



## CHAPTER IV

### RESULTS AND DISCUSSIONS

In this study, the experiments are classified into three sections. First, preliminary experiment is conducted to find suitable operating condition. Second, repeatability experiments 1 to 3 are conducted to study the repeatability of the experiments. Third, deactivation experiments 4 to 8 are conducted to study influence of nitrogen compounds on catalytic reforming of hexanes on commercial Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalyst.

The feedstock is hexanes. The major compositions of hexanes are 88% of n-hexane, 9.45% of methylcyclopentane and other trace hexane isomers approximately 2.55%. Nitrogen compounds are used to doctor the feedstocks in each deactivation experiment. They are pyridine, quinoline, 1,2,3,4-tetrahydroquinoline, 2,6-dimethylpyridine and pyrrole. All nitrogen compounds are analytical grade from suppliers. Properties of each reactant are shown in Chapter III. Details of feedstocks and operating condition of each experiment are given in Tables 4.1 to 4.3.

During each experiment, liquid samples are taken every 6 hours without interruption to the system. After each experiment, liquid samples are labeled and kept for analyses. The liquid samples are analyzed for their composition by gas chromatographic analysis technique. The outputs from chromatogram show unconvert n-hexane, methylcyclopentane and products from the reactions. All the compositions are identified by comparison with standard retention time.

Table 4.1 Procedure of Preliminary Experiments

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Feedstock:

FeedI - Hexanes + 10 ppm Cl as CH<sub>2</sub>Cl<sub>2</sub>

Operating conditions:

LHSV (hr<sup>-1</sup>) - 5

Catalyst - 1 gram dilute with inert glass beads ratio 3:1

Sampling - every 6 hours

Condition variables:

1. Pressure 100 psig, Temperature 450°C, H<sub>2</sub>:H/C mole ratio = 6:1
2. Pressure 100 psig, Temperature 400°C, H<sub>2</sub>:H/C mole ratio = 6:1
3. Pressure 200 psig, Temperature 450°C, H<sub>2</sub>:H/C mole ratio = 6:1
4. Pressure 200 psig, Temperature 400°C, H<sub>2</sub>:H/C mole ratio = 6:1
5. Pressure 100 psig, Temperature 450°C, H<sub>2</sub>:H/C mole ratio = 9:1
6. Pressure 100 psig, Temperature 450°C, H<sub>2</sub>:H/C mole ratio = 6:1
7. Pressure 100 psig, Temperature 450°C, H<sub>2</sub>:H/C mole ratio = 3:1

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Table 4.2 Procedure of Repeatability Experiments\*

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Feedstock:

FeedI - Hexanes + 10 ppm Cl as CH<sub>2</sub>Cl<sub>2</sub>

Operating conditions:

Catalyst - 1 gram dilute with inert glass beads ratio 3:1

LHSV (hr<sup>-1</sup>) - 5

Temperature (°C) 450

Pressure (psig) 100

H<sub>2</sub>:H/C mole ratio 6:1

Sampling - every 6 hours

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\* Experiments are called Ref1, Ref2, and Ref3.

Table 4.3 Procedure of Deactivation Experiments

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Feedstocks:

Feed I - Hexanes + 10 ppm Cl as  $\text{CH}_2\text{Cl}_2$   
 Feed II - Hexanes + 10 ppm Cl as  $\text{CH}_2\text{Cl}_2$  + 10 ppm N as nitrogen compounds

Operating conditions:

Temperature (°C) 450  
 Pressure (psig) 100  
 $\text{H}_2$  :H/C mole ratio 6:1  
 LHSV ( $\text{hr}^{-1}$ ) 5  
 Sampling every 6 hours

Switch feedstocks:

Period I	Feed I	Duration 48 hours ( 0 - 48 hrs)
Period II	Feed II	Duration 24 hours ( 49 - 72 hrs)
Period III	Feed I	Duration 24 hours ( 73 - 96 hrs)
Period IV	Feed II	Duration 24 hours ( 97 -120 hrs)
Period V	Feed I	Duration 24 hours (121 -144 hrs)

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The integrating areas show on the chromatogram are used to calculate concentration of compounds in samples. The concentration of compounds in sample is used to calculate weight percent of product components in sample by;

$$\text{Weight (\%)} \text{ of each product component} = \text{Conc. in liquid sample} \times \% \text{ Weight recovery}$$

and

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

$$\text{Weight (\%)} \text{ loss} = \frac{\text{Feed weight} - \text{Sample weight}}{\text{Feed weight}} \times 100\%$$

Conversion of n-hexane is then calculated by



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$$\text{Conversion of n-hexane} = \frac{(C_{t0} - C_t)}{C_{t0}} \times 100$$

where

$C_{t0}$  = Weight (%) of n-hexane in feed

$C_t$  = Weight (%) of n-hexane in sample

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

From the experiments, the main reaction products in liquid sample are 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 (EB), xylenes and propylbenzene (PB).

From the previous literature survey, the reaction network in this study is proposed in Figure 4.1. The results indicate that n-hexane isomerizes to four isomers (i.e. 2,2-DMB, 2,3-DMB, 2-MP and 3-MP), cyclize to two naphthenes (MCP and cyclohexane) and hydrocrack to cracking products ( $C_1-C_5$ ). Furthermore, the four hexane isomers isomerize to n-hexane, cyclize to the naphthenes and hydrocrack to the cracking products. Moreover, the four hexane isomers also isomerize to each other. Similar results were obtained by Christoffel (1979). He described the interconversion of five hexane isomers and their hydrocracking to cracking products.

Moreover, the above results indicate that the five member ring naphthene (MCP) isomerizes to the six member ring naphthene (cyclohexane) and hydrodecyclizes to both n-hexane and four hexane isomers. Cyclohexane isomerizes to methylcyclopentane, hydrodecyclizes to both n-hexane and four hexane isomers and dehydrogenates to benzene.

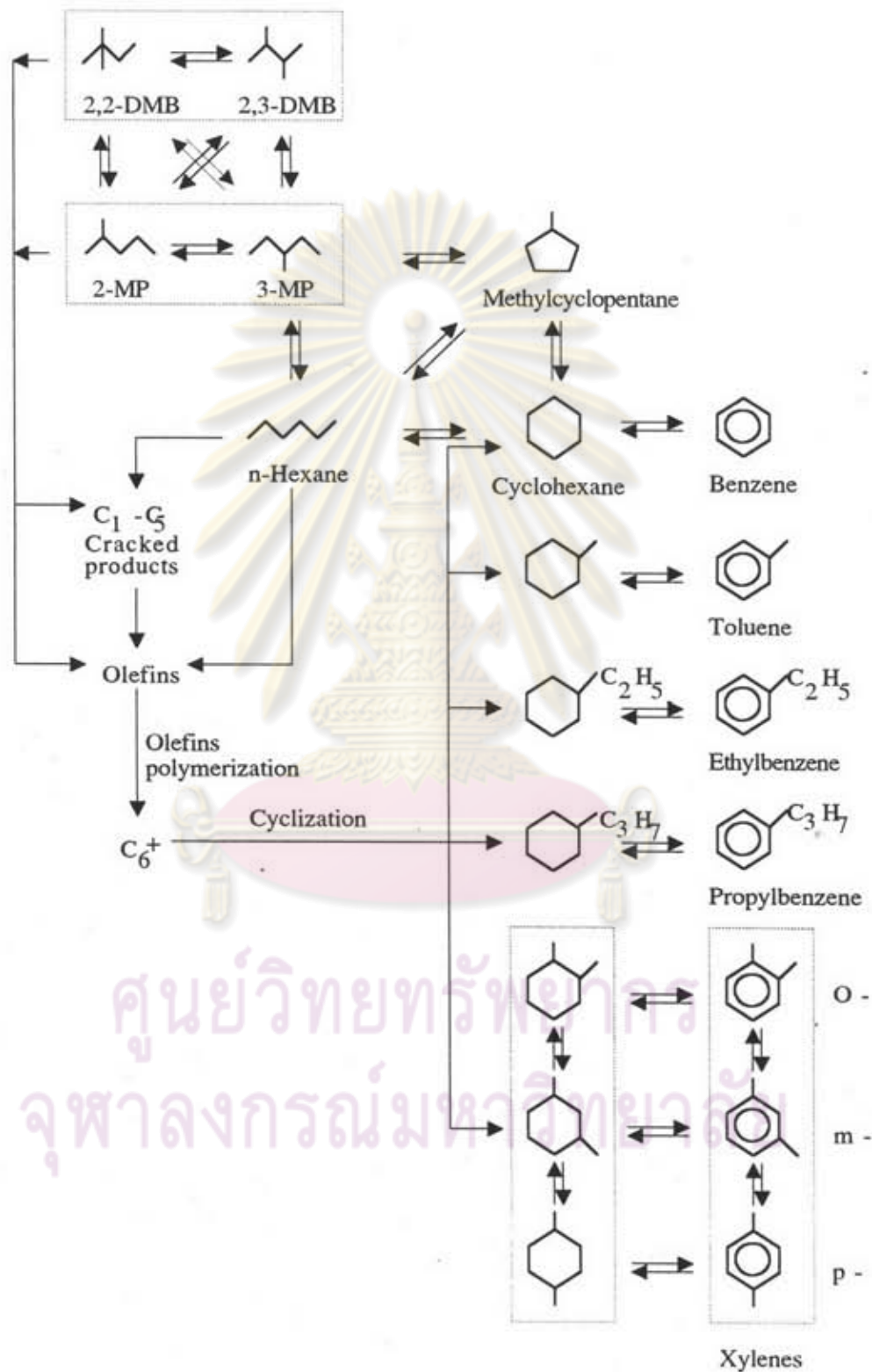


Figure 4.1 Reaction Network of Catalytic Reforming of Hexanes on Commercial Pt-Re/Alumina.

In addition, the higher aromatic compounds are 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. Since the straight-chain paraffins are converted into isoparaffins by proceed through the olefins. Therefore, the olefins from these reactions and the olefins from other reactions (for example partly of cracking products and dehydrogenation of n-hexane) polymerize to  $C_6^+$ -paraffins.

Then,  $C_6^+$ -paraffins cyclize to cyclohexane and its derivatives such as methylcyclohexane, ethylcyclohexane, propylcyclohexane and dimethylcyclohexanes. Then, these  $C_6$ -ring naphthenes dehydrogenate to benzene, toluene, ethylbenzene, propylbenzene, and xylenes, respectively. The aromatic compounds (benzene and its derivatives) also hydrogenate to the naphthenes. Similar whole reaction patterns have been thoroughly reported in several papers as mentioned above. Cyclohexane in this result is not detected. It converts 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 occurred very rapidly.

Feed in this study is paraffin (n-hexane). Therefore, each product shows the corresponding reaction (especially three main reactions). This means that the aromatic compounds show the dehydroisomerization or aromatization reaction, the hexane isomers show the isomerization reaction, and the cracking products show the hydrocracking reaction.

From the results in the first 48 hours of reference experiments, the total weight loss is 56.8% (by weight), the weight of n-hexane is 11.3%, the weight of



methylcyclopentane is 0.76%, the weight of four hexane isomers is 15.8%, the weight of benzene is 6.07%, and total weight of the higher aromatics is 4.18%. In this study, the blank test precedes the reaction with the same operating conditions of other experiments but without the catalyst. The weight loss of the blank test shows the weight loss of n-hexane that vaporize into the gas phase. It found that the weight loss of the blank test is 32% which corresponding to the result from vapour-liquid equilibrium calculation by simulation program. Therefore, the weights (%) of hydrocracking products are obtained by the difference value between the total weight loss and the weight loss of the blank test. Thus the weight of hydrocracking products is approximately 24.8%. The last 5.09% is the amount of trace other compounds that slightly exist in the liquid products. The weights of all products are compared with the weight of feed. They are summarized in Table 4.4.

Table 4.4 The Weight (%) of Feed and Products in the First 48 Hours of Reference Experiment.

Composition	Weight (%) in feed	Weight (%) in products
n-hexane	88.0	11.30
Methylcyclopentane	9.45	0.76
Cracking products	-	24.80
Hexane isomer products	2.55	15.80
Benzene	-	6.07
Higher aromatics	-	4.18
Trace of other compounds	-	5.09
Lost by Vapour-Liquid equilibrium	-	32.0

For clarity, all products in this study will categorize into four groups. First, products from cracking reaction and flow concurrently with gas sample are grouped together as cracking products. Second, all  $C_6$  molecules that are hexane isomers categorize as isomerization products. Third, benzene is the main aromatic product. The last "higher aromatics" represents aromatic products with the exception of benzene.

