

CHAPTER III

EXPERIMENTAL

Apparatus and Instruments

1. Condenser cooled with Acetone-Dry Ice
Adapted from the digestion apparatus in reference number [33]
2. Tubing Reactors
Annealed 316 Stainless Steel Tubing ASTM A269 ,
O.D. 1/4 in. x Wall Thickness 0.035 in. x Length 6 feet
3. Furnace for Reaction Unit
Adapted from some units of Gas Chromatograph Instrument from
Pye Unicam GC model Pye Series 104 Chromatograph
4. Furnace
Carbolite Furnace model Eurotherm 808P
5. Instrument for P.I.A.N.O. and/or P.I.O.N.A.* Analysis
Perkin-Elmer Autosystem GC model Series 9000 and/or
Hewlett Packard AC PIONA model HP5890 Series II

* Either P.I.A.N.O. or P.I.O.N.A. is a commercial name of one type of GC Instrument which P. stands for Paraffins, I. stands for Isoparaffins, A. stands for Aromatics, N. stands for Naphthenes, and O. stands for Olefins.

6. Gas Chromatograph (GC)

Hewlett Packard GC model HP5890 Series II

7. Cooperative Fuels Research (CFR) Standard Engine

ASTM method D2699

Materials

1. Natural Gas Liquid (NGL), Reformate, and Methyl t-Butyl Ether (MTBE) were supplied from Petroleum Authority of Thailand (PTT).

2. Chloroplatinic Acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was available from Merck.

3. Ammonium Fluoride (NH_4F) was available from Merck.

4. Alumina Powder Support (Alumina Catalyst Al-3912P is a powdered gamma alumina.) was supplied from a dealer of Engelhard, Holland. (surface area = $185 \text{ m}^2/\text{g}$, total pore volume = 0.50 cc/g , partical size < 90 microns = 85 wt%, density = $0.7\text{-}0.85 \text{ g/cm}^3$)

5. Hydrogen Gas (Purity 99.986% minimum) was high purity grade and available from TIG Trading Limited.

6. Nitrogen Gas (Purity 99.99% minimum) was high purity grade and available from TIG Trading Limited.

Preparation, Activation and Regeneration of Catalysts [3,34,35]

1. Preparation of Catalysts

1.1 Impregnation of Platinum on Alumina Support : for an example of catalyst containing 0.6% Pt on Alumina Support.

An aqueous impregnating solution was prepared by dissolving 1 g of chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) in 32 ml of deionized water (the volume of aqueous equivalent to pore volume of alumina support). The alumina powder support (62.78 g) was impregnated with this prepared solution. The impregnated support was dried at 120-140°C for 2-3 hrs and then calcined in air flow at 500°C for 3 hrs to obtain the calcined 0.6% Pt on alumina support catalyst.

1.2 Impregnation of Fluoride on Pt/Alumina Catalyst : for an example of catalyst containing 0.6% Pt-1.0% F on Alumina Support.

Following the same procedure mentioned in impregnation of platinum on alumina support in 1.1, and then the calcined catalyst (0.6% Pt on alumina) was reimpregnated with 32 ml of aqueous solution containing NH_4F (1.22 g) and left at room temperature for one hour, dried at 120-140°C for 16 hrs to obtain the fluorided catalyst. This fluorided catalyst was calcined in air flow at 500°C for 3 hrs to obtain the 0.6%Pt-1.0%F on alumina support catalyst.

2. Activation of Catalysts

In the isomerization reaction, both Pt on alumina and Pt-F on alumina catalysts had to be activated under hydrogen pressure before use. Any calcined catalyst in this research was packed in a tubing reactor. Then the tubing reactor packing with calcined catalyst was installed in a furnace and was heated at 450°C while maintained the flow of hydrogen at 60 psi for 6 hrs to obtain the activated catalyst.

3. Regeneration of Catalysts

The used catalyst was taken out of the tubing reactor and brought to decoke with a furnace at 550°C for 10 hrs minimum, and then was activated, following activation procedure mentioned, before reuse.

