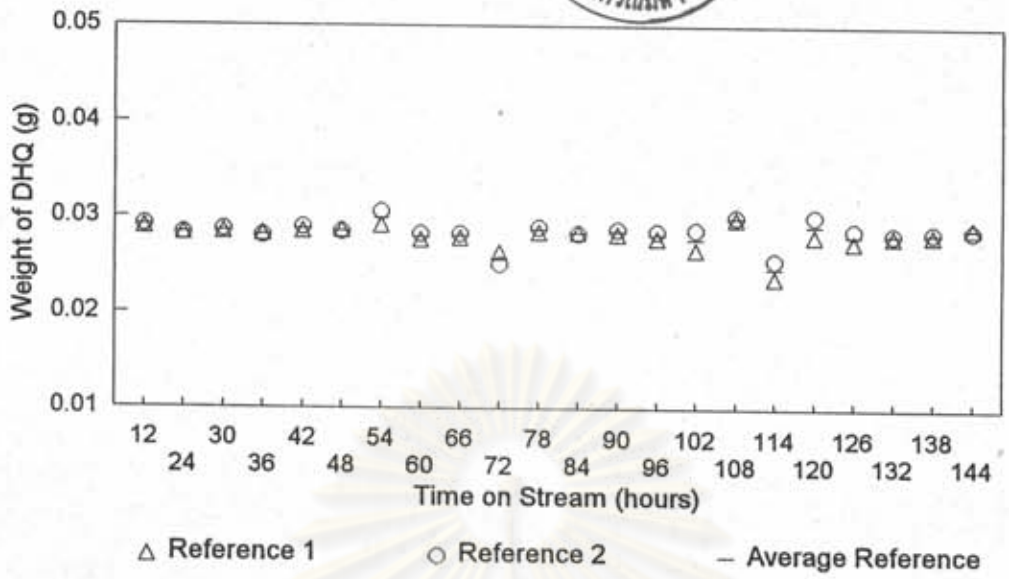



Figure 4.9 Weight of Decahydroquinoline in Samples with Time

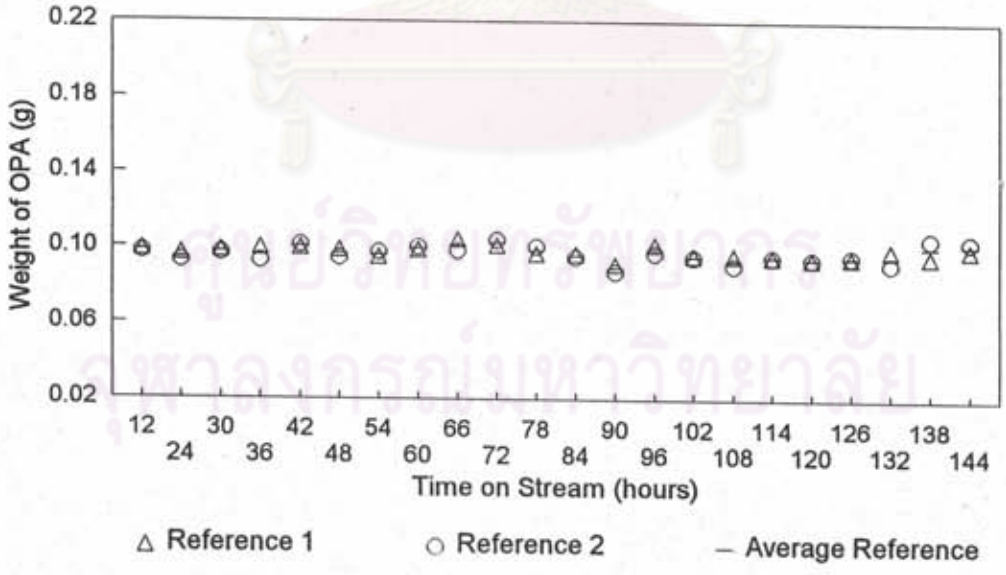



Figure 4.10 Weight of o-Propylaniline in Samples with Time

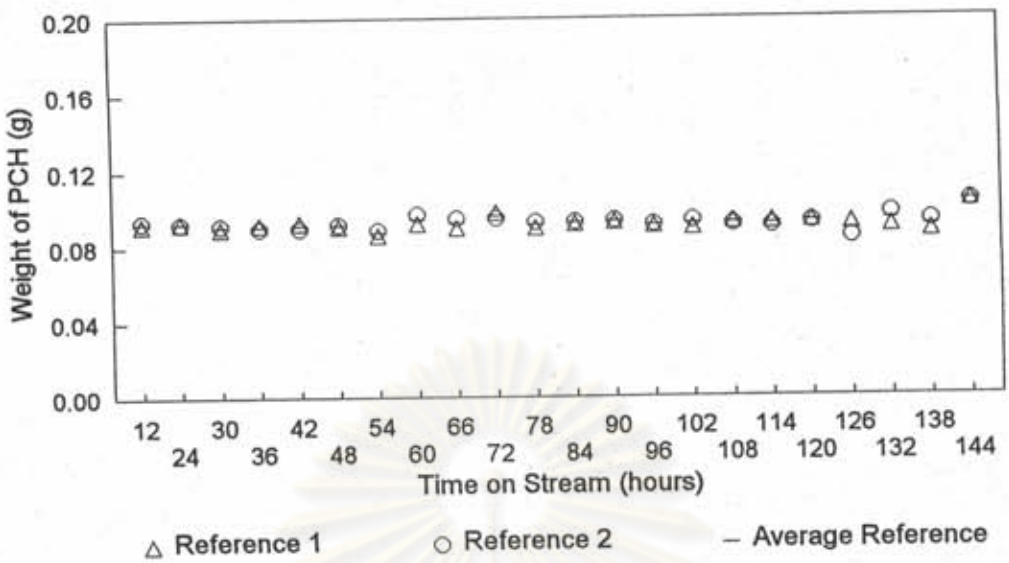



Figure 4.11 Weight of Propylcyclohexane in Samples with Time

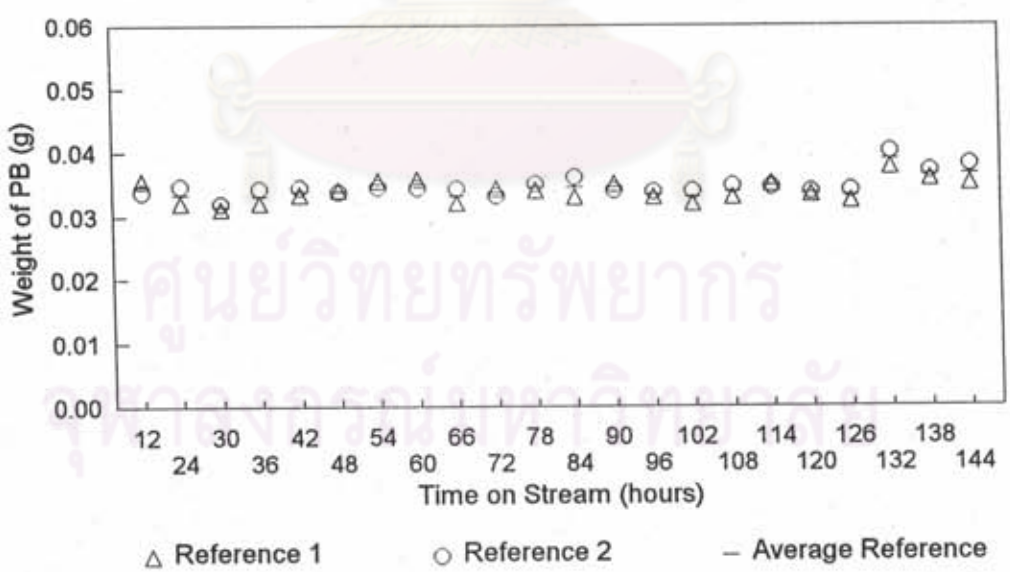



Figure 4.12 Weight of Propylbenzene in Samples with Time

## 4.3 Study Effects of Sulfur Compounds on Catalyst and Hydrodenitrogenation of Quinoline

Under hydrodenitrogenation conditions, sulfur compounds can react with hydrogen via hydrodesulfurization reaction to produce hydrogen sulfide. The presence of hydrogen sulfide has a slight inhibiting effect on the intermediate hydrogenation-dehydrogenation steps involved in the overall hydrodenitrogenation of quinoline but a marked accelerating effect on the intermediate hydrogenolysis steps. The net effect is an increase in the overall hydrodenitrogenation rate. Satterfield and Gultekin (1981) reached this conclusion in investigations of the effect of hydrogen sulfide on the catalytic hydrodenitrogenation of quinoline. They reported that hydrogenation-dehydrogenation reactions might be retarded by competitive adsorption between hydrogen sulfide and nitrogen compounds for hydrogenation sites. The enhancement in hydrogenolysis reactions might be caused by an increase in the surface acidity from the hydrogen sulfide; as a result the quantities of o-propylaniline, propylcyclohexane and propylbenzene were increased in the presence of hydrogen sulfide. For the quantity of 5,6,7,8-tetrahydroquinoline was increased in the presence of hydrogen sulfide because hydrogen sulfide inhibited the hydrogenation of quinoline to 5,6,7,8-tetrahydroquinoline much lower than the hydrogenation of 5,6,7,8-tetrahydroquinoline to decahydroquinoline and hydrogen sulfide also slightly inhibited the dehydrogenation of decahydroquinoline to 5,6,7,8-tetrahydroquinoline. Besides, hydrogen sulfide caused significant decreased the quantity of decahydroquinoline since hydrogen sulfide had a definite enhancement effect on the hydrogenolysis of decahydroquinoline but there was a slight inhibition effect on the hydrogenation of

5,6,7,8-tetrahydroquinoline to decahydroquinoline, the hydrogenation of 1,2,3,4-tetrahydroquinoline to decahydroquinoline and the dehydrogenation of decahydroquinoline to 5,6,7,8-tetrahydroquinoline. In addition, in the presence of hydrogen sulfide reduced the quantity of 1,2,3,4-tetrahydroquinoline so that hydrogen sulfide markedly increased the hydrogenolysis of 1,2,3,4-tetrahydroquinoline, resulting in the reduction of quinoline because quinoline reacted very rapidly to form an equilibrium mixture with 1,2,3,4-tetrahydroquinoline. Yang and Satterfield (1984) obtained similar results for catalytic hydrodenitrogenation of quinoline in a trickle-bed reactor at 350, 375, and 390°C and 6.9 MPa (1,001.0 psig). They found that the quantity of decahydroquinoline produced markedly decreased while the quantity of o-propylaniline increased, and as these results they suggested that hydrogen sulfide increased the rate of decahydroquinoline to form propylcyclohexylamine, which was readily converted to hydrocarbons and ammonia, and increased the hydrogenolysis of 1,2,3,4-tetrahydroquinoline to form o-propylaniline. Furthermore, these results were consistent with the observations of Gultekin et al. (1989) for combined effects of hydrogen sulfide, water and ammonia on hydrodenitrogenation of quinoline at 7 MPa (1,015 psig) and 330, 350, and 375°C. They reported that hydrogen sulfide decreased the concentration of decahydroquinoline and increased the concentration of 5,6,7,8-tetrahydroquinoline because hydrogen sulfide enhanced the hydrogenolysis reaction rate and inhibited hydrogenation.