Therefore, the results are analyzed in the point of conversion (%) of feed and the weights (%) of the products.

#### 4.1 Suitable operating condition.

Preliminary experiments are conducted to find a suitable operating condition such as temperature, pressure and  $H_2:H/C$  mole ratio for reforming reaction of hexanes. The experiments are divided to two parts.

Part I, study the effects of temperature and pressure, temperatures are  $400^\circ C$  and  $450^\circ C$ , and pressures are 100 psig and 200 psig. The effects of temperature and pressure are plotted in Figures 4.2 to 4.7. The data are given in the Appendix (Table 1A to 6A). From this set of experiments, the suitable temperature and pressure are chosen.

Conversions (%) of n-hexane and methylcyclopentane are plotted versus time and presented in Figures 4.2 and 4.3, respectively. The results indicate that the conversion (%) of n-hexane and methylcyclopentane at higher temperature ( $450^\circ C$ ) are clearly higher than the conversion at lower temperature ( $400^\circ C$ ). At higher temperature, the difference of pressure 100 psig and 200 psig are not significant.

Similar result is obtained in the weight (%) loss. The weight (%) loss, as shows in Figure 4.4, at higher temperature is also higher than the weight loss at lower temperature.



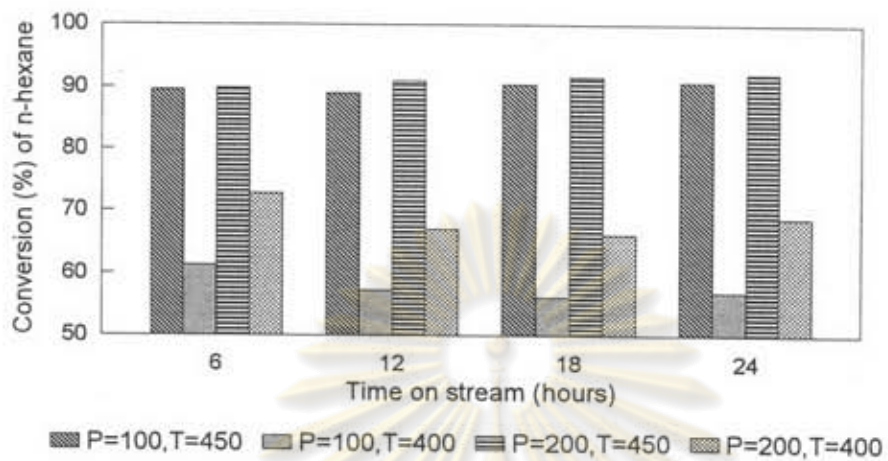


Figure 4.2 Conversion (%) of n-Hexane with Time (The Effects of Temperature and Pressure)

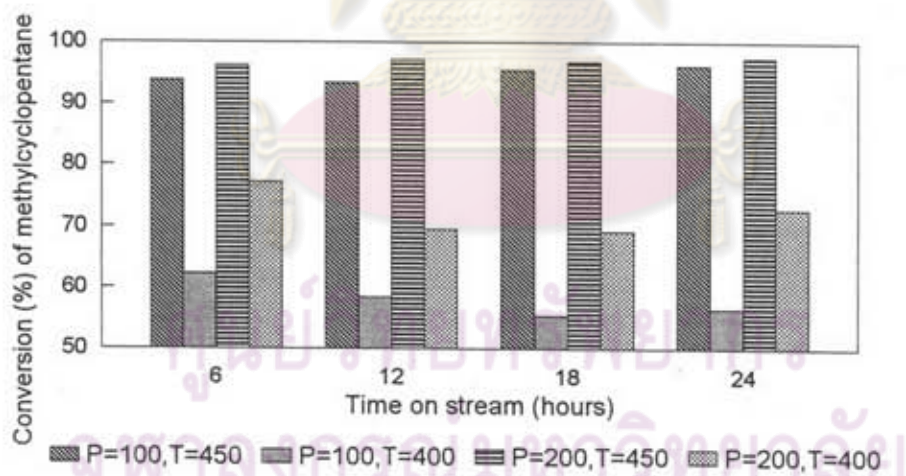


Figure 4.3 Conversion (%) of Methylcyclopentane with Time (The Effects of Temperature and Pressure)

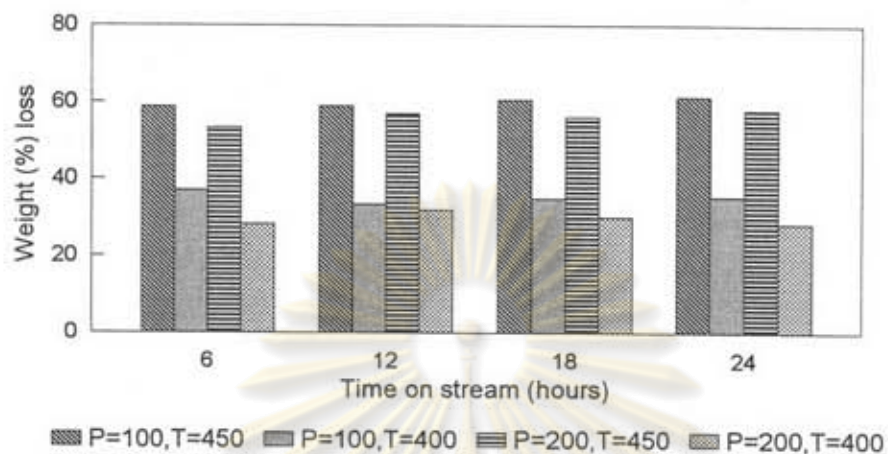


Figure 4.4 Weight (%) Loss with Time  
(The Effects of Temperature and Pressure)

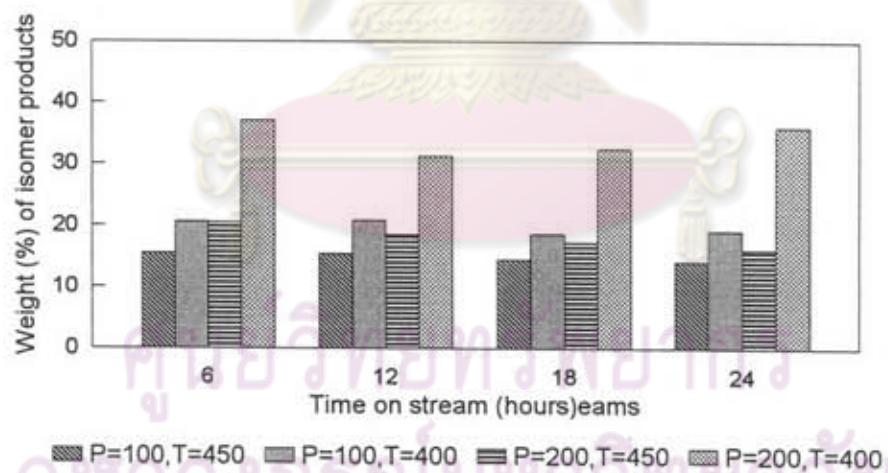


Figure 4.5 Weight (%) of Isomer Products with Time  
(The Effects of Temperature and Pressure)

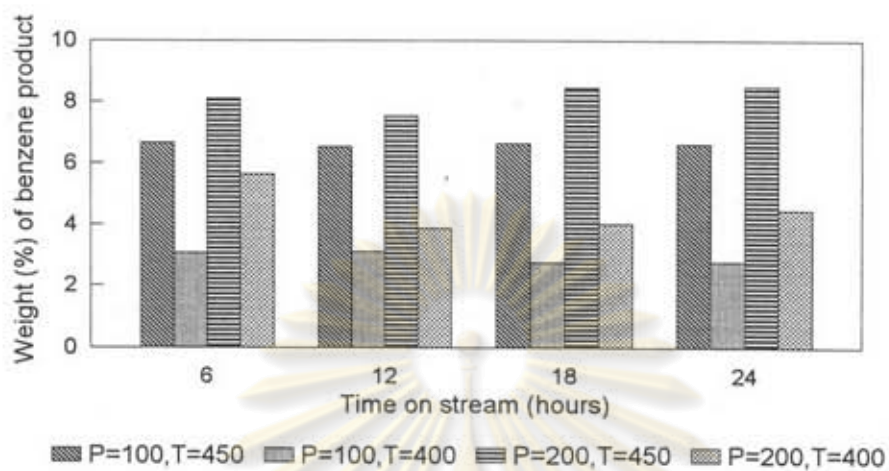


Figure 4.6 Weight (%) of Benzene Product with Time (The Effects of Temperature and Pressure)

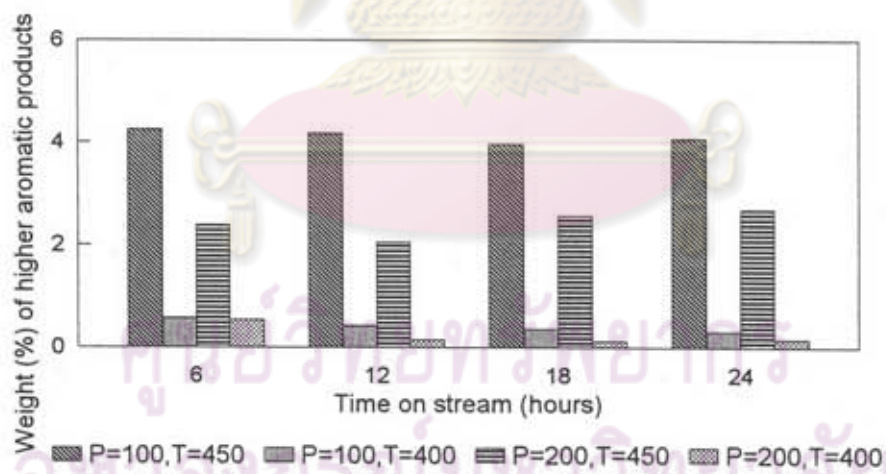


Figure 4.7 Weight (%) of Higher Aromatic Products with Time (The Effects of Temperature and Pressure)



The weight (%) of isomer products, as shows in Figure 4.5, at higher temperature are 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 (%) of benzene, as shows in Figure 4.6, at higher temperature is higher than the weight at lower temperature. From the previous literature survey, the selectivity of aromatic increases when the temperature increases. Furthermore, the benzene weight at higher pressure are higher than the benzene weight at lower pressure. In contrast, the weights (%) of higher aromatics, as shows in Figure 4.7, at lower pressure are higher than the weight at higher pressure. In addition, the weights of higher aromatics at higher pressure are too less for this study.

Therefore, the suitable temperature and pressure are  $450^{\circ}\text{C}$  and 100 psig, respectively.

Part II, study the effects of  $\text{H}_2$ :H/C mole ratio, are 9:1, 6:1, and 3:1. The effects of  $\text{H}_2$ :H/C mole ratios are plotted in Figures 4.8 to 4.13. The data are given in the Appendix (Table 1A to 6A). The suitable  $\text{H}_2$ :H/C mole ratios are chosen.

The conversions (%) of n-hexane, as show in Figure 4.8, increase when the hydrogen to hydrocarbon mole ratio increase. Similar result is obtained in the conversion (%) of methylcyclopentane, as show in Figure 4.9. The order of conversion depends on hydrogen to hydrocarbon mole ratio are  $9 > 6 > 3$ . Because the selectivity of cracking products increase when hydrogen to hydrocarbon mole ratio increase (Gates, Katzer, and Schuit, 1979). Corresponding to the weight (%) loss, as show in Figure 4.10, the order of weight loss are also  $9 > 6 > 3$ .

