

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

##### 3.1.1 Feedstock

- Hydrogenated biodiesel derived from jatropha oil (obtained from PTT RTI)

##### 3.1.2 Chemicals for Catalyst Preparation

- Sodium aluminate (53.5% Al, Sigma-Aldrich)
- Colloidal silica (Ludox HS-40, Sigma-Aldrich)
- Sodium hydroxide (97% purity, Ajax Finechem)
- Ammonium hydroxide (Merck)(99wt%, Ajax Finechem)
- Tetraammineplatinum (II) chloride hydrate (99.99 %, Aldrich)

##### 3.1.3 Standard Chemicals and Others

- Carbon disulphide (99.5% PS, Panreac)
- Acetone (99% purity, LabScan)
- Methanol (99% purity, LabScan)
- Deionized water

##### 3.1.4 Gases

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

## 3.2 Equipment

### 3.2.1 Preparation and Characterization of Pt/HY Catalyst

- Microwave digestion system (CEM Mars-5)
- Oven
- Hot & stirring plate (Cole Parmer)
- Bruker D8 Advance X-ray diffractometer
- Bruker SRS3400 X-ray fluorescence spectrometer
- Scanning electron microscopy (Hitachi/S-4800)
- BET surface area analyzer (Quantachrome/Autosorb-1)
- Thermo finnigan TPDRO 1100 equipped with flame ionization detector
- Atomic absorption spectroscopy (SpectrAA,300)

### 3.2.2 Catalyst Performance Testing

- High pressure packed-bed continuous flow reactor system consisting of
  - Mass flow controller (Brooks instrument 5850E)
  - High pressure liquid pump (Waters 515 HPLC)
  - Back pressure regulator (SIEMENS)
  - 3/4" O.D.x16" long stainless steel reactor
  - Tubular furnace with a temperature controller
- Gas chromatograph (Shimadzu GC-17A) equipped with a capillary HP-PLOT/Al<sub>2</sub>O<sub>3</sub> "S" deactivated column and FID detector
- Gas chromatograph (Agilent GC 7890 equipped with FID/TCD)
- Gas chromatograph-simulated distillation (Varian/CP-3800)

### 3.3 Methodology

#### 3.3.1 Synthesis of NaY Zeolite Catalyst in Different Crystal Size ( $4\text{Na}_2\text{O} : 1\text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 180\text{H}_2\text{O}$ )

Colloidal silica and sodium aluminate was used as Si and Al sources, respectively. Na source was obtained from sodium hydroxide while the organic cation agent was tetramethylammonium hydroxide.

a) Solution A was prepared by mixing colloidal silica and deionized water. Then, the mixture was kept under stirring at room temperature and atmosphere for 1 h.

b) Solution B was prepared by mixing the sodium aluminate and deionized water. The mixture was then kept under stirring at room temperature and atmosphere for 1 h.

c) Solution B was slowly added to solution A, followed by sodium hydroxide under vigorous stirring.

d) The mixture was then stirred in to a closed glass vessel for different aging times (1, 2, 4, 6 days) at room temperature.

e) The solution was treated at different temperatures (90, 100, 110 °C) for 2 h in a vessel lined with Teflon using a microwave digestion system.

f) The prepared Y zeolite was then cooled down to ambient temperature, and then was centrifuged at 3,000 rpm for 0.5 h. After that the solid was washed several times with deionized water to remove excess NaOH. The washed sample was dried overnight at 100 °C and calcined at 500 °C for 2.5 h.

#### 3.3.2 Preparation of the Proton- Type Y Zeolite (HY Zeolite)

##### 3.3.2.1 *Ammonium Ion-exchange of NaY Zeolite*

NaY zeolite was added by 0.5 M  $\text{NH}_4\text{OH}$  aqueous solution; the zeolite to ammonium hydroxide solution ratio was 1:80, after that the mixture was heated at 80 °C for 1 h and then the residue was filtered and washed with distilled water to remove ions by using a centrifugation. The above cycle was repeated three times. Last step, the synthesized HY was dried overnight in an oven at 110 °C. The Na-form crystal was thus changed to  $\text{NH}_4$  - form catalyst.

### 3.3.2.2 *HY-Type Zeolite*

The  $\text{NH}_4\text{Y}$  zeolite was converted to HY zeolite by removing  $\text{NH}_3$  from the catalyst surface. The  $-\text{NH}_3$  can be removed by thermal treatment of the  $\text{NH}_4\text{Y}$  zeolite. This was done by heating a sample in an air stream at  $500\text{ }^\circ\text{C}$  for 2.5 h by heating them from room temperature to  $500\text{ }^\circ\text{C}$  at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . After the catalyst was cooled down, it was stored in a glass bottle in desiccators for further study.

### 3.3.3 Preparation of Pt/HY Catalyst by Incipient Wetness Impregnation (IWI)

HY zeolite was calcined at  $500\text{ }^\circ\text{C}$  for 3 h with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  to remove organic residues from the zeolite. After that, the zeolite was loaded with 0.1 wt% Pt by incipient wetness 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 5 g of zeolite drop wise using a micro syringe to obtain a Pt/HY catalyst with a desired Pt loading. Thirdly, the wet zeolite was dried in an oven at  $110\text{ }^\circ\text{C}$  for overnight. Finally, catalyst was calcined in a furnace at  $350\text{ }^\circ\text{C}$  for 3 h with the heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . Then, a bifunctional catalyst was obtained in metal oxide forms.

