

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of catalysts

The concentration of platinum in catalysts were determined by X-ray Fluorescence (XRF) spectroscopy. The percentage of platinum was calculated by the library search program. XRF chromatograms of catalysts are shown in Figure E1-E4 in Appendix E, and its percentage of platinum is shown in Table 4.1.

Table 4.1 The percentage of platinum in catalysts.

| catalyst | feed | impregnation |
|---|------|-----------------------|
| | | concentration (wt. %) |
| 0.3 % Pt/Al ₂ O ₃ | 0.3 | 0.268 |
| 0.6 % Pt/Al ₂ O ₃ | 0.6 | 0.569 |
| 0.3 % Pt/4A molecular sieve | 0.3 | 0.252 |
| 0.6 % Pt/4A molecular sieve | 0.6 | 0.519 |

4.2 Characterization of NGL and products

The NGL feedstream and all obtained products were characterized by Gas Chromatography according to ASTM D5443-93. Their compositions were identified by visually matching they with standard in the hydrocarbon test mixed which already existed in the library search program. GC chromatogram of NGL is shown in Figure A1, and its percentage of compositions and retention times are presented in Table 4.2. All percentages of

composition in NGL and the products were calculated from area of the GC peaks. The performance characteristics of the molecular sieve column and the sample composition result in separation of the normal and iso-paraffins, by carbon number. These groups can be combined in the calculations and reported as paraffins, by carbon number. Each of the aromatic components may elute in several of the aromatic fractions. All groups were reported in percent by weight, normalized to 100 %. The area associated was multiply with each of the identified group by the appropriated response factor to produce corrected area for each of the groups. Then the corrected areas were add all of the individual to total of corrected areas. The normalized percent by weight of an identified group were obtained from divide each of the identified corrected area groups by the total corrected area.

These data indicated that there were many types of hydrocarbons in NGL, i.e., naphthenes, paraffins and aromatics. Nevertheless, the C₅ and C₆ paraffins were the major compositions of NGL. Chromatograms of the NGL products are presented in Appendix A. These compositions were similar to the NGL composition but were not the same, such as the product from using 0.6 % Pt & 0.5 % F/Al₂O₃ were especially different because of the disappearance of C₅ naphthenes and lighter hydrocarbons and there was an increasing of benzene.

Table 4.2 Compositions of NGL

| injection | | retention time | | area | | wt. % | |
|-----------|-------------------------|----------------|-------|------------------------|-----------------------|-------|-------|
| | | 1 | 2 | 1 | 2 | 1 | 2 |
| peak no. | name | | | | | | |
| 1 | <i>n</i> -butane | 2.32 | 2.26 | 58597 | 63302 | 0.02 | 0.03 |
| 2 | cyclopentane | 3.62 | 3.58 | 6765757 | 5404372 | 1.68 | 1.62 |
| 3 | isopentane | 3.98 | 4.02 | 7.583×10 ⁷ | 6.347×10 ⁷ | 20.42 | 20.34 |
| 4 | <i>n</i> -pentane | 4.13 | 4.13 | 8.211×10 ⁷ | 6.077×10 ⁷ | 19.68 | 18.07 |
| 5 | cyclohexane | 5.98 | 5.88 | 3.088×10 ⁷ | 2.621×10 ⁷ | 7.90 | 7.87 |
| 6 | isohexane | 6.44 | 6.46 | 4645527 | 3864728 | 1.38 | 1.18 |
| 7 | <i>n</i> -hexane | 6.71 | 6.74 | 9.472×10 ⁷ | 8.251×10 ⁷ | 23.84 | 25.14 |
| 8 | methylcyclohexane | 8.92 | 8.81 | 2.980×10 ⁷ | 2.571×10 ⁷ | 7.39 | 7.72 |
| 9 | <i>n</i> -heptane | 9.77 | 9.60 | 2.841×10 ⁷⁰ | 2.482×10 ⁷ | 7.19 | 7.60 |
| 10 | 1,4-dimethylcyclohexane | 11.92 | 11.94 | 3057611 | 4418304 | 0.72 | 0.76 |
| 11 | 1,2-dimethylcyclohexane | 12.21 | 12.50 | 4325116 | 4623433 | 1.11 | 1.13 |
| 12 | <i>n</i> -octane | 12.92 | 12.88 | 7377104 | 8590213 | 1.86 | 1.93 |
| 13 | 2,2-dimethylheptane | 15.39 | 15.57 | 394924 | 425854 | 0.11 | 0.16 |
| 14 | 2,4-dimethylheptane | 16.00 | 15.98 | 1437932 | 1694252 | 0.35 | 0.37 |
| 15 | benzene | 31.58 | 31.57 | 1.586×10 ⁷ | 1.144×10 ⁷ | 3.65 | 3.42 |
| 16 | toluene | 31.77 | 31.77 | 6689894 | 776467 | 1.22 | 1.20 |
| | toluene | 41.85 | 41.85 | 1105777 | 987934 | 0.62 | 0.60 |
| 17 | polynaphthene | 34.38 | 34.28 | 52220 | 54594 | 0.01 | 0.01 |
| 18 | ethylbenzene | 42.24 | 42.25 | 2882433 | 2389935 | 0.34 | 0.32 |
| 19 | xylene | 42.37 | 42.47 | 337435 | 47509 | 0.42 | 0.43 |
| 20 | 1,2,4-trimethylbenzene | 42.88 | 42.84 | 241736 | 34994 | 0.05 | 0.06 |
| 21 | 1,2,3-trimethylbenzene | 58.20 | 58.01 | 155756 | 17085 | 0.04 | 0.04 |
| | total | | | 3.972×10 ⁷ | 3.281×10 ⁷ | 100 | 100 |

4.3 The Various Effects in Aromatization Reactions

The percentage of all conversion in Appendix C indicated the important conversion of the compositions including the conversion of total C₅ (C₅ Naphthenes & C₅ Paraffins), conversion of C₆ (C₆ Naphthenes & C₆ Paraffins), conversion of C₇⁺ (C₇⁺ Naphthenes & C₇⁺ Paraffins) and total conversion. The percentages of these conversions were calculated from decreasing of corresponding paraffins and naphthenes according to the calculation methods shown in Appendix C.

