

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Feedstocks

- Pentadecane (99% purity, Aldrich)
- Hexadecane (99% purity, Aldrich)
- Heptadecane (99% purity, Aldrich)
- Octadecane (99% purity, Aldrich)

3.1.2 Catalyst Supports and Metal Precursors

- Tetraammineplatinum (II) chloride hydrate (99.99%, Aldrich)
- HY zeolite (SiO₂/Al₂O₃ ratio of 100, Tosoh Company)

3.1.3 Standard Chemicals and Others

- Carbon disulphide (99.5% purity, Panreac Synthesis)
- Acetone (98% purity, Labscan)
- Methanol (99.9% purity, Labscan)
- Distilled water

3.1.4 Gases

- Hydrogen (99.99% purity, BIG)
- Nitrogen (99.99% purity, Linde)
- Helium (99.99% purity, Linde)
- Air zero (99.99% purity, Linde)

3.2 Equipment

- High pressure packed-bed continuous flow reactor system consisting of a mass flow controller (Brooks instrument 5850E), a high pressure liquid pump (Waters 515 HPLC), a back pressure regulator (SIEMENS), $\frac{3}{4}$ " O.D. x 16" long stainless steel reactor, and a three-zone tubular furnace with a temperature controller (Cabolite).
- Gas chromatograph (Agilent GC 7890A equipped with injector, DB-5 column, and FID)
- Gas chromatograph- mass spectrometry (GC-MS)
- Shimadzu GC-17A gas chromatograph equipped with a capillary HP-PLOT/ Al_2O_3 "S" deactivated column and FID detector
- Atomic absorption spectroscopy (SpectrAA, 300)
- Surface area analyzer (SAA, Quantachrome/Autosorb 1MP)
- Temperature programmed reduction (TPR) apparatus
- Temperature programmed oxidation (TPO) apparatus
- Temperature programmed desorption (TPD) apparatus
- Hot & stirrer plate (Cole Parmer)

3.3 Methodology

3.3.1 Pt/HY Catalyst Preparation

3.3.1.1 *Incipient Wetness Impregnation Method*

HY zeolite was dried overnight at 110 °C and calcined at 500 °C for 3 h with a heating rate of 10 °C/min to remove organic residues from the zeolite. After that, the zeolite was loaded with Pt by an incipient wetness impregnation technique consisting of 4 steps. Firstly, a desired amount of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ compound was dissolved in 6 mL of deionized water. Secondly, the $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ solution was added on the zeolite drop wise using a micro syringe to obtain a Pt/HY catalyst with a desired Pt loading, which was 0.1 wt% Pt/HY catalysts in this work. Thirdly, the wet zeolite was dried in an oven at 110 °C for overnight. Finally, catalyst was

calcined in a furnace at 350 °C for 3 h with a heating rate of 10 °C/min. Then, a bi-functional Pt/HY catalyst was obtained in metal oxide form.

3.3.1.2 *Ion-Exchange Method*

The HY zeolite was first dried overnight at 110 °C and calcined at 500 °C for 3 h with a heating rate of 10 °C/min to remove organic residues from the zeolite. One gram of HY zeolite was suspended in 150 mL of 1.7 M $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ aqueous solution in a beaker. Then, the beaker was placed into a water bath and stirred at 90 °C for 12 h. The precipitate of ion-exchanged Pt/HY zeolite was thoroughly washed with deionized water until pH value of catalyst reached to 7.5. Finally, the catalyst slurry was dried at 110 °C for overnight, and calcined for 3 h at 350 °C with a heating rate of 10 °C/min. Then, a bifunctional 0.1 wt% Pt/HY catalyst was obtained in metal oxide form.

3.3.2 Catalyst Characterization

3.3.2.1 *Atomic Absorption Spectroscopy (AAS)*

Atomic absorption spectroscopy (SpectrAA-300) is used to determine the concentration of a particular element in a sample. Chemical element absorbs ultraviolet light when they are excited by heat. Each element has a characteristic wavelength that will be absorbed. The AAS instrument seeks for a particular element by focusing a beam of UV light at a specific wavelength through a flame and into a detector. The sample of interesting element is aspirated into the flame. If the element is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance. As a concentration increases, an absorbance increases. A standard calibration curve is constructed by standard solutions at various concentrations. A sample preparation was divided in 4 steps. Firstly, samples were dissolved in hydrofluoric acid for 1 h. Secondly, samples were dissolved in aqua regia composed of mixing concentrated nitric acid and hydrochloric acid in a volume ratio of 1:3 and heated by a hot & stirrer plate at 80 °C for 2 h. Thirdly, samples were filtered by a syringe filter. Finally, samples were transferred into volumetric flask to make a desired volume using water.