Isomerization Reactions Procedure

1. Reaction Unit

All studies in this research were performed by the reaction unit as shown in Figure 3.1. Isomerization reactions were operated in a tubing reactor (B) containing packed catalyst. This tubing reactor was installed in a furnace (D) that the temperature could be controlled for desired reaction temperatures. There was a temperature gauge (C) over the furnace for checking the accuracy of reaction temperatures which were controlled by the temperature control unit (E) (adapted from some GC units).

A hydrogen tank was connected to the inlet side of the tubing reactor passed an injection unit (A) (also adapted from some GC units) to use

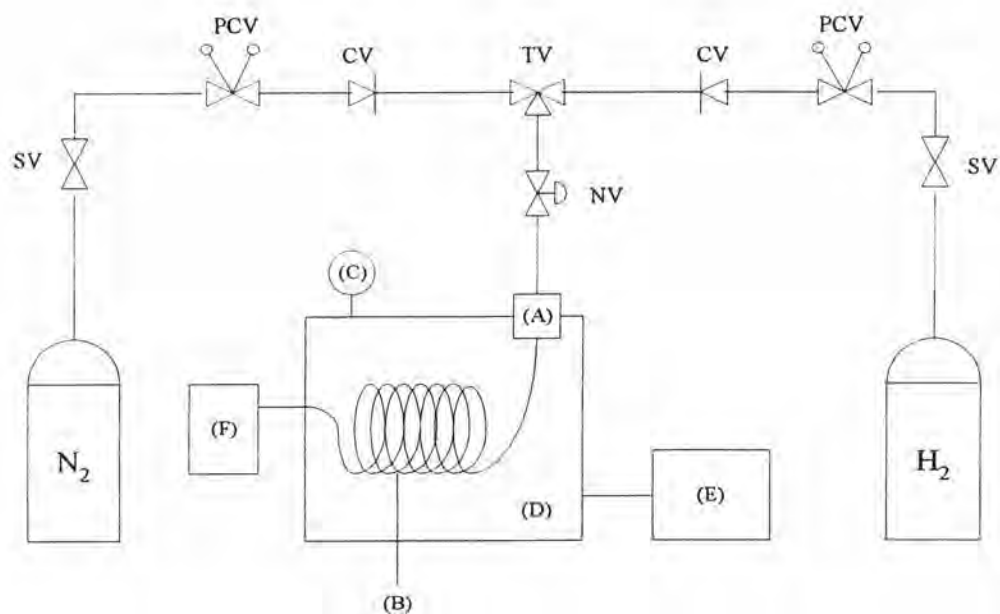


Figure 3.1 Schematic drawing of the reaction unit

CV = CHECK VALVE

NV = NEEDLE VALVE

PCV = PRESSURE CONTROL VALVE (REGULATOR)