The percentage yield of aromatic compounds are given in Appendix D. There were percentage yields of benzene, toluene, and C₈ and heavier aromatics, and total aromatics. The calculation method is shown in Appendix D.

All studies of the effect in aromatization of NGL in this research were shown by graphs, which were plotted between the reaction temperature (as the X-axis) and the conversion or percent yield of aromatic compounds (as the Y-axis).

(1) Effect of Hydrogen Pressure

The effect of hydrogen pressure was carried out by varying the hydrogen pressure to 20, 40 and 60 psi at temperature of about 350°-430° C on 0.6% Pt & 0.5% F/Al₂O₃ and 0.6% Pt & 1% F/Al₂O₃ catalyst.

The results from Appendix C3 and C4 were plotted and gave the graph in Figure 4.1 and Figure 4.2.

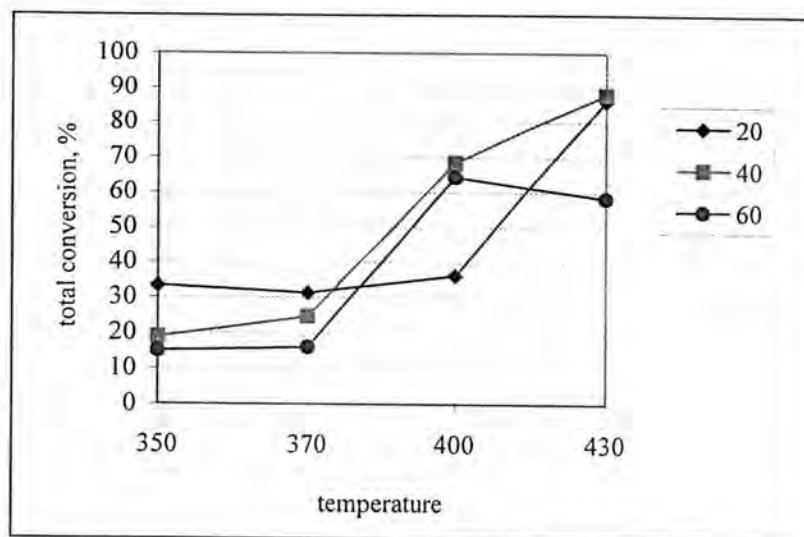


Figure 4.1 The comparison of the percent conversion at different hydrogen pressure on 0.6% Pt & 0.5% F/Al₂O₃.

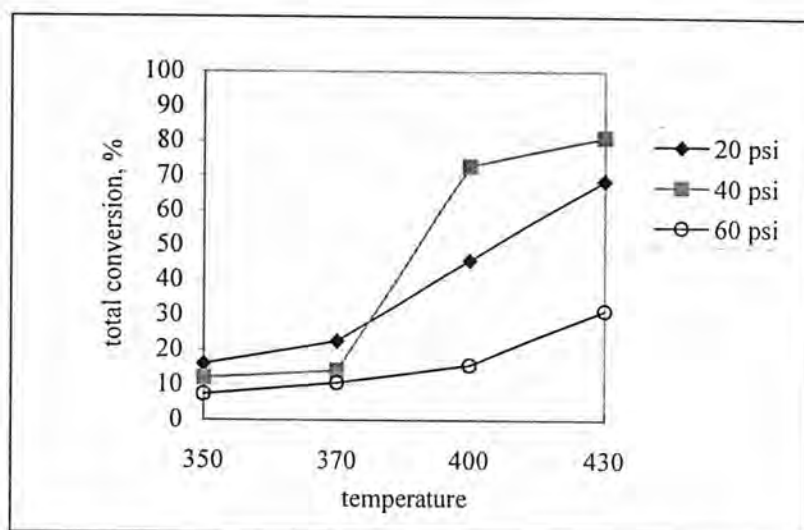


Figure 4.2 The comparison of the percent conversion at different hydrogen pressure on 0.6% Pt & 1% F/Al₂O₃.

The use of different hydrogen pressure gave the different conversions of hydrocarbons, the conversion increased when the temperature increased. The percent yields of aromatics (figure 4.3 and 4.4) indicate that at 40 psi of hydrogen pressure there is a better yield of aromatics than at 20 and 60 psi.

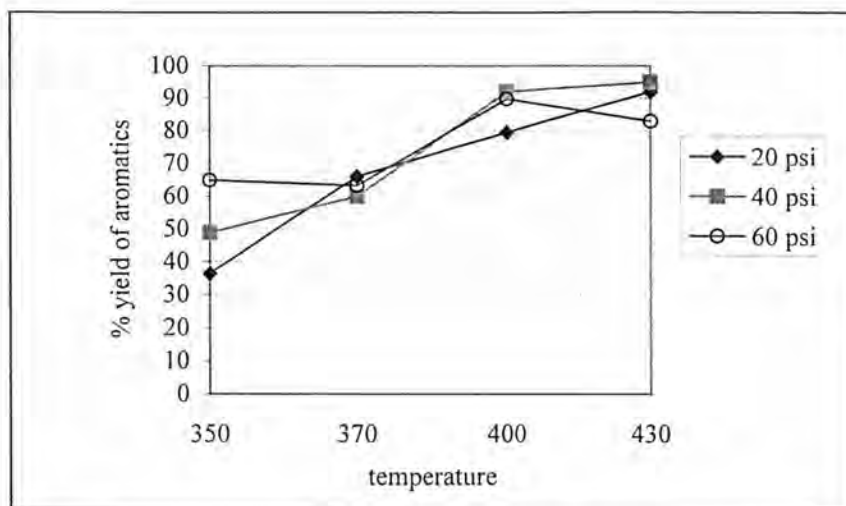


Figure 4.3 The comparison of the percent yield of aromatics related to total conversion at different hydrogen pressure on 0.6% Pt & 0.5% F/Al₂O₃.