Satterfield and Yang (1984) explained effects of hydrogen sulfide on catalytic hydrodenitrogenation of quinoline in the point of nature of the active sites. They proposed two types of catalytic sites on sulfided

$NiMo/Al_2O_3$ catalyst: site I was a sulfur anion vacancy associated with Mo and was responsible for both hydrogenolysis and hydrogenation reaction; site II was Bronsted acid type which was responsible for the hydrogenolysis reaction. Hydrogen sulfide interacted with sulfur anion vacancies (site I) to convert into Bronsted acid type (type II). Consequently, the presence of hydrogen sulfide markedly accelerated the hydrogenolysis reaction and slightly reduced the hydrogenation reaction. Furthermore, hydrogen sulfide had little effect on the activation energies for the hydrogenation reactions but it significantly reduced those for the hydrogenolysis reactions. This suggested that vacancies activity was slightly decreased in the presence of hydrogen sulfide and the Bronsted acid sites for the hydrogenolysis reactions were more active than vacancies. Maternova (1982) established the existence of SH groups on a sulfided commercial $CoMo/Al_2O_3$ catalyst by a technique involving adsorption of silver ions from a pyridine solution. The dissociation of hydrogen sulfide was similar to the dissociative adsorption of water onto a zeolite or alumina, in which a surface vacancy was converted to a Bronsted acid site. Voorhoeve (1971) demonstrated by an ESR study that the number of vacancies on a sulfided $NiW/Al_2O_3$ catalyst decreased with an increase of hydrogen sulfide partial pressure when the catalyst was exposed to an $H_2S/H_2$ environment.

### 4.3.1 Straight Chain and Cyclic

The effects of structure of sulfur compounds are compared between ethyl sulfide (straight chain) and thiophene (cyclic). Figures 4.13 to 4.19 show that, in the presence of sulfur compounds, the quantities of quinoline, 1,2,3,4-tetrahydroquinoline and decahydroquinoline are decreased while the quantities of 5,6,7,8-tetrahydroquinoline, o-propylaniline,

propylcyclohexane and propylbenzene are increased. These results indicate that sulfur compounds inhibit hydrogenation and dehydrogenation reactions but markedly accelerate hydrogenolysis reactions. Ethyl sulfide has stronger effect than thiophene, as shown in Table 4.4, since ethyl sulfide reacts to form hydrogen sulfide and hydrocarbons easier than thiophene. To explain the effect of structure, Massoth and Murali Dhar (1982) proposed a possible mechanism of hydrodesulfurization of thiophene. There were two pathways in this reaction. The first pathway was called hydrogenolysis and the second pathway was called hydrogenation. The second path was not rapid compared with the first path. So, if thiophene reacted via hydrogenation of heterocyclic ring pathway, it would react slow to form hydrogen sulfide. In addition, in the case of hydrogenolysis pathway, since sulfur atom in both compounds has two lone pair electrons but structure of thiophene is aromatic compound which has resonance effect. Therefore, a lone pair electrons

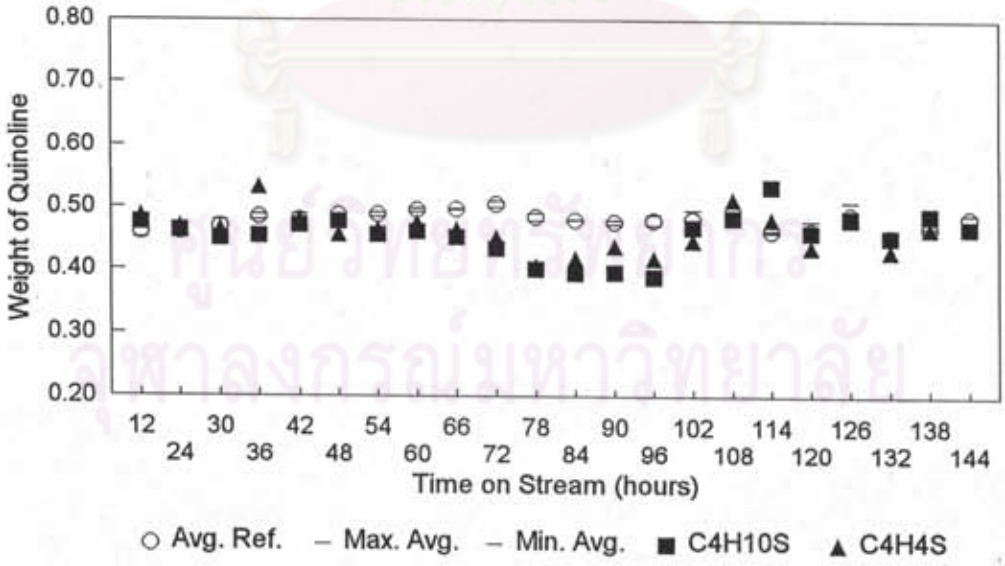



Figure 4.13 Effects of Ethyl Sulfide and Thiophene on Weight of Quinoline in Samples with Time

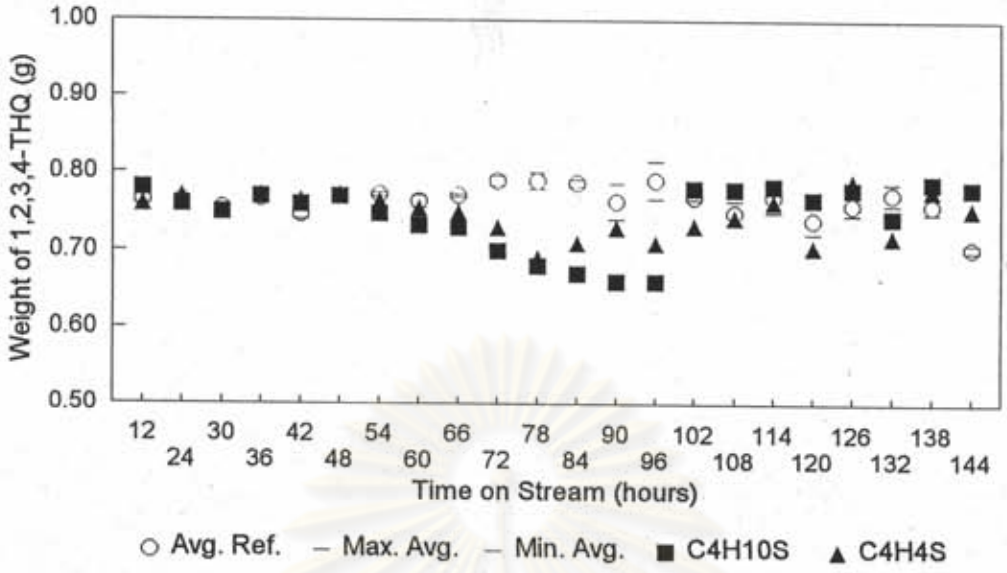



Figure 4.14 Effects of Ethyl Sulfide and Thiophene on Weight of 1,2,3,4-Tetrahydroquinoline in Samples with Time

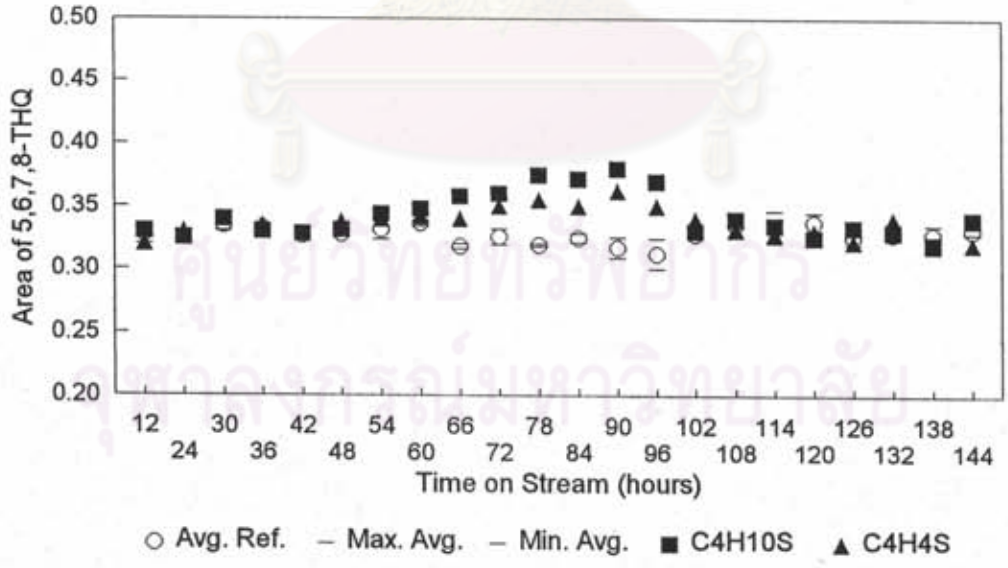



Figure 4.15 Effects of Ethyl Sulfide and Thiophene on Area of 5,6,7,8-Tetrahydroquinoline in Samples with Time