Moreover, in Figures 4.8 and 4.9, the hydrogen to

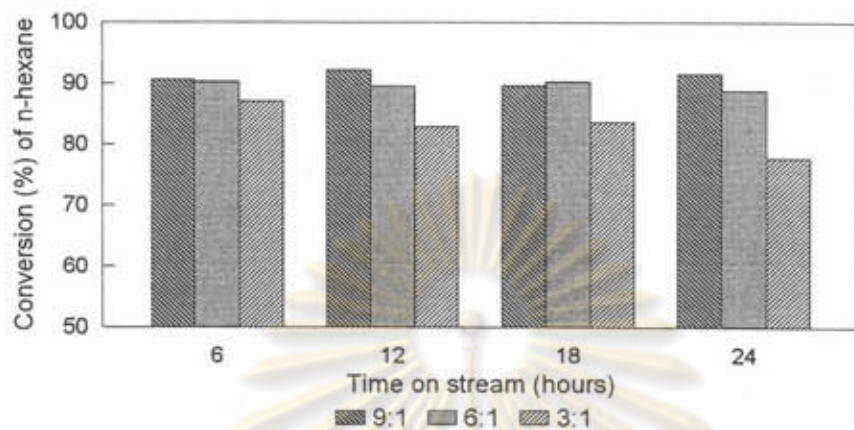


Figure 4.8 Conversion (%) of n-Hexane with Time  
(The Effects of Mole Ratio of Hydrogen:H/C)

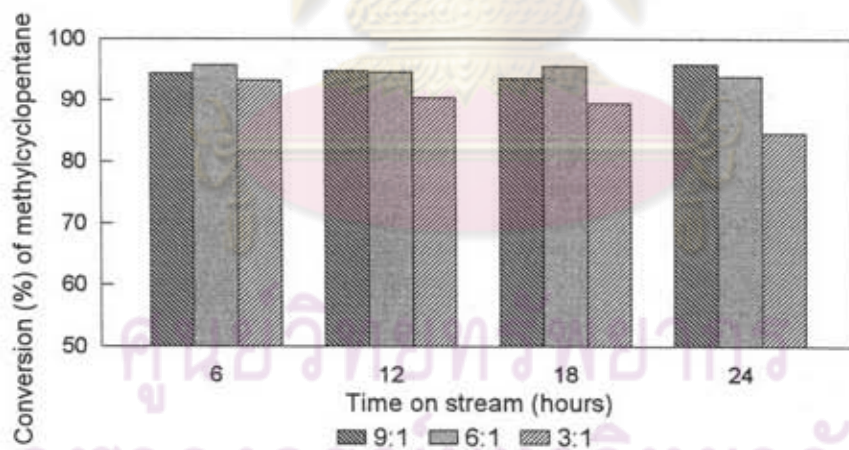


Figure 4.9 Conversion (%) of Methylcyclopentane with Time  
(The Effects of Mole Ratio of Hydrogen:H/C)

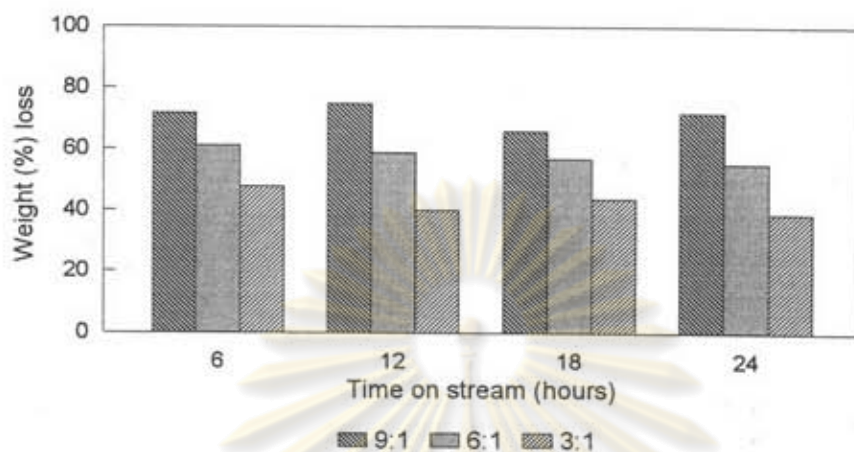


Figure 4.10 Weight (%) Loss with Time  
(The Effects of Mole Ratio of Hydrogen:H/C)

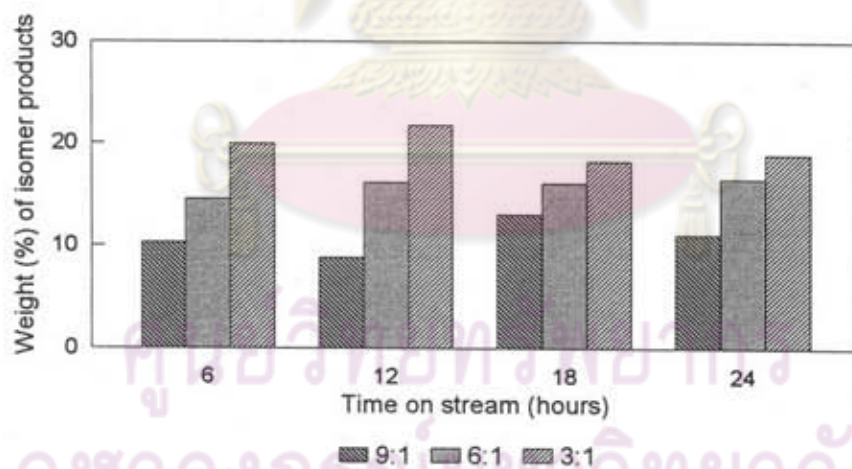


Figure 4.11 Weight (%) of Isomer Products with Time  
(The Effects of Mole Ratio of Hydrogen:H/C)



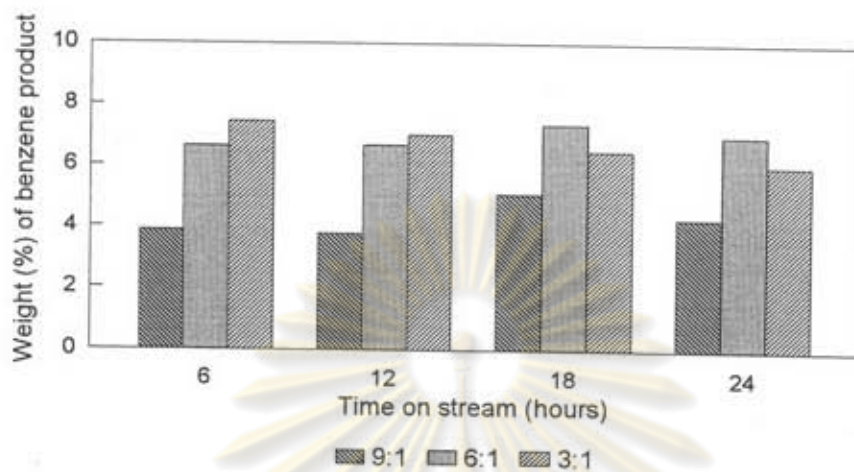


Figure 4.12 Weight (%) of Benzene Product with Time  
(The Effects of Mole Ratio of Hydrogen:H/C)

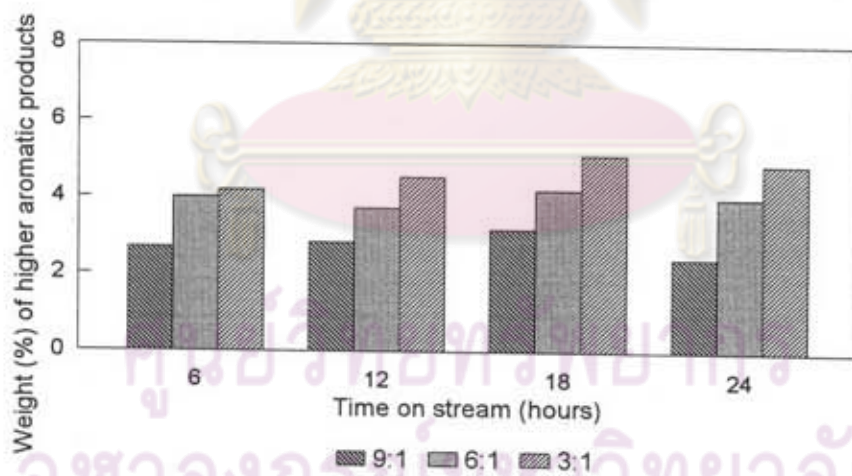


Figure 4.13 Weight (%) of Higher Aromatic Products with Time  
(The Effects of Mole Ratio of Hydrogen:H/C)

hydrocarbon mole ratio of 3 is seems to be rapidly decline with time. Because too low hydrogen to hydrocarbon mole ratio will be increased the catalyst deactivation rates because of coke laydown on the catalyst (Ciapetta et al., 1958).

The weight (%) of isomer products, as show in Figure 4.11, increase when the hydrogen to hydrocarbon mole ratio decrease. The weights of isomer products are increase in the following order of  $H_2:H/C$  mole ratios are  $3 > 6 > 9$ . Same results to the weight (%) of benzene and higher aromatics, as show in Figures 4.12 and 4.13, the orders of their weights are also  $3 > 6 > 9$ . Low hydrogen to hydrocarbon mole ratio increase the aromatization reaction (Gates, Katzer, and Schuit, 1979). The  $H_2:H/C$  mole ratios of 6 is the most constant weight. The results also indicated that the ratio of 9 is the lowest weight of, desirable products, benzene and higher aromatics.

Therefore, the suitable hydrogen to hydrocarbon mole ratio is 6.

From the above analysis results of preliminary experiments, the suitable operating conditions are as follow: the temperature is  $450^{\circ}C$ , the pressure is 100 psig.

#### 4.2 Repeatability and Stability

Reference experiments are conducted to find repeatability of the experiments and the suitable time to reach steady state. Three additional experiments are also conducted at the same conditions as the operating condition chosen, to verify their repeatability and to find their average results. The data are given in the Appendix (Tables 7A to 12A). The average maximum and minimum deviation (%) of reference experiments are summarized in Table 4.5.

Table 4.5 The average maximum and minimum deviation (%) of reference experiments

	Average deviation (%) of reference experiments	
	Maximum	Minimum
Conversion of n-hexane	1.81	2.02
Conversion of MCP	1.64	1.44
Cracking product	7.90	8.66
Isomer products	5.27	6.32
Benzene product	4.81	4.89
Higher aromatic products	5.98	5.16

Average results of reference experiments are used as basis results at the same duration of time for comparison with each deactivation experiment.

From the experiments, the steady state operation reaches after 24 hours from start up. Total time to cover the whole range of experiment is 144 hours. The conversion (%) of n-hexane decreases from 87.98% to 77.28% and conversion (%) of methylcyclopentane decreases from 92.20% to 83.25%.

The conversion (%) of n-hexane decreases corresponding to the weight of benzene (the main of aromatic product) declines because the catalyst activity is 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 ( $\text{Al}_2\text{O}_3$ ) 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 (Das, Srivastava, and Saraf, 1988).

Myers, Lang and Weisz (1961) proposed that large paraffinic molecules quickly deactivated the catalyst. They suggested the deactivation mechanism as follows: Initially, unsaturated reaction intermediates were formed mainly at the platinum sites. These precursors were then reversibly adsorbed on the platinum



and migrated to acid sites where they were irreversibly adsorbed. These adsorbed precursors can 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-catalyzed reaction and also slower than the process of transferring the precursors to the acid sites.

Nevertheless, the reactions produce many kinds of products. In these studies are classified to group of products by difference types of structures and path ways of reactions. The product groups are cracking, hexane isomers, benzene and higher aromatics products.

#### 4.3 Effects of nitrogen compounds

Deactivation experiments are designed to verify influence of each nitrogen compound on catalytic reforming of hexanes. Conversion (%) of n-hexane and methylcyclopentane and weight (%) of each product group (for example cracking, isomers, benzene and aromatic products) are compared with average result of reference experiments.

There are many difference types of nitrogen compounds in nature. They differ in their features, such as characteristic structure and basicity. In the deactivation experiments, the effects of nitrogen compounds on catalytic reforming of hexanes on Pt-Re/Al<sub>2</sub>O<sub>3</sub> commercial catalyst are categorized to studies the influence of their types and structures as follows;

- The effects of number of ring.
- The effects of steric hindrance.
- The effects of ring saturation.
- The effects of basicity.

The results are compared with the average reference experiment result. The data are given in the Appendix (Tables 13A to 18A).

The each of deactivation experiments will divide to five periods that;

- Period I :The feed is Feed I which contain 10 ppm chloride as  $\text{CH}_2\text{Cl}_2$  and keep steady state proceeds for 48 hours.
- Period II :The feed is Feed II which contains 10 ppm nitrogen as nitrogen compounds and 10 ppm chloride as  $\text{CH}_2\text{Cl}_2$  and proceeds for 24 hours.
- Period III :The feed is Feed I proceeds for 24 hours.
- Period IV :The feed is Feed II and proceeds for 24 hours.
- Period V :The feed is Feed I and proceeds for 24 hours.

