CHAPTER IV

RESULTS AND DISCUSSIONS

In this study, the experiments were classified into three sections. First, preliminary experiment was conducted to find suitable operating condition. Second, reference experiments 2 to 4 were conducted in order to study the repeatability of the experiments at the conditions chosen. Third, deactivated experiments 5 to 9 were conducted to study influence of sulfur compounds on catalytic reforming of n-hexane. The sulfur compounds used in this study were carbon disulfide, methyl disulfide, methyl sulfide, ethyl sulfide and thiophene. Details of feedstock and operating conditions of each experiment were given in Tables 4.1 to 4.3.

The reaction was performed in a fixed-bed reactor. Before start-up of each experiment, the reactor was packed in the middle part with 1 gram of catalyst. The catalyst used was a commercial Pt-Re/Al_2O_3 which contained 0.22 wt% of Pt, 0.44 wt% of Re and 1.0-1.1 wt% of Cl. The top part of the reactor was left empty and used as vaporizing zone. The bottom part was packed with glass bead and used as cooling zone. The reactor was connected to a gas feed line and a liquid feed line at the top of the reactor, and connected to a sample bomb at the bottom.

In this study, the feedstock was hexanes which contained 88 wt% of n-hexane, 9.45 wt% of methylcyclopentane and approximately 2.55 wt% of other trace hexane isomers. The results showed that the main reaction products of the catalytic reforming of n-hexane

Table 4.1 Procedure of Preliminary Experiment
           (Experiment 1)

Feedstock :
     Feed I   - Hexanes + 10 ppm chloride as
                       dichloromethane

- -

Operating Conditions :
     Catalyst   - $Pt\text{-}Re/Al_2O_3$ 1 gram (dilute with
                       glass bead by volume ratio 1:3)
     Sampling   - every 6 hours

- -

Run Variable :
     Pressure, Temperature, H_2:H/C mole ratio
     1) 100 psig, 450°C, 6:1 Duration of run 24 hours
     2) 100 psig, 400°C, 6:1 Duration of run 24 hours
     3) 200 psig, 450°C, 6:1 Duration of run 24 hours
     4) 200 psig, 400°C, 6:1 Duration of run 24 hours
     5) 100 psig, 450°C, 3:1 Duration of run 24 hours
     6) 100 psig, 450°C, 6:1 Duration of run 24 hours
     7) 100 psig, 450°C, 9:1 Duration of run 24 hours

Table 4.2 Procedure of Reference Experiment*
            (Experiment 2, 3 and 4)

Feedstock :

    Feed I   - Hexanes + 10 ppm chloride as
                                  dichloromethane

- -

Operating Conditions :

Temperature	- 450°C
Pressure	- 100 psig
H_2:H/C Mole Ratio	- 6:1
LHSV	- 5
Feed Flow rate	- 5 cm^3/hour
Catalyst	- Pt-Re/Al_2O_3 1 gram (dilute with glass bead by volume ratio 1:3)
Sampling	- every 6 hours
Duration of Run	- 144 hours

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* The experiments 2, 3 and 4 would be called Ref.1,
Ref.2, and Ref.3, respectively.

Table 4.3 Procedure of Deactivated Experiments
         (Experiment 5, 6, 7, 8 and 9)

Feedstock :
      Feed I   - Hexanes + 10 ppm chloride as
                            dichloromethane
      Feed II   - Feed I + 10 ppm sulfur as
                            sulfur compounds

Operating Conditions :
      Temperature   - 450°C
      Pressure   - 100 psig
      H_2:H/C Mole Ratio - 6:1
      LHSV   - 5
      Feed Flow rate   - 5 cm^3/hour
      Catalyst   - Pt-Re/Al_2O_3 1 gram (dilute with
                            glass bead by volume ratio 1:3)
      Sampling   - every 6 hours
      Duration of Run   - 144 hours

Switching Feedstock :
      Feed I   - Duration of run 48 hours
      Feed II   - Duration of run 24 hours
      Feed I   - Duration of run 24 hours
      Feed II   - Duration of run 24 hours
      Feed I   - Duration of run 24 hours

on commercial Pt-Re/Al_2O_3 in liquid product sample detected by the gas chromatographic technique were 2,2-dimethylbutane (2,2-DMB), 2,3-dimethylbutane (2,3-DMB), 2-methylpentane (2-MP), 3-methylpentane (3-MP), n-hexane, methylcyclopentane (MCP), benzene, toluene, ethylbenzene, xylenes and propylbenzene.

All products in this study would be categorized into five groups. The first group was the unconverted feed, i.e. n-hexane and methylcyclopentane. The second group was the cracking products, i.e. C_1-C_5 products. The third group was the isomerization products, i.e. 2,2-DMB, 2,3-DMB, 2-MP and 3-MP. The forth group was the main aromatization product (benzene). The last group was the higher aromatic products, i.e. toluene, ethylbenzene, xylenes and propylbenzene. Therefore, the results were analyzed in the point of conversion of feed and the weight percent of the main reaction products.

These results indicated that n-hexane reforming consisted of four major reactions. They were (1) hydrocracking of hydrocarbons to lower molecular weight hydrocarbons, (2) isomerization of paraffins to isoparaffins and C_5-ring naphthenes to C_6-ring naphthenes, (3) dehydrocyclization of paraffins to aromatics and (4) dehydrogenation of naphthenes to aromatics. The last two reactions could be called aromatization reaction. Similar results were obtained by Ciapetta and Wallace (1972) and Gary and Handwerk (1991).

During each experiment, liquid samples were taken every 6 hours. The samples were analyzed for quantities of n-hexane, methylcyclopentane and the main reaction products. Conversion of n-hexane was calculated by

$$\% \text{ Conversion of n-hexane} = \frac{(C_{to} - C_t)}{C_{to}} \times 100$$

where

C_{to} = weight % of n-hexane in feed.

C_t = weight % of n-hexane in product sample.

Conversion of methylcyclopentane was calculated with the same procedure as conversion of n-hexane.

4.1 Reaction Network of Catalytic Reforming of n-Hexane

In this study, the cracking products were C_1-C_5 products and the isomerization products were 2,2-DMB, 2,3-DMB, 2-MP and 3-MP. Similar results were obtained by Christoffel (1979). He described the interconversion of five hexane isomers and their hydrocracking to cracking products. The reaction pattern indicated that n-hexane isomerized to four isomers (i.e., 2,2-DMB, 2,3-DMB, 2-MP and 3-MP), and hydrocracked to cracking products (C_1-C_5). Furthermore, the four hexane isomers isomerized to n-hexane and hydrocracked to the cracking products. The four hexane isomers also isomerized to each other.

Product distribution and reaction intermediates during catalytic reforming reaction have been thoroughly reviewed in several papers, for example, Blue and Gould (1975) purposed the main reactions of catalytic reforming. Because of the wide range of paraffins and naphthenes included in the platformer feed and because the reaction rates varied considerably with the carbon number of the reactant, these reactions occurred in series and in parallel to each other, forming the rather complicated overall reaction. The main reactions of catalytic reforming composed of hydrocracking, paraffin

isomerization, paraffin dehydrocyclization, naphthene
isomerization and naphthene dehydrogenation. Similar
results were reported by Henningsen et al. (1970), Kmak
et al. (1973), Kleelman (1976), Kugelman (1976) and
Mayers (1986).

From the previous literature surveys, the
reaction network in this study was proposed in Figure
4.1. The results indicated that n-hexane isomerized to
four isomers (i.e., 2,2-DMB, 2,3-DMB, 2-MP and 3-MP),
cyclized to two naphthenes (MCP and cyclohexane) and
hydrocracked to cracking products (C_1-C_5). Furthermore,
the four hexane isomers isomerized to n-hexane, cyclized
to the naphthenes and hydrocracked to the cracking
products. The four hexane isomers also isomerized to
each other.

Moreover, the above results indicated that the
five-membered-ring naphthene (methylcyclopentane)
isomerized to the six-membered-ring naphthene
(cyclohexane) and hydrodecyclized to both n-hexane and
four hexane isomers. Cyclohexane isomerized to
methylcyclopentane, hydrodecyclized to n-hexane and
rapidly dehydrogenated to benzene.

In addition, the reaction network showed that
the higher aromatic compounds were occurred such as
toluene, ethylbenzene, propylbenzene and xylenes.
Speight (1991) previously proposed that the olefin
polymerization can be taken place on the acid catalyst
sites. The straight-chain paraffins were converted into
isoparaffins which proceeded through the olefin
intermediates. Thus, the olefins from this reaction
and other reactions (e.g., partial dehydrogenation
species of cracking products and n-hexane) could be
polymerized to C_6^+-hydrocarbons. Then, C_6^+-hydrocarbons
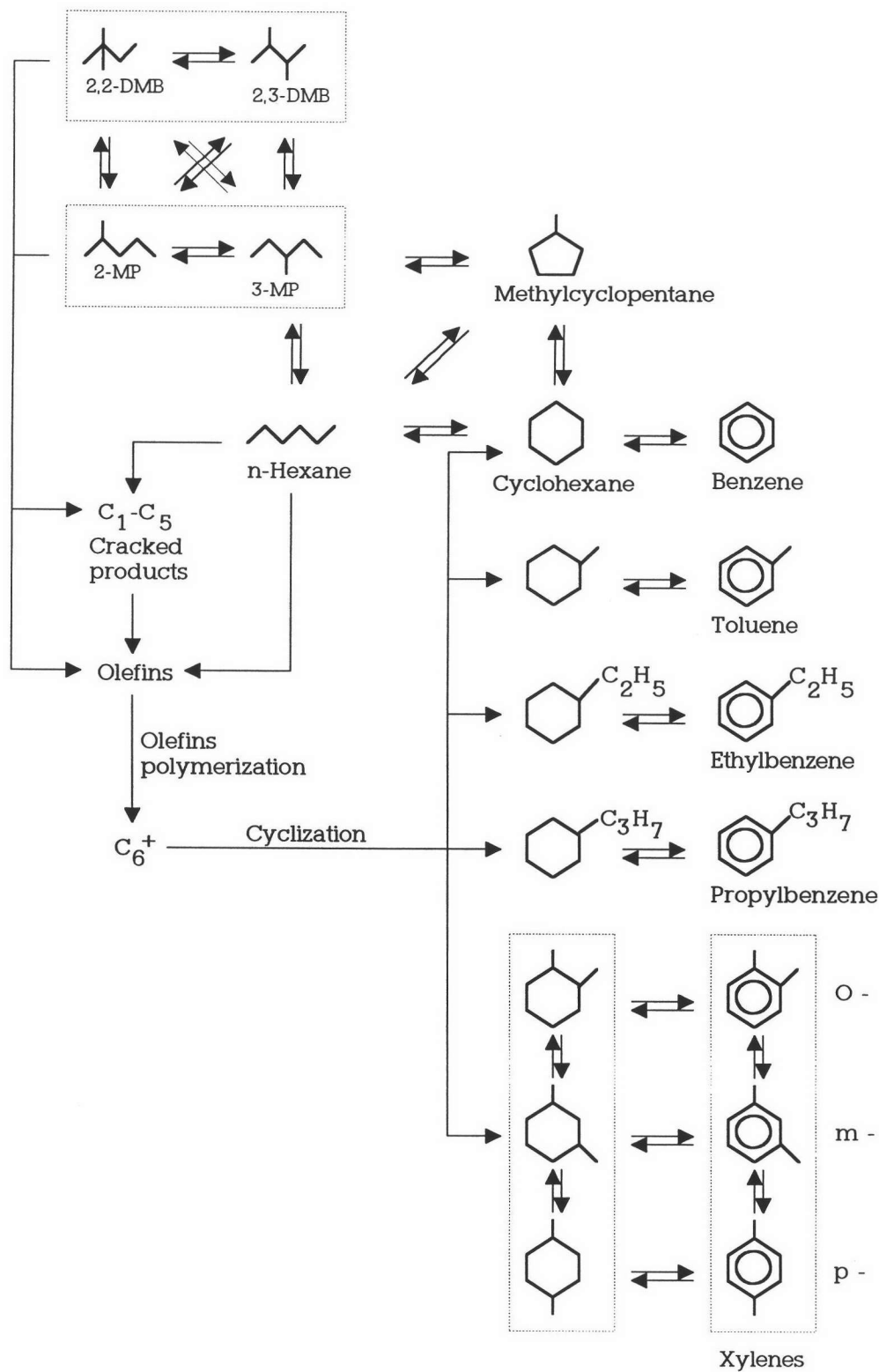were cyclized to cyclohexane and its derivatives such as

Figure 4.1 Reaction Network of Catalytic Reforming
of n-Hexane on Commercial Pt-Re/Alumina

methylcyclohexane, ethylcyclohexane, propylcyclohexane and dimethylcyclohexanes. These C_6-ring naphthenes rapidly dehydrogenated to benzene, toluene, ethylbenzene, propylbenzene and xylenes, respectively. Aromatic compounds also hydrogenated to naphthenes.

Cyclohexane in this study was not detected because it was converted to benzene in close to 100% efficiency on platinum-rhenium/alumina catalyst. (Kirk-Othmer, 1982). Similar result was obtained by Marin and Froment (1982) who studied reforming of C_6 hydrocarbons on a Pt-Al_2O_3 catalyst. They found that cyclohexane was not detected because the dehydrogenation of cyclohexane to benzene was rapidly occurred. In addition, the experimental results indicated a good conversion of cyclohexane derivatives to the corresponding aromatics since cyclohexane derivatives were not observed. Earlier study (Kobe and Mcketta, 1958) elucidated that the conversion of C_6-ring naphthenes to the corresponding aromatics was a rapid and clean reaction.

The conversion of five-membered-ring naphthenes to aromatics was considerably slower than the corresponding conversion of the six-membered-ring naphthenes. There was no doubt that the intermediate isomerization step necessary for the five-membered-ring naphthenes was rate controlling step (Kobe and Mcketta, 1958). The reaction was visualized as proceeding through a cyclohexane derivative intermediate.