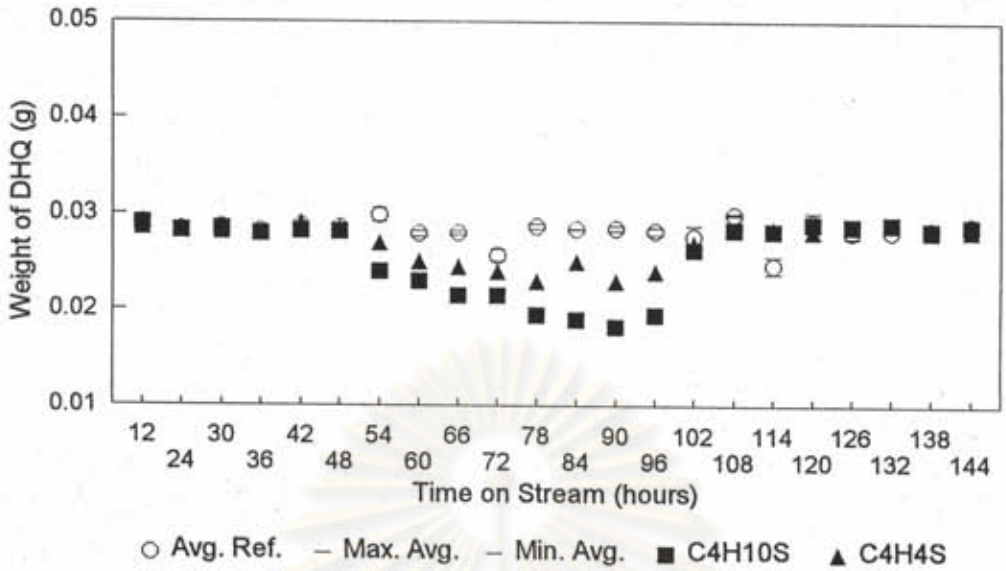



Figure 4.16 Effects of Ethyl Sulfide and Thiophene on Weight of Decahydroquinoline in Samples with Time

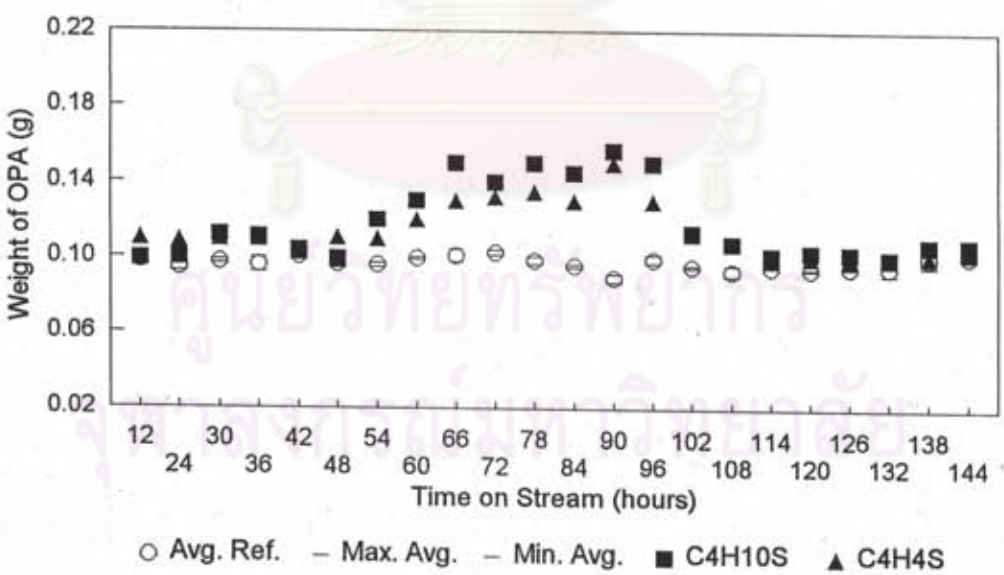



Figure 4.17 Effects of Ethyl Sulfide and Thiophene on Weight of o-Propylaniline in Samples with Time

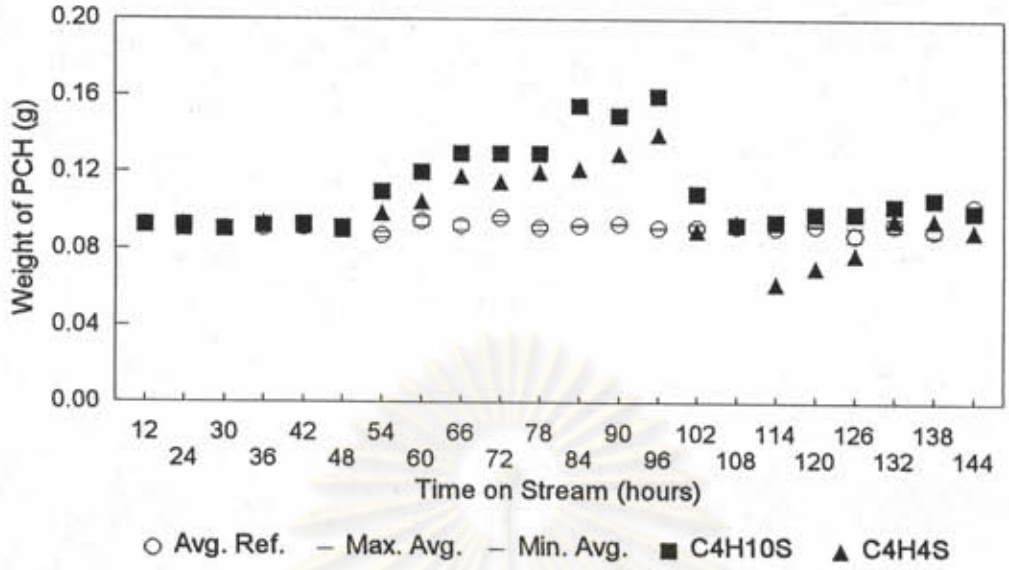



Figure 4.18 Effects of Ethyl Sulfide and Thiophene on Weight of Propylcyclohexane in Samples with Time

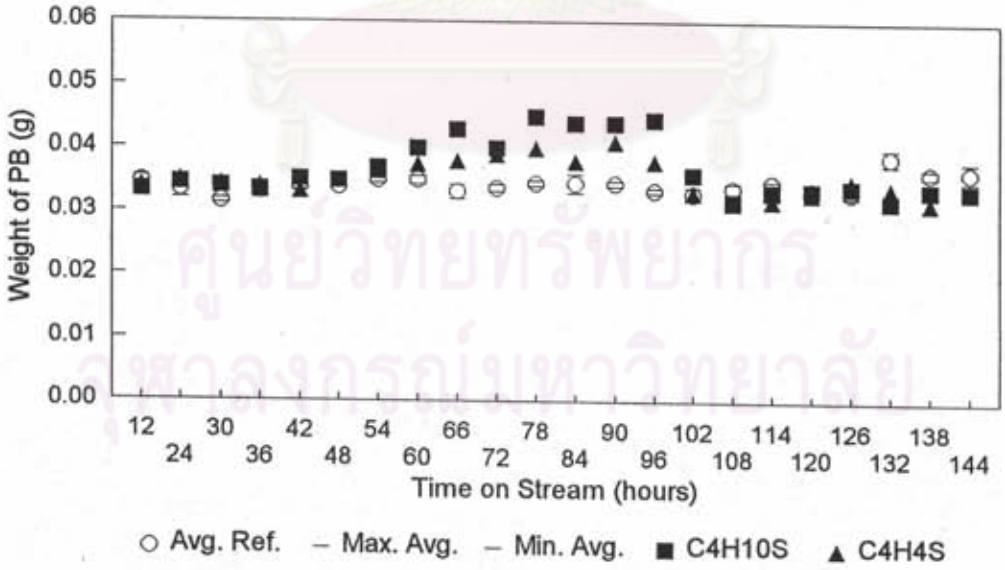



Figure 4.19 Effects of Ethyl Sulfide and Thiophene on Weight of Propylbenzene in Samples with Time

Table 4.4 Effects of Ethyl Sulfide and Thiophene on Various Compounds in Samples

| Compounds | $C_4H_{10}S$** | $C_4H_4S$** | $C_4H_{10}S$/ $C_4H_4S$ | Deviation (%)*** |
|---|---|---|---|---|
| Quinoline | -13.39 | -9.39 | 1.42 | -4.71 |
| 1,2,3,4-THQ | -10.38 | -6.25 | 1.66 | -4.80 |
| 5,6,7,8-THQ | 12.63 | 8.03 | 1.57* | 4.01 |
| DHQ | -26.23 | -13.33 | 1.96 | -18.13 |
| OPA | 46.17 | 32.82 | 1.41 | 9.15 |
| PCH | 46.73 | 28.36 | 1.65 | 12.26 |
| PB | 23.35 | 12.48 | 1.87 | 8.51 |

* The average area ratio

** Average deviation (%) which compared with average reference experiment at an addition interval of sulfur compound

*** Average deviation (%) of thiophene which compared with ethyl sulfide at an addition interval of sulfur compound (These values show that average deviations of various compounds between thiophene and ethyl sulfide are more than experimental deviation (as shown in Table 4.3))

of sulfur atom in thiophene is used for delocalizing inside cyclic. Sulfur atom in thiophene only remains a lone pair electrons. Sulfur atom of ethyl sulfide has two lone pair electrons due to its straight chain structure. Accordingly, the chance of ethyl sulfide adsorbs on active site more than thiophene; as a result hydrogenolysis of ethyl sulfide reacts greater than thiophene. The analogous behavior of straight chain and cyclic was reported by Schuit and Gates (1973) and Satterfield (1980). They found that the reactivity of R-S-R' was greater than thiophene. Besides, Obolentsev

and Mashkina (1960) investigated hydrogenolysis of organic sulfur compounds under conditions of hydrorefining and pointed out that hydrogenolysis of ethyl sulfide reacted easier than thiophene.

In addition, in studying performance evaluation of hydrodesulfurization catalysts by distribution of sulfur compounds in naphtha, Anabtawi et al. (1995) stated that the reactivities of sulfur compounds decreased in the order: mercaptan > disulfide > sulfide > thiophene > benzothiophene > alkyl benzothiophene. This also agreed with the report of Gates et al. (1979). It was stated that thiophenic compounds were the least reactive organosulfur compounds in petroleum and other fossil fuels.

After a sulfur compound addition interval, the solution is switched to original liquid feed. The quantities of compounds in samples reach to steady-state level. These results show that the change in catalyst activity is reversible.