From the previous literature survey, the alumina support may have been acidified by the incorporation of chloride into the structure. Organic nitrogen compounds which present in the feed, are converted into ammonia under reforming conditions and this neutralizes acid sites on the catalyst. The inhibition proceeding through neutralization by forming volatile ammonium chloride that removed chloride from the support. The halogen could be replaced and may be restored by adding small amounts of an organic chloride to the feedstock. These results are supported by Limido et al. (1987); Gates, Katzer and Schuit (1979); Satterfield (1980); Cocchetto and Satterfield (1976) and Speight (1991).

In this study, each experiment proceeds for 144 hours which can be divided into five periods. The effects of all deactivation experiments are plotted in Figures 4.14 to 4.19 and the data are given in the Appendix (Tables 13A to 18A). The first period is the first 48 hours of the experiment and proceeds with only the feed solution. In period II, the feed is feed II which contains nitrogen impurities proceed for 24 hours.

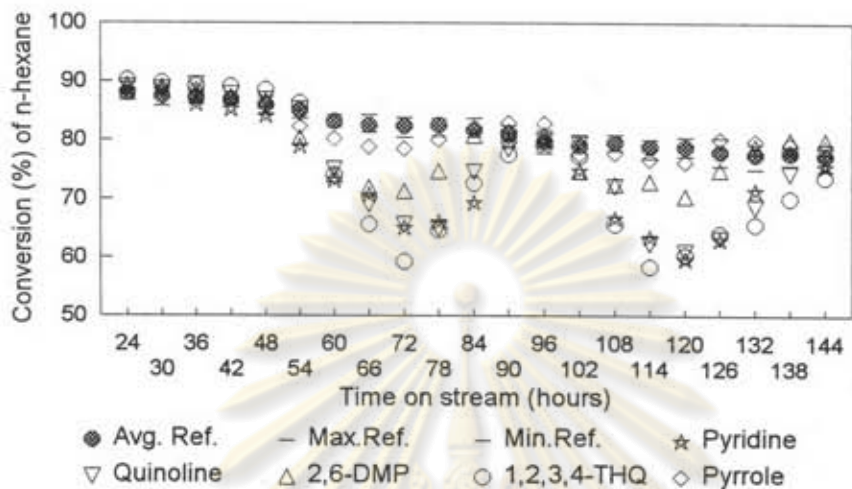


Figure 4.14 Conversion (%) of n-Hexane with Time  
(All of Deactivated Experiments Compare with Average Reference Experiment)

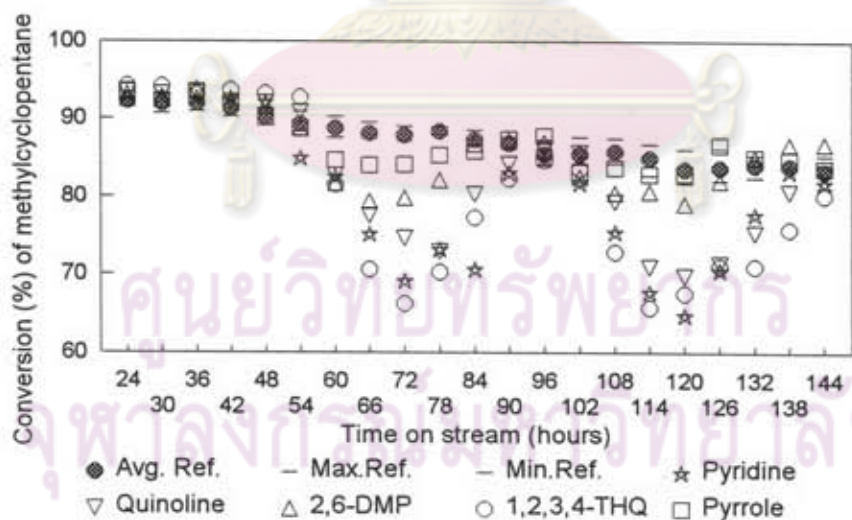


Figure 4.15 Conversion (%) of Methylcyclopentane with Time  
(All of Deactivated Experiments Compare with Average Reference Experiment)



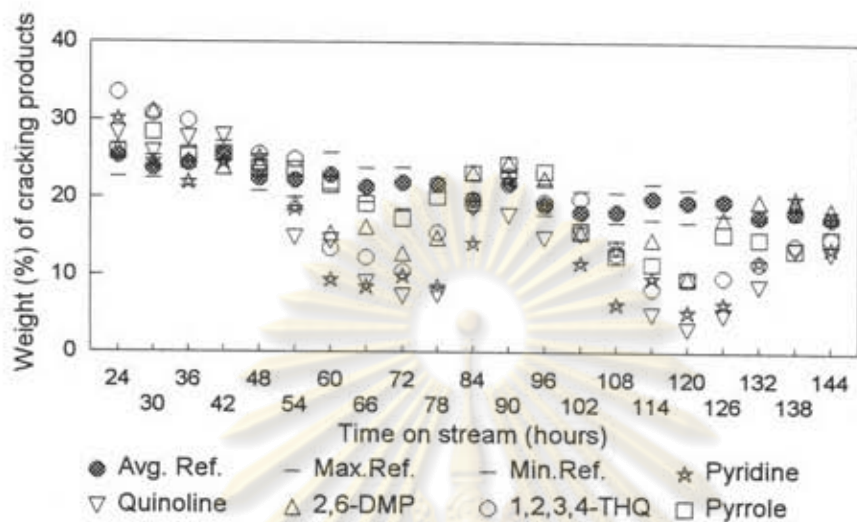


Figure 4.16 Weight (%) of Cracking Products with Time (All of Deactivated Experiments Compare with Average Reference Experiment)

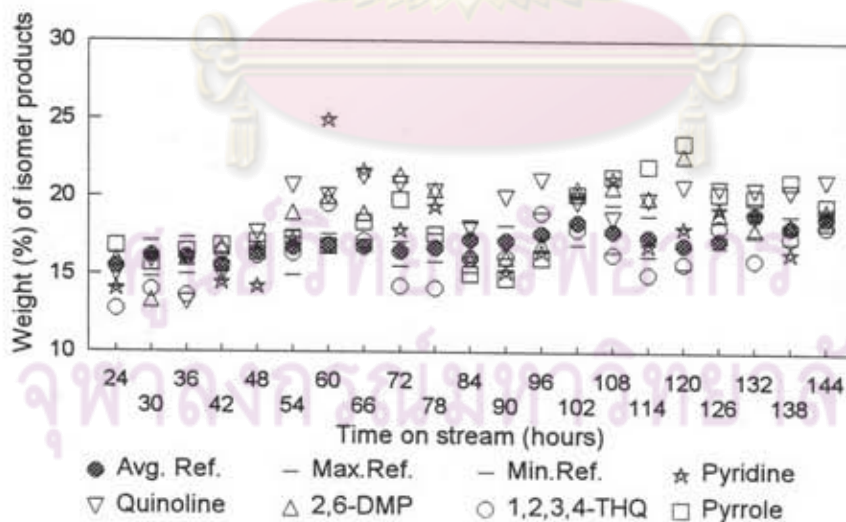


Figure 4.17 Weight (%) of Isomer Products with Time (All of Deactivated Experiments Compare with Average Reference Experiment)

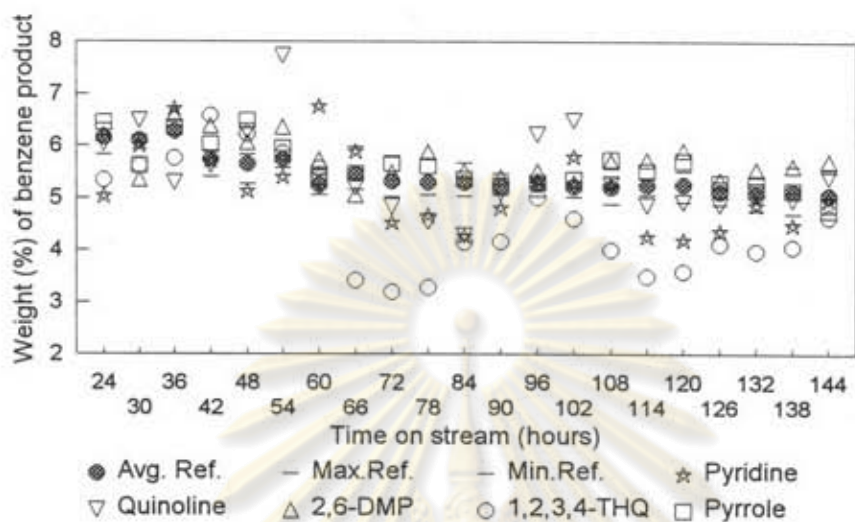


Figure 4.18 Weight (%) of Benzene Product with Time (All of Deactivated Experiments Compare with Average Reference Experiment)

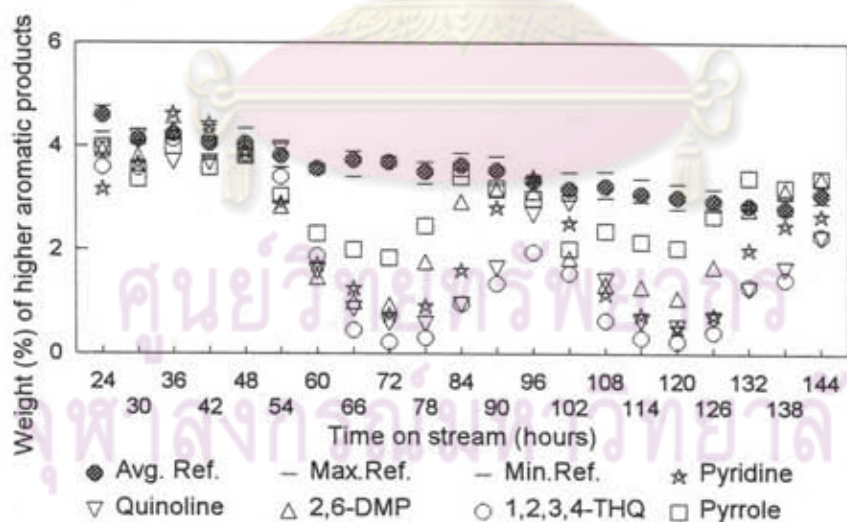


Figure 4.19 Weight (%) of Higher Aromatic Products with Time (All of Deactivated Experiments Compare with Average Reference Experiment)

The deviation (%) of deactivation experiments in period II are compared with the average reference experiment and summarized in Table 4.6 and Table 4.7.

Table 4.6 The Deviation (%) of Conversion in Deactivation Experiments from Average Reference Experiment

Conversion of	Deviation (%) from average reference				
	Pyridine	Quinoline	2,6-DMP	1234-THQ	Pyrrole
n-Hexane	-20.86	-20.34	-13.33	-28.10	-4.74
Methylcyclopentane	-21.36	-15.10	-9.18	-24.62	-4.29

Table 4.7 The Deviation (%) of Weight (%) of Product Groups in Deactivation Experiments from Average Reference Experiment

Product groups	Deviation (%) from average reference				
	Pyridine	Quinoline	2,6-DMP	1234-THQ	Pyrrole
Cracking	-54.79	-66.74	-41.51	-52.42	-21.26
Isomers	8.37	26.44	29.96	-13.58	20.13
Benzene	-14.85	-9.02	3.20	-40.04	6.39
Higher aromatic	-79.73	-84.05	-74.32	-94.32	-50.27

The conversion (%) of n-hexane and methylcyclopentane are sharply decreased with time by loss of activity of the catalyst. The maximum effect is 1,2,3,4-tetrahydroquinoline that reduces conversion (%) of n-hexane and methylcyclopentane from average reference approximately 28.10% and 24.62%, respectively. The minimum effect is pyrrole that reduces conversion (%) of n-hexane and methylcyclopentane from average reference approximately 4.74% and 4.29%, respectively.

In period III, the feed is feed I which unrepresent of nitrogen impurities. The conversion (%) eventually regain to the former level of activity of average reference. The further experiments in period IV and V are the similar results as period II and III,



respectively. However, there is a difference in behavior of the various nitrogen compounds.

Moreover, the effects of nitrogen compounds to the reforming reaction are considered by distinguish of product groups.

In the case of weight (%) of cracking products, that is main of reaction of n-hexane. The weights (%) of cracking products in deactivation period are lower than the average weight from reference experiments. The maximum effect is decreased 66.74% by quinoline. The minimum effect is decreased 21.26% by pyrrole. These results show that nitrogen impurities are highly affected on cracking reaction.