3.3.2.2 Temperature Programmed Reduction (TPR)

Temperature programmed reduction is employed for evaluating the quantity of the reducible species present in the prepared catalyst and the temperature, at which the reduction itself takes place as a function of temperature. In each test, 50 mg of catalyst was placed in a quartz reactor, and heated (10 °C/min) under a He flow up to 500 °C, and held at the temperature for 3 h in order to remove moisture from the catalyst surface. The sample was cooled down to 30 °C. Then, the sample was exposed to a stream of 5% H₂/Ar with a flow rate of 20 mL/min. After that, the sample was heated to 800 °C with a heating rate of 10 °C/min. The amount of hydrogen consumed was monitored on-line by an SRI model 110 TCD detector as a function of temperature.

3.3.2.3 Brunauer-Emmett-Teller Method (BET)

The surface area of the fresh catalysts is measured by BET surface area analyzer (Quantachrome/Autosorb-1). The sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 150 °C for 4 h prior to the analysis. Then, N₂ was purged to adsorb on surface, measuring the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium is established. This volume-pressure data will be used to calculate the BET surface area.

3.3.2.4 Temperature Programmed Desorption (TPD) of *Isopropylamine*

The acidity of prepared catalysts is tested by the amine TPD technique. First, 50 mg of sample was reduced at 500 °C in a flow of H₂ for 3 h. After reduction, the sample was cooled in H₂ to room temperature and then isopropylamine was injected in to sample. After removing the excess isopropylamine, the sample was linearly heated in He to 800 °C at a heating rate of 20 °C/min. Masses 44, 41, and 17 were monitored to determine the evolution of isopropylamine, propylene, and ammonia, respectively.

3.3.2.5 Temperature Programmed Oxidation (TPO)

This technique is employed to analyze the amount and characteristics of the coke deposited on the catalysts during reaction. TPO of the spent catalysts was performed in a continuous flow of 2% O₂ in He while the temperature was linearly increased with a heating rate of 12 °C/min. The oxidation was conducted in a 1/4" quartz fixed-bed reactor after the spent catalyst was dried at 110 °C overnight, weighed (30 mg), and placed between two layers of quartz wool. The sample was further purged at room temperature by flowing 2% O₂ in He for 30 min to stabilize the signal before starting a run. The CO₂ produced by the oxidation of the coke species was converted to methane using a methanizer filled with 15% Ni/Al₂O₃ and operated at 400 °C in the presence of H₂. The evolution of methane was analyzed using an FID detector.

3.3.2.6 H₂ Chemisorption

H₂ Chemisorption is used to determine the degree of metal dispersion on the catalyst support. The extent of dispersion is defined as the ratio of the number of surface metal atoms in a catalyst to the total number present. A value of unity means that all metal atoms are exposed to reactants. Firstly, 50 mg of the prepared catalyst was pretreated in a 100 mL/min flow of hydrogen at 500 °C for 30 min. Then, the pretreated catalyst was purged in nitrogen at 500 °C for 1 h to remove chemisorbed hydrogen. After that, catalysts were cooled down in 10 mL/min flow of nitrogen to room temperature. The H₂ chemisorption was performed at room temperature and carried out by pulsing H₂ over clean metal surfaces until saturation. A thermal conductivity detector (TCD) measured the composition of the gas at the exit from the tube. Hydrogen chemisorption onto the metal surface depleted the H₂ content of the exist gas passing through the TCD. The consumption of H₂ due to chemisorption was determined by integration of the TCD signal output for metal dispersion determination.

3.3.3 Catalytic Activity Testing

The hydrocracking of *n*-paraffin feedstocks was carried out in a 3/4" O.D. continuous flow fixed-bed reactor under high pressure conditions. The schematic of the reactor system is shown in Figure 3.1 and the description of flow diagram is

shown in Table 3.1. The catalyst was firstly reduced for 3 h under flowing of hydrogen gas at the reduction temperature 500 °C. After the reduction, the temperature and pressure of the reactor were set to 310 °C and 500 psig in flowing of hydrogen gas. Then, the stream of *n*-paraffin feedstocks was fed into the reactor by using a high-pressure liquid pump. The flow of hydrogen gas and the reaction pressure were controlled by a mass flow controller and a back pressure regulator, respectively.

The liquid product was trapped and collected in a condenser while the gas product was analyzed online by using a Shimadzu GC-17A gas chromatograph equipped with a capillary HP-PLOT/Al₂O₃ “S” deactivated column and FID detector. Amount of gas product was corrected by using wet test gas meter (Ritter TG 05/2). The liquid product was analyzed by another gas chromatograph, Agilent 7890A equipped with a DB-5HT column and FID detector. Both gas and liquid products were collected and analyzed hourly.