### 4.3.2 Structures Which Consist of Equal Carbon Atoms but Different Sulfur Atoms

The effects of structures which consist of equal carbon atoms but different sulfur atoms are compared between methyl sulfide (1 sulfur atom) and methyl disulfide (2 sulfur atoms). The change in the product composition of quinoline hydrodenitrogenation is shown in Figures 4.20 to 4.26. The quantities of quinoline, 1,2,3,4-tetrahydroquinoline and decahydroquinoline are decreased while the quantities of 5,6,7,8-tetrahydroquinoline, o-propylaniline, propylcyclohexane and propylbenzene are increased. These results indicate that sulfur compounds inhibit hydrogenation and dehydrogenation reactions but markedly accelerate hydrogenolysis reactions. Methyl disulfide has stronger effect than methyl sulfide, as shown in

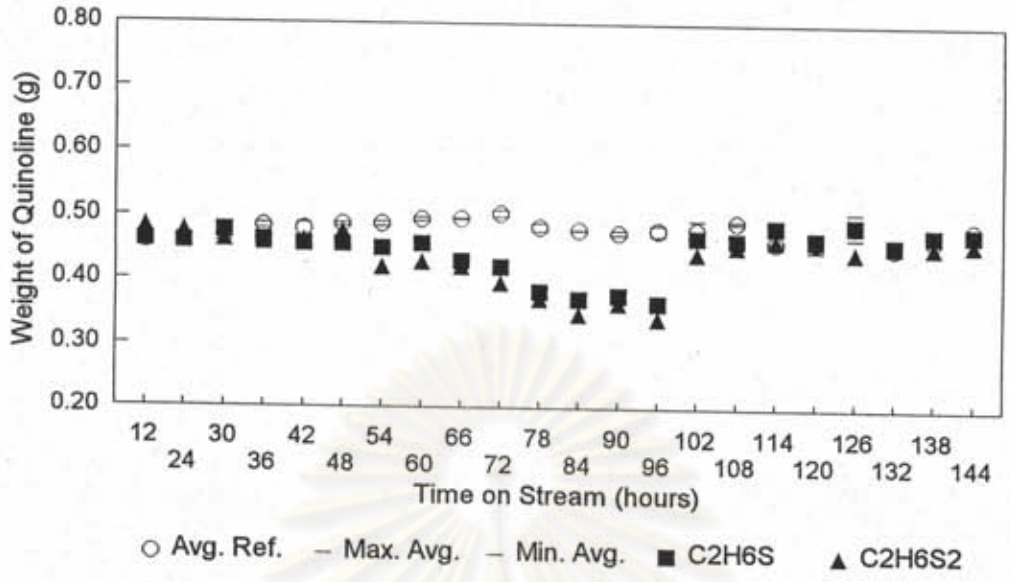



Figure 4.20 Effects of Methyl Sulfide and Methyl Disulfide on Weight of Quinoline in Samples with Time

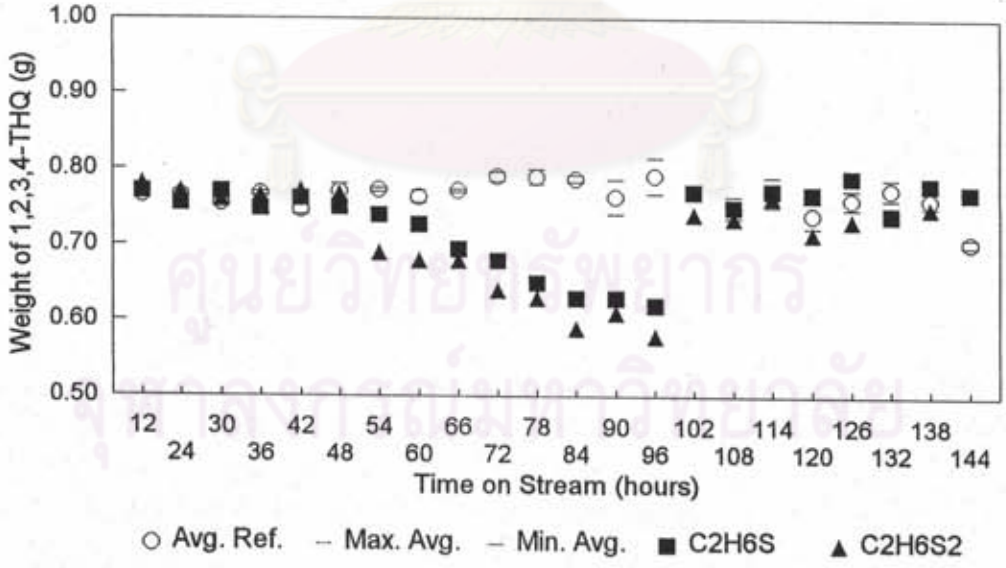



Figure 4.21 Effects of Methyl Sulfide and Methyl Disulfide on Weight of 1,2,3,4-Tetrahydroquinoline in Samples with Time

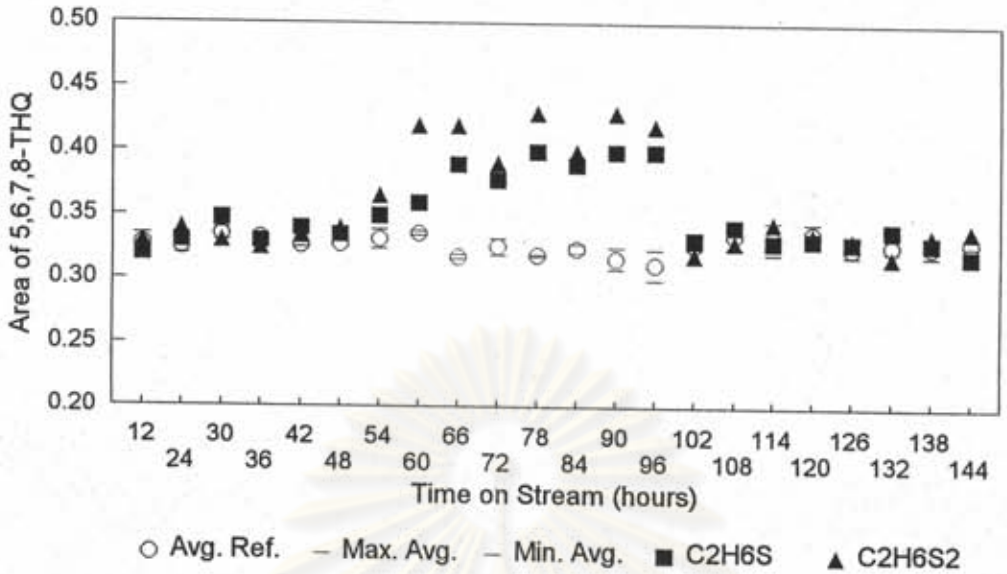



Figure 4.22 Effects of Methyl Sulfide and Methyl Disulfide on Area of 5,6,7,8-Tetrahydroquinoline in Samples with Time

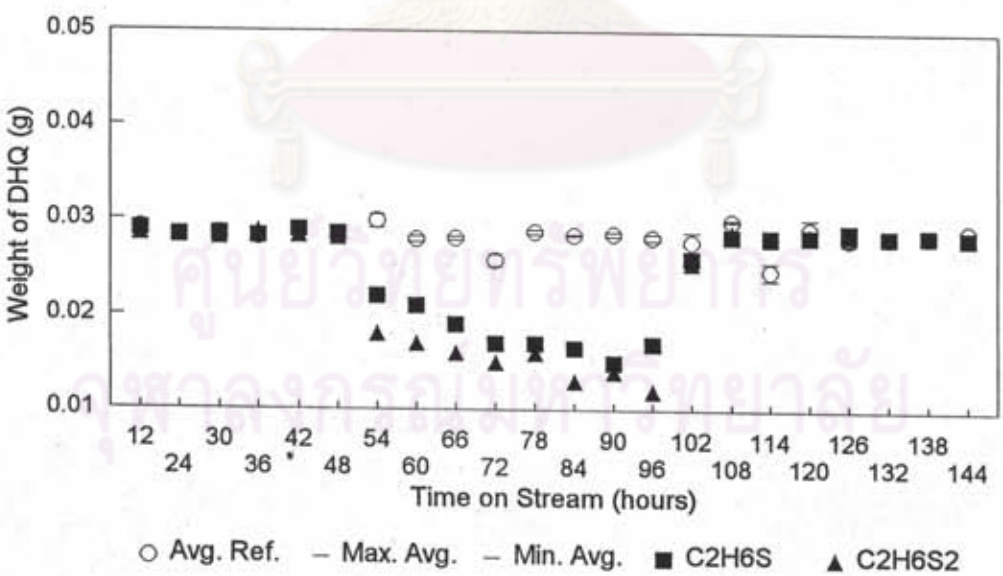



Figure 4.23 Effects of Methyl Sulfide and Methyl Disulfide on Weight of Decahydroquinoline in Samples with Time

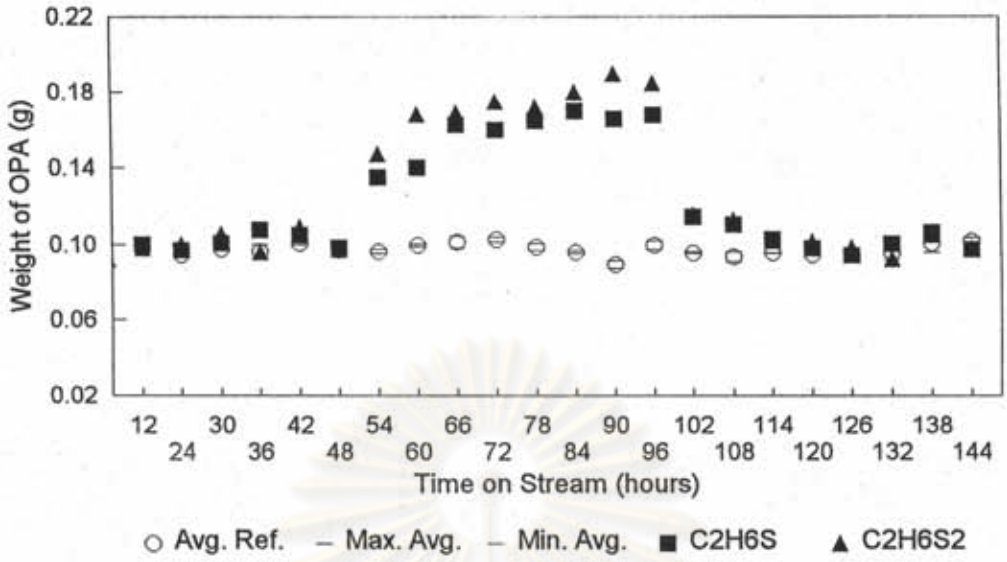



Figure 4.24 Effects of Methyl Sulfide and Methyl Disulfide on Weight of o-Propylaniline in Samples with Time