The weights (%) of higher aromatics are significantly affected by nitrogen impurities. The weights (%) of higher aromatics in deactivation period are lower than the average weight from reference experiment. The maximum effect is decreased 94.32% by 1,2,3,4-tetrahydroquinoline. The minimum effect is decreased 50.27% by pyrrole. From the previous mention in reaction network, as shows in Figure 4.1, the olefin polymerization from cracking reactions can be taken place on the acid catalyst sites to  $C_6^+$ -paraffins.

$C_6^+$ -paraffins cyclize to cyclohexane and their's derivatives. These  $C_6$ -ring naphthenes dehydrogenate to benzene and higher aromatics. Therefore, higher aromatics are suppressed by decreasing of cracking reaction and olefins polymerization on an acidic site.

In contrast, nitrogen compounds affect on the weight (%) of isomer products and benzene. The hexane isomers in deactivation period are higher than the average weight of reference experiment. Because the nitrogen compounds highly affects on cracking reaction which is the main of reaction of n-hexane and proceeds on acidic function. The acidic function is suppressed by nitrogen compounds. Thus isomerization reaction increase

by proceeds on metal function. This result is supported by Sterba and Haensel (1976). They concluded that the slowing down of the faster reaction accentuates the participation of an otherwise slower reaction.

The effects on the weight (%) of benzene depend on the type of nitrogen. In the case of pyridine and quinoline effect on the weight (%) of benzene product. The weight (%) of benzene product are higher than the average weight of reference experiment in the initial time of deactivation and follow by decline approximately to 19.25% and 19.06%, respectively. In the case of poison by 1,2,3,4-tetrahydroquinoline, weight (%) of benzene simultaneous decreases approximately to 40.04% but the poisons by 2,6-dimethylpyridine and pyrrole have not significantly effects. Therefore, the different effects depending on their type and structure.

These results indicate that the addition of nitrogen compounds accelerate catalyst deactivation. The catalytic deactivation reduces total conversion of the reactant. The poisoning effects of nitrogen compounds on n-hexane reforming also depend upon the nature of their types and structures as in the following.

#### **4.3.1 The effects of number of ring.**

The effects of number of ring in nitrogen compounds are observed by comparing experiments using feedstock containing quinoline and feedstock containing pyridine. Quinoline is the nitrogen compound which structure consists one aromatic ring attach to pyridine parent compound. The effects of number of ring are plotted in Figures 4.20 to 4.25.

Figure 4.20 shows a comparison of n-hexane conversion (%) in the presents of pyridine and quinoline with average reference experiment, at any time taken. The figure shows that introduction of 10 ppm nitrogen as nitrogen compounds in period II gradually decreases the



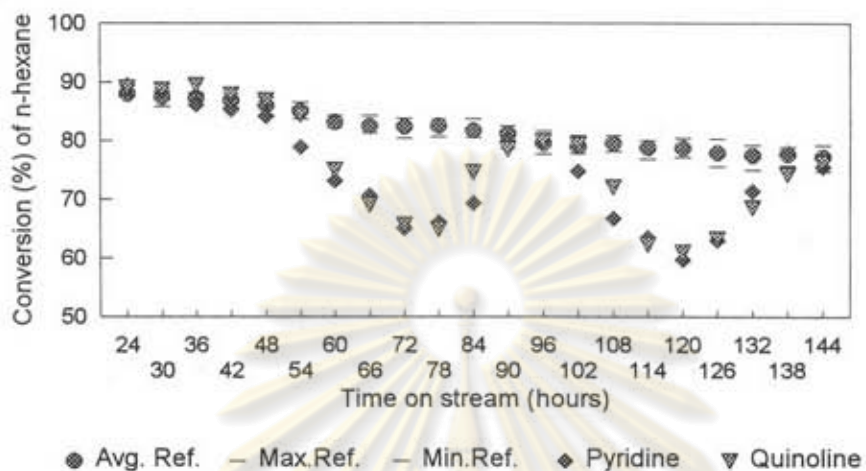


Figure 4.20 Conversion (%) of n-Hexane with Time (The Effects of Number of Ring)

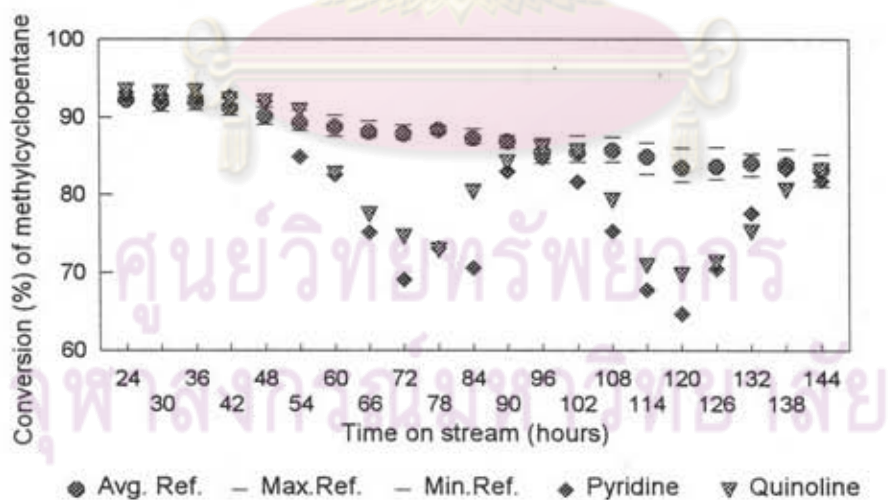


Figure 4.21 Conversion (%) of Methylcyclopentane with Time (The Effects of Number of Ring)



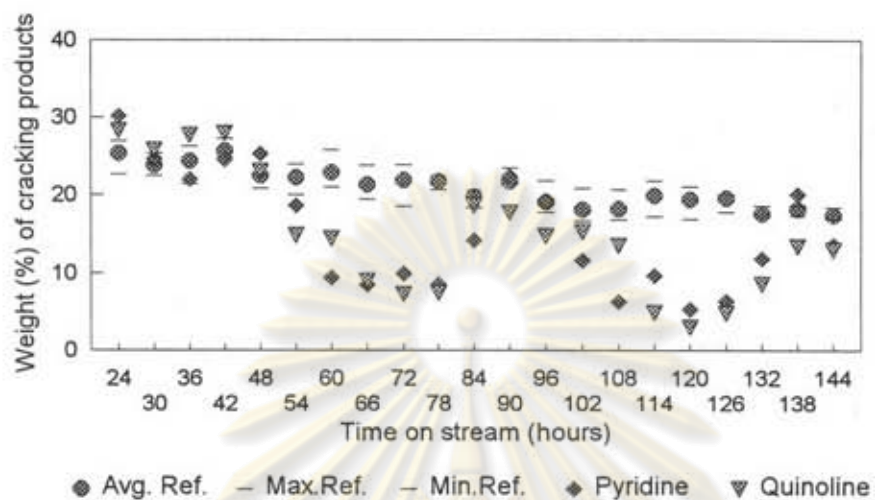


Figure 4.22 Weight (%) of Cracking Products with Time (The Effects of Number of Ring)

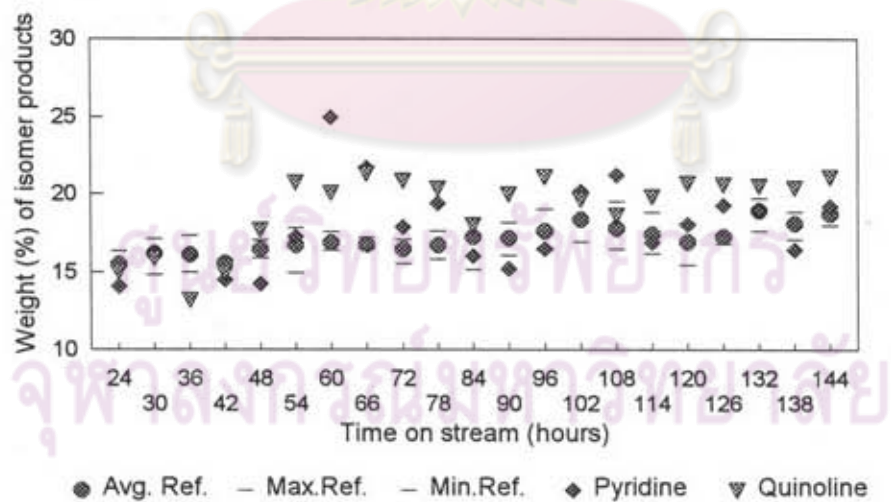


Figure 4.23 Weight (%) of Isomer Products with Time (The Effects of Number of Ring)

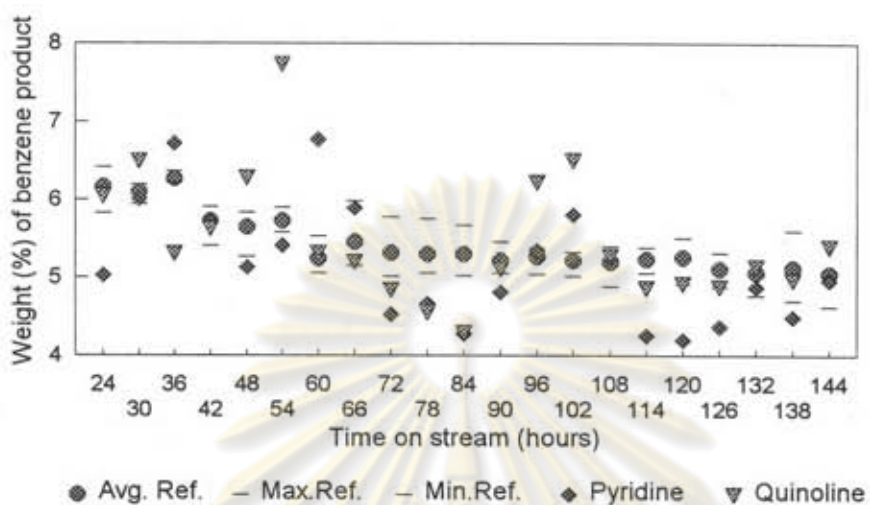


Figure 4.24 Weight (%) of Benzene Product with Time (The Effects of Number of Ring)

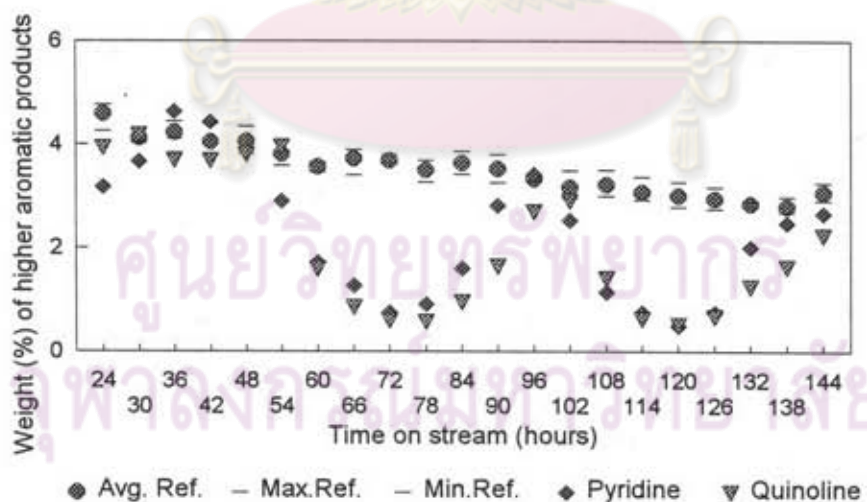


Figure 4.25 Weight (%) of Higher Aromatic Products with Time (The Effects of Number of Ring)

conversion (%) of n-hexane. Pyridine eventually decrease the conversion (%) of n-hexane in period II approximately 20.86%. The result is not significantly differ to the result of quinoline that decrease approximately 20.34%. The difference in conversion of n-hexane fall in the experimental error range. Figure 4.21 shows the conversion (%) of methylcyclopentane gradually decreases similar as the conversion of n-hexane. While pyridine decreases in the conversion of methylcyclopentane with a small higher than quinoline.

Alternating to pure feed in period III shows the recovery of n-hexane conversion (%) and methylcyclopentane conversion (%) to a nearly level of the average reference experiment. These results indicate that the nitrogen compounds are reversible poisons.