In this study, the blank test proceeded the reaction with the same operating conditions as other experiments but without the catalyst. The weight loss of the blank test showed the weight loss of feed due to its vaporization into the gas phase. It found that the weight loss of the blank test was 30% which corresponding

to the result from vapor-liquid equilibrium calculation by simulation program. Weight loss of feed was calculated by

$$\% \text{ Weight loss of feed} = \frac{(W_{to} - W_t) \times 100}{W_{to}}$$

where

W_{to} = weight % of feed.

W_t = weight % of product sample.

Weight recovery of feed was calculated by

$$\% \text{ Weight recovery} = 100 - (\% \text{ Weight loss})$$

Therefore, weight of each product was calculated by

$$\% \text{ Weight of product} = (\text{Concentration of product}) \times (\% \text{ Weight recovery})$$

The experimental results indicated that the total weight loss was 57%, the weight of n-hexane was 11%, the weight of methylcyclopentane was 1.4%, the weight of four hexane isomers was 16.5%, the weight of benzene was 6.1%, and total weight of the higher aromatics was 4.3%. It also found that the weight loss of the blank test was 30%. Therefore, the weight of hydrocracking products was obtained by the different value between the total weight loss and the weight loss of the blank test. The weight of hydrocracking products was approximately 26%. Thus the last 4.7% was the amount of trace other compounds which slightly existed in the liquid products. The weight of all products was compared with the weight of feed and summarized in Table 4.4.

Table 4.4 Weight Percent of Feed and Products in the
First 48 Hours of Reference Experiment

Composition	Weight (%)	
	Feed	Products
n-Hexane	88.00	11.00
Methylcyclopentane	9.45	1.40
Cracking products	-	26.00
Hexane isomers	2.55	16.50
Benzene	-	6.10
Higher aromatics	-	4.30
Trace other compounds	-	4.70
Weight loss from vapor - liquid equilibrium	-	30.00
	100.00	100.00

Figures 4.2 and 4.3 showed the conversion of
n-hexane and the weight of benzene of average reference
experiment. They showed that the conversion of n-hexane
decreased corresponding to the weight of benzene (the
main aromatic product) declined because the catalyst
activity was lost. Ostrovskii et al. (1990)
previously suggested that the main reason for the
deactivation of reforming catalysts was coke formation
and coke was deposited on both support (Al_2O_3) and metals
(Pt-Re). The platinum function activity decreased
because of loss of platinum dispersion while alumina
function activity was loss because of coke deposition
(Shantanu et al., 1988).
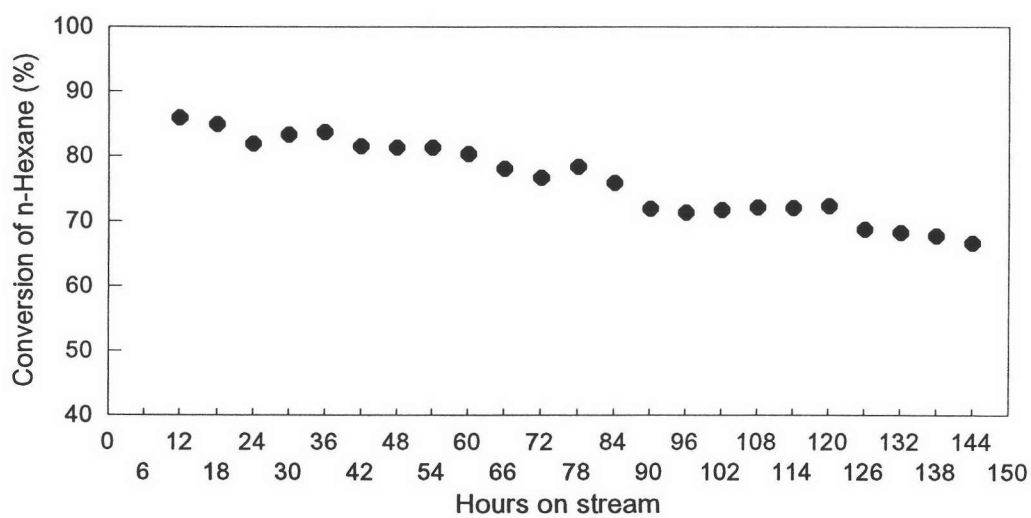
Figure 4.2   Deactivation of Reforming Catalyst
on Conversion of n-Hexane of Average Reference
Experiment.
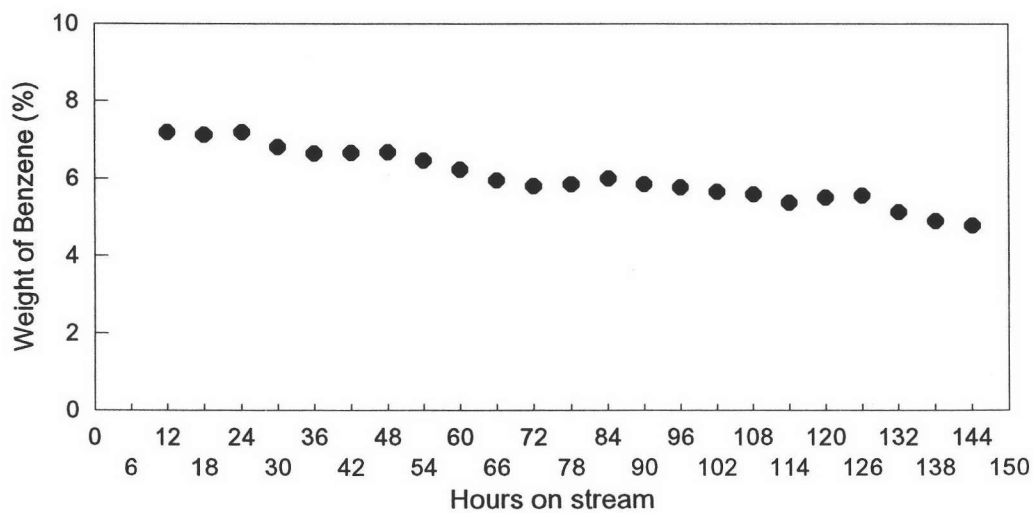
Figure 4.3   Deactivation of Reforming Catalyst
on Weight (%) of Benzene of Average Reference
Experiment.

Myers and co-workers (1961) proposed that large paraffinic molecules deactivated the catalyst relatively quickly. They suggested the following deactivation mechanism. Initially, unsaturated reaction intermediates were formed mainly at the platinum sites. These precursors were then reversibly adsorbed on the platinum and migrate to acid sites where they were irreversibly adsorbed. These adsorbed precursors could then polymerize to form the cokes having several double bonds per molecule. The polymerization process was viewed as the rate-limiting step, being slower than the platinum catalysed reaction and also slower than the process of transfer the precursors to the acid sites.

4.2 Preliminary Experiments

A preliminary study was conducted to find suitable operating conditions for other experiments. From the previous literature summary in section 2.9 in Chapter II, the general operating temperatures were varied from 450°C to 527°C, the operating pressures were varied from 100 psig to 600 psig and the hydrogen to hydrocarbon mole ratio of 3-10 were most frequently used.

In this study, the temperatures were 400°C and 450°C because the maximum operating temperature of the experimental apparatus was 500°C. The pressures were 100 psig and 200 psig. The hydrogen to hydrocarbon mole ratios were 3, 6 and 9. The effects of temperature and pressure on the reactions were presented in Appendix (Table 1A. to 6A.). Figures 4.4 to 4.9. indicated that the conversion of n-hexane and methylcyclopentane at higher temperature (450°C) was clearly higher than the conversion at lower temperature (400°C). At higher temperature, the results of different pressure were not significant. Similar result was obtained in the weight
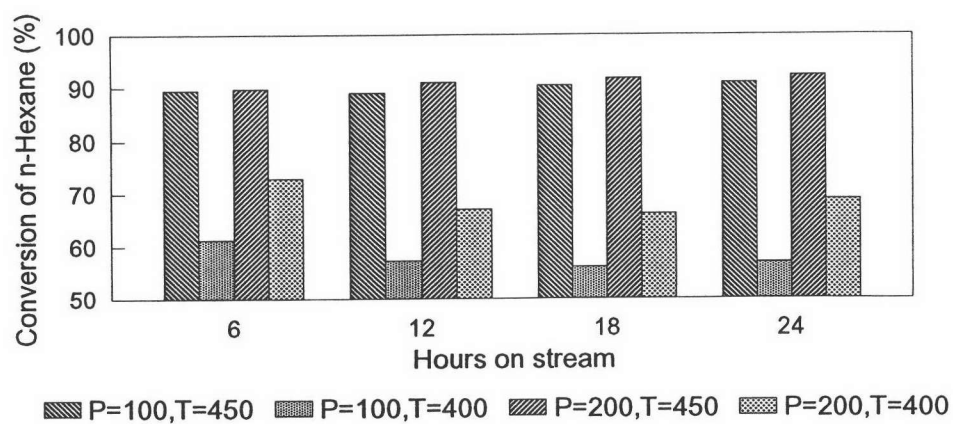
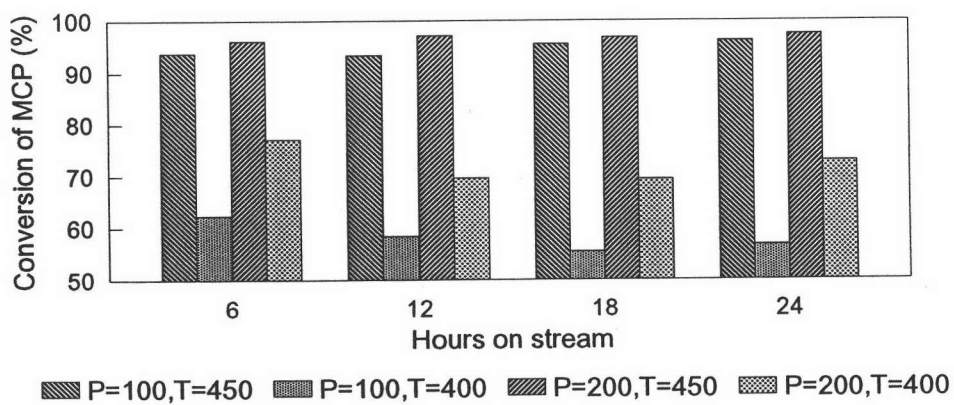Figure 4.4 Effect of Temperature and Pressure on Conversion of n-Hexane.

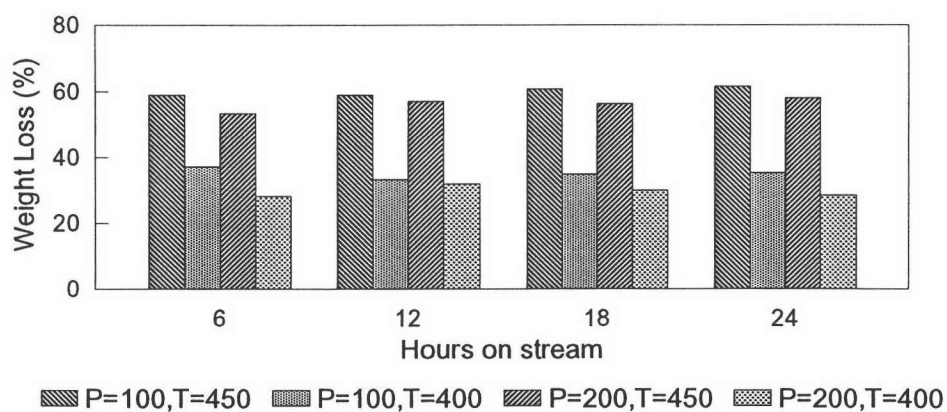Figure 4.5 Effect of Temperature and Pressure on Conversion of Methylcyclopentane.

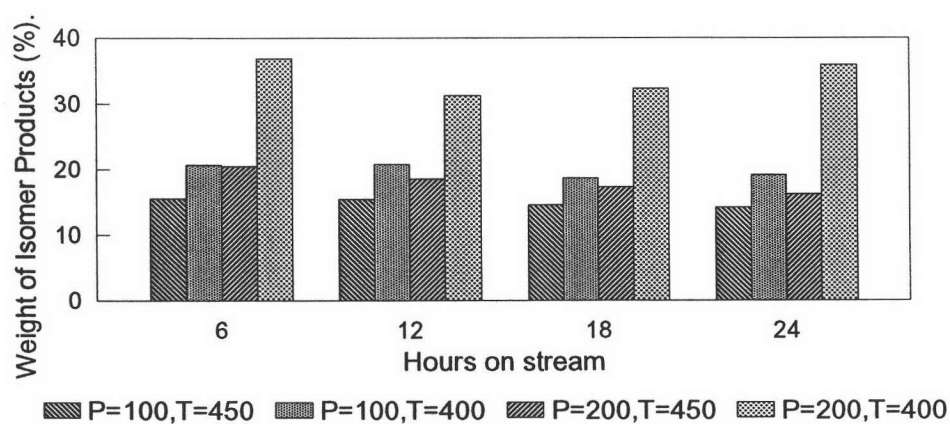Figure 4.6 Effect of Temperature and Pressure on Weight Loss (%).

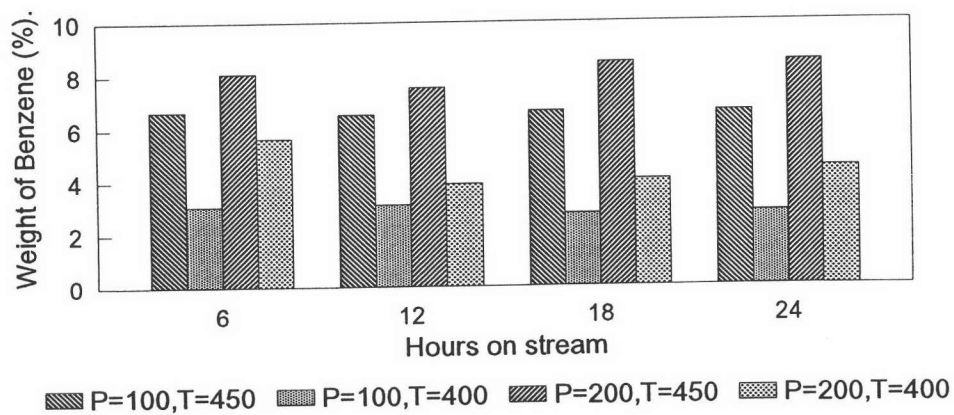Figure 4.7 Effect of Temperature and Pressure on Weight (%) of Isomer Products.