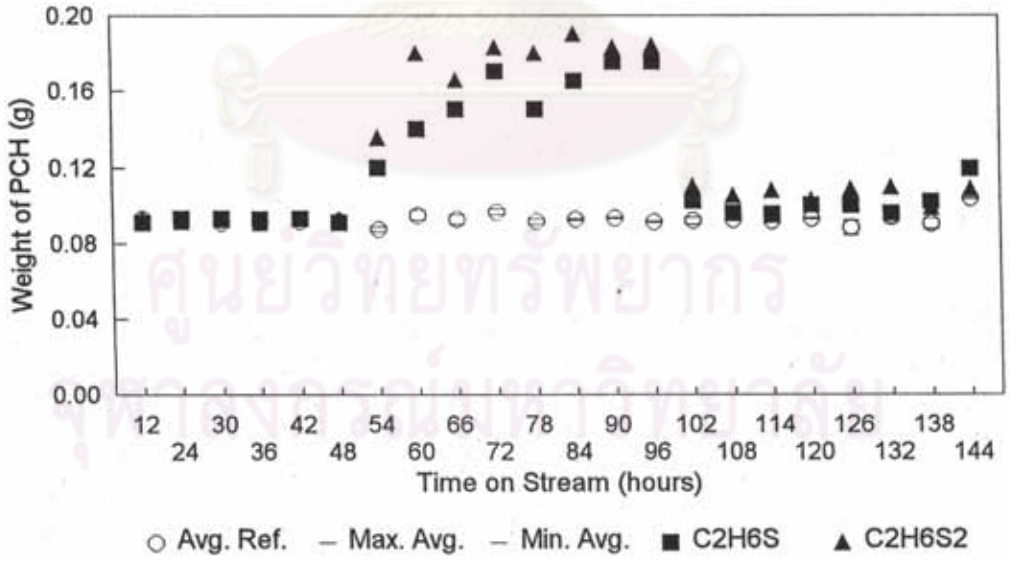



Figure 4.25 Effects of Methyl Sulfide and Methyl Disulfide on Weight of Propylcyclohexane in Samples with Time

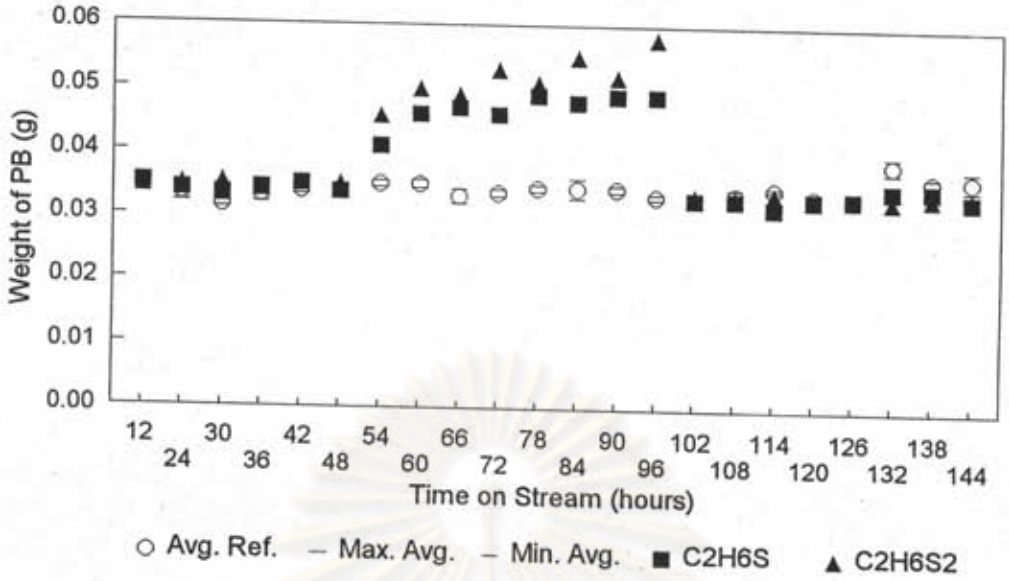



Figure 4.26 Effects of Methyl Sulfide and Methyl Disulfide on Weight of Propylbenzene in Samples with Time

Table 4.5. This effect can explain that methyl disulfide reacts to form hydrogen sulfide and hydrocarbons easier than methyl sulfide. Methyl disulfide has two sulfur atoms while methyl sulfide has one sulfur atom. In addition, adsorption of the sulfur molecule at the anion vacancy on catalyst was favored because of the high electron density inside molecule (Houalla et al., 1977). The comparatively high reactivity of methyl disulfide is probably a result of higher electron density. Thus hydrogenolysis of methyl disulfide reacts easier than that of methyl sulfide. The analogous behavior of structure which had different the number of sulfur atoms was reported by Schuit and Gates (1973) and Satterfield (1980). They reported that the reactivity of R-S-S-R' was greater than R-S-R'. Besides, Anabtawi et al. (1995) studied performance evaluation of hydrodesulfurization catalysts by distribution of sulfur compounds in naphtha. They showed that the reactivities of sulfur compounds decreased in the order: mercaptan > disulfide > sulfide

Table 4.5 Effects of Methyl Sulfide and Methyl Disulfide on Various Compounds in Samples

| Compounds | $C_2H_6S_2$** | $C_2H_6S$** | $C_2H_6S_2$/ $C_2H_6S$ | Deviation (%)*** |
|---|---|---|---|---|
| Quinoline | -20.84 | -16.62 | 1.25 | -5.35 |
| 1,2,3,4-THQ | -18.10 | -13.73 | 1.32 | -5.60 |
| 5,6,7,8-THQ | 26.94 | 18.92 | 1.42* | 6.26 |
| DHQ | -46.38 | -35.99 | 1.29 | -19.98 |
| OPA | 77.49 | 62.09 | 1.25 | 8.59 |
| PCH | 89.27 | 68.18 | 1.31 | 11.17 |
| PB | 51.16 | 37.00 | 1.38 | 9.19 |

* The average area ratio

** Average deviation (%) which compared with average reference experiment at an addition interval of sulfur compound

*** Average deviation (%) of methyl sulfide which compared with methyl disulfide at an addition interval of sulfur compound (These values show that average deviations of various compounds between methyl sulfide and methyl disulfide are more than experimental deviation (as shown in Table 4.3))

> thiophene > benzothiophene > alkyl benzothiophene. Similar results were reported by Gates et al. (1979).

After a sulfur compound addition interval, the solution is switched to original liquid feed. The quantities of compounds in samples reach to steady-state level. These results show that the change in catalyst activity is reversible.

### 4.3.3 Structures Which Consist of Equal Sulfur Atoms but Different Carbon Atoms

The effects of structures which consist of equal sulfur atoms but different carbon atoms are divided into two groups:

The first group consists of methyl disulfide (2 carbon atoms) and carbon disulfide (1 carbon atom). The change in the product composition of quinoline hydrodenitrogenation is shown in Figures 4.27 to 4.33. The quantities of quinoline, 1,2,3,4-tetrahydroquinoline and decahydroquinoline are decreased while the quantities of 5,6,7,8-tetrahydroquinoline, o-propylaniline, propylcyclohexane and propylbenzene are increased. These results indicate that sulfur compounds inhibit hydrogenation and dehydrogenation reactions but markedly accelerate hydrogenolysis reactions. Methyl disulfide has stronger effect than carbon disulfide, as shown in Table 4.6. This effect can explain that methyl disulfide reacts to form hydrogen sulfide and hydrocarbons easier than carbon disulfide, with the result that bonds of methyl disulfide are single bond (C-S) while bonds of carbon disulfide are double bond (C=S). The comparatively high reactivity of methyl disulfide is probably a result of lower bond energy, bond energy of C-S bond and C=S bond is approximately 255 and 477 kJ/mol, respectively (Chang, 1994). Thus hydrogenolysis of methyl disulfide is easier than that of carbon disulfide.

After a sulfur compound addition interval, the solution is switched to original liquid feed. The quantities of compounds in samples reach to steady-state level. These results show that the change in catalyst activity is reversible.

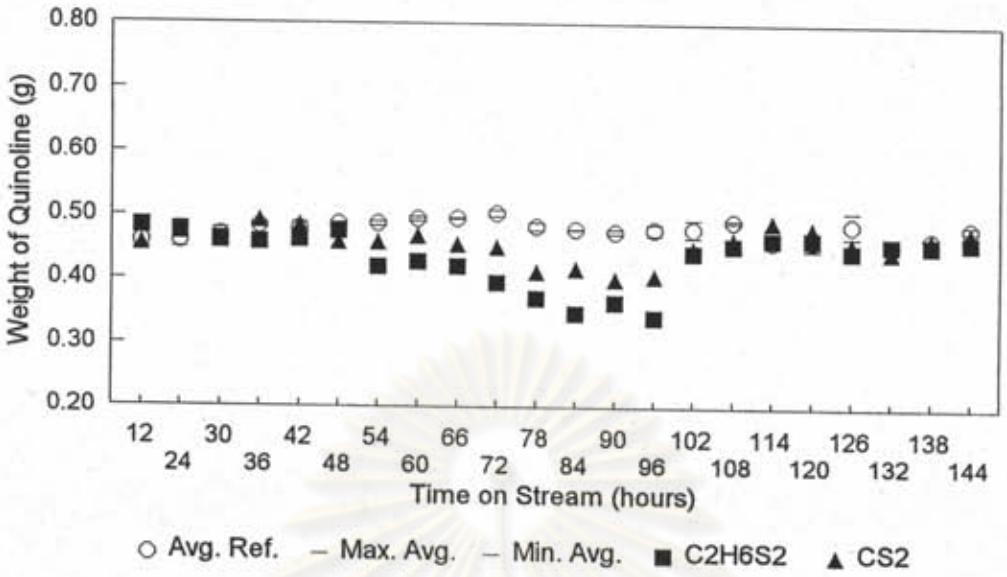



Figure 4.27 Effects of Methyl Disulfide and Carbon Disulfide on Weight of Quinoline in Samples with Time