Figures 4.22 to 4.25 show the comparison of the effects of number of ring on cracking, isomerization and aromatization products. Figure 4.22 shows the weight (%) of cracking products which are gradually decreased in deactivation period. Figure 4.23 shows the weight (%) of isomer products in deactivation period. The hexane isomers in deactivation period are higher than the average weight of reference experiment. Figure 4.24 shows the weight (%) of benzene products in deactivation period. The weight (%) of benzene product are higher than the average weight of reference experiment in the initial time of deactivation and follow by decline approximately to 19.25% by pyridine and 19.06% by quinoline. Figure 4.25 shows the weight (%) of higher aromatic products which are rapidly decrease in deactivation period. Higher aromatics are suppressed by decreasing of cracking reaction and olefins polymerization on an acidic site.

From the results, all of the product groups are affected by the impurities but these effects have not significant difference between pyridine and quinoline.



The difference in deactivation results are fallen in the experimental error range. Thus it is difficult to conclude that the addition of aromatic ring to pyridine has any difference effect on the deactivation of these experiments.

In the mechanism of deactivation, Speight (1991) reported that organic nitrogen compounds were converted into ammonia under reforming conditions and neutralizes acid sites on the catalyst by forming volatile ammonium chloride. In general of the hydrodenitrogenation of heterocyclic ring compounds, the heterocyclic ring was first saturated, followed by ring fracture at a C-N bond. Nitrogen was removed from the resulting amine or aniline as ammonia (Cocchetto and Satterfield, 1976). With pyridine, the ring was first hydrogenated to piperidine, which forms, in turn, pentylamine and pentane plus ammonia (McIlvried, 1971).

In the case of quinoline, analogous reactions occur but a greater variety of intermediate compounds were formed. These compounds include 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, and decahydroquinoline, followed by hydrocracking to form aromatic and saturated cyclic amines, and then cyclic hydrocarbons. The overall reaction network was relatively complex (Satterfield and Cocchetto, 1975).

#### **4.3.2 The effects of stearic hindrance.**

The effects of stearic hindrance in nitrogen compounds are observed by comparing experiments using feedstock containing pyridine and 2,6-dimethylpyridine, respectively. Pyridine is nonstearic hindrance in structure while 2,6-dimethylpyridine is stearic hindrance in structure. The effects of stearic hindrance are plotted in Figures 4.26 to 4.31.

Figure 4.26 shows a comparison of n-hexane conversion (%) in the presents of pyridine and

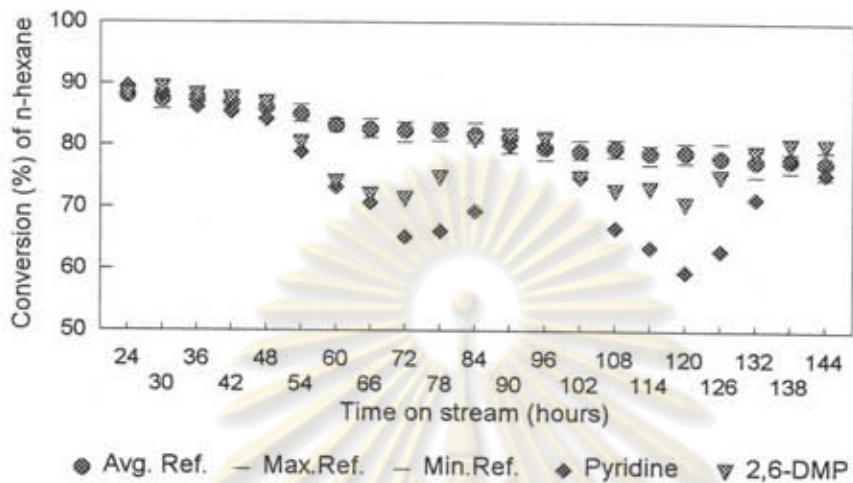


Figure 4.26 Conversion (%) of n-Hexane with Time (The Effects of Stearic Hindrance)

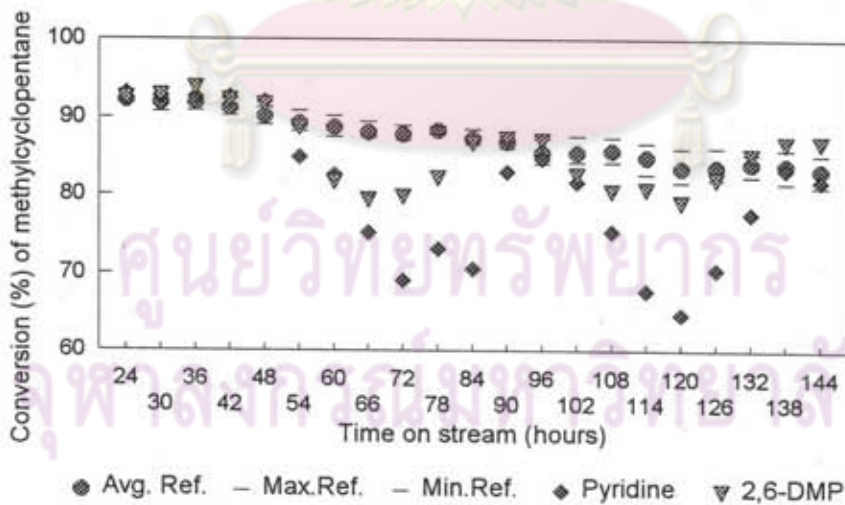


Figure 4.27 Conversion (%) of Methylcyclopentane with Time (The Effects of Stearic Hindrance)

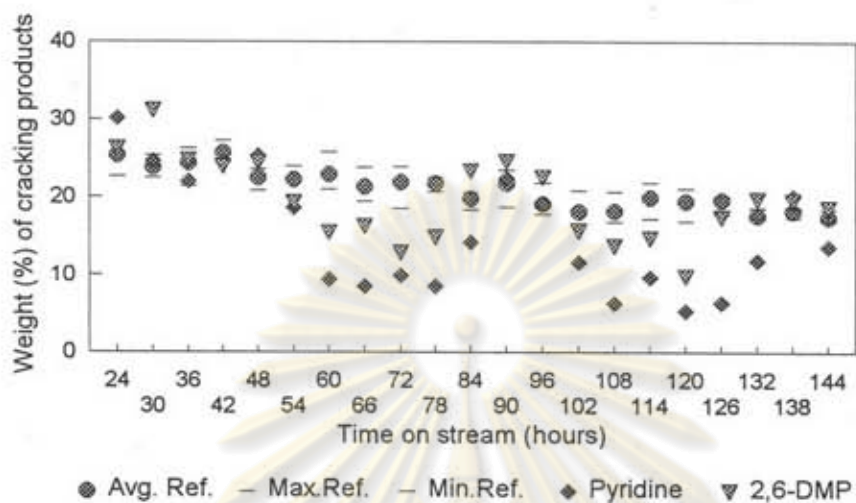


Figure 4.28 Weight (%) of Cracking Products with Time (The Effects of Stearic Hindrance)

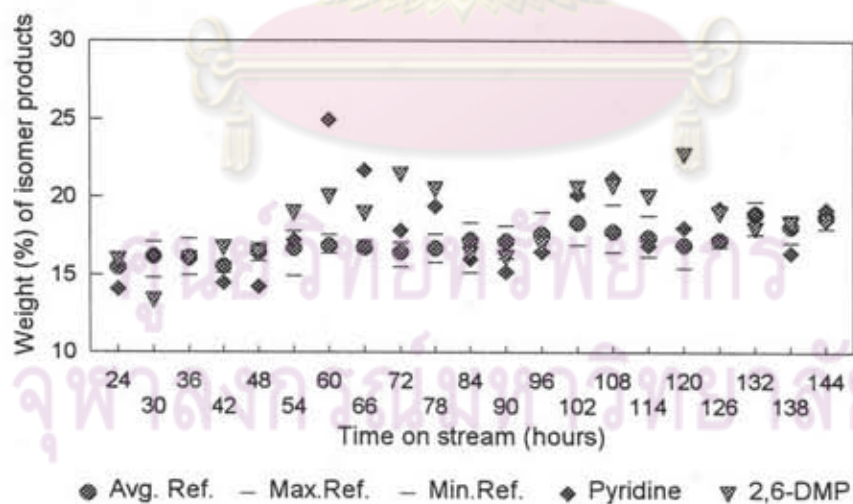


Figure 4.29 Weight (%) of Isomer Products with Time (The Effects of Stearic Hindrance)



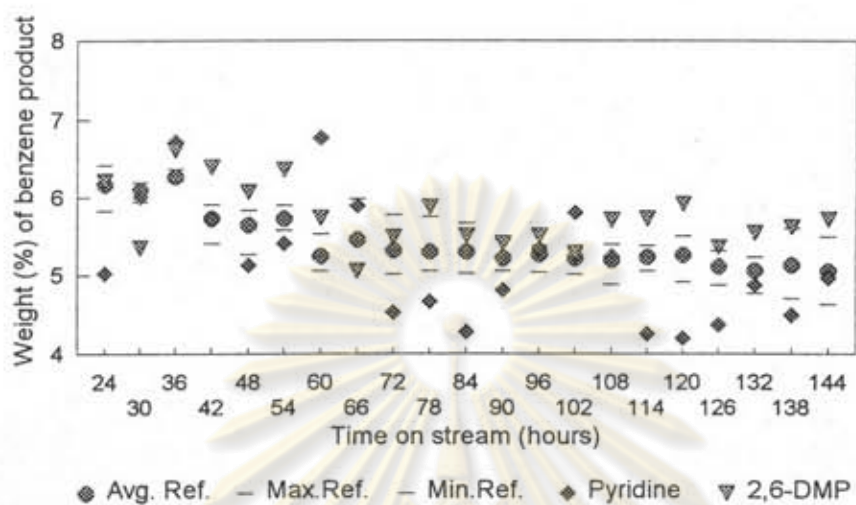


Figure 4.30 Weight (%) of Benzene Product with Time (The Effects of Stearic Hindrance)

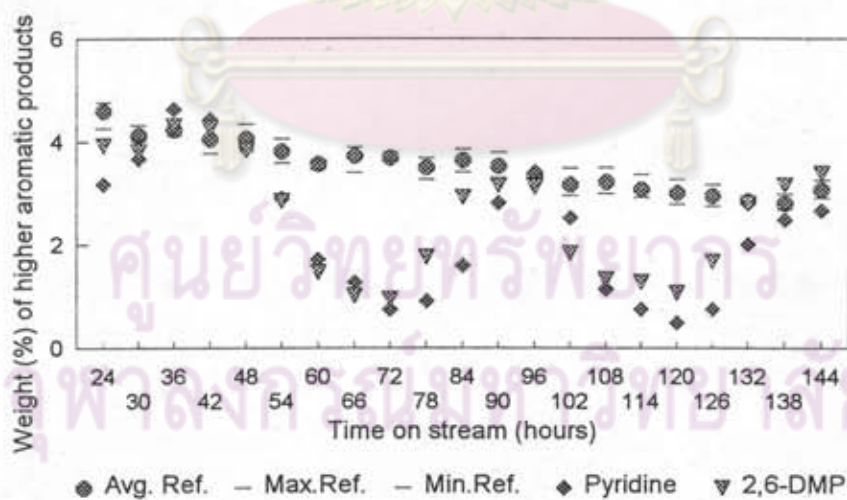


Figure 4.31 Weight (%) of Higher Aromatic Products with Time (The Effects of Stearic Hindrance)

2,6-dimethylpyridine with average reference experiment, at any time taken. The figure shows that introduction of 10 ppm nitrogen as nitrogen compounds in period II gradually decreases the conversion (%) of n-hexane. Pyridine eventually decreases the conversion (%) of n-hexane in period II approximately 20.86%. The result significantly differs to the result of 2,6-dimethylpyridine that decrease approximately 13.33%.

From Figures 4.27, the results show that introduction of 2,6-dimethylpyridine eventually decreases the conversion (%) of methylcyclopentane approximately 9.18% from average reference. These effects are differ from effects by pyridine which decreases approximately 21.36%. While pyridine decreases the conversion of n-hexane and methylcyclopentane higher than 2,6-dimethylpyridine about 1.56 time and 2.32 time, respectively.

Figures 4.28 to 4.31 show the comparison of the effects of number of ring on cracking, isomerization and aromatization products. Figure 4.28 shows the weight (%) of cracking products which are gradually decrease in deactivation period. Figure 4.29 shows the weight (%) of isomer products in deactivation period. The hexane isomers in deactivation period are higher than the average weight of reference experiment. Figure 4.30 shows the weight (%) of benzene products in deactivation period. The weight (%) of benzene product are higher than the average weight of reference experiment in the initial time of deactivation and follow by decline. Figure 4.31 shows the weight (%) of higher aromatic products which are rapidly decrease in deactivation period. Higher aromatics are suppressed by decreasing of cracking reaction and olefins polymerization on an acidic site.