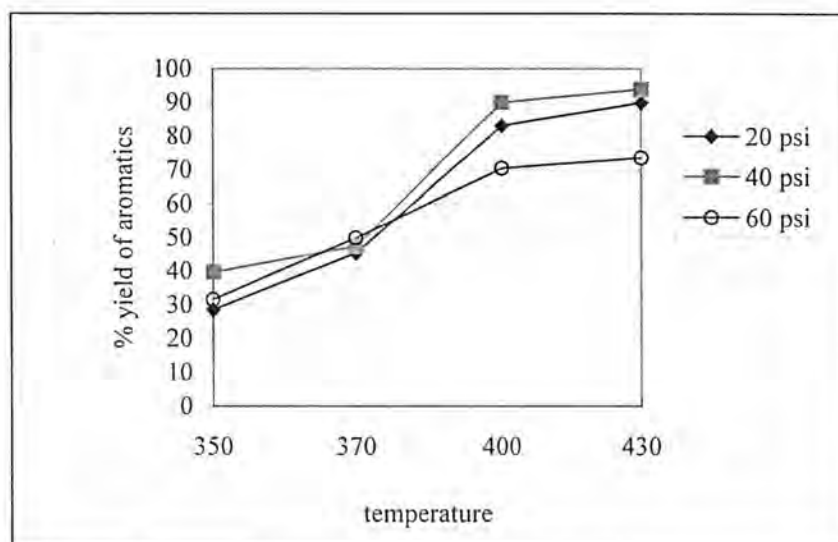


Figure 4.4 The comparison of the percent yield of aromatics related to total conversion at different hydrogen pressure on 0.6% Pt & 1% F/Al₂O₃.

Since only Pt sites are required for dehydrogenation, the effect of hydrogen appears to be associated with the platinum. It is suggested that in the absence of hydrogen the platinum is almost completely covered with hydrocarbon residues, formed by side reactions involving extensive

dehydrogenation and polymerization. The primary role of hydrogen is then to keep the surface clean.

Rohrer et al. [35] found that the rate of dehydrogenation increased with increasing hydrogen partial pressure up to a maximum value, beyond which the rate fell off with a further increase of hydrogen pressure. Experiment which nitrogen was substituted for hydrogen showed no isomerization or dehydrocyclization of n-heptane, indicated that the presence of hydrogen was necessary for both reactions.

Although reactions which involve the loss of hydrogen (dehydrogenation of alkanes to unsaturated product or to aromatics) could occur without hydrogen, the active life of the catalyst would be very short under these conditions. One of the possible role of hydrogen could be to form metal-hydrogen combined sites which accordingly would be the active centers for hydrocarbon reactions. Lower hydrogen pressure favor the formation of more unsaturated intermediates [27].

The presence of hydrogen was found to be necessary for isomerization-dehydroisomerization, since no cyclohexane or benzene could be detected when nitrogen replaced hydrogen. Furthermore, the rate was found to pass through a maximum with increasing hydrogen pressure, so that at sufficiently high hydrogen pressure the rate decreased with increasing hydrogen pressure. The rate then decreases with increasing hydrogen pressure because of the inverse effect of hydrogen on the equilibrium concentration of alkene intermediates [36].

(2) Effect of Temperature

The study of temperature effect in aromatization of NGL was performed by various reaction temperatures (350, 370, 400 and 430°C) on 0.6% Pt & 0.5% F/Al₂O₃ and 0.6% Pt & 1% F/Al₂O₃ catalyst under 40 psi of hydrogen pressure.

The result is given in Table C3, C4, D3 and D4 in Appendix C and D respectively. The graph of these results are shown Figure 4.5 - 4.6 below.

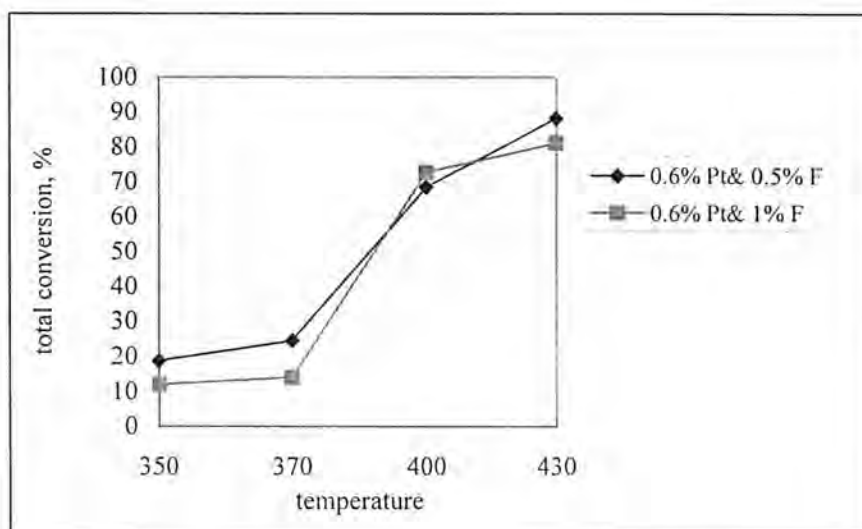


Figure 4.5 The comparison of the percent conversion at different temperatures on 0.6% Pt & 0.5% F/Al₂O₃ and 0.6% Pt & 1% F/Al₂O₃ under 40 psi H₂.

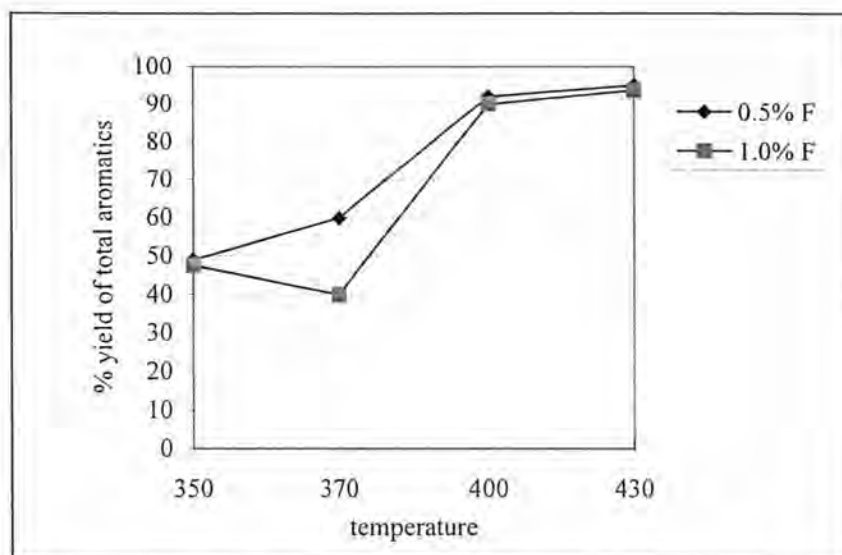


Figure 4.6 The comparison of the percent yield of total aromatics related to total conversion at different temperatures on 0.6% Pt & 0.5% F/Al₂O₃ and 0.6% Pt & 1% F/Al₂O₃ under 40 psi H₂.