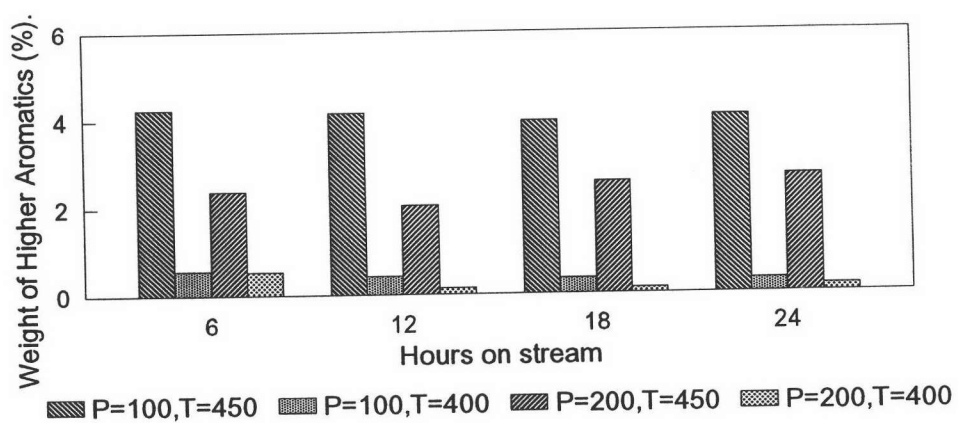Figure 4.8 Effect of Temperature and Pressure on Weight (%) of Benzene.

Figure 4.9 Effect of Temperature and Pressure on Weight (%) of Higher Aromatics.

loss. The weight loss at higher temperature was also higher than the weight loss at lower temperature.

The weight percent of isomer products at higher temperature seem to be less than the isomer products at lower temperature. Goble and Lawrence (1965) previously described that the chloride alumina readily isomerized paraffins under relatively mild conditions because of their high activity.

The weight percent of benzene at higher temperature was higher than the weight percent at lower temperature. From the previous literature surveys, the selectivity of aromatic would be increased when the temperature increased. Furthermore, the weight percent of benzene at higher pressure was higher than the weight percent at lower pressure but the weight percent of higher aromatics at lower pressure was higher than the weight percent at higher pressure. In addition, the weight percent of higher aromatics at higher pressure seem to be too less for this study. Therefore, the suitable temperature and pressure were 450°C and 100 psig, respectively.

The effects of hydrogen to hydrocarbon mole ratio on the reactions were presented in Figures 4.10 to 4.15. The conversion of n-hexane and conversion of methylcyclopentane increased when the hydrogen to hydrocarbon mole ratio increased. The order of conversion was 9 > 6 > 3 because the selectivity of cracking products increased when hydrogen to hydrocarbon mole ratio increased (Gates et al., 1979). Corresponding to the weight loss, the order of weight loss was also 9 > 6 > 3.

Moreover, in the case of conversion of n-hexane and conversion of methylcyclopentane, the hydrogen to hydrocarbon mole ratio of 3 seem to be rapidly declined
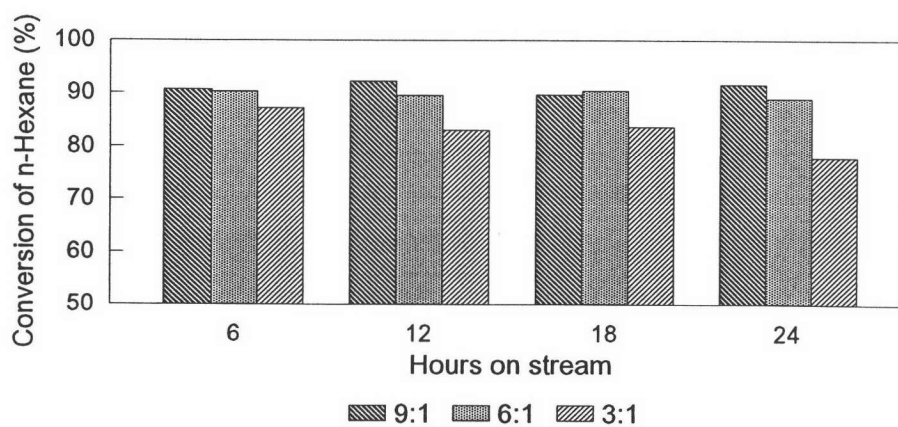
Figure 4.10 Effect of Hydrogen to Hydrocarbon Mole
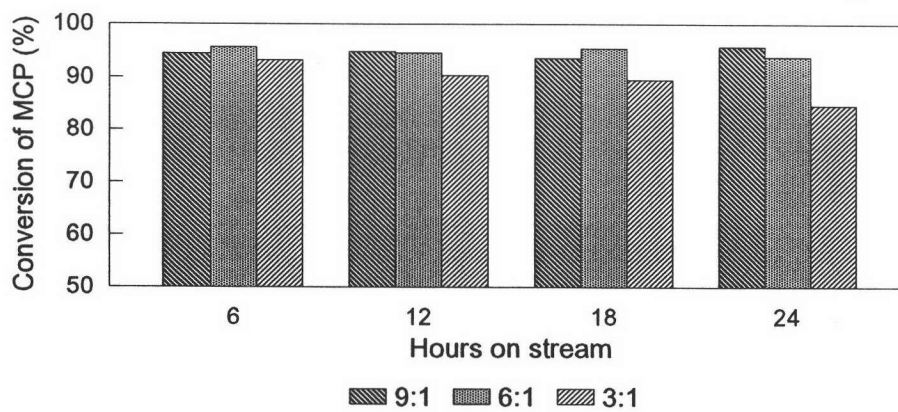Ratio on Conversion of n-Hexane.

Figure 4.11 Effect of Hydrogen to Hydrocarbon Mole
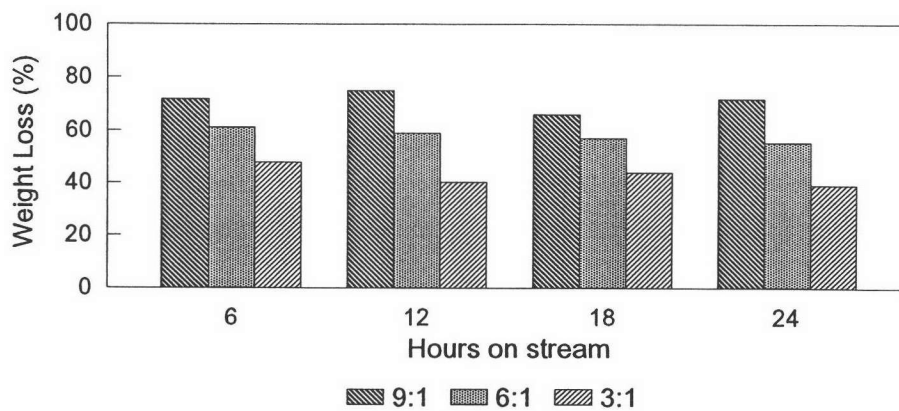Ratio on Conversion of Methylcyclopentane.

Figure 4.12 Effect of Hydrogen to Hydrocarbon Mole
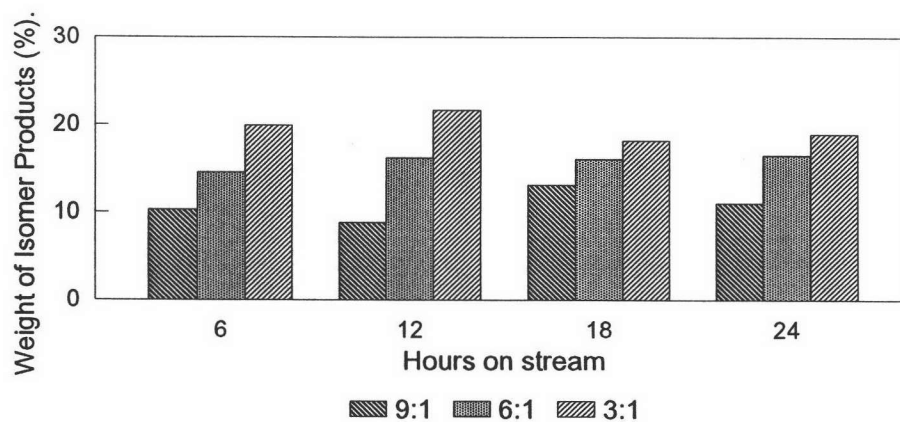Ratio on Weight Loss (%).

Figure 4.13 Effect of Hydrogen to Hydrocarbon Mole
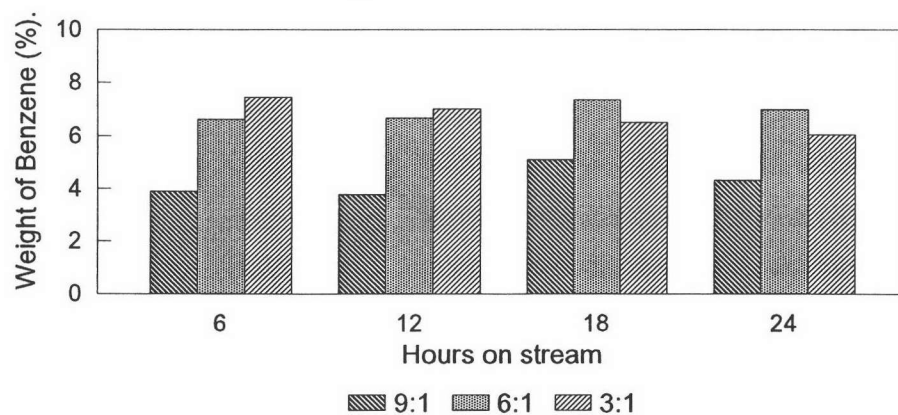Ratio on Weight (%) of Isomer Products.

Figure 4.14 Effect of Hydrogen to Hydrocarbon Mole Ratio on Weight (%) of Benzene.
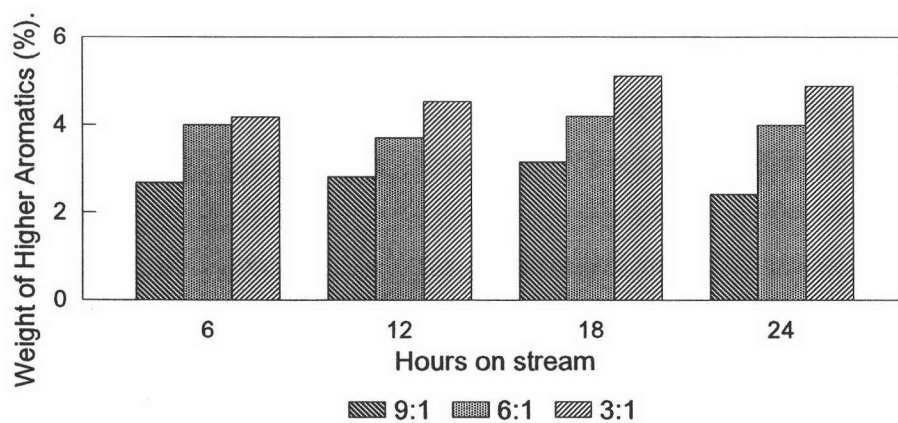

Figure 4.15 Effect of Hydrogen to Hydrocarbon Mole Ratio on Weight (%) of Higher Aromatics.

with time because too low hydrogen to hydrocarbon mole ratio would increase the catalyst deactivation rates because of coke lay down on the catalyst (Ciapetta et al., 1958).

The weight percent of isomer products would be increased when decreased the hydrogen to hydrocarbon mole ratio. The order of the weight percent of isomer products was 3 > 6 > 9. Similar results were obtained in the weight percent of benzene and higher aromatics. The order of their weight percent was also 3 > 6 > 9. Low hydrogen to hydrocarbon mole ratio increased the aromatization reaction (Gates et al., 1979). The results indicated that the ratio of 9 was the lowest weight of desirable products (benzene and higher aromatics). The most constant weight of desirable products was obtained in the ratio of 6. Therefore, the suitable hydrogen to hydrocarbon mole ratio was 6.

From the analysis results of preliminary experiments, the suitable temperature, pressure and hydrogen to hydrocarbon mole ratio were chosen. The suitable temperature and pressure were the ones that gave a high conversion of n-hexane and a high weight percent of aromatic compounds. The suitable hydrogen to hydrocarbon mole ratio was the low mole ratio due to a high aromatization activity but was not too low mole ratio because of rapid catalyst deactivation by coke. Therefore, the temperature, pressure and hydrogen to hydrocarbon mole ratio were chosen as follow: the temperature was 450°C, the pressure was 100 psig, and the hydrogen to hydrocarbon mole ratio was 6. These operating conditions were subsequently used to study in other experiments.

4.3 Experimental Error

Experiments 2,3 and 4 were conducted at the same conditions as the operating conditions chosen, 450°C, 100 psig and hydrogen to hydrocarbon mole ratio of 6, in order to study the repeatability of the experiments. The experiments 2, 3 and 4 would be called Ref.1, Ref.2, and Ref.3, respectively. Deviations of the experiments were shown in Appendix (Table 7A. to 12A.). In this study, the experimental error was presented in the deviation of conversion of n-hexane because of its main reactant. Conversion of n-hexane at any time of reference experiments was shown in Table 4.5. From the data, the steady-state operation was reached after 48 hours from start-up. Duration of each experiment was 144 hours. Average results of reference experiment were used as basis results. Therefore, the effects of each sulfur compound on weight percent of product and on conversion of feed were carried out by comparison of the average results of reference experiment with the results of each deactivated experiment. From the results of three reference experiments, an experimental error was calculated to be in the range of ± 2.35%.