From the results, all of the product groups are affected by the impurities. Stearic hindrance effects



have significant difference between pyridine and 2,6-dimethylpyridine. These results show that 2,6-dimethylpyridine is lower effects than pyridine. The difference in deactivation results are higher than the experimental error range. Although, the basicity (base upon pKa and proton affinity as show in Table 2.5) of 2,6-dimethylpyridine is higher than that of pyridine.

These results can be explained by the basicity of nitrogen compounds will adsorb on acidic sites of catalyst. The adsorption of nitrogen compounds on the catalyst that occur through nitrogen atom rather than p-bonding of the ring. In addition, nitrogen atom of pyridine does not hinder by the methyl group as that of 2,6-dimethylpyridine. So, it indicates that increasing stearic hindrance to structure causes decreasing inhibition effects.

#### 4.3.3 The effects of ring saturation.

The effects of ring saturation in nitrogen compounds are observed by comparing experiments using feedstock containing quinoline and 1,2,3,4-tetrahydroquinoline, respectively. The effects of ring saturation are plotted in Figures 4.32 to 4.37.

Figure 4.32 shows a comparison of n-hexane conversion (%) in the presents of quinoline and 1,2,3,4-tetrahydroquinoline with average reference experiment, at any time taken. The figure shows that introduction of 10 ppm nitrogen as nitrogen compounds in period II gradually decreases the conversion (%) of n-hexane. Quinoline eventually decreases the conversion (%) of n-hexane in period II approximately 20.34%. The result is significantly differ from the result of 1,2,3,4-tetrahydroquinoline which decrease approximately 28.10%. The difference in conversion of n-hexane is higher than the experimental error range.



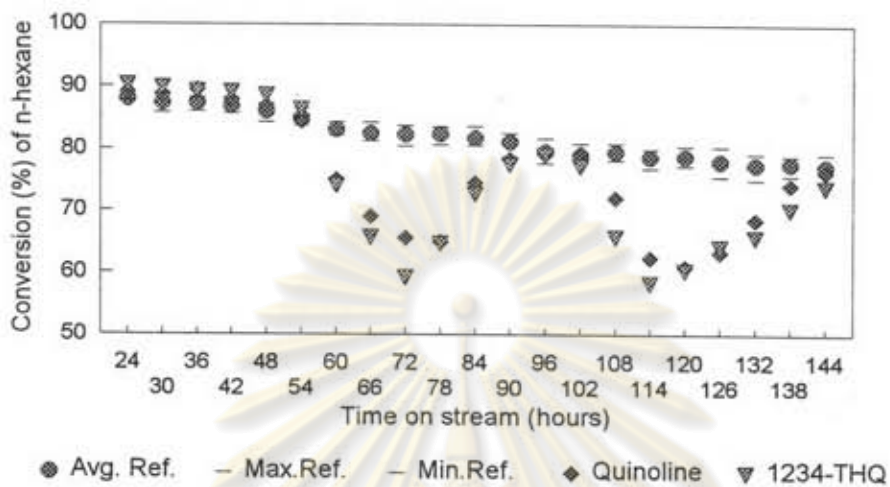


Figure 4.32 Conversion (%) of n-Hexane with Time (The Effects of Ring Saturation )

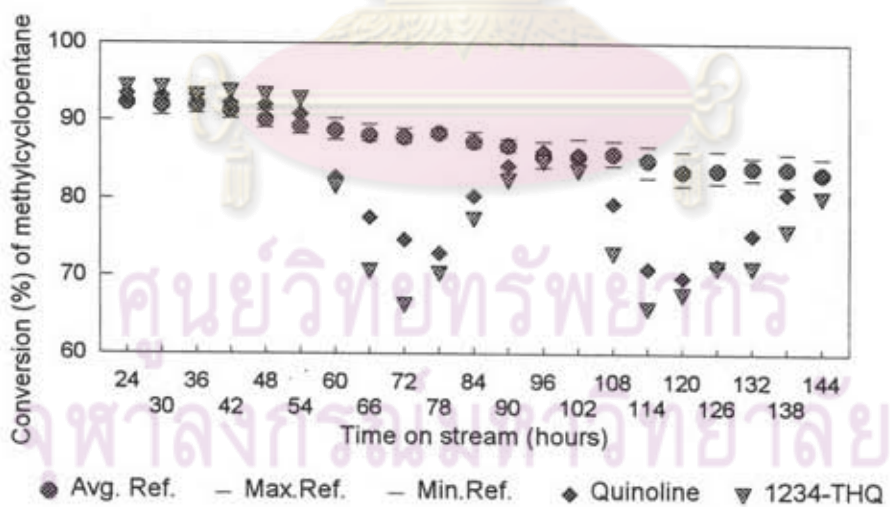


Figure 4.33 Conversion (%) of Methylcyclopentane with Time (The Effects of Ring Saturation )

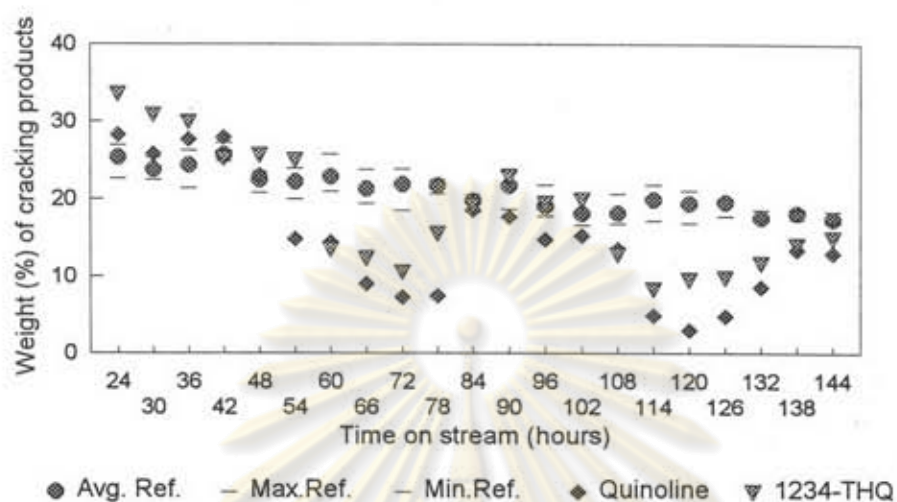


Figure 4.34 Weight (%) of Cracking Products with Time (The Effects of Ring Saturation )

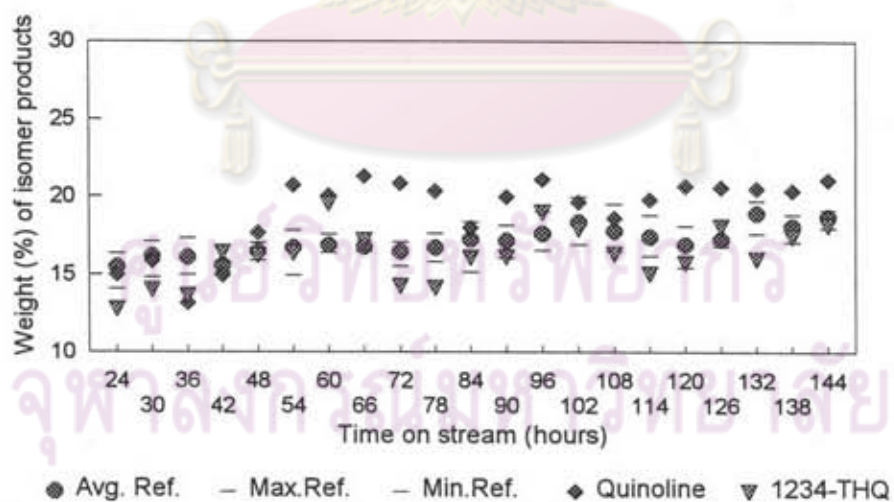


Figure 4.35 Weight (%) of Isomer Products with Time (The Effects of Ring Saturation )

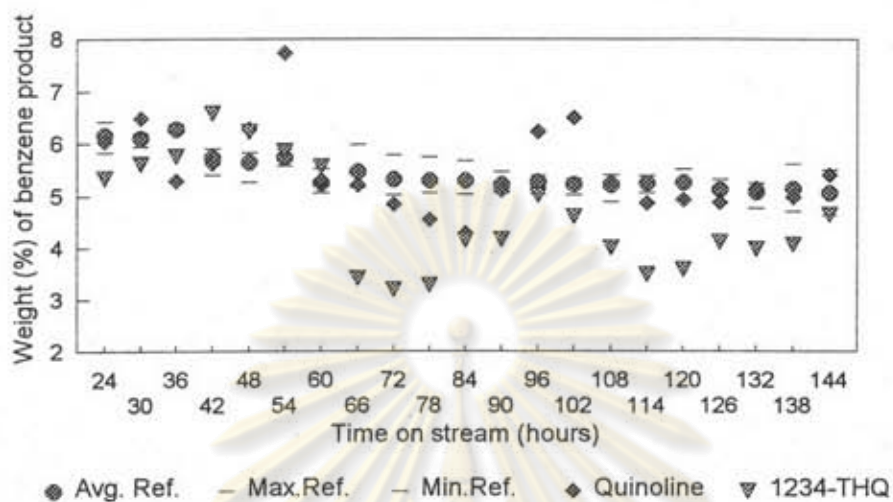


Figure 4.36 Weight (%) of Benzene Product with Time (The Effects of Ring Saturation )

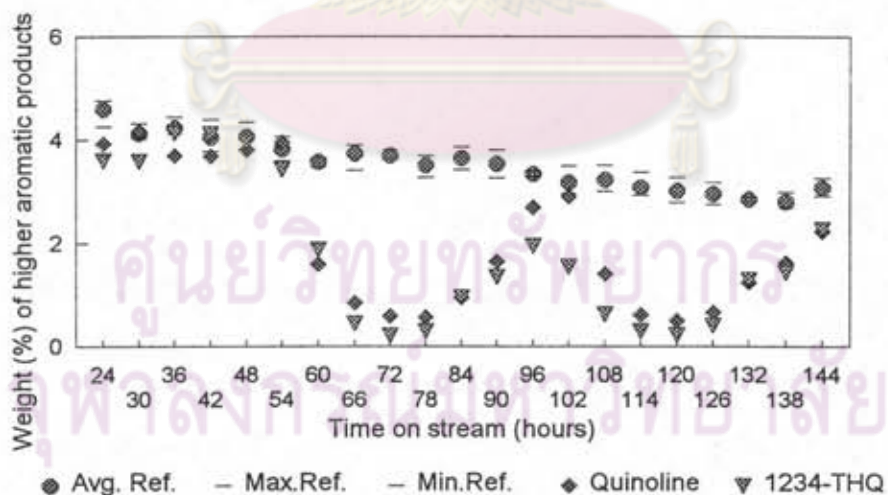


Figure 4.37 Weight (%) of Higher Aromatic Products with Time (The Effects of Ring Saturation )



From Figures 4.33, the results show that introduction of quinoline eventually decreases the conversion (%) of methylcyclopentane approximately 15.10% from average reference. These effects are different from effects by 1,2,3,4-tetrahydroquinoline which decreases approximately 24.62% while 1,2,3,4-tetrahydroquinoline decreases the conversion of n-hexane and methylcyclopentane higher than quinoline about 1.38 time and 1.63 time, respectively.

Alternating to pure feed in period III shows recovery of the n-hexane conversion (%) and methylcyclopentane conversion (%) to a nearly level of the average reference experiment. These results indicate that the nitrogen compounds are reversible poisons.

Figures 4.34 to 4.37 show the comparison of the effects of ring saturation on cracking, isomerization and aromatization products. Figure 4.34 shows the weight (%) of cracking products which are gradually decreased in deactivation period. Figure 4.35 shows the weight (%) of isomer products in deactivation period. The weight (%) of isomer products in the deactivation period of quinoline are higher than the average weight of reference experiment but the weight (%) of isomer products in the case of 1,2,3,4-tetrahydroquinoline is not higher than the average weight of reference experiment.