The graphs shown above indicated that the optimum reaction temperatures for aromatization of NGL was 430 °C, both 0.6 % Pt & 0.5 % F/Al₂O₃ and 0.6 % Pt & 1 % F/Al₂O₃ catalyst gave high conversion and production of total aromatics at this temperature.

Table 2.3 shows that the dehydrocyclization reaction, a significant reaction in reforming to give aromatics product, can occurred well at high temperatures. So, the higher the temperature, the higher the amount of aromatics. The dehydrogenation of naphthenes is favored thermodynamically at low hydrogen partial pressure and high temperatures. Important aromatization reactions are the dehydrogenation of naphthenes and the dehydrocyclization reaction of paraffins.

(3) Effect of Catalyst Concentration

Effect of hydrogenation-dehydrogenation concentration

The study of hydrogenation-dehydrogenation concentration effect was carried out by comparing two different concentrations of Pt (0.3 % Pt and 0.6 % Pt) in 1 % F/Al₂O₃ catalysts under 40 psi of hydrogen pressure.

The results from Table C2 and C4 in Appendix C and Table D2 and D4 were plotted to give the graphs in Figure 4.7 - 4.8 for comparison of the dehydrogenation effect in aromatization reaction.

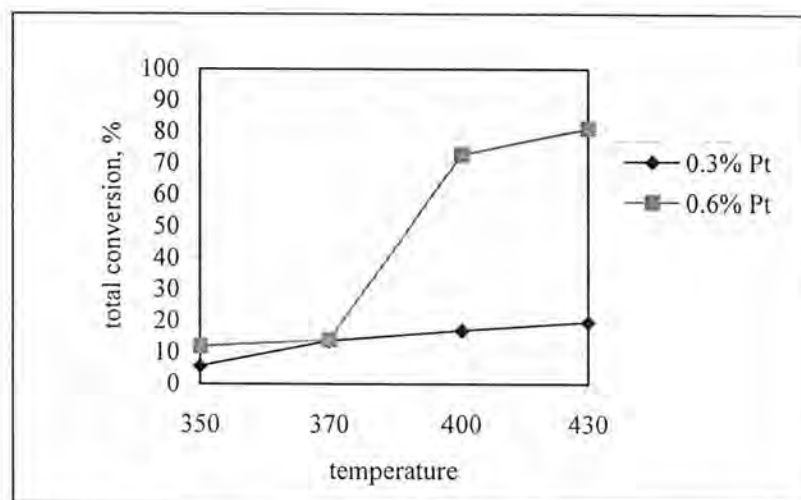


Figure 4.7 The comparison of the percent conversion at different concentrations of Pt-site in 1 % F/Al₂O₃ under 40 psi H₂.

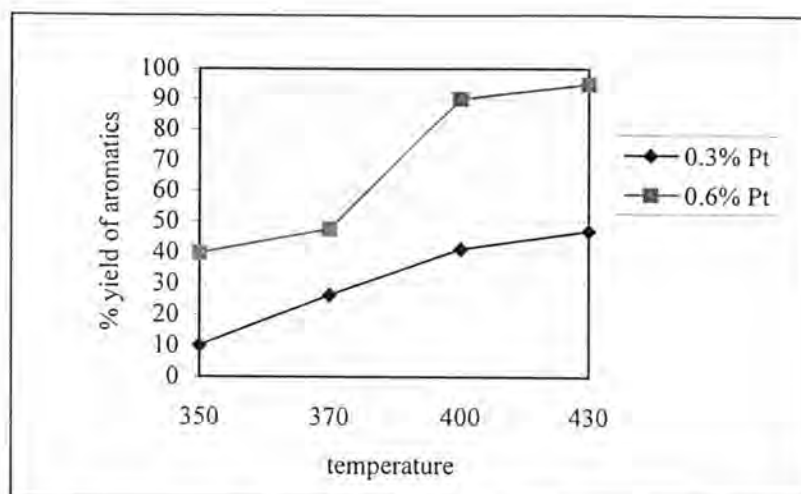


Figure 4.8 The comparison of the percent yield of aromatics related to total conversion at different concentrations of Pt-site in 1 % F/Al₂O₃ under 40 psi H₂.

These graphs indicated that increasing platinum content from 0.3 to 0.6 wt. % had essentially effect on the conversion of hydrocarbons and percent yield of aromatic, at 430°C the yield increased from 47.03 % to 93.66 %.

An abundant amount of platinum can catalyze the aromatization reactions to give the desired aromatics. Platinum is the metal of choice because it is the only one that has the activity for the desired reactions without being more than moderately active for undesired reactions such as hydrogenolysis of paraffins.

The reforming reaction need dehydrogenation site-Pt according to the reaction network which was proposed by Menon. et al. [30]. A suitable concentration of metal needs to be used. In previous studies on isomerization of NGL over supported metals, it has been concluded that 0.9 % Pt is not good for production of aromatics.

Effect of acidic concentration

The study of acid concentration effect was carried out by comparing two different concentrations of F in catalyst, 0.5 % F and 1 % F in 0.6 % Pt/Al₂O₃ catalysts under 40 psi of hydrogen pressure.

The results from Table C3, C4, D3 and D4 in Appendix C were plotted as shown in Figure 4.9 - 4.10 for comparison of acidic site effect in aromatization reaction.