Table 4.5 Conversion of n-Hexane with Time of
Reference Experiments

Time (hr)	Conv. of n-Hexane (%)			Average Ref.	Deviation (%)	
	Ref.1	Ref.2	Ref.3		Max	Min
12	87.34	85.29	85.04	85.89	1.69	1.00
18	86.45	83.56	84.74	84.91	1.80	3.54
24	84.27	82.47	79.02	81.92	2.87	3.54
30	83.61	82.85	83.46	83.31	0.37	0.55
36	84.50	83.04	83.61	83.71	0.93	0.81
42	82.69	81.34	80.46	81.50	1.46	1.27
48	82.27	79.70	81.95	81.30	1.18	1.97
54	80.19	80.71	83.03	81.31	2.11	1.38
60	81.76	78.51	80.67	80.31	1.80	2.25
66	80.13	75.38	78.72	78.07	2.64	3.46
72	76.05	74.91	79.22	76.73	3.25	2.37
78	75.65	79.65	79.62	78.31	1.71	3.39
84	75.74	75.75	76.13	75.87	0.33	0.17
90	71.80	69.30	74.80	71.97	3.94	3.70
96	70.97	69.17	73.84	71.33	3.52	3.02
102	71.27	69.97	73.91	71.72	3.06	2.44
108	72.41	70.65	73.39	72.15	1.72	2.08
114	70.14	70.23	75.65	72.01	5.06	2.59
120	72.94	68.87	75.23	72.35	3.98	4.81
126	68.59	65.95	71.64	68.73	4.24	4.03
132	66.89	66.03	71.72	68.21	5.14	3.19
138	67.14	68.16	68.05	67.78	0.56	0.95
144	65.95	66.89	67.09	66.64	0.67	1.03
	Average Deviation				2.35	2.33

4.4 Effects of Sulfur Compounds

In this research, the effects of sulfur compounds on catalytic reforming of n-hexane were studied over commercial platinum-rhenium/alumina catalyst. The sulfur compounds used in this study were carbon disulfide (CS_2), methyl disulfide ($(CH_3)_2S_2$), methyl sulfide ($(CH_3)_2S$), ethyl sulfide ($(C_2H_5)_2S$) and thiophene (C_4H_4S). The deactivated experiments were conducted by adding these compounds directly to the feedstock prior to the experiments 5, 6, 7, 8 and 9, respectively.

Duration of each experiment was 144 hours. The feedstock was hexanes containing 10 ppm chloride as dichloromethane (CH_2Cl_2) to stabilize acid site of the catalyst. Each sulfur compound was added into the feedstock twice in each deactivated experiment at a concentration of 10 ppm sulfur as sulfur compound and was reacted at the same operating conditions as in the reference experiment. The first sulfur compound addition period was between the hours of 48 to 72 and the second sulfur compound addition period was between the hours of 96 to 120.

The effects of each sulfur compound on conversion of the feedstock and on weight percent of the products were carried out by comparison of the average results of reference experiment with the results of each deactivated experiment. The products were characterized by gas chromatographic techniques to investigate the effects of sulfur compounds on each reaction in catalytic reforming of n-hexane.

Furthermore, the sulfur compounds were chosen to compare the effects of type and structure on catalytic reforming of n-hexane as in the following:

1) The effect of structure was compared between ethyl sulfide (straight chain) and thiophene (cyclic).

2) The effect of number of sulfur atom was compared between methyl sulfide (1 sulfur atom) and methyl disulfide (2 sulfur atoms).

3) The effect of number of carbon atom was compared between methyl sulfide (2 carbon atoms) and ethyl sulfide (4 carbon atoms) and was also compared between carbon disulfide (1 carbon atom) and methyl disulfide (2 carbon atoms).

The effects of sulfur compounds on catalytic reforming of n-hexane were shown in Appendix (Table 13A. to 18A.) and summarized in Table 4.6. The results showed that the addition of sulfur compounds affected catalytic reforming of n-hexane on commercial Pt-Re/alumina.

Table 4.6 Effects of Sulfur Compounds on Catalytic Reforming of n-Hexane

Composition	Effects of Sulfur Compounds	Percent
Conversion of n-Hexane	Decrease	15
Conversion of Methylcyclopentane	Decrease	14
Weight (%) of Isomer Products	Decrease	34
Weight (%) of Benzene	Decrease	60
Weight (%) of Cracking Products	Increase	30
Weight (%) of Higher Aromatics	Increase	25

Conversion of n-hexane and methylcyclopentane were lower than the ones in the reference experiments approximately 15% and 14%, respectively. The weight percent of isomer products was also lower than the average weight from reference experiment approximately 34%. The weight percent of benzene was obviously lower than the average reference weight approximately 60%.

In contrast, the weight percent of cracking products was higher than the average weight of reference experiment approximately 30%. The weight percent of higher aromatics was also higher than the average weight of reference experiment approximately 25%.

These results indicated that the sulfur compounds adsorbed on active sites of catalyst, resulting in the reduction of the reactant being adsorbed on the catalytic sites which reduced the total conversion of the reactant. Furthermore, the poisoning effect of sulfur compounds on n-hexane reforming depend upon the nature of sulfur compounds type as in the following.

4.4.1 Effects of Structure of Sulfur Compounds

The effects of structure of sulfur compounds were compared between ethyl sulfide (straight chain) and thiophene (cyclic). The effects were analyzed in the point of conversion of feed and weight percent of the reaction products. The results were shown in Figures 4.16 to 4.21. Figures 4.16 showed the conversion of n-hexane at any time of three data (average conversions of reference experiments, experiment of ethyl sulfide and experiment of thiophene) and Figures 4.17 showed the conversion of methylcyclopentane. The results indicated that the effects of ethyl sulfide on conversion of both n-hexane and methylcyclopentane did not differ to the effects of thiophene in the first sulfur compound addition period. Introduction of 10 ppm sulfur decreased the conversion of n-hexane and methylcyclopentane approximately 17.5% and 10%, respectively.
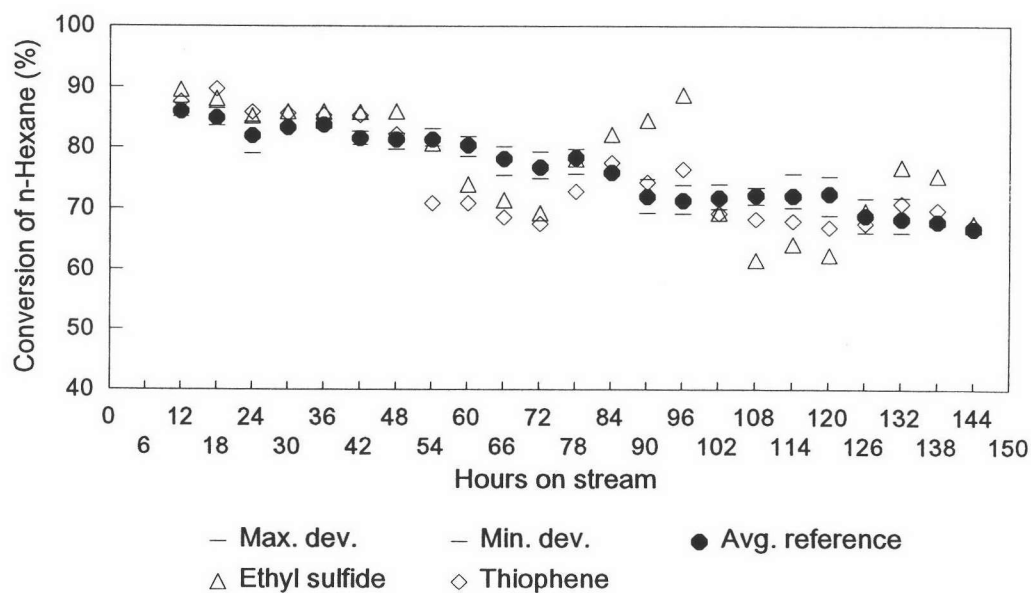
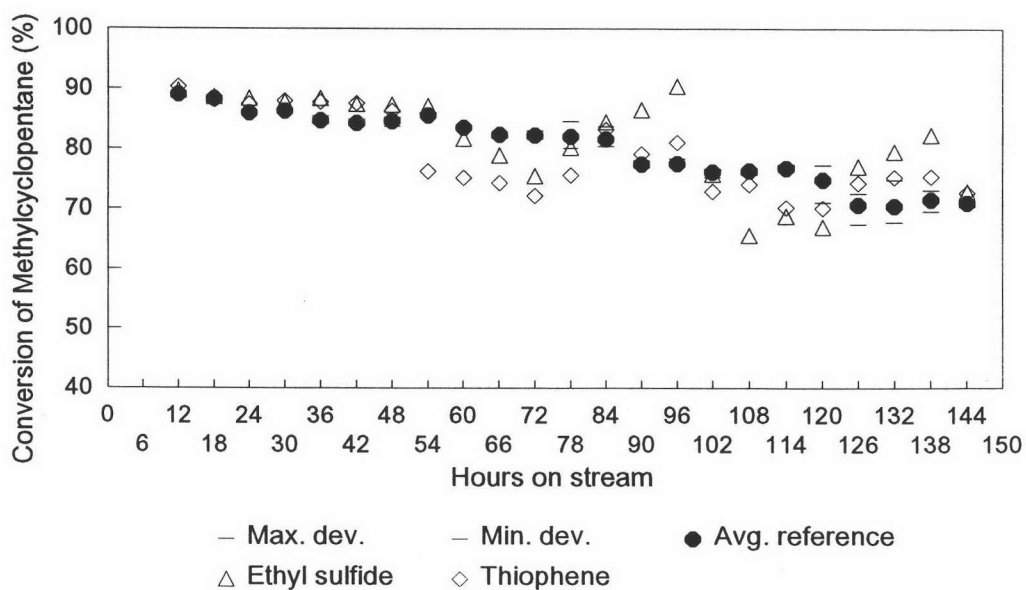Figure 4.16 Effect of Structure of Sulfur Compounds on Conversion of n-Hexane.

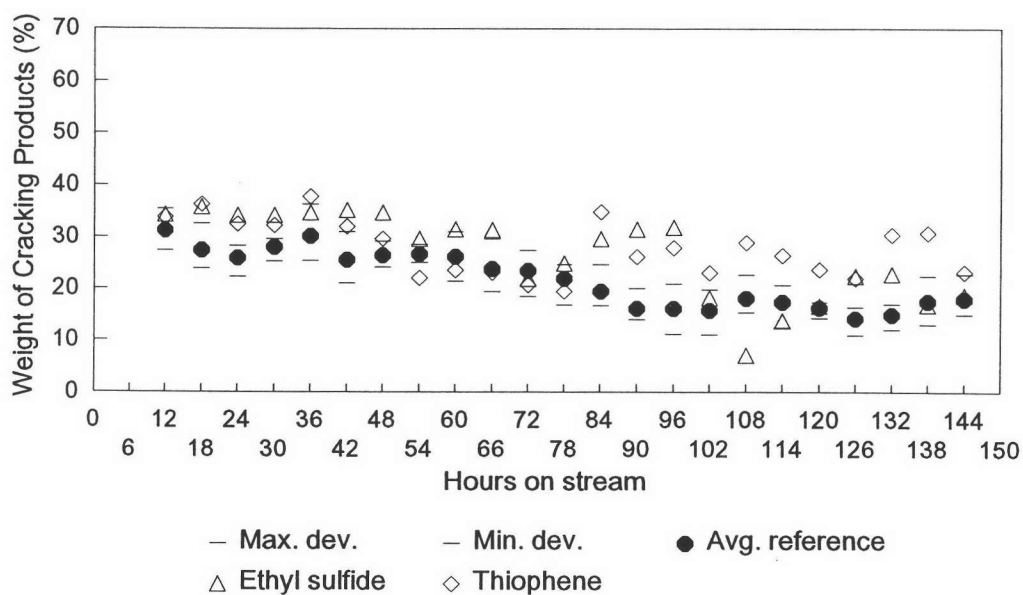Figure 4.17 Effect of Structure of Sulfur Compounds on Conversion of Mthylcyclopentane.

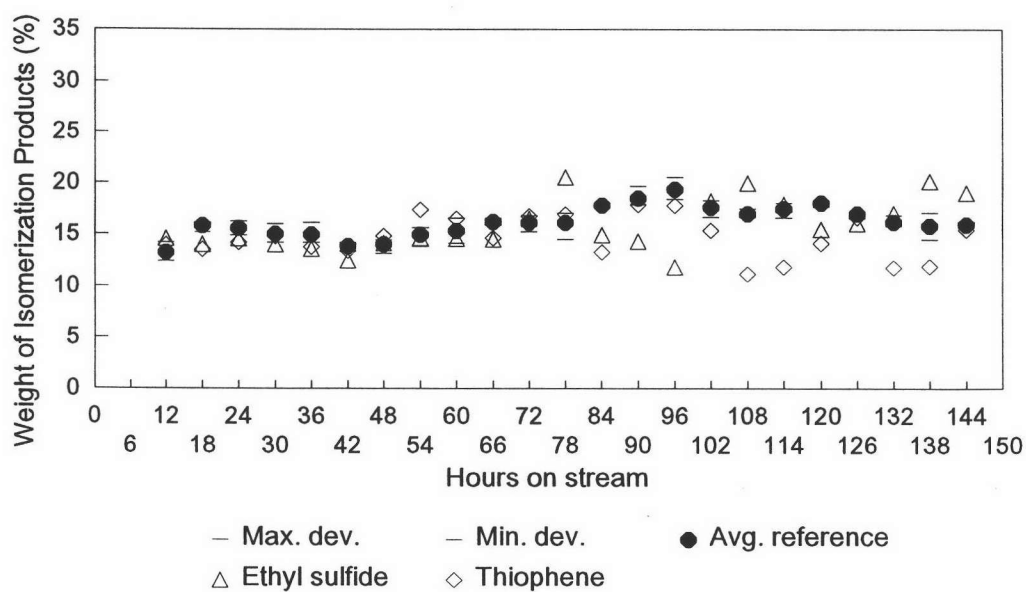Figure 4.18 Effect of Structure of Sulfur Compounds on Weight (%) of Cracking Products.