Figure 4.36 shows the weight (%) of benzene products in deactivation period of quinoline. The weight (%) of benzene product are higher than the average weight of reference experiment in the initial time of deactivation and follow by decline but the weight (%) of benzene is obviously decreased approximately to 40.04% from the average reference experiment when introduction the feed contains 1,2,3,4-tetrahydroquinoline into the reactions. Figure 4.37 shows the weight (%) of higher aromatic products which are rapidly decreased in deactivation period. Higher aromatics are suppressed by

decreasing of cracking reaction and olefins polymerization on an acidic site.

From the results, all of the product groups are affected by the impurities. Ring saturation effects have significant difference between quinoline and 1,2,3,4-tetrahydroquinoline. The difference in deactivation results are higher than the experimental error range. These results indicate that 1,2,3,4-tetrahydroquinoline is higher effects than quinoline. The difference of deactivation can be explained by the hydrodenitrogenation of nitrogen compounds. In general the heterocyclic ring is first saturated, followed by ring fracture at a C-N bond to form ammonia and poisons the acid function of catalyst. In the case of 1,2,3,4-tetrahydroquinoline is the nitrogen compound with saturated structure that can be hydrodenitrogenated easier than quinoline. Girgis (1991) proposed that, if the carbon-nitrogen bond energy in a typical heterocyclic compound was close to that of carbon-nitrogen double bond, a reaction breaking the carbon-nitrogen double bond was expected to have a high activation energy. This propose was supported by Streitwieser and Heathcock (1976), hydrogenation of the heteroring was required to reduce the relatively large energy of the carbon-nitrogen bonds in such rings and permit more facile carbon-nitrogen bond scission. The energies of carbon-nitrogen double bonds and single bonds were 147 and 73 kcal/mole, respectively.

In case of quinoline, the hydrodenitrogenation was first hydrogenated. These products are included 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, and decahydroquinoline, followed by hydrocracking. Maxed (1951) proposed that the slow hydrogenation rate of heterocyclic nitrogen compounds itself being a self-poisoning effect due to the obstructively long adsorbed life on the catalytic surface.



#### 4.4.4 The effects of basicity.

The effects of basicity in nitrogen compounds are observed by comparing experiments using feedstock containing pyridine and feedstock containing pyrrole. Pyridine is a basic nitrogen compound while pyrrole is a nonbasic nitrogen compound. The effects of basicity are plotted in Figures 4.38 to 4.43.

Figure 4.38 shows a comparison of n-hexane conversion (%) in the presents of pyridine and pyrrole with average reference experiment, at any time taken. The figure shows that introduction of 10 ppm nitrogen as nitrogen compounds in period II gradually decreases the conversion (%) of n-hexane. Pyridine eventually decreased the conversion (%) of n-hexane in period II approximately 20.86%. The result is significantly differ to the result of pyrrole that decrease approximately 4.74%.

From Figures 4.39, the results show that introduction of pyrrole eventually decreases the conversion (%) of methylcyclopentane approximately 4.29% from average reference. These results are differ from effects by pyridine which decreases approximately 21.36%. Pyridine decreases the conversion of n-hexane and methylcyclopentane higher than pyrrole about 4.4 time and 4.97 time, respectively. The results show that introduction of pyrrole slightly declines the conversion (%) of n-hexane and methylcyclopentane.

Figures 4.40 to 4.43 show the comparison of the effects of basicity on cracking, isomerization and aromatization products. Figure 4.40 shows the weight (%) of cracking products which are gradually decreased in deactivation period. Figure 4.41 shows the weight (%) of isomer products in deactivation period. The hexane isomers in deactivation period are higher than the average weight of reference experiment. Figure 4.42 shows the weight (%) of benzene products in deactivation



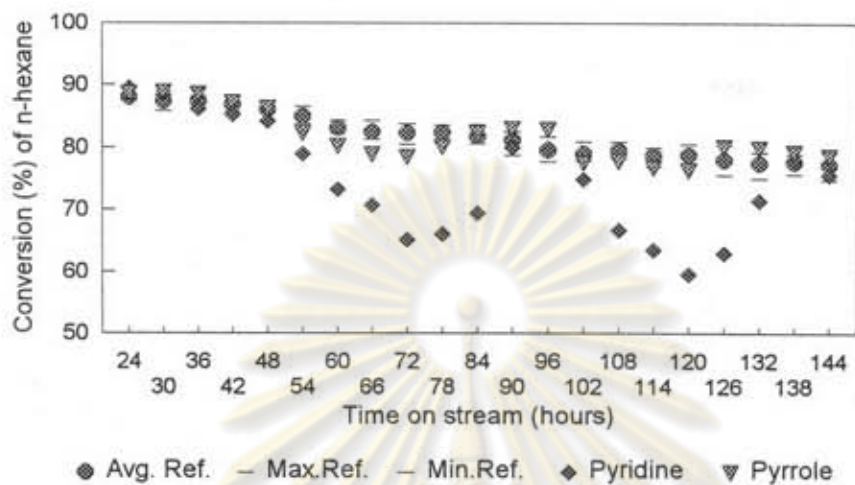


Figure 4.38 Conversion (%) of n-Hexane with Time (The Effects of Basicity)



Figure 4.39 Conversion (%) of Methylcyclopentane with Time (The Effects of Basicity)

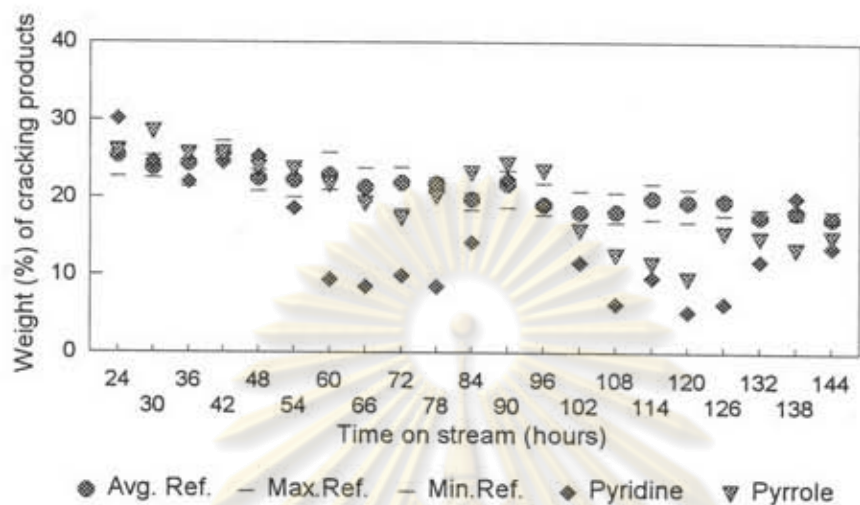


Figure 4.40 Weight (%) of Cracking Products with Time (The Effects of Basicity)

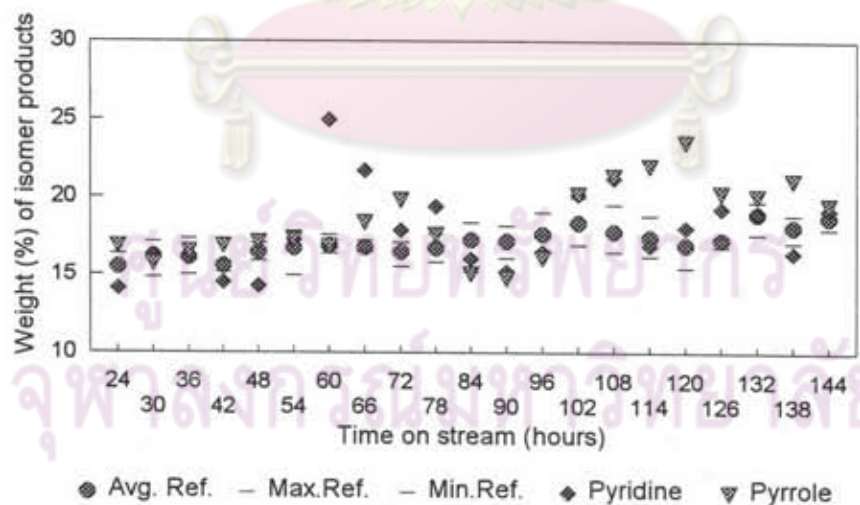


Figure 4.41 Weight (%) of Isomer Products with Time (The Effects of Basicity)

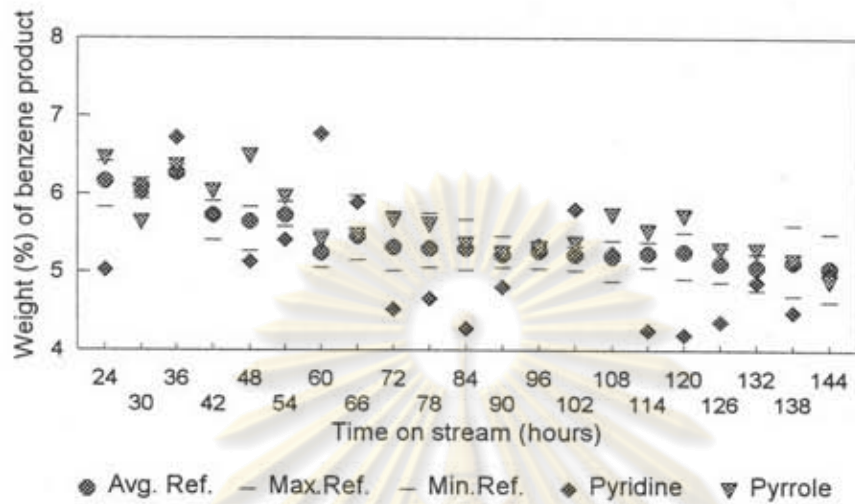


Figure 4.42 Weight (%) of Benzene Product with Time (The Effects of Basicity)

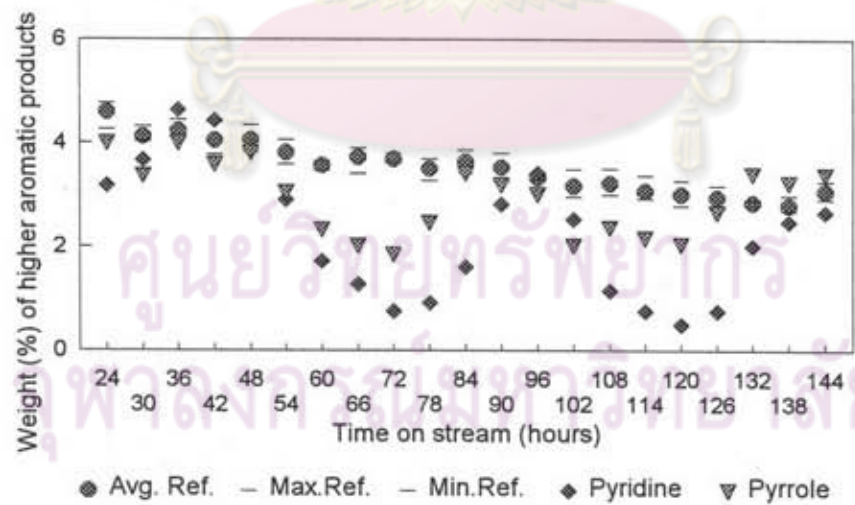


Figure 4.43 Weight (%) of Higher Aromatic Products with Time (The Effects of Basicity)



period. In the case of pyridine, the weight (%) of benzene product are higher than the average weight of reference experiment in the initial time of deactivation and follow by decline but the weight (%) of benzene product has not significantly effected when introduction the feed contains pyrrole into the reactions. Figure 4.43 shows the weight (%) of higher aromatic products which are decreased in deactivation period. Higher aromatics are suppressed by decreasing of cracking reaction and olefins polymerization on an acidic site.

From the results, all of the product groups are affected by the impurities. Basicity effects have significant difference between pyridine and pyrrole. These results show that pyrrole is lower effects than pyridine. The difference in deactivation results are higher than the experimental error range.

Pyrrole is a small effect when compare with pyridine. These results indicate that the basic of nitrogen compounds increase the effects on catalyst. This result can also be explained by the acidity of the catalyst. The support of the catalyst is acidic sites which are believed to be poisoned by basic compound. These results are supported by Satterfield (1980) that concluded, the strong basic compounds were of particular concern in acid-catalized reaction, such as cracking, since they will poison acidic sites.

The structure of pyrrole differ from pyridine or others basic nitrogen compounds. In pyrrole or others nonbasic compounds as in Table 2.4. They have one hydrogen atom on nitrogen atom. This effects fall into line with the principle of influence, respectively, of an unshilded or shilded nitrogen atom (Maxed, 1951).