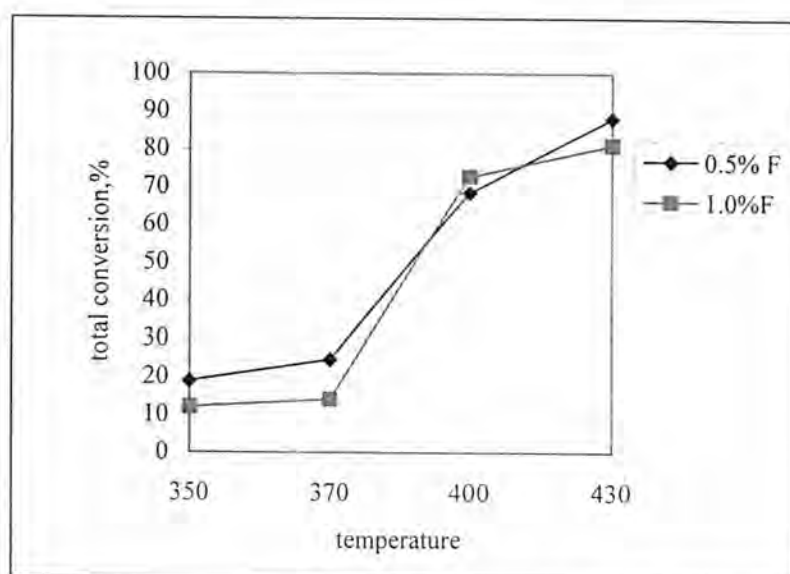


Figure 4.9 The comparison of total conversion at different concentrations of acid site under 40 psi H₂ on 0.6 % Pt/Al₂O₃ catalyst.

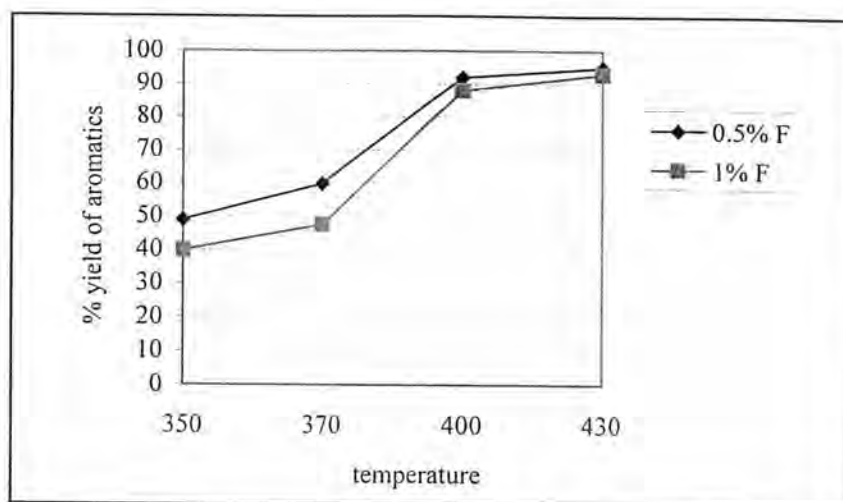
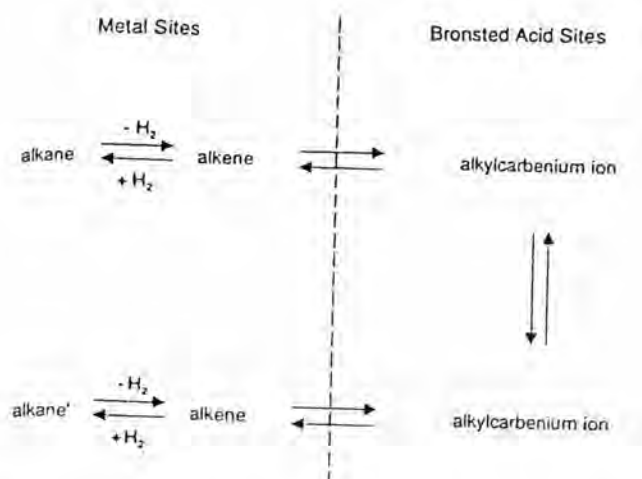


Figure 4.10 The comparison of percent yield of total aromatics at different concentrations of acid site under 40 psi H_2 on 0.6 % Pt/ Al_2O_3 .

The increasing platinum content from 0.5 to 1 wt. % F had essentially no effect on total conversion and the total percentage yield of aromatics had a few differences (Figure 4.9 and 4.10). The aromatization proceeds with much higher yield on the 0.6 % Pt & 0.5% F/ Al_2O_3 catalyst than on the 0.6 % Pt & 1% F/ Al_2O_3 catalyst. But, at 400°C the latter could have given a higher percentage yield of toluene.

As mentioned previously about the metal-acid bifunction catalyst, the reaction of the olefin intermediates on acid site could form a carbenium ion mechanism (Scheme 4.1). The adsorption of the olefins resulted in the formation of a carbenium ion by addition of a proton from the catalyst surface. The carbenium ion then rearranges on the surface. The isomerized carbenium ion could revert to isoolefins by elimination of a proton. The isoolefins then migrate to platinum sites where they are hydrogenated to the corresponding isoparaffins. The isomerization rate is therefore controlled by the acid activity of the catalyst [37].



Scheme 4.1 Bifunctional reaction scheme [38].

According to kinetic studies the first step in the aromatization reaction was the dehydrogenation of alkanes to the corresponding alkenes. In the presence of 0.6 % Pt & 1 % F/Al₂O₃ catalyst n-hexenes produced from n-hexane would undergo skeletal isomerization to methylpentenes. Therefore, the latter could then not be aromatized to benzene by a simple ring closure reaction. Methylpentanes, on the other hand, undergo aromatization to benzene much easier on 0.6 % Pt & 1 % F/Al₂O₃ catalyst than on 0.6 % Pt & 0.5 % F/Al₂O₃ catalyst.

(4) Effect of Solid Support

The effect of solid support on aromatization of NGL was observed by using different support between the alumina and the 4A molecular sieve.

The results from Table C3, and C5-C8 in Appendix C and Table D3, and D5-D8 in Appendix D were plotted and gave the graphs for comparing the activity of the support.