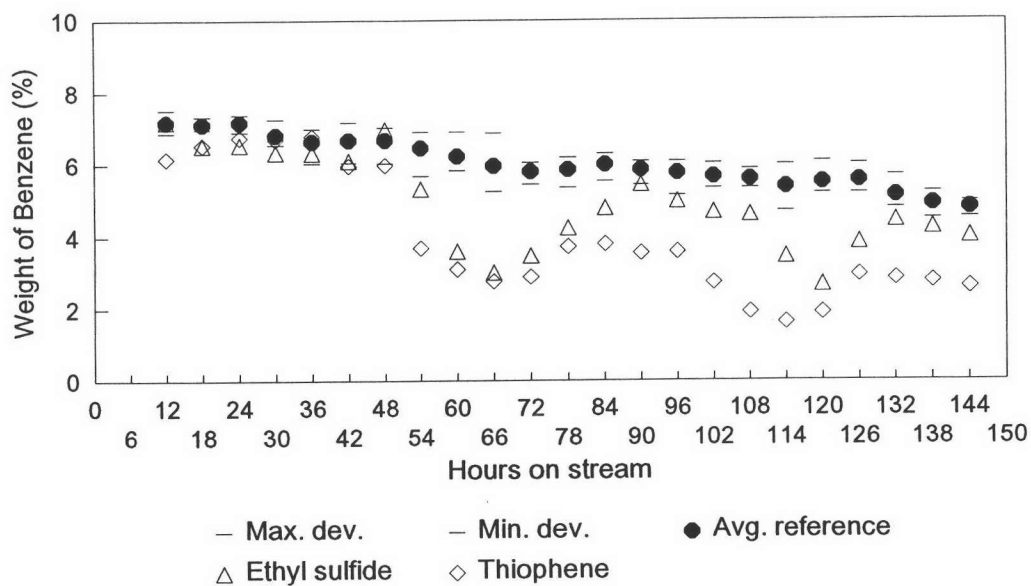Figure 4.19 Effect of Structure of Sulfur Compounds on Weight (%) of Isomer Products.

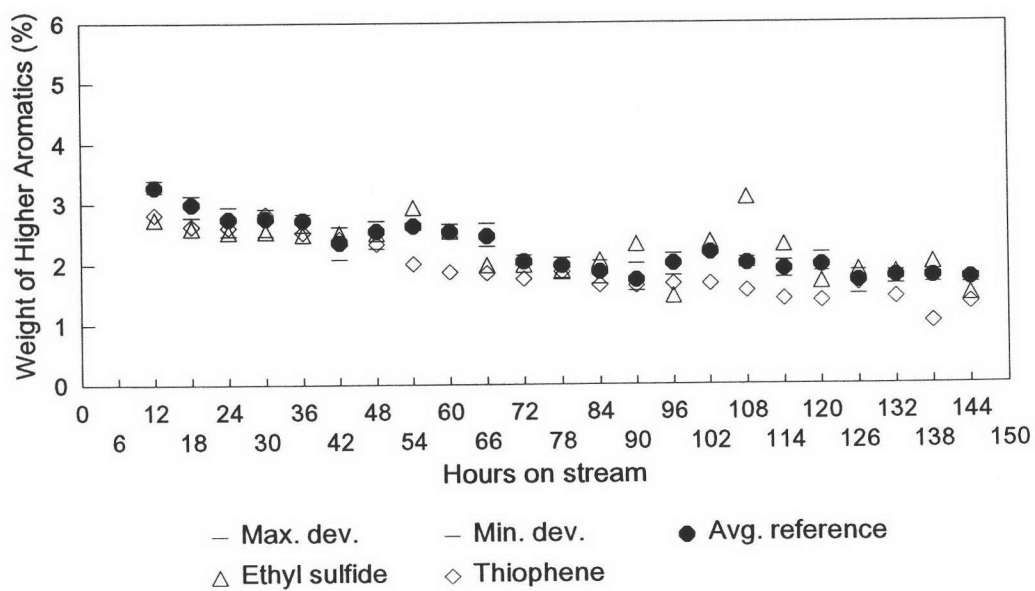Figure 4.20   Effect of Structure of Sulfur Compounds on Weight (%) of Benzene.

Figure 4.21   Effect of Structure of Sulfur Compounds on Weight (%) of Higher Aromatics.

Bickle et al. (1990) proposed that when sulfur compound was first introduced to the system, preferential adsorption of the compound on rhenium would occur. They produced Re-S bonds (due to the strength of this bond) until all surface rhenium atoms were capped. The adsorption of sulfur then occurred on the platinum face atoms (as irreversible sulfur) that were free of an electronic interaction with rhenium until saturation level was reached. Any further sulfur adsorption would be via reversible sulfur to the platinum low-coordination sites, controlled by equilibrium with the gaseous hydrogen sulfide concentration. Meerbott et al. (1954) proposed that deactivation of platinum on reforming catalyst was caused by the formation of a chemical compound between platinum and sulfur or by hydrogen sulfide on the platinum surface. Garetto et al. (1992) also proposed that reforming catalyst poisoning typically results from strong chemisorption of sulfur compounds on the surface of the metal. In this study, the conversion of n-hexane and methylcyclopentane were decreased due to sulfur adsorption on metal sites.

Alternating to pure feedstock (during the period of 72 to 96 hours) showed recovery of the conversion of n-hexane and methylcyclopentane to a level higher than the average reference conversion in the case of ethyl sulfide approximately 20% and 17.8%, respectively. Conversely, in the effect of thiophene, conversion of n-hexane and methylcyclopentane did not greatly differ from average reference conversion. The results showed that ethyl sulfide gave the sulfur adsorption on the metal site higher than thiophene. The hydrocarbons (as feed or partially dehydrogenated species) could still be adsorbed to the platinum site, but they could not react, they split over to the alumina surface. From the

previous literature summary in section 2.9 in Chapter II, acid site on alumina surface was not only used for carbon skeletal rearrangement (isomerization or cyclization) but also used for hydrocracking. The effects of ethyl sulfide exhibited that the reactants were split over to the acid sites for hydrocracking and cracked higher than the effects of thiophene.

Ethyl sulfide had two lone pair electrons on the sulfur atom which could adsorb with one or two metal sites. Contractor and Lal (1979) previously proposed that sulfur atoms were either adsorbed with one sulfur atom strongly bond to two Pt atoms or with one sulfur atom weakly bonded to only one Pt atom. Although thiophene had two lone pair electrons on the sulfur atom like ethyl sulfide, a lone pair electron of thiophene could delocalize inside its ring because thiophene had resonance stability due to its aromatic structure. These indicated that at least a lone pair electron of thiophene did not exist on the sulfur atom for all time. Therefore, the chance of sulfur of thiophene adsorption on metal sites seem to be less than sulfur of ethyl sulfide adsorption.

In addition, when ethyl sulfide was adsorbed on the metal sites, it would dissociate easier than thiophene and gave sulfur to cover the metal sites higher than thiophene because thiophene was aromatic compound which was difficult to hydrogenate in reforming condition on the catalyst (Pt-Re/alumina). Corresponding to the result of benzene reforming, the experiment using only benzene feed indicated that no reaction occurred in the same condition of reference experiment.

Ethyl sulfide affected conversion of n-hexane and methylcyclopentane by increasing of their conversion during the period of 72 to 96 hours (first alternating to

pure feedstock). Conversion of both n-hexane and methylcyclopentane increased by increasing of hydrocracking on acid sites of the catalyst. Corresponding to the weight percent of cracking products of the effect ethyl sulfide, as shown in Figure 4.18, weight percent of cracking products in the same period was higher than the average reference weight approximately 50%. The weight percent of isomer products, as shown in Figure 4.19, in the same period decreased 37.5% from the average reference weight because the cracking products occurred in high rate and the olefin intermediates of isomer products were rapidly reduced due to sulfur adsorption on the metal sites.

The weight percent of benzene, as shown in Figure 4.20, was obviously decreased 56% from the average reference weight when sulfur compounds were first introduced in the reaction. The effect of ethyl sulfide did not differ from the effect of thiophene in the first sulfur compound addition period. In the second sulfur compound addition period, weight percent of benzene of the effect of ethyl sulfide was decreased 55% from the average reference weight and weight percent of benzene of the effect of thiophene was decreased approximately 73% from the average reference weight. In the same period, the weight of higher aromatics, as shown in Figure 4.21, of the effect of ethyl sulfide was higher than the average reference weight approximately 26% whereas no difference was found between the effect of thiophene and average reference weight. These results showed that although ethyl sulfide poisoned the metal sites higher than thiophene resulting in more inhibition of aromatization but the acid site activity in the case of the effect of ethyl sulfide was higher than acid site activity in the case of thiophene effect. From previous

mentioned in reaction network, as shown in Figure 4.1, the olefin polymerization could be taken place on the acid sites to C_6^+-hydrocarbons. Then, they were cyclized to C_6-ring naphthenes and these C_6-ring naphthenes rapidly dehydrogenated to benzene and higher aromatics. Therefore, benzene weight and higher aromatics weight of ethyl sulfide effect were higher than thiophene effect. These results agreed with the study of Satterfield (1980) who studied the hydrodesulfurization of sulfur compounds. He found that the order of activity was R-S-R' > thiophene.

4.4.2 Effects of Number of Sulfur Atom

The effects of number of sulfur atom were compared between methyl sulfide (CH_3-S-CH_3, 1 sulfur atom) and methyl disulfide (CH_3-S-S-CH_3, 2 sulfur atoms). The results were shown in Figures 4.22 to 4.27. From Figures 4.22 and 4.23, the results indicated that the effects of methyl sulfide did not differ to the effects of methyl disulfide in the first sulfur compound addition period. Introduction of 10 ppm sulfur decreased the conversion of n-hexane and methylcyclopentane approximately 12.5% and 9.52%, respectively.

Alternating to pure feedstock (during the period of 72 to 96 hours) showed recovery of the conversion of both n-hexane and methylcyclopentane to a level higher than the average reference conversion in both sulfur compounds approximately 17.65% and 12.64%, respectively. The difference in conversion of feed of both sulfur compounds fell in the experimental error range. Thus it was difficult to conclude that the difference in the number of sulfur atom in the molecule affected the conversion of feed.
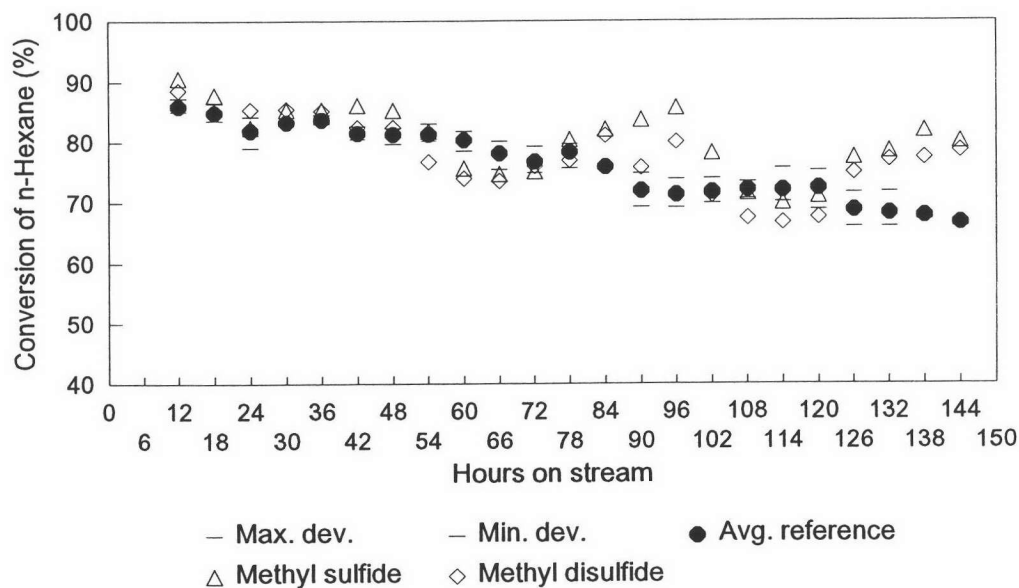
Figure 4.22 Effect of Number of Sulfur Atom of Sulfur Compounds on Conversion of n-Hexane.
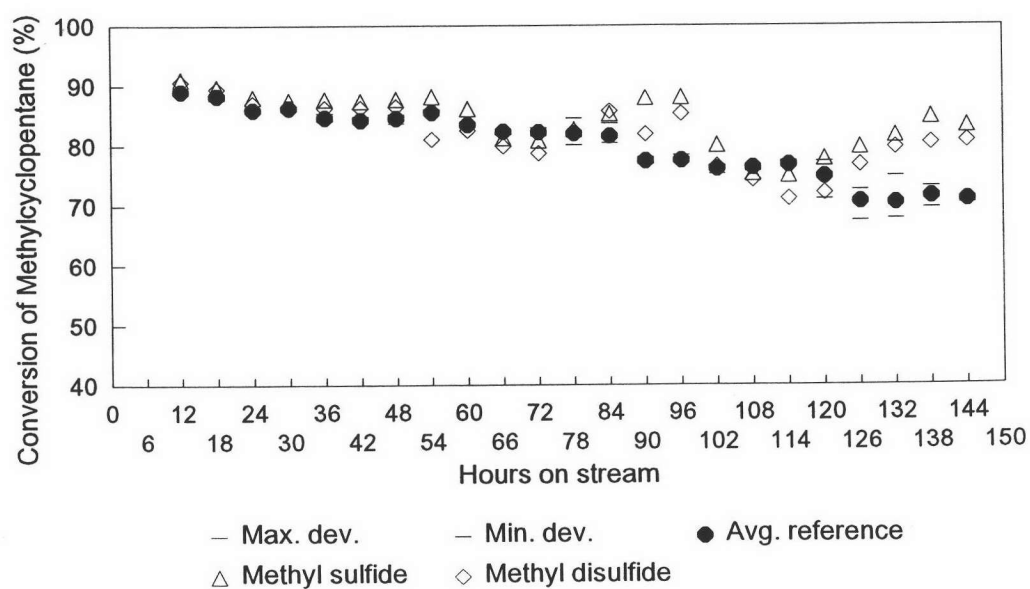