SV = STOP VALVE

TV = THREE-WAY VALVE

A = INJECTION UNIT

B = TUBING REACTOR

C = TEMPERATURE GAUGE

D = FURNACE

E = TEMPERATURE CONTROL UNIT

F = CONDENSATION UNIT

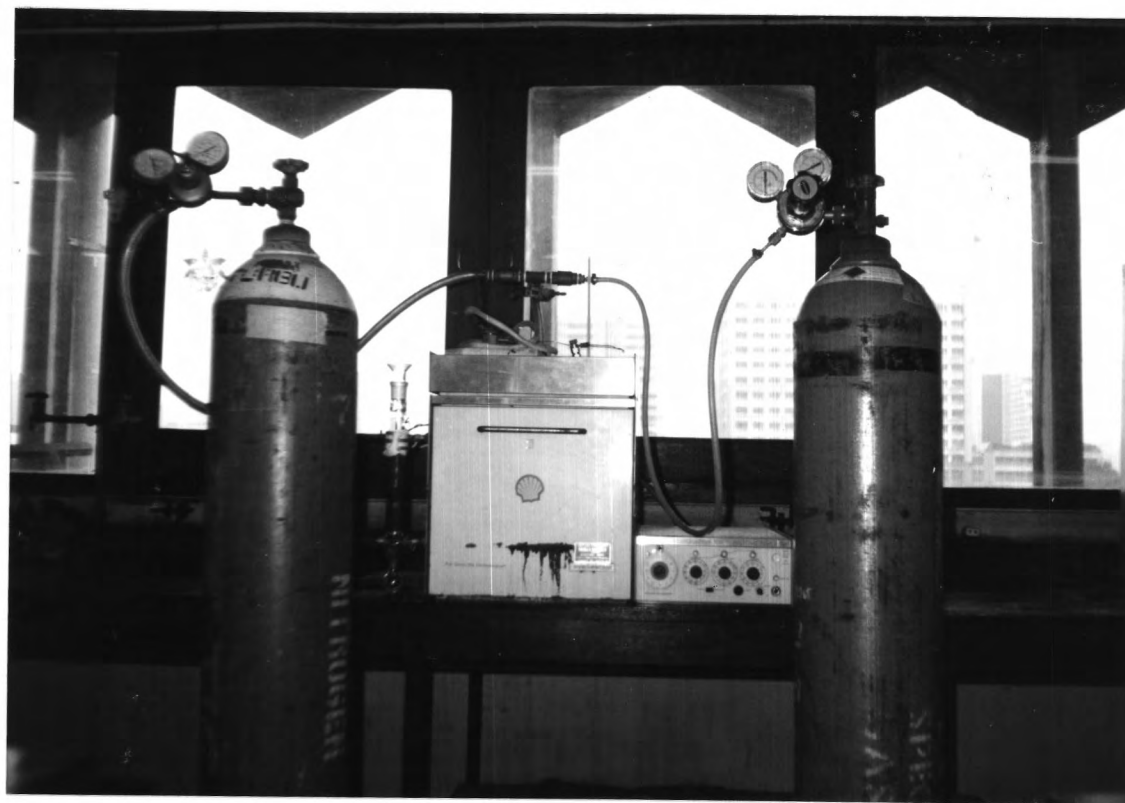


Figure 3.2 The reaction unit

for supplying hydrogen gas into the tubing reactor all over the reaction operation. A tank of nitrogen gas was also connected in the same direction of hydrogen to the tubing reactor for supplying nitrogen gas in order to flush the rest of products remaining in the tubing reactor after reaction took place.

The condensation unit (F) was composed of a condenser cooled with acetone-dry ice and a reservoir set. The condenser was connected to the outlet terminal of the tubing reactor for condensing the products from reactions, as it was able to condense the products that having boiling point higher than -78°C . Then the condensed products from the condenser were collected into a reservoir flask which was dipped in a bath which also cooled with acetone-dry ice.

2. Reaction Procedure

NGL (as the feed) was injected into the heated tubing reactor packing with catalysts during flowing hydrogen gas for 30 mins. The products in gaseous phase were taken out by hydrogen carrying, and then were condensed with a condenser cooled with acetone-dry ice into a receiving flask. In any reaction operation of this research, nitrogen gas was used for flushing out the rest of products remaining in the tubing reactor after the reaction time (30 mins) to collect all of the products absolutely.

Procedures in Study of Various Effects on Isomerization of NGL

1. Study of Temperature Effect

The temperature effect on isomerization of NGL was studied by various reaction temperatures (270, 320, 370, 400, 420, and 450°C) over 0.3% Pt-0.5% F/Al₂O₃ catalyst under 60 psi hydrogen pressure to search for the optimum reaction temperature in isomerization of NGL.

The data of percentages of composition and percentages of total conversion in this study were shown in Table B1 (in Appendix B) and Table C1 (in Appendix C), respectively.

2. Study of Hydrogen Pressure Effect

The effect of hydrogen pressure on isomerization of NGL was studied under different hydrogen pressure (40, 60, and 80 psi) at the optimum reaction temperatures (370, 400, 420, and 450°C) to search for the optimum hydrogen pressure. The study of hydrogen pressure effect was performed over several concentrations of catalyst, they were:

- 0.3% Pt-0.5% F/Al₂O₃ catalyst, as the data of percentages of composition and percentages of total conversion shown in Table B1 (in Appendix B) and Table C1 (in Appendix C), respectively.

- 0.6% Pt-0.5% F/Al₂O₃ catalyst, as the data of percentages of composition and percentages of total conversion shown in Table B3 (in Appendix B) and Table C3 (in Appendix C), respectively.

- 0.9% Pt-0.5% F/Al₂O₃ catalyst, as the data of percentages of composition and percentages of total conversion shown in Table B4 (in Appendix B) and Table C4 (in Appendix C), respectively.