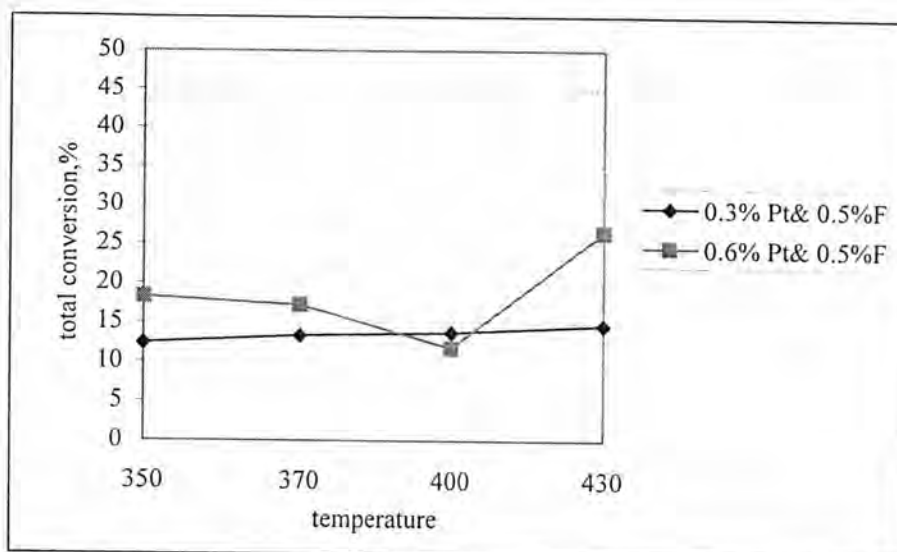


Figure 4.11 The comparison of the total conversion at different concentrations of metal site at 40 psi H₂ by using 4A molecular sieve support instead of alumina.

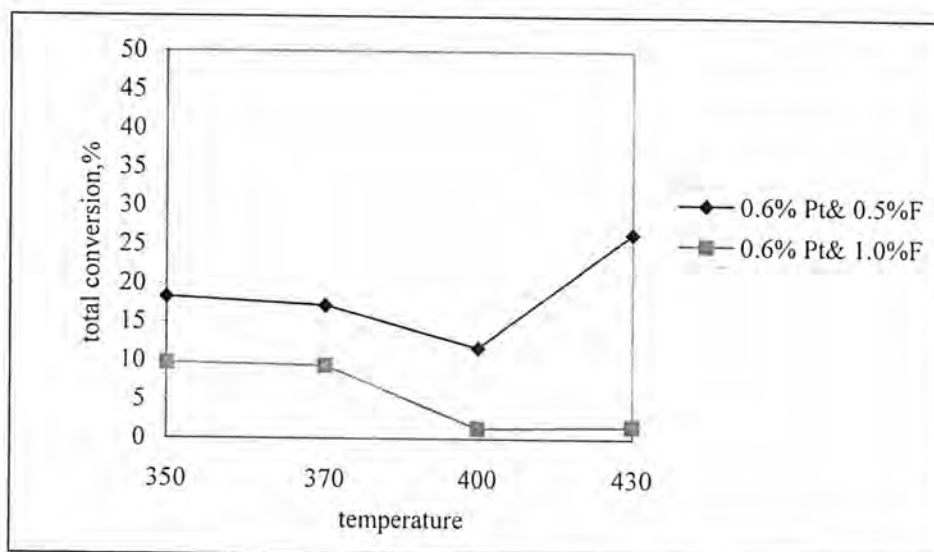


Figure 4.12 The comparison of the total conversion at different concentrations of acid site on 0.6% Pt at 40 psi H₂ by using 4A molecular sieve as a solid support.

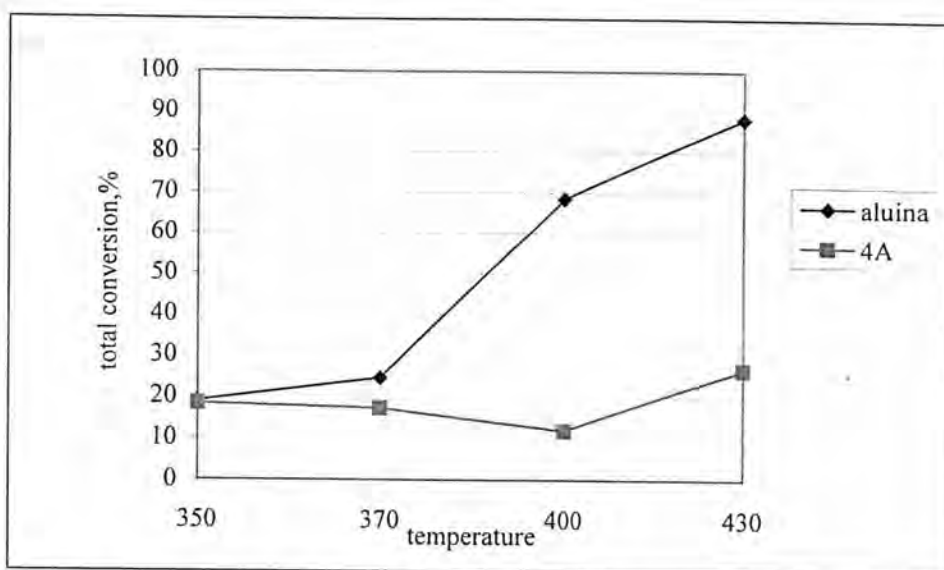


Figure 4.13 The comparison of the total conversion of different supports on 0.6% Pt & 0.5% F at 40 psi H₂.