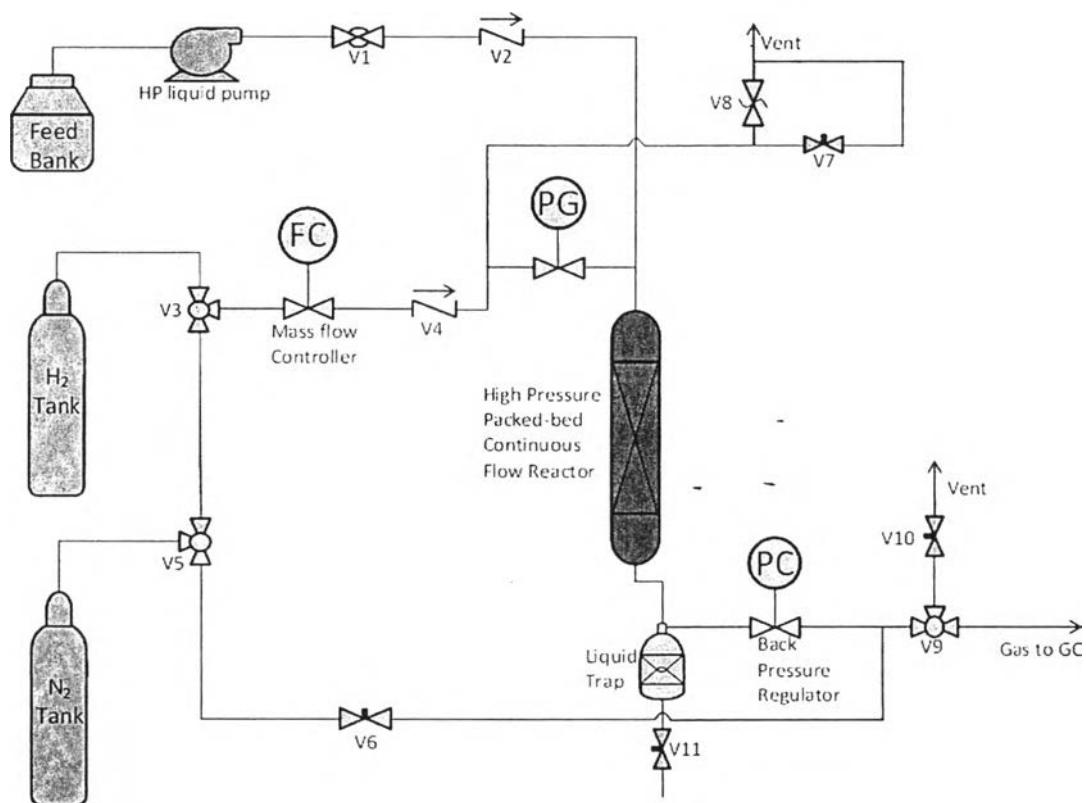


Figure 3.1 A schematic flow diagram of the hydrocracking of *n*-paraffin feedstocks experiment in high pressure packed-bed continuous flow reactor system.

Table 3.1 Description of flow diagram of the hydrocracking of *n*-paraffin feedstocks experiment in high pressure packed-bed continuous flow reactor system

No.	Items	Functions
1	V1	On-off valve for feedstock from high pressure liquid pump
2	V2	Checking valve for avoiding the backward flow of the feedstock
3	V3	Three ways valve for switching between nitrogen gas and hydrogen gas flow
4	V4	Checking valve for avoiding the backward flow of hydrogen or nitrogen gas
5	V5	Three ways valve for switching the direction of nitrogen gas flow
6	V6	Needle valve for controlling pressure in back pressure regulator
7	V7	Needle valve for releasing gas from the system
8	V8	Relief valve for releasing pressure overload in the system
9	V9	Three ways valve for switching between vent gas and gas to GC lines
10	V10	On-off valve for releasing pressure from back pressure regulator
11	V11	Metering valve for gathering the liquid product from condenser
12	FC	Flow controller to set flow rate for the desired H ₂ /feed molar ratio
13	PG	Pressure gauge for indicating pressure in packed bed reactor
14	PC	Back pressure regulator for controlling the pressure in reactor

The hydrocracking of *n*-paraffin feedstocks was conducted at temperature, pressure, LHSV, and H₂/Feed ratio as shown in Table 3.2.