- 0.6% Pt/Al₂O₃ catalyst, as the data of percentages of composition and percentages of total conversion shown in Table B5 (in Appendix B) and Table C5 (in Appendix C), respectively.

- and 0.6% Pt-1.0% F/Al₂O₃ catalyst, as the data of percentages of composition and percentages of total conversion shown in Table B6 (in Appendix B) and Table C6 (in Appendix C), respectively.

3. Studies of Catalyst Concentration Effects

3.1 Study of Hydrogenation-Dehydrogenation Center Effect

The effect of hydrogenation-dehydrogenation center (Pt-concentration effect) was performed by using 0.3% Pt, 0.6% Pt, and 0.9% Pt impregnated on 0.5% F/Al₂O₃ catalysts under the optimum hydrogen pressure (60 psi H₂) and the optimum reaction temperatures (370, 400, 420, and 450°C) to search for the optimum concentration of platinum for isomerization of NGL.

The data of percentages of composition and percentages of total conversion in this study were shown in Table B1, B3, and B4 (in Appendix B) and Table C1, C3, and C4 (in Appendix C), respectively.

3.2 Study of Acidic Center Effect

The effect of acidic center (Fluoride-concentration effect) was performed by using 0% F, 0.5% F, and 1.0% F impregnated on 0.6% Pt/Al₂O₃ catalysts (0.6% Pt was the optimum concentration of platinum which received from the study of hydrogenation-dehydrogenation center effect) under the optimum hydrogen pressure (60 psi H₂) and the optimum reaction temperatures

(370, 400, 420, and 450°C) to search for the optimum concentration of fluoride for isomerization of NGL.

The data of percentages of composition and percentages of total conversion in this effect study were shown in Table B5, B3, and B6 (in Appendix B) and Table C5, C3, and C6 (in Appendix C), respectively.

4. Further Studies of Activities of Used Catalysts and Reproducibility

The reproducibility of reactions and the activities of used catalysts were studied by the 0.3% Pt-0.5% F/Al₂O₃ catalyst, and their data of percentages of composition and percentages of total conversion were shown in Table B2 (in Appendix B) and Table C2 (in Appendix C), respectively.

Analysis of Reactant and Products

NGL and its products were characterized by P.I.A.N.O. autosystem GC, their hydrocarbon compositions were identified by this instrument with the library search program. Quantitative analysis was studied by GC, then the calculations of percentages of conversion in the isomerization reactions were studied from percentages of compositions represented by the peak areas of the reactant and the products.

Operation Condition in GC Analysis

Column : CBP-1, 25 m x 0.22 mm I.D.

Carrier Gas : Helium gas

Injection Port : 200°C, Split 200:1

Detector : 250°C, FID

Oven : Temperature program by :

30°C for 5 min,

30-120°C for 15°C/min,

120°C for 4 min

The GC chromatogram of NGL was shown in Figure 4.1, and the identification of its compositions was presented in Table 4.1. The GC chromatograms of some products from some selected reaction conditions were shown in Figure A1-A13 (in Appendix A). All the data of percentages of compositions and percentages of total conversion were presented in Table B1-B6 (in Appendix B) and Table C1-C6 (in Appendix C), respectively. Furthermore, percentages of total conversion in any isomerization reaction were presented versus the reaction temperatures by graph features in Figure 4.2, and Figure 4.4-4.23 (in Chapter IV).

Determination of Antiknock Property [36]

The research octane number (RON) determinations, by ASTM method D2699, were performed by Petroleum Authority of Thailand (PTT). NGL and its product (Isomate) from the optimum reaction condition were determined in RON for comparison, and there were some extraordinary studies in comparing RON of them by blending with Reformate and MTBE to be a gasoline. The extraordinary studies were performed by blending 6% NGL

into mixture of 84% Reformate and 10% MTBE ; and 15% NGL in mixture of 75% Reformate and 10% MTBE, similarly the isomerase from the optimum reaction condition was blended and studied as NGL mentioned for comparison RON in the same blended proportion to NGL.

Analysis of Total Aromatics and Benzene [36]

Percentages of total aromatics and benzene of any blended gasoline were determined by AC P.I.O.N.A. GC of Petroleum Authority of Thailand (PTT) following the ASTM method D4420 and D3606, respectively.