Figure 4.23 Effect of Number of Sulfur Atom of Sulfur Compounds on Conversion of Methylcyclopentane.
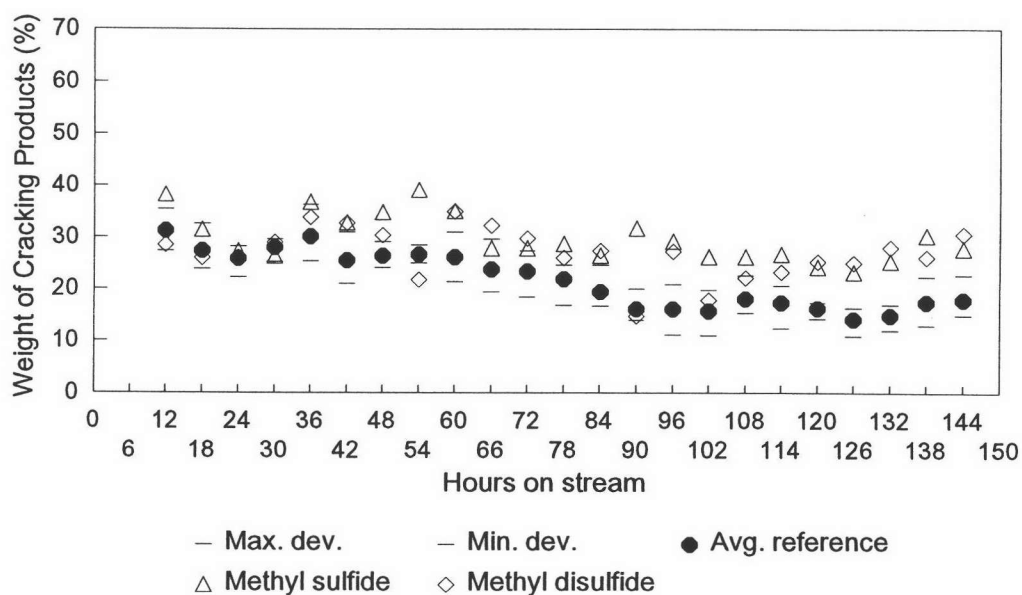
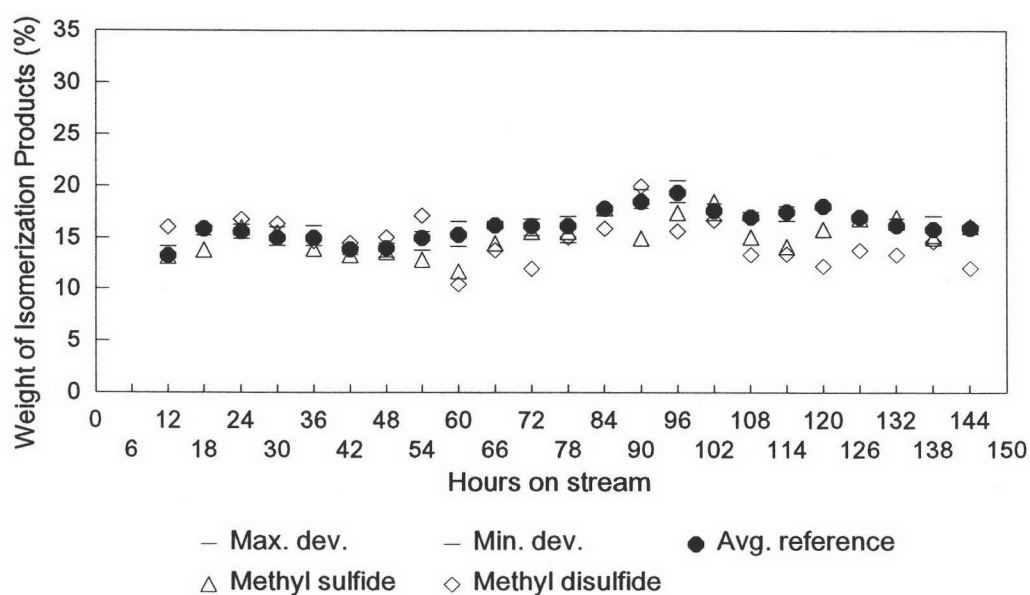Figure 4.24   Effect of Number of Sulfur Atom of Sulfur Compounds on Weight (%) of Cracking Products.

Figure 4.25   Effect of Number of Sulfur Atom of Sulfur Compounds on Weight (%) of Isomer Products.
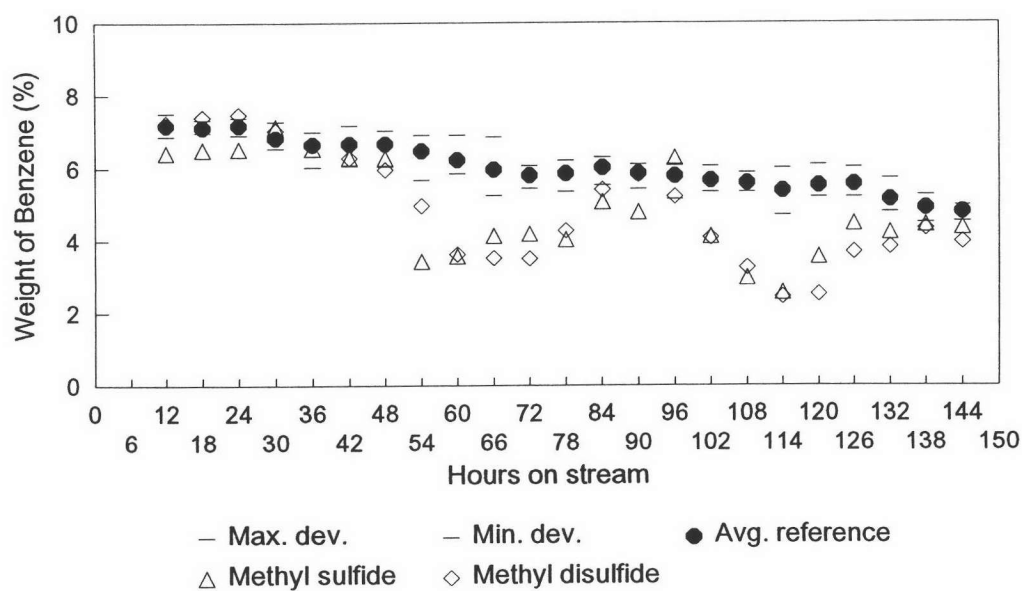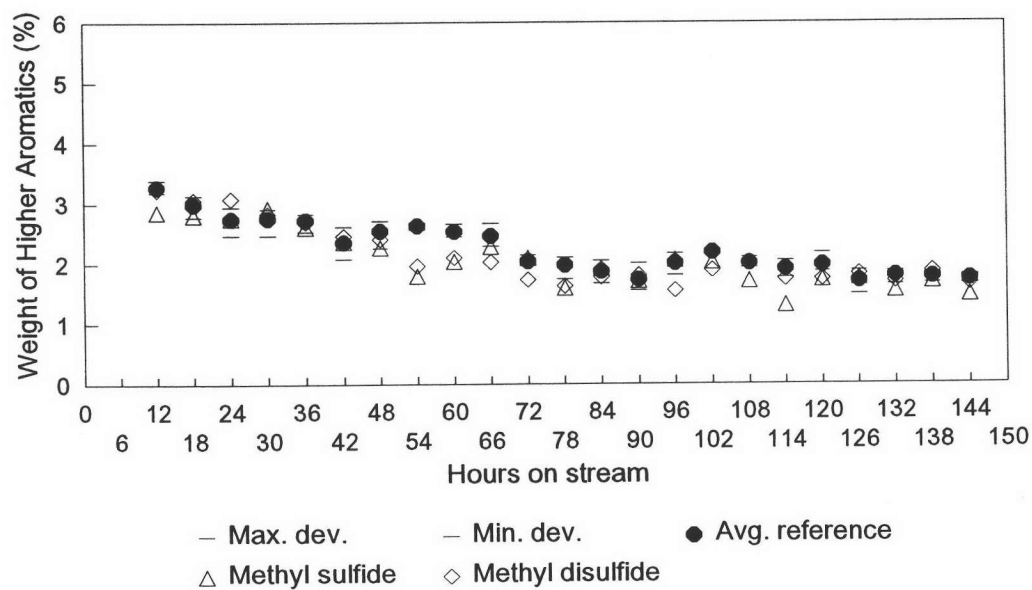
Figure 4.26 Effect of Number of Sulfur Atom of Sulfur Compounds on Weight (%) of Benzene.

Figure 4.27 Effect of Number of Sulfur Atom of Sulfur Compounds on Weight (%) of Higher Aromatics.

Figures 4.24 and 4.25 showed that methyl sulfide and methyl disulfide gave the same results in cracking and isomerization reactions. In the first sulfur compound addition period, addition of sulfur compounds increased the weight percent of cracking products approximately 30% from average reference weight percent whereas the weight percent of isomerization products was decreased approximately 30% from average reference weight percent.

The weight percent of benzene and higher aromatics was presented in Figures 4.26 and 4.27, respectively. The sulfur compounds decreased the formation of benzene approximately 46% in the first sulfur compound addition period and 60% in the second sulfur compound addition period due to sulfur adsorption on metal sites. No effect of these sulfur compounds on higher aromatics was found. These results showed that no difference was found again for these two sulfur compounds.

However, the structure of two sulfur compounds was considered and found that both compounds had the same C-S bond (average bond energy 255 kJ/mol (Chang, 1994)). Methyl disulfide had S-S bond which differed to methyl sulfide, and S-S bond (average bond energy 268 kJ/mol (Chang, 1994)) was slightly higher than C-S bond. Thus, when both sulfur compounds were adsorbed on active sites of the catalyst, the dissociation ability was nearly the same rate. Similar results were obtained by Maxed (1951). He previously found that ethyl sulfide ($CH_3-CH_2-S-CH_2-CH_3$) did not differ greatly molecular toxicity from ethyl disulfide ($CH_3-CH_2-S-S-CH_2-CH_3$) inspite of doubled sulfur content.

4.4.3 Effects of Number of Carbon Atom
(Similar Bond)

The effects of number of carbon atom were compared between methyl sulfide (CH_3-S-CH_3, 2 carbon atoms) and ethyl sulfide (CH_3-CH_2-S-CH_2-CH_3), 4 carbon atoms). The results were shown in Figures 4.28 to 4.33. Figures 4.28 and 4.29 showed that introduction of ethyl sulfide in the first sulfur compound addition period decreased the conversion of both n-hexane and methylcyclopentane approximately 17.5% and 13.1%, respectively. Methyl sulfide decreased in the conversion of n-hexane and methylcyclopentane approximately 11.5% and 8.5%, respectively. Thus, ethyl sulfide decreased conversion of feed higher than methyl sulfide approximately 1.5 times.

Alternating to pure feedstock (during the period of 72 to 96 hours) showed recovery of the conversion of n-hexane and methylcyclopentane conversion of ethyl sulfide effect to a level higher than the average reference conversion approximately 19.5% and 21%, respectively. Methyl sulfide increased the conversion of n-hexane and methylcyclopentane approximately 13.8% and 13.2%, respectively. Thus, ethyl sulfide effects at this period increased conversion of feed higher than methyl sulfide approximately 1.4-1.6 times.

The results indicated that ethyl sulfide dissociated easier than methyl sulfide when it was adsorbed on the metal sites and gave sulfur to cover the the metal sites higher than methyl sulfide because the structure of ethyl sulfide was larger than methyl sulfide. Gates et al. (1979) suggested that the rate of hydrocracking increased rapidly with reactant molecular weight. For example, n-C_{16} paraffin cracked 3 times as fast as n-C_{12} paraffin. Therefore, ethyl sulfide seem to
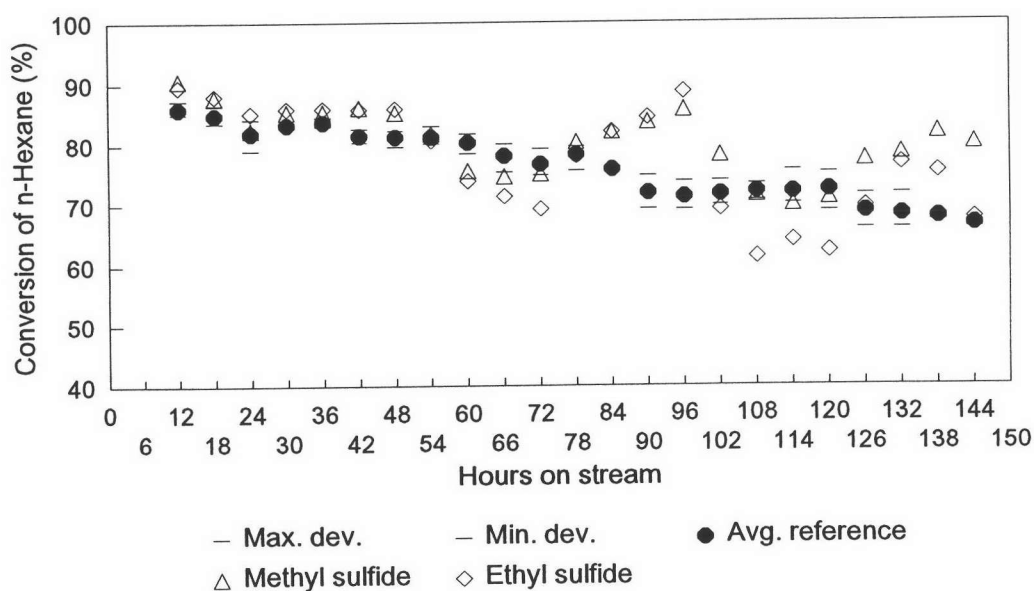
Figure 4.28 Effect of Number of Carbon Atom of
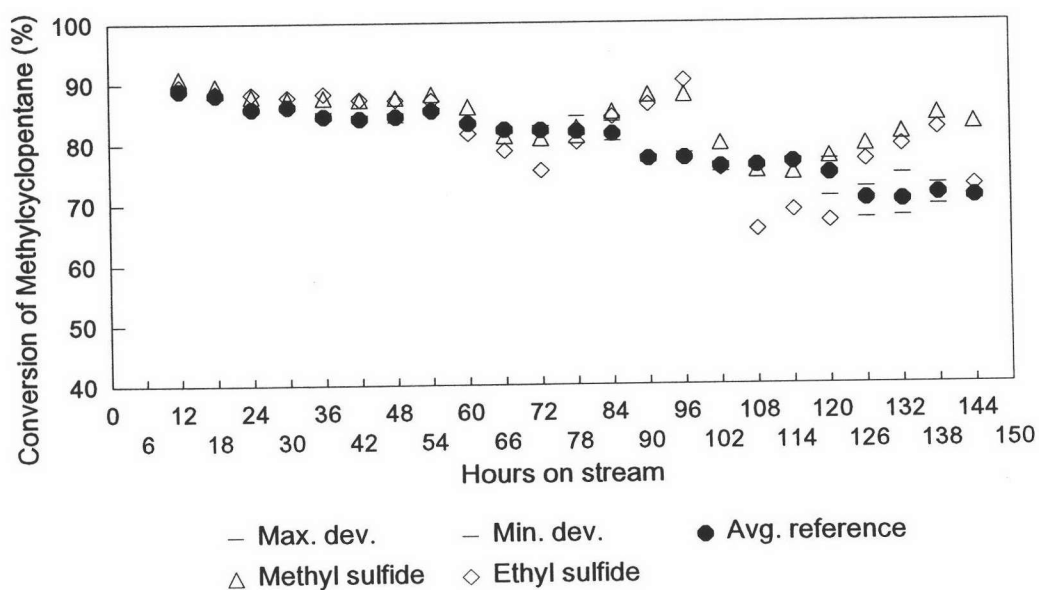Sulfur Compounds on Conversion of n-Hexane.