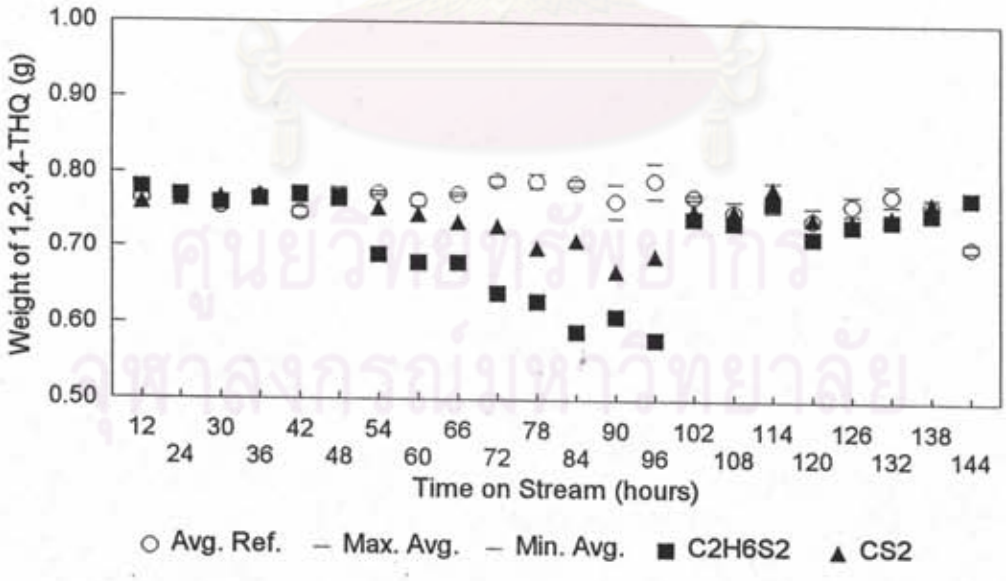



Figure 4.28 Effects of Methyl Disulfide and Carbon Disulfide on Weight of 1,2,3,4-Tetrahydroquinoline in Samples with Time

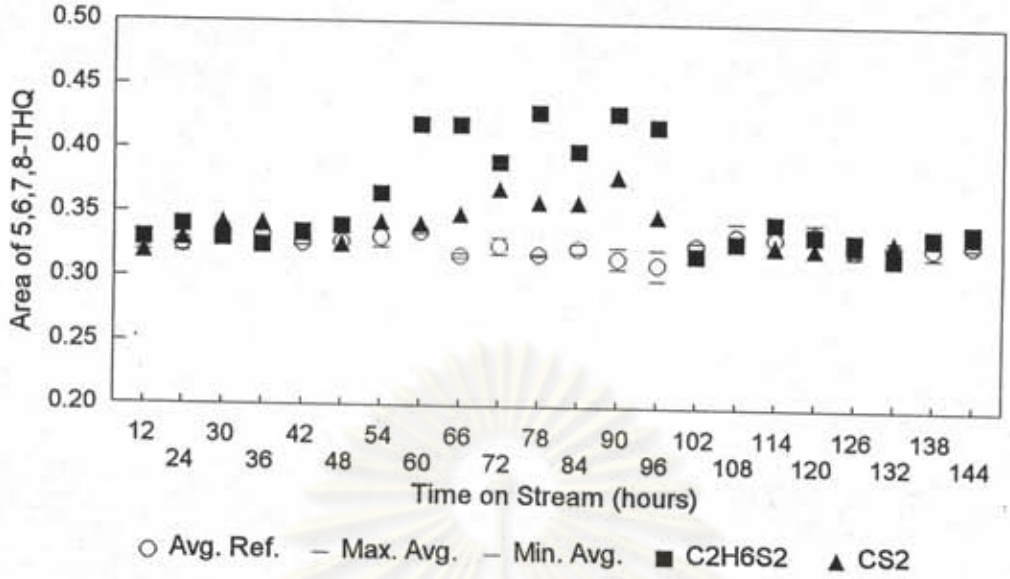



Figure 4.29 Effects of Methyl Disulfide and Carbon Disulfide on Area of 5,6,7,8-Tetrahydroquinoline in Samples with Time

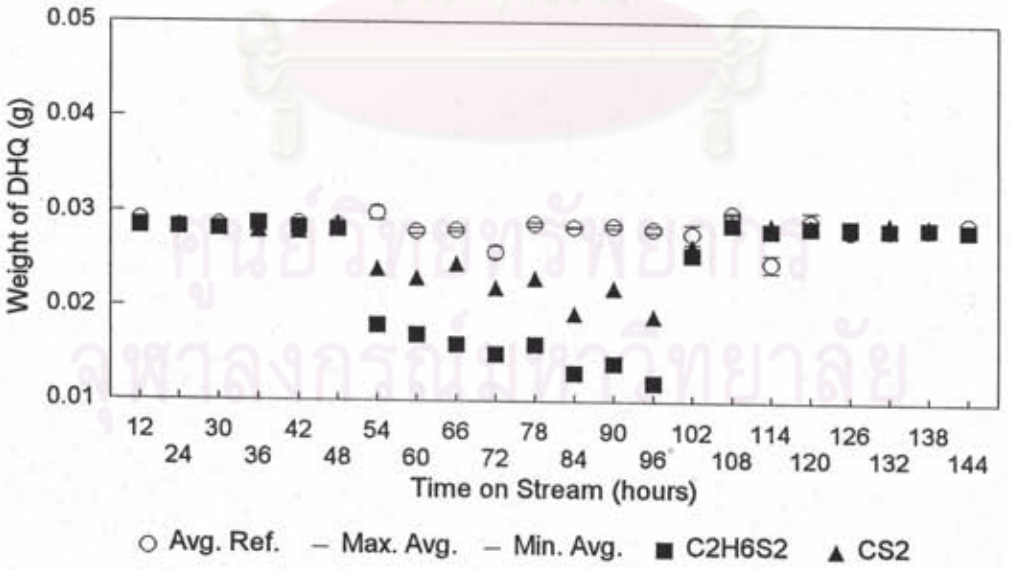



Figure 4.30 Effects of Methyl Disulfide and Carbon Disulfide on Weight of Decahydroquinoline in Samples with Time

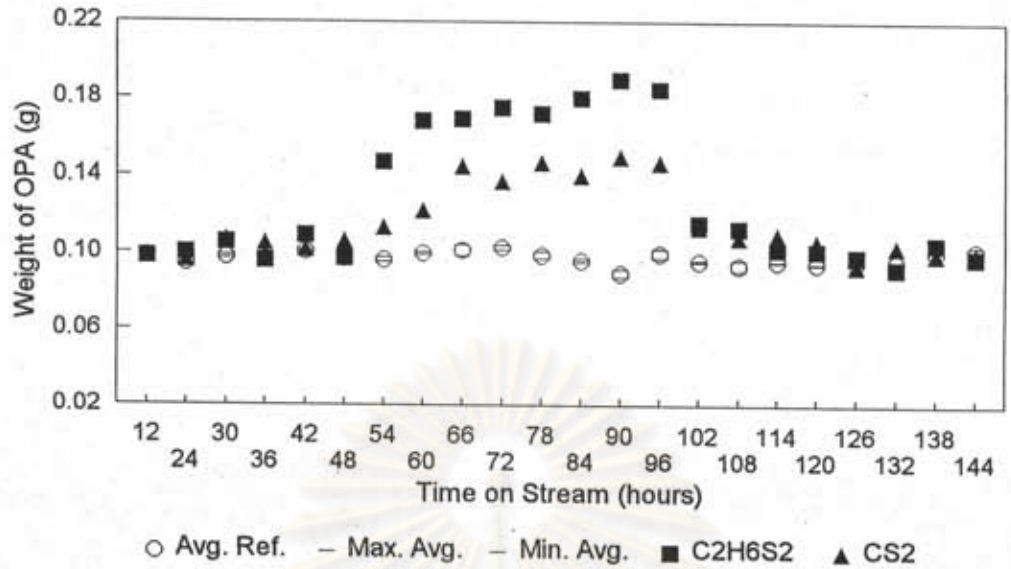



Figure 4.31 Effects of Methyl Disulfide and Carbon Disulfide on Weight of o-Propylaniline in Samples with Time

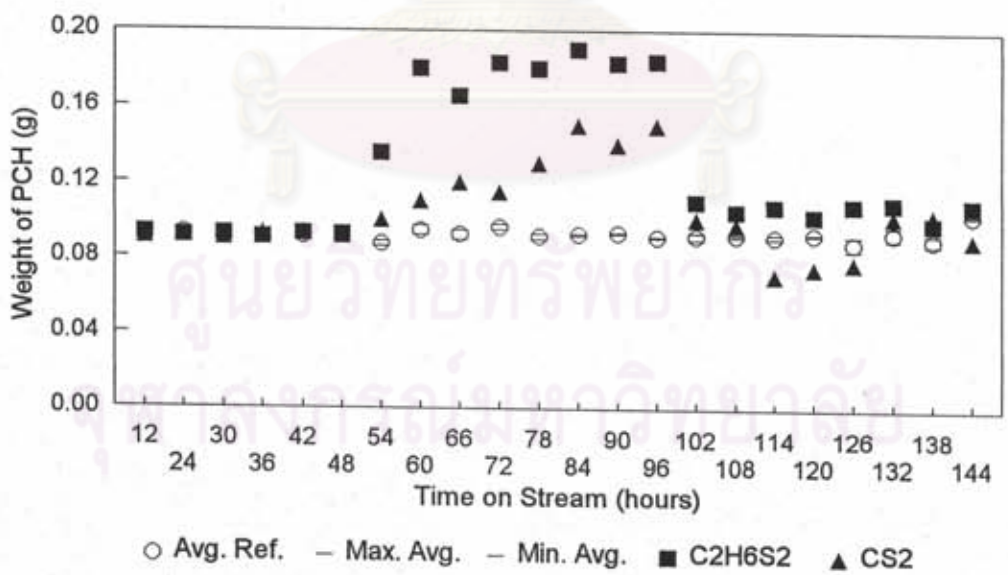



Figure 4.32 Effects of Methyl Disulfide and Carbon Disulfide on Weight of Propylcyclohexane in Samples with Time