## 3.4 **Characterization of Synthesized HY Zeolite**

### 3.4.1 X-ray Diffractometer (XRD)

The crystalline phase of prepared HY zeolite was analyzed by a Rigaku X-ray diffractometer, RINT-2200 with Cu tube for generating  $\text{CuK}\alpha$  radiation ( $1.5406\text{ \AA}$ ). The system consists of a voltage generator of 40 kV. The  $2\theta$  is in the range between 10 and 70 with a scanning rate of  $5^\circ/\text{s}$ . This analysis is generally performed based on the fact that an X-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between the pattern of an unknown and sample, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. When comparing the same crystalline substance of different samples, the

higher intensity indicates the higher content. The average crystallite sizes ( $D$ ) of the metals in the samples will be estimated by Scherrer equation,  $D = 0.9\lambda/\beta \cos\theta$ , where  $\theta$  is the diffraction angles, and  $\beta$  is the full width at half maximum.

#### 3.4.2 X-ray Fluorescence Spectrometer (XRF)

The quantity of Si and Al on the HY zeolite were analyzed by XRF technique, Philips model PW 4400. With a primary X-ray excitation source from an X-ray tube, the X-ray can be absorbed by the atom, and transfer all of its energy to an innermost electron. During the process, if the primary X-ray has sufficient energy, electrons are ejected from the inner shell, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells, and the process gives off a characteristic X-ray, whose energy is the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces X-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. The intensities of observed lines for a given atom vary according to the amount of that atom present in the specimen.

#### 3.4.3 Scanning Electron Microscopy (SEM)

SEM analysis was done on a Hitachi/S-4800 scanning electron microscope (SEM). To prepare the sample for SEM, a drop of dilute colloidal solution of the uncalcined sample was dropped onto the SEM sample stud surface, and the sample stud was then dried at 60 °C for 3 h. Shortly before acquiring an SEM image, the sample was coated with gold. From the SEM images, small NaY crystals are envisioned as cubic particles in order to estimate the particle size.

#### 3.4.4 Brunauer-Emmett-Teller Method (BET)

The total surface area and external surface area of catalysts was 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,  $N_2$  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.

#### 3.4.5 Temperature Programmed Desorption (TPD) of Isopropylamine

Bronsted acid sites of Pt/HY catalyst was measured by isopropylamine TPD technique. First, 50 mg of sample was pretreated at 500 °C in a flow of He for 1 h. After the pretreatment, the sample was cooled in He to 30 °C and then isopropylamine was injected with He into the sample. After removing the excess of isopropylamine by flowing He, the sample was linearly heated 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. The amount of Bronsted site was calibrated with propene.

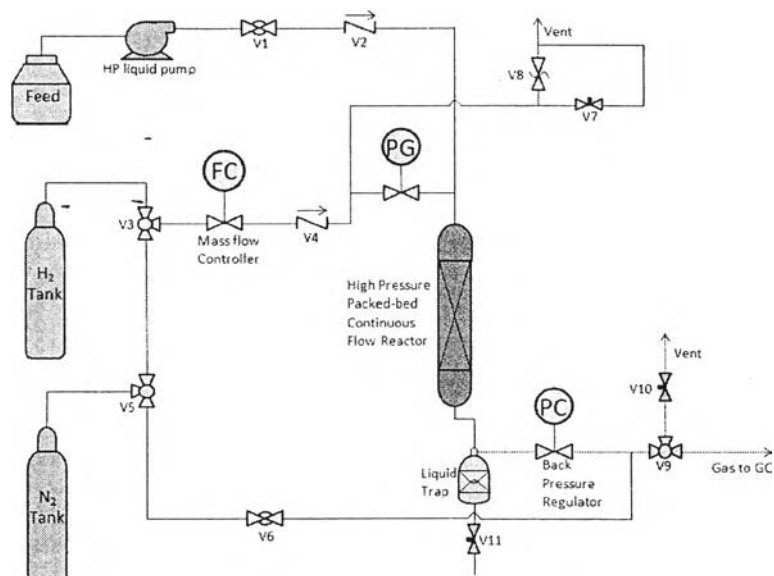
#### 3.4.6 Temperature Programmed Oxidation (TPO)

This technique was 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% O<sub>2</sub> 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% O<sub>2</sub> in He for 30 min to stabilize the signal before starting a run. The CO<sub>2</sub> produced by the oxidation of the coke species was converted to methane using a methanizer filled with 15% Ni/Al<sub>2</sub>O<sub>3</sub> and operated at 400 °C in the presence of H<sub>2</sub>. The evolution of methane was analyzed using an FID detector.

### 3.5 Catalytic Activity Testing

The hydrocracking of hydrogenated biodiesel derived from jatropha oils was carried out in a stainless steel 3/4" O.D., continuous flow fixed-bed reactor under high pressure conditions. The schematic of the reactor system and the description of flow diagram are shown in Figure 3.1. The catalyst was firstly reduced for 3 h under flowing H<sub>2</sub> at 500 °C. After the reduction, temperature and pressure of the reactor