Figure 4.29 Effect of Number of Carbon Atom of
Sulfur Compounds on Conversion of Methylcyclopentane.
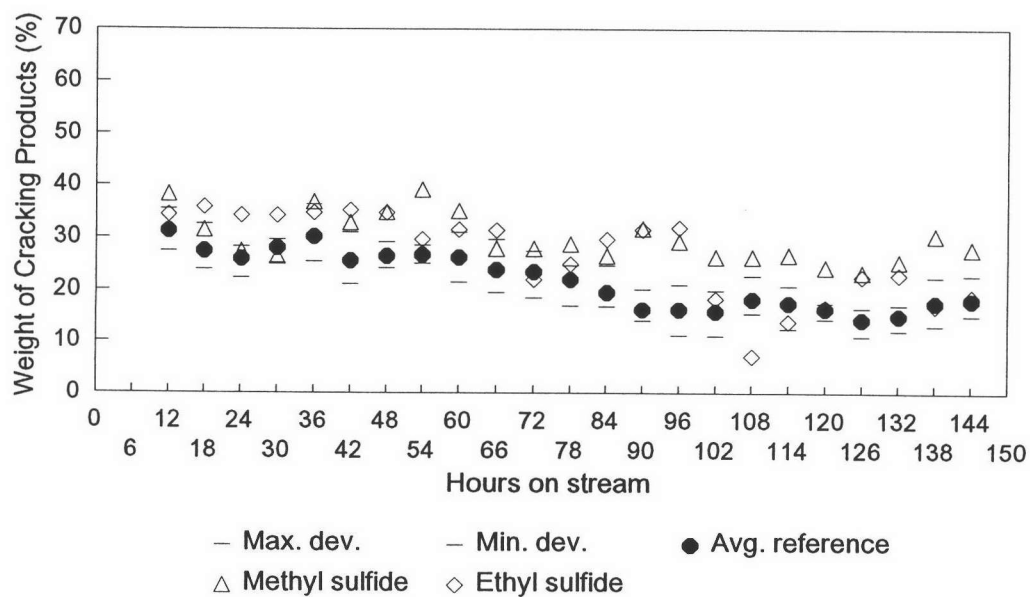
Figure 4.30   Effect of Number of Carbon Atom of
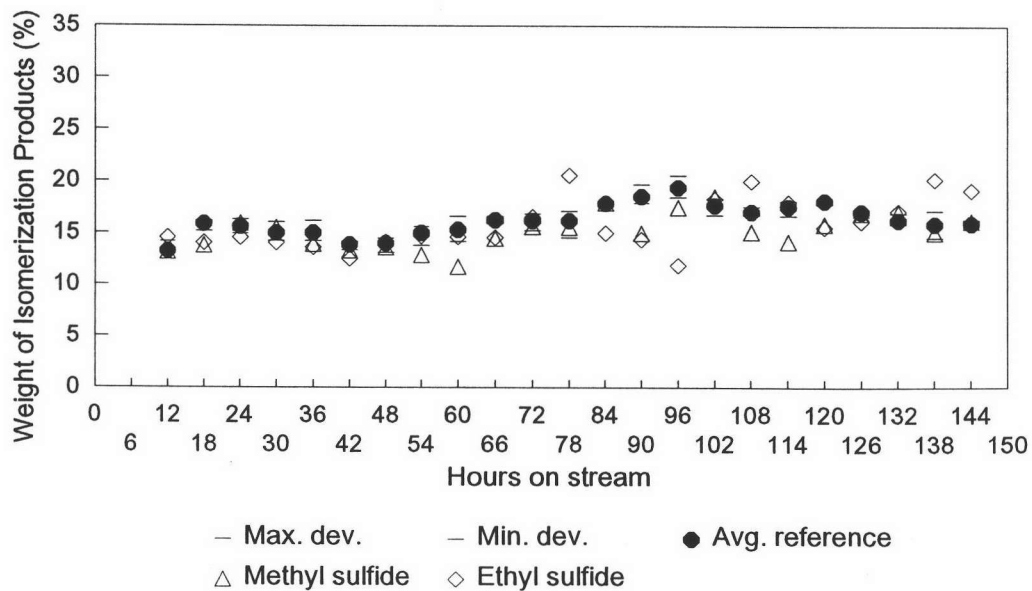Sulfur Compounds on Weight (%) of Cracking Products.

Figure 4.31   Effect of Number of Carbon Atom of
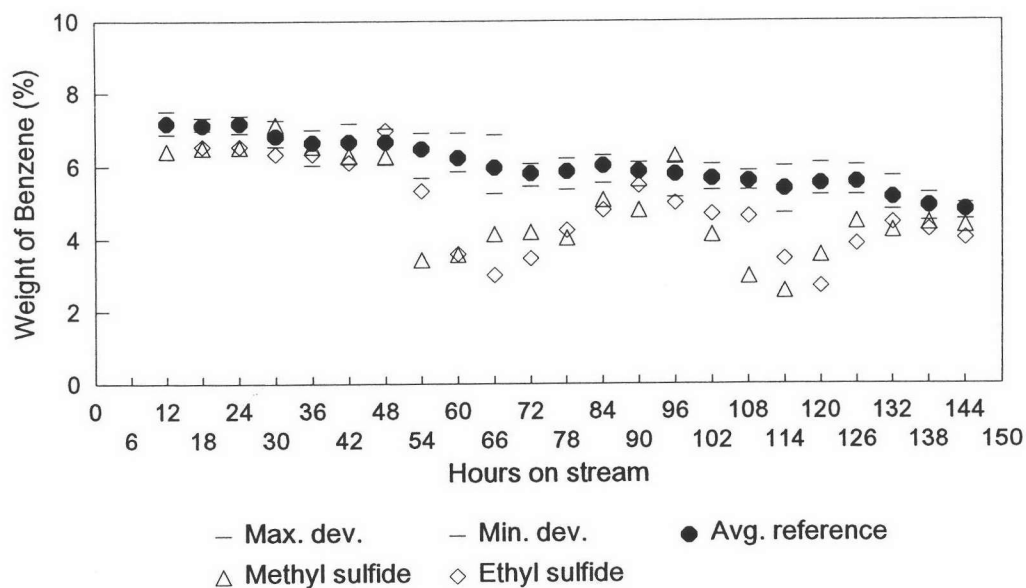Sulfur Compounds on Weight (%) of Isomer Products.

Figure 4.32 Effect of Number of Carbon Atom of
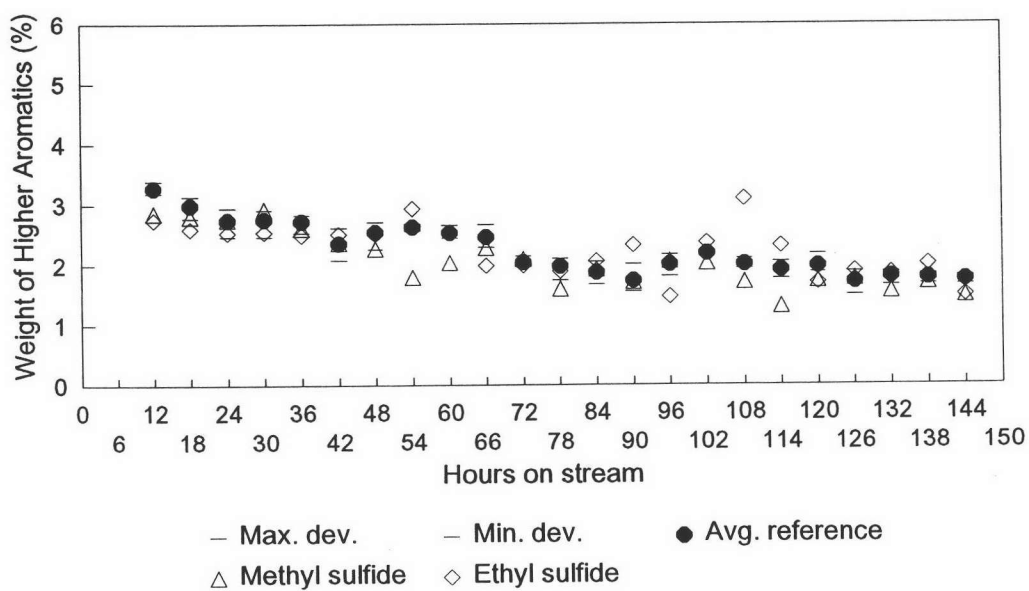Sulfur Compounds on Weight (%) of Benzene.

Figure 4.33 Effect of Number of Carbon Atom of
Sulfur Compounds on Weight (%) of Higher Aromatics.

be cracked easier than methyl sulfide. Furthermore, when ethyl sulfide cracked, it proceeded through primary carbonium ion ($+CH_2CH_3$) intermediate. Methyl sulfide proceeded through methyl carbonium ion ($+CH_3$) intermediate. Gates et al. also suggested that the stability of carbonium ion increased in the order:

Tertiary > Secondary > Primary > Methyl

This reason indicated that ethyl sulfide dissociated easier than methyl sulfide because ethyl sulfide proceeded through more stable intermediate than methyl sulfide.

Ethyl sulfide affected conversion of n-hexane and methylcyclopentane by increasing of their conversion during the period of 72 to 96 hours (first alternating to pure feedstock). The increasing of conversion of both n-hexane and methylcyclopentane caused by hydrocracking on acid sites of the catalyst. Corresponding to the weight percent of cracking products, as shown in Figure 4.30, cracking products of ethyl sulfide effect in the same period were higher than the average reference weight percent approximately 113% which higher than weight percent of methyl sulfide (73.3%) approximately 1.5 times. The weight percent of isomer products, as shown in Figure 4.31, in the same period decreased with 33.3% from the average reference weight percent because the cracking products occurred in high rate and the olefin intermediates of isomer products were rapidly reduced due to sulfur adsorption on the metal sites.

The weight percent of benzene, as shown in Figure 4.32, was obviously decreased with 56% from the average reference weight percent when sulfur compounds were first introduced in the reaction. The effects of ethyl sulfide did not differ to the effects of methyl sulfide in both the first and the second sulfur compound

addition period but in the second sulfur compound
addition period, the weight percent of higher aromatics,
as shown in Figure 4.33, of the effect of ethyl sulfide
was higher than the average reference approximately 40%
whereas no difference between the effect of methyl
sulfide and average reference weight percent. This
result showed that ethyl sulfide poisoned the metal sites
higher than methyl disulfide. The acid site activity in
the case of ethyl sulfide was higher than acid site
activity in the case of methyl sulfide.

4.4.4 Effects of Number of Carbon Atom (Different Bond).

The effects of number of carbon atom were
compared between carbon disulfide (S=C=S, 1 carbon atom)
and methyl disulfide (CH_3-S-S-CH_3, 2 carbon atoms).
The results were shown in Figures 4.34 to 4.39. Figures
4.34 and 4.35 showed that introduction of carbon
disulfide in the first sulfur compound addition period
decreased the conversion of both n-hexane and
methylcyclopentane approximately 18.5% and 15.7%,
respectively. Methyl disulfide decreased the conversion
of n-hexane and methylcyclopentane approximately 11.1%
and 8.4%, respectively. Thus effects of carbon disulfide
at this period decreased conversion of feed higher than
effects of methyl disulfide approximately 1.7-1.9 times.