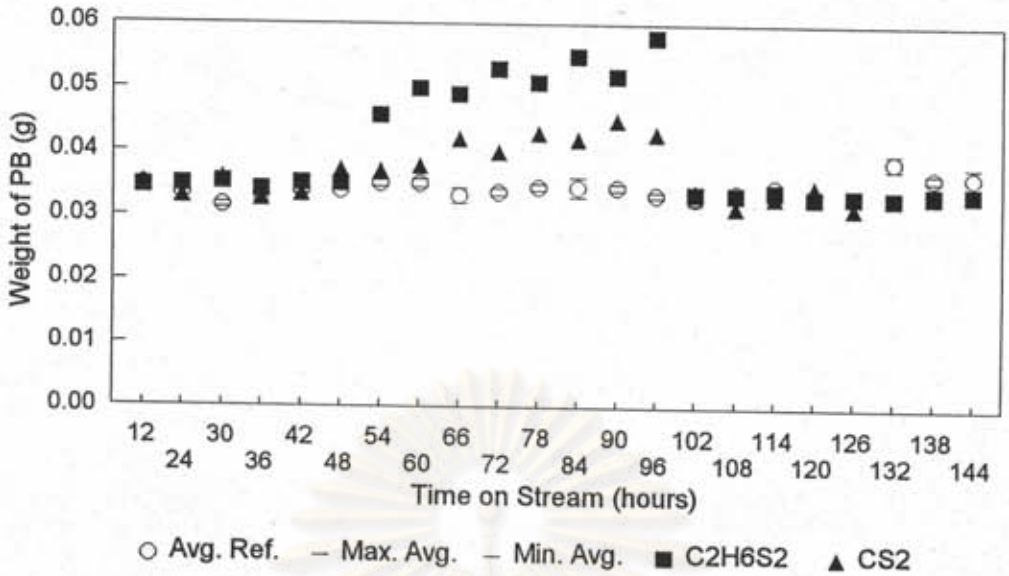



Figure 4.33 Effects of Methyl Disulfide and Carbon Disulfide on Weight of Propylbenzene in Samples with Time

The second group consists of methyl sulfide (2 carbon atoms) and ethyl sulfide (4 carbon atoms). The change in the product composition of quinoline hydrodenitrogenation is shown in Figures 4.34 to 4.40. The quantities of quinoline, 1,2,3,4-tetrahydroquinoline and decahydroquinoline are decreased while the quantities of 5,6,7,8-tetrahydroquinoline, o-propylaniline, propylcyclohexane and propylbenzene are increased. These results indicate that sulfur compounds inhibit hydrogenation and dehydrogenation reactions but markedly accelerate hydrogenolysis reactions. Ethyl sulfide has less effect than methyl sulfide, as shown in Table 4.7. This effect can explain that ethyl sulfide reacts to form hydrogen sulfide and hydrocarbons more difficult than methyl sulfide as a hindrance effect. Ethyl sulfide which has longer in chain than methyl sulfide restricts its access to the active site on the catalyst surface. The hindrance effect caused by this longer chain is

Table 4.6 Effects of Methyl Disulfide and Carbon Disulfide on Various Compounds in Samples

| Compounds | $C_2H_6S_2$** | $CS_2$** | $C_2H_6S_2$/ $CS_2$ | Deviation (%)*** |
|---|---|---|---|---|
| Quinoline | -20.84 | -11.04 | 1.89 | -12.64 |
| 1,2,3,4-THQ | -18.10 | -7.96 | 2.27 | -12.70 |
| 5,6,7,8-THQ | 26.94 | 10.59 | 2.54* | 12.66 |
| DHQ | -46.38 | -21.60 | 2.15 | -47.01 |
| OPA | 77.49 | 40.89 | 1.89 | 20.63 |
| PCH | 89.27 | 37.30 | 2.39 | 27.58 |
| PB | 51.16 | 20.50 | 2.50 | 20.11 |

* The average area ratio

** Average deviation (%) which compared with average reference experiment at an addition interval of sulfur compound

*** Average deviation (%) of carbon disulfide which compared with methyl disulfide at an addition interval of sulfur compound (These values show that average deviations of various compounds between carbon disulfide and methyl disulfide are more than experimental deviation (as shown in Table 4.3))

expected to be even more pronounced in case of ethyl sulfide. The analogous behavior of hindrance was reported by Houalla et al. (1977). It was found that the alkyl thiophenes were in general less reactive than thiophene, presumably by hindrance effect, and their experimental results confirmed that 4,6-dimethyldibenzothiophene was 10 times less reactive than dibenzothiophene, whereas 4-methyldibenzothiophene was approximately 6 times less reactive. Satterfield (1980) also reported that the reactivity of R-S-R' decreased with increased molecular size. Besides,

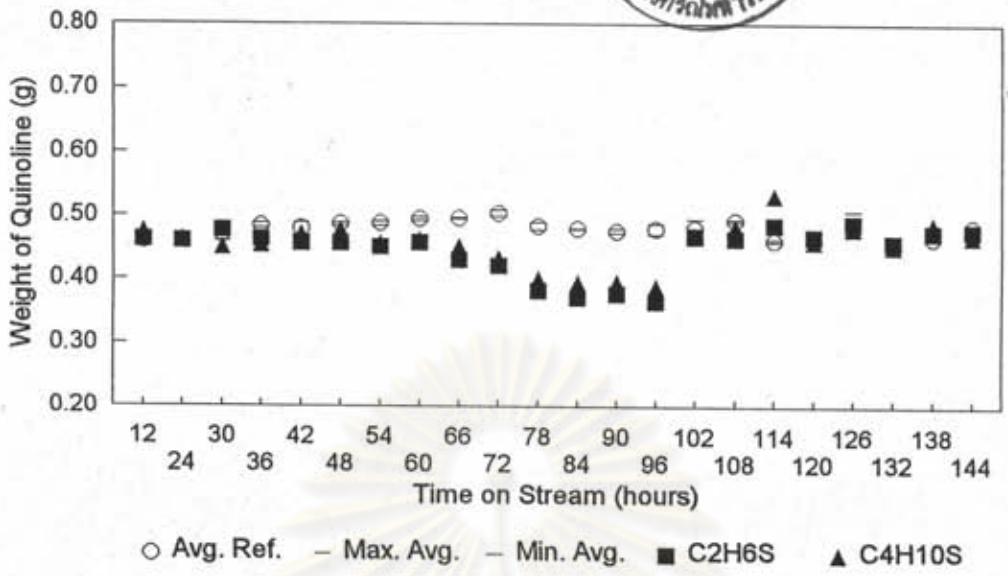



Figure 4.34 Effects of Methyl Sulfide and Ethyl Sulfide on Weight of Quinoline in Samples with Time

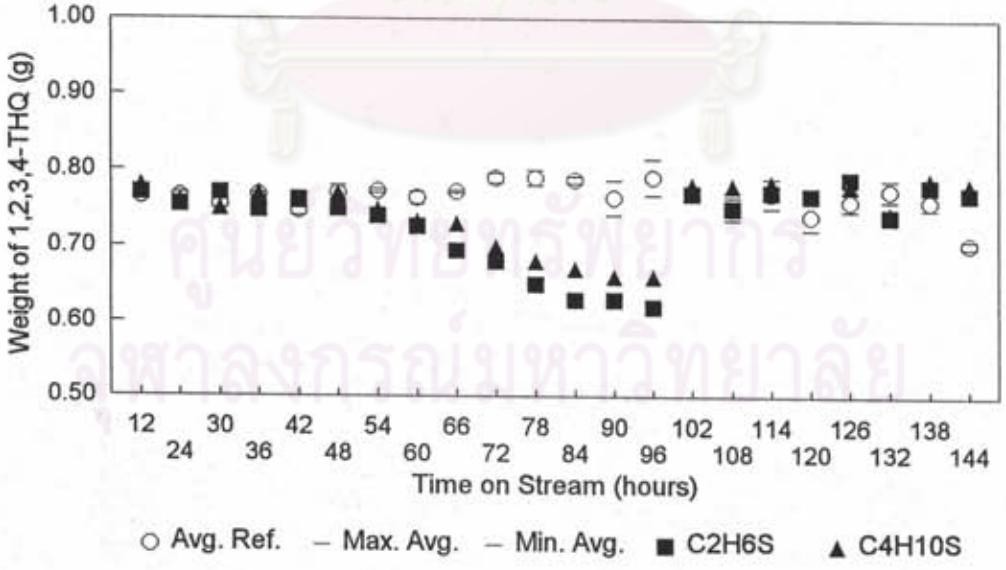



Figure 4.35 Effects of Methyl Sulfide and Ethyl Sulfide on Weight of 1,2,3,4-Tetrahydroquinoline in Samples with Time

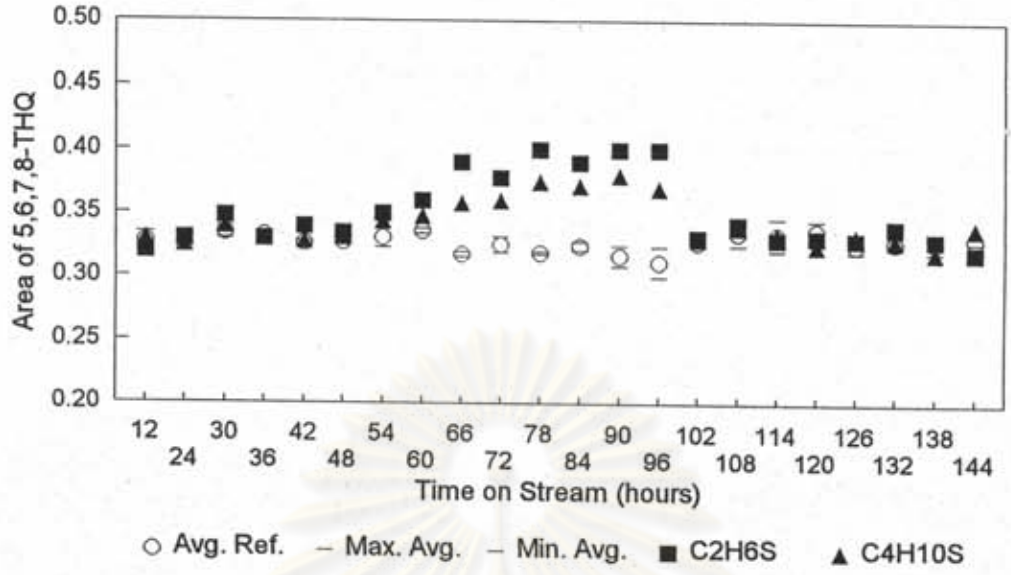



Figure 4.36 Effects of Methyl Sulfide and Ethyl Sulfide on Area of 5,6,7,8-Tetrahydroquinoline in Samples with Time