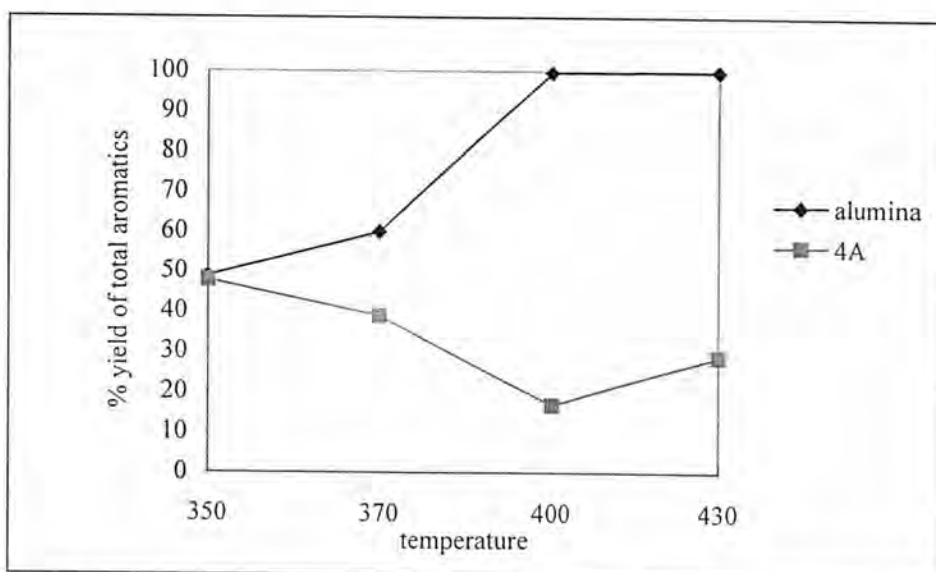


Figure 4.14 The comparison of the percent yield of total aromatics on different supports on 0.6% Pt & 0.5% F at 40 psi H₂.

The above graphs indicate that the suitable support in aromatization of NGL was γ -alumina when compared with the 4A molecular sieve. Even though 4A molecular sieve was the suitable solid support for improving the octane number of gasoline, because the isomers of octane and higher

hydrocarbons were found when 4A molecular sieve solid support was used in reaction. The straight-chain hydrocarbons fit into the zeolite pores and undergoes catalytic hydration much faster than the branched-chain alcohol which could not fit [39,40]. The data in table 4.3 demonstrates that the straight-chain reactant is selectively converted in the presence of the small-pore zeolite A.

Table 4.3 Demonstrating of shape-selective cracking of paraffins by zeolite [40].

| Reactant | Conversion, % ^a | | | |
|-----------------|----------------------------|------------|------------|----------------|
| | No catalyst ^b | 4A Zeolite | 5A Zeolite | Silica-alumina |
| n-Hexane | 1.1 | 1.4 | 9.2 | 12.2 |
| 3-methylpentane | <1.0 | <1.0 | <1.0 | 28.0 |

^a Reaction conditions: 500°C, contact time = 7 S.

^b Conversion determined with reactor packed with quartz chips.

(5) Reproducibility and Activity of Used Catalyst

Reproducibility

The reproducibility of the reaction was observed on 0.6% Pt & 0.5 % F/Al₂O₃ catalyst, under 40 psi of hydrogen pressure and at 350°- 430°C.

The results from Tables C3 and D3 in Appendix C and D respectively were plotted and gave the graphs as shown in Figure 4.22 and 4.23 below.

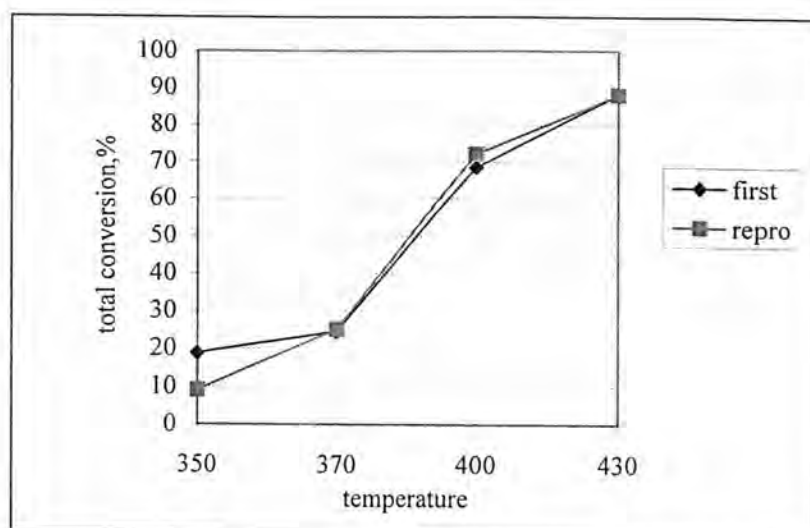


Figure 4.15 The reproducibility of the total conversion on 0.6% Pt & 0.5% F/Al₂O₃ at 40 psi H₂.

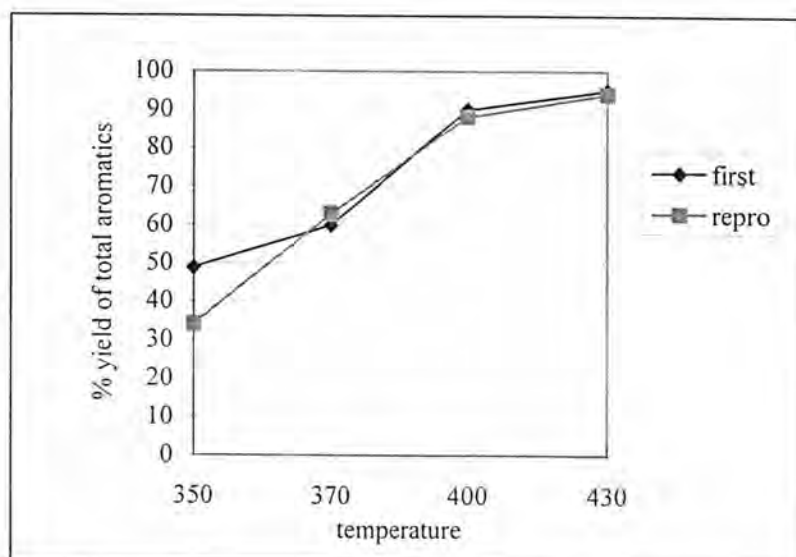


Figure 4.16 The reproducibility of the percent yield of total aromatics on 0.6% Pt & 0.5% F/Al₂O₃ at 40 psi H₂.