Alternating to pure feedstock (during the period
of 72 to 96 hours) showed recovery of conversion of
n-hexane to a level higher than the average reference
conversion in both sulfur compounds approximately 14.3%.
In the case of methylcyclopentane conversion, carbon
disulfide increased the conversion approximately 13.2%
whereas methyl disulfide increased the conversion
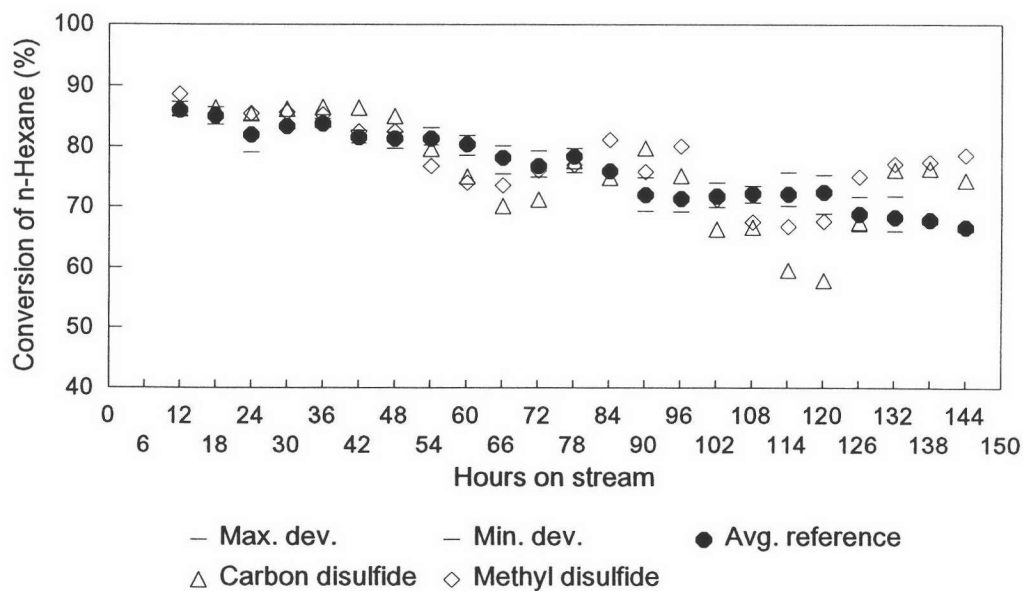approximately 7.9%.

Figure 4.34 Effect of Number of Carbon Atom of
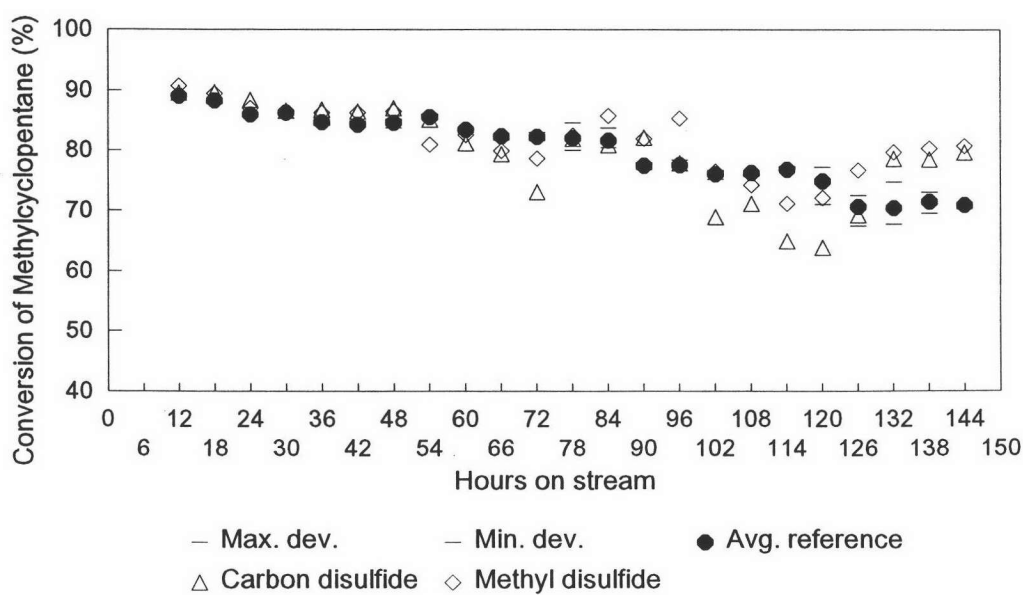Sulfur Compounds on Conversion of n-Hexane.

Figure 4.35 Effect of Number of Carbon Atom of
Sulfur Compounds on Conversion of Methylcyclopentane.
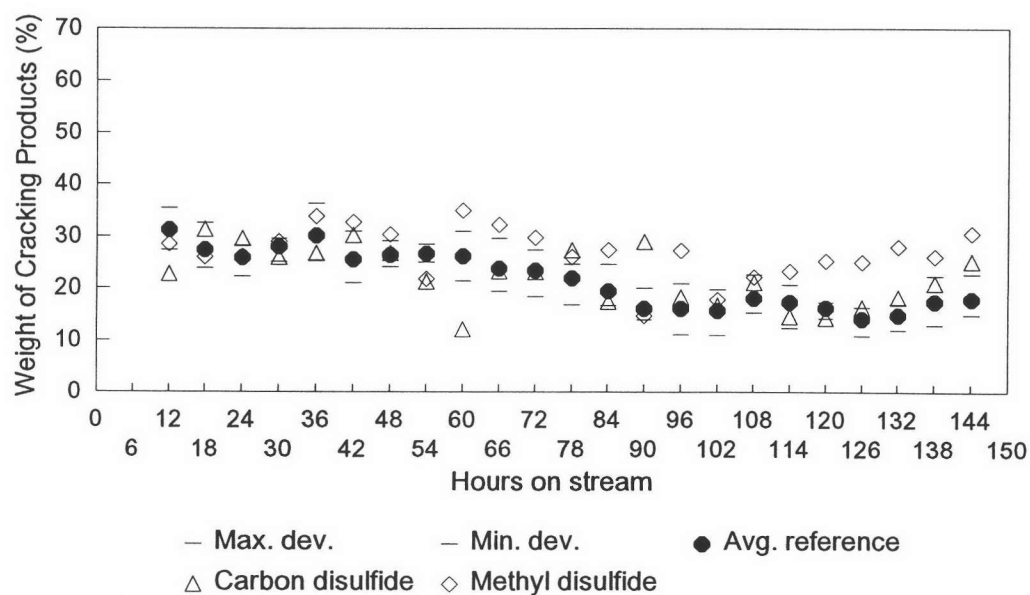
Figure 4.36 Effect of Number of Carbon Atom of Sulfur Compounds on Weight (%) of Cracking Products.
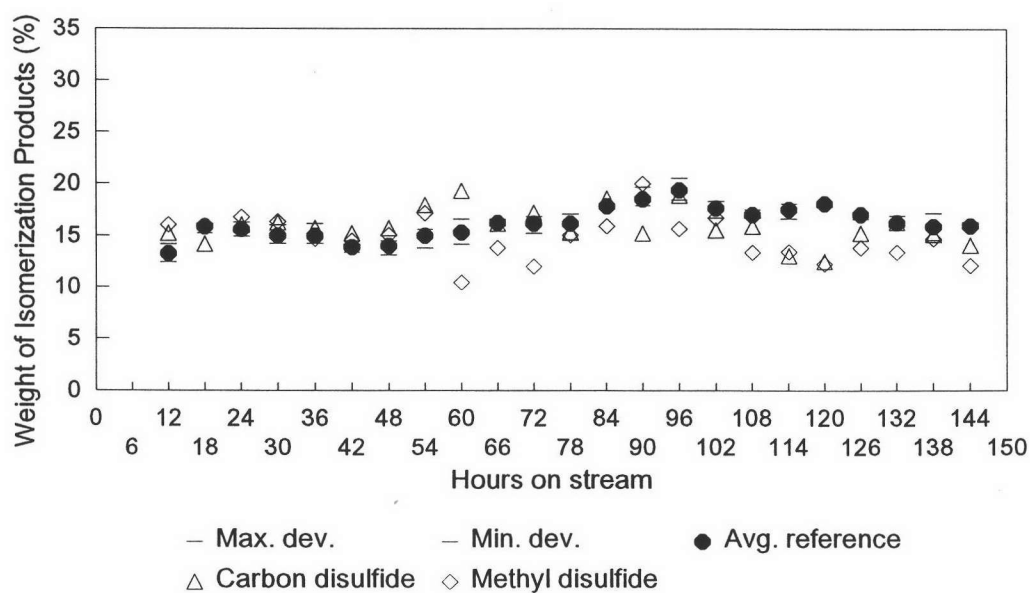

Figure 4.37 Effect of Number of Carbon Atom of Sulfur Compounds on Weight (%) of Isomer Products.
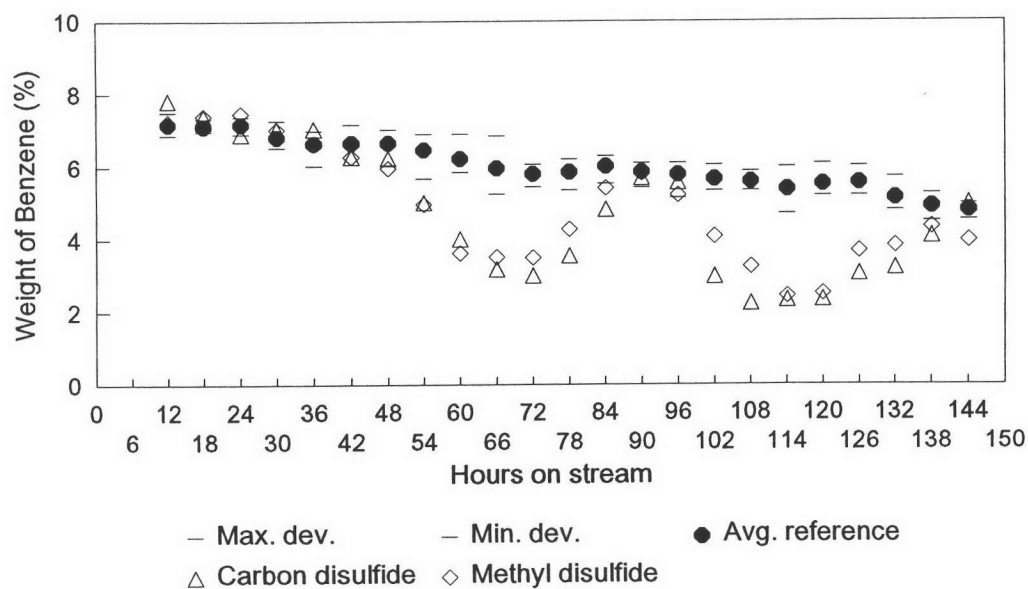
Figure 4.38 Effect of Number of Carbon Atom of
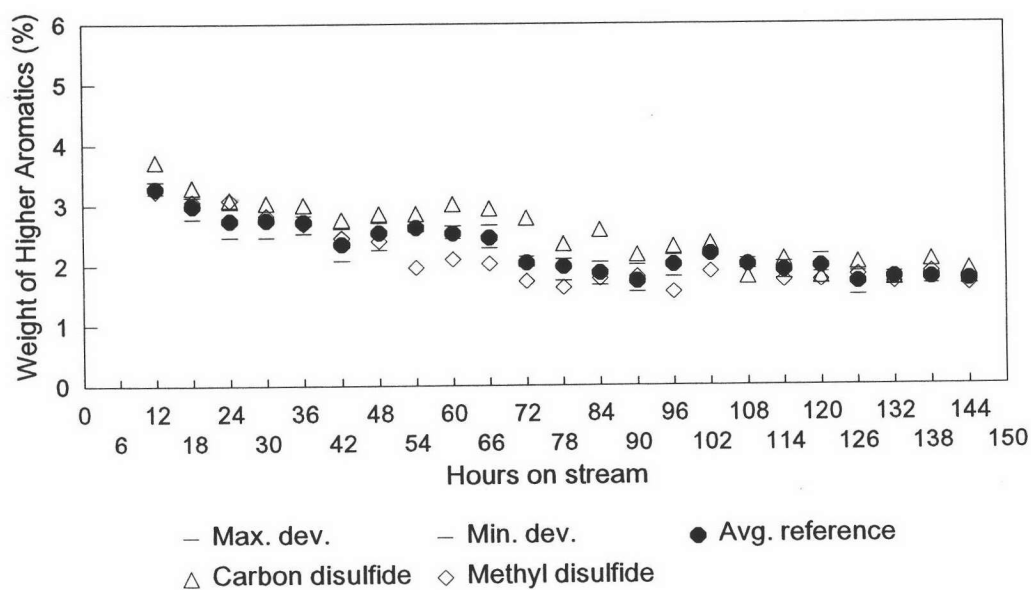Sulfur Compounds on Weight (%) of Benzene.

Figure 4.39 Effect of Number of Carbon Atom of
Sulfur Compounds on Weight (%) of Higher Aromatics.

The second sulfur compound addition period (during the period of 96 to 120 hours), the results showed that carbon disulfide decreased the conversion of n-hexane and methylcyclopentane approximately 20% and 17.3%, respectively. Methyl disulfide decreased the conversion of n-hexane and methylcyclopentane approximately 7.1% and 7.7%, respectively. Therefore, carbon disulfide effect at this period decreased conversion of feed higher than methyl disulfide approximately 2.8 and 2.25 times.

The results indicated that although methyl disulfide dissociated easier than carbon disulfide when it was adsorbed to the metal sites because it had single bond of C-S bond (average bond energy 255 kJ/mol (Chang, 1994)). Carbon disulfide had the double bonds of C=S bond (average bond energy 477 kJ/mol (Chang, 1994)) which was difficult to dissociate. Therefore, carbon disulfide had a chance to adsorb on the active sites with its molecule and covered the metal sites higher than methyl disulfide.

Weight percent of cracking products, as shown in Figure 4.36, of both sulfur compound effect at the period of alternating to pure feedstock (during the period of 72 to 96 hours) was higher than the average reference weight percent approximately 87.5%. The difference in isomer products of these two sulfur compounds was not significant. The isomer products, as shown in Figure 4.37, decreased 20% from the average reference weight percent in the same period because the cracking products occurred in high rate and the olefin intermediates of isomer products were rapidly reduced due to sulfur adsorption on the metal sites.

Weight percent of benzene, as shown in Figure 4.38, was obviously decreased with 60% from the average

reference weight percent when sulfur compounds were introduced in the reaction. The effect of carbon disulfide slightly differed to the effect of methyl disulfide in both the first and the second sulfur compound addition period but in the first sulfur compound addition period, the weight percent of higher aromatics, as shown in Figure 4.39, of carbon disulfide effect was higher than the average reference weight percent approximately 26% whereas it was a slightly difference between methyl disulfide effect and average reference weight percent. This result showed that carbon disulfide poisoned the metal sites higher than methyl disulfide due to its stronger bond. Thus the acid site activity in the case of carbon disulfide was higher than the acid site activity in the case of methyl disulfide.