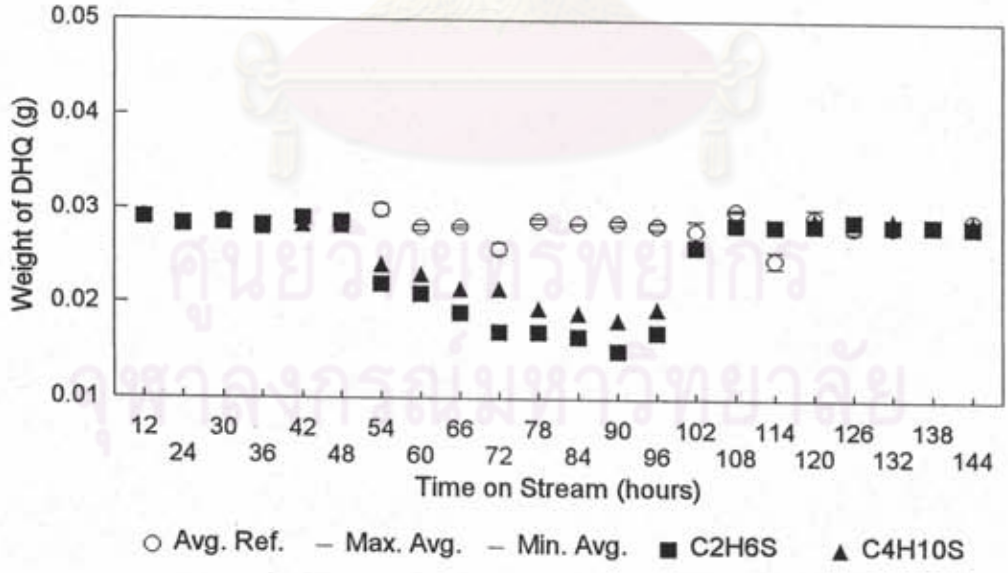



Figure 4.37 Effects of Methyl Sulfide and Ethyl Sulfide on Weight of Decahydroquinoline in Samples with Time

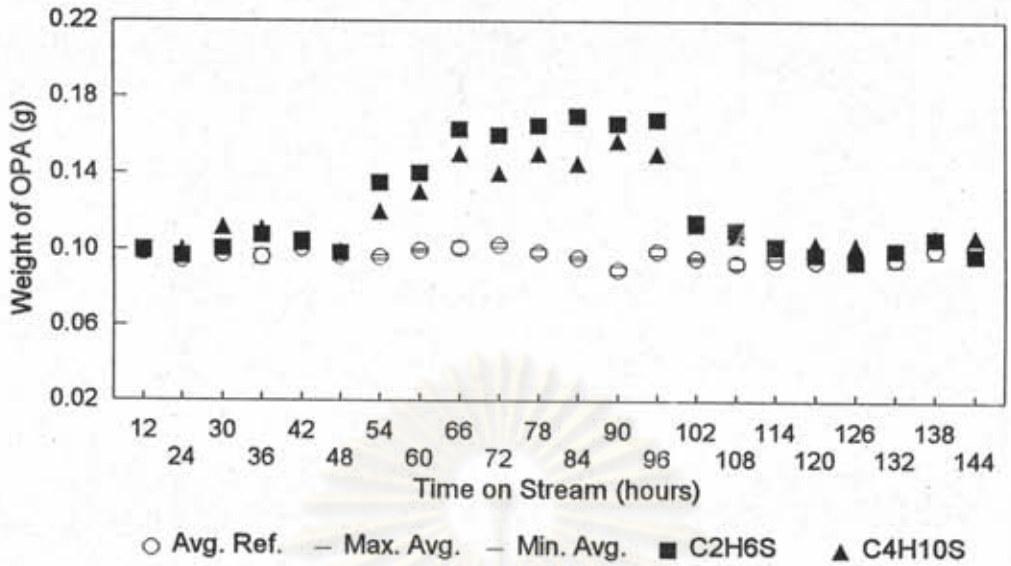



Figure 4.38 Effects of Methyl Sulfide and Ethyl Sulfide on Weight of o-Propylaniline in Samples with Time

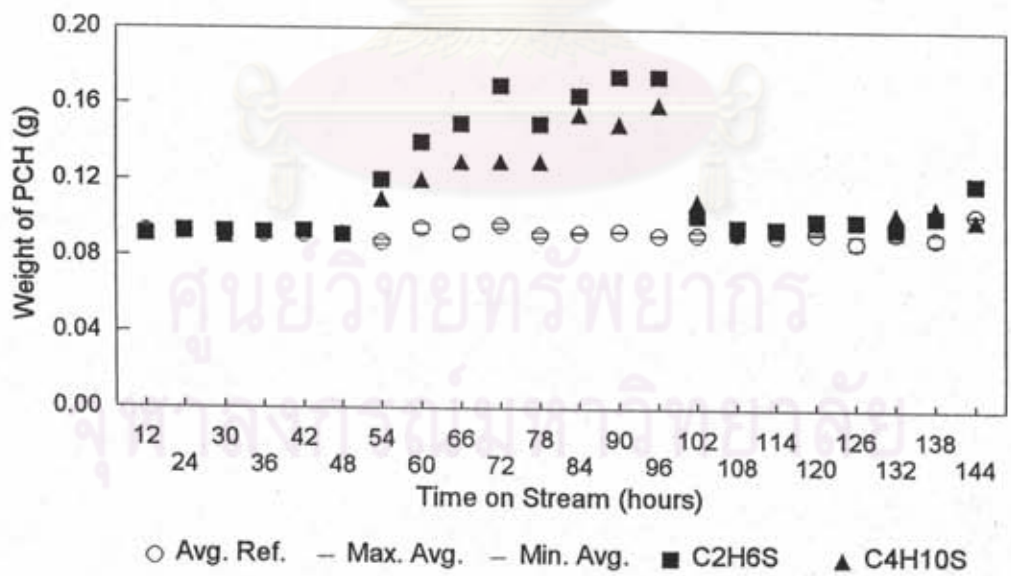



Figure 4.39 Effects of Methyl Sulfide and Ethyl Sulfide on Weight of Propylcyclohexane in Samples with Time

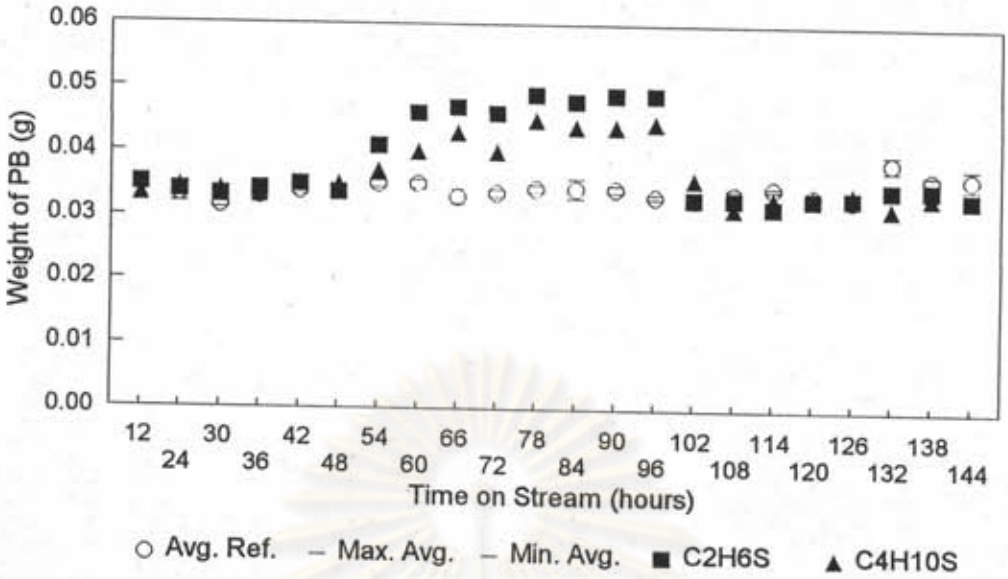



Figure 4.40 Effects of Methyl Sulfide and Ethyl Sulfide on Weight of Propylbenzene in Samples with Time

Obolentsev and Mashkina (1960) investigated hydrogenolysis of organic sulfur compounds under conditions of hydrorefining employing commercial CoMo/$Al_2O_3$ and pointed out that hydrogenolysis of methyl sulfide reacted easier than ethyl sulfide.

After a sulfur compound addition interval, the solution is switched to original liquid feed. The quantities of compounds in samples reach to steady-state level. These results show that the change in catalyst activity is reversible.

Table 4.7 Effects of Methyl Sulfide and Ethyl Sulfide on Various Compounds in Samples

| Compounds | $C_2H_6S$** | $C_4H_{10}S$** | $C_2H_6S$/ $C_4H_{10}S$ | Deviation (%)*** |
|---|---|---|---|---|
| Quinoline | -16.62 | -13.39 | 1.24 | -4.01 |
| 1,2,3,4-THQ | -13.73 | -10.38 | 1.32 | -4.08 |
| 5,6,7,8-THQ | 18.92 | 12.63 | 1.50* | 5.17 |
| DHQ | -35.99 | -26.23 | 1.37 | -15.60 |
| OPA | 62.09 | 46.17 | 1.34 | 9.83 |
| PCH | 68.18 | 46.73 | 1.46 | 12.72 |
| PB | 37.00 | 23.35 | 1.58 | 10.00 |

* The average area ratio

** Average deviation (%) which compared with average reference experiment at an addition interval of sulfur compound

*** Average deviation (%) of ethyl sulfide which compared with methyl sulfide at an addition interval of sulfur compound (These values show that average deviations of various compounds between ethyl sulfide and methyl sulfide are more than experimental deviation (as shown in Table 4.3))