The graphs shown in Figure 4.23 and 4.24 indicate that there was a reproducibility of the reactions performed on the 0.6 % Pt & 0.5 % F/Al₂O₃ catalyst, since there was no significant difference in the total conversion and the percentage yield of aromatics.

Activity of used catalyst

The activities of used catalyst was observed on 0.6% Pt & 0.5 % F/Al₂O₃ catalyst, under 40 psi of hydrogen pressure and at 350°- 430°C.

The results from Table C3 and D3 in Appendix C and D, respectively, were plotted and gave the graphs as shown in Figure 4.24 and 4.25 below.

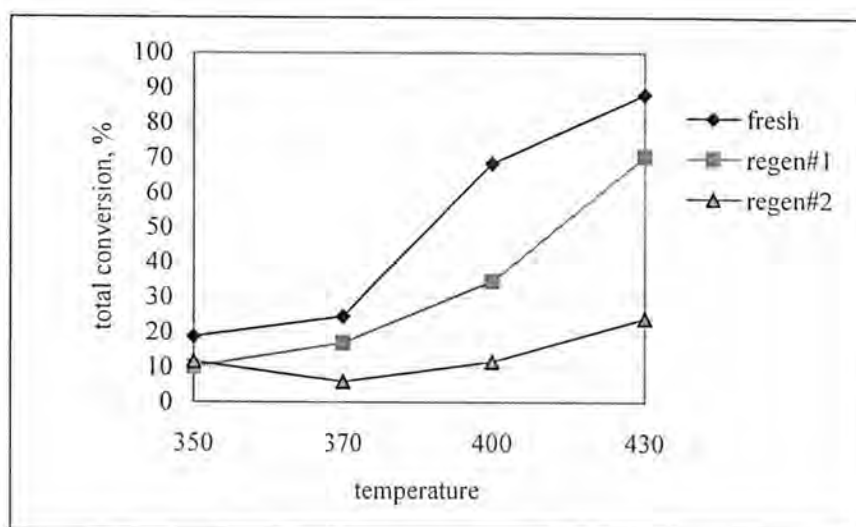


Figure 4.17 The total conversion on 0.6% Pt & 0.5% F/Al₂O₃ compared with used catalysts, under 40 psi H₂.

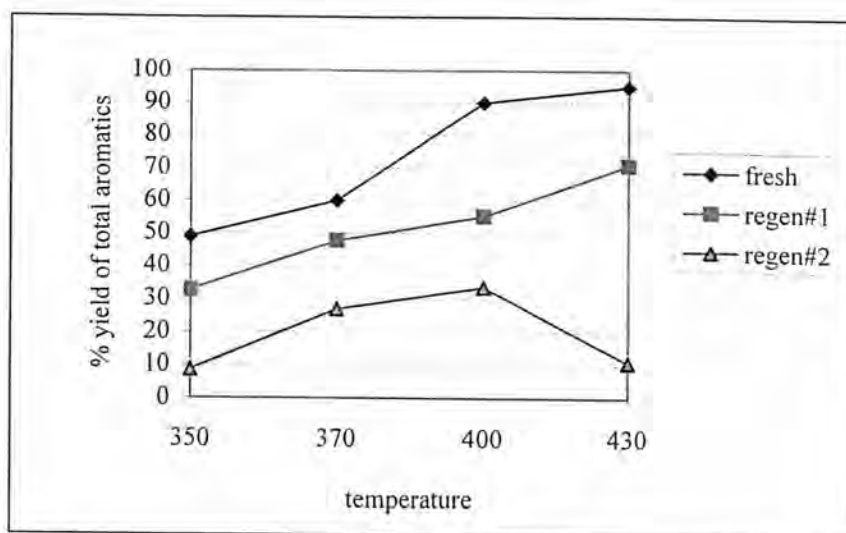


Figure 4.18 The percent yield of total aromatics on 0.6% Pt & 0.5% F/Al₂O₃ compared with used catalysts, under 40 psi H₂.

The graphs shown in Figure 4.24 and 4.25 indicated that the fresh catalyst gave the highest total conversion and yield of total aromatics. When the catalysts was regenerated, the efficiency of the catalyst was reduced. Moreover, the second regeneration of the catalyst resulted in the worst activity of the catalyst compared to those of the fresh catalyst and the first regeneration catalyst. When the first regeneration of catalyst was used in reaction, that catalyst had lost about 20 % of its initial activity. A fresh catalyst will produce more aromatics than the first regeneration of catalyst. As the used catalyst had coke formation. The coke appeared to covered the catalyst surface so that its activity was reduced.

This research have many advantages when compare with the other researches. Table 4.4 shows in different ways of comparison such as feedstream. This research used the mixed hydrocarbons, NGL, as a feed but in Le Van Mao's work or Bannett's work used a pure hydrocarbon as a feed. The advantage of using the mixed feed was the feed no need separating before used in process.

Table 4.4 Comparison this research with the other researches.

| | This research | Bour-nonville | Brand | Kuchar | Le Van Mao | Bannett |
|----------------------|---|-----------------------------------|---|---------------------------------|-------------|--------------------------------|
| feedstream | mixed | 90 % C ₅ | 26.8 % C ₇ 36.7 % C ₈ | C5/C6 | pure butane | pure ethylene, pure propane |
| catalyst | 0.6 % Pt & 0.5 %F /Al ₂ O ₃ | 0.3 % Pt & 0.2 %Sn /zeolite | 0.4 % Pt & 0.5 % Zr /Al ₂ O ₃ | ZSM & aluminium phosphate | ZSM 5 | 0.8 % Ga /zeolite |
| step | 1 | 1 | 1 | 2 | 1 | 2 |
| temperature (°C) | 430 | 480 | 500 | 450 | 540 | 550 |
| pressure (psi) | 40 | 36.3 | 0.69 | 50 | - | 3 |
| % conversion | 88 | 95 | - | 25 | - | 56 |
| % yield of aromatics | 95 | 70 | 40 | (30 wt. %) | (47.3 wt.%) | 36 |

The step of process in this research had only one step, which was not a complicated process when compare with the Bannett's research which was two steps process or the Kuchar's work that have to used two reactors in operation. This research used the lowest temperature and give the most percent yield of aromatics per total conversion when compare with the other researches.