Table 3.2 The reaction condition for hydrocracking of *n*-paraffin feedstocks

Parameters	Condition
Reaction temperature	310 °C
Reaction pressure	500 psig
LHSV	1.0 h ⁻¹
H ₂ /feed molar ratio	30.0

3.3.4 Product Analysis

3.3.4.1 *GC/FID*

The liquid products were analyzed by a gas chromatograph (Agilent 7890A) equipped with FID detector. The liquid products from the hydrocracking of *n*-paraffin feedstocks contain non-polar hydrocarbons. And the non-polar hydrocarbons were determined by using DB-5 column (non-polar column). The GC operating condition was summarized as follows:

Injector-temperature:	50 °C
Detector temperature:	380 °C
Carrier gas:	He
Column type:	Capillary column (DB-5HT: diameter 0.32 mm length 30 m)

Table 3.3 shows the chromatographic temperature program was used for liquid product analysis.

Table 3.3 The chromatographic temperature program for liquid product analysis

Step	Temperature (°C)	Rate (°C/min)	Hold time (min)
1	50	-	10
2	160	5	-5

For the quantitative calculations of liquid product, the areas of each peak analyzed hourly by a GC/FID (Agilent 7890A) were converted to gram unit by Equation 3.1. Because each peak of products can convert from area unit to gram unit directly.

$$\text{Weight of product } i \text{ (g)} = \frac{(\text{areas of product } i) \times (\text{grams of liquid product})}{\text{total areas of liquid product}} \quad (3.1)$$

The conversion and products selectivity of each product were calculated by Equations 3.2 and 3.3:

$$\text{Conversion (\%)} = \frac{\text{moles of feed converted} \times 100}{\text{moles of feed input}} \quad (3.2)$$

$$\text{Selectivity to product } i \text{ (\%)} = \frac{(\text{moles of product } i) \times 100}{\text{moles of overall product}} \quad (3.3)$$

The composition of gas product was analyzed qualitatively online hourly by GC/FID (Shimadzu GC-17A). The GC operating condition was summarized as follows:

Injection temperature:	150 °C
Detector temperature:	250 °C
Carrier gas:	He
Column type:	capillary HP-PLOT/Al ₂ O ₃ "S" deactivated column

The following chromatographic temperature program was used for gas product analysis:

Table 3.4 The chromatographic temperature program for gas-phase product analysis

Step	Temperature (°C)	Rate (°C/min)	Hold time (min)
1	40	-	3
2	70	15	0
3	170	5	0
4	190	1	1

For the quantitative calculations of gas product, the areas of each peak analyzed hourly by GC/FID (Shimadzu GC-17A) were converted to gram unit by using comparing with the area of methane from gas standard by mol % (equal to vol %), as shown in Equations 3.4 and 3.5.

$$\text{Volume of product } i \text{ (mL)} = \frac{(\text{areas of product } i) \times (\text{volume of gas product})}{(\text{molecular weight of product } i) \times (\text{total area of gas product})} \quad (3.4)$$

$$\text{Weight of product } i \text{ (g)} = \frac{(\text{volume of product } i) \times (\text{molecular weight } i)}{(22.4) \times (1,000)} \quad (3.5)$$

The calculations of conversion, products selectivity and yield of product are defined as shown in Equations 3.6, 3.7 and 3.8, respectively.

$$\text{Conversion (\%)} = \frac{(\text{weight of total products}) \times 100}{\text{weight of (total products + remaining feed)}} \quad (3.6)$$

$$\text{Selectivity of product } i \text{ (\%)} = \frac{(\text{weight of product } i) \times 100}{\text{weight of total products}} \quad (3.7)$$

$$\text{Yield of product } i \text{ (\%)} = (\text{conversion}) \times (\text{selectivity of product } i) \quad (3.8)$$

3.3.4.2 Gas Chromatography–Mass Spectrometry (GC-MS)

Gas chromatography–mass spectrometry (GC-MS) is an analytical technique that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances in a test sample. The main application of GC-MS is identification of unknown samples. The GC-MS is composed of two major building blocks: the gas chromatograph and the mass spectrometer. The gas chromatograph utilizes a capillary column which depends on the column's dimensions (length, diameter, film thickness) and the phase properties. The difference in the chemical properties of each molecule in a mixture and their relative affinity for the stationary phase of the column will promote separation of the molecules as the sample move along with the length of the column. The molecules are retained by the column and then elute from the column at different times, and this allows the mass spectrometer downstream to capture, ionize, accelerate, deflect, and detect the ionized molecules separately. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass-to-charge ratio.

The GC operating condition was summarized as follows:

Injector temperature:	320 °C
Detector temperature:	380 °C
Carrier gas:	He
Column type:	Capillary column (Rxi-5Sil: diameter 0.25 mm length 30 m)

Table 3.5 shows the chromatographic temperature program used for liquid product analysis.

Table 3.5 The chromatographic temperature program for liquid product analysis

Step	Temperature (°C)	Rate (°C/min)	Hold time (min)
1	40	-	10
2	55	1	5
3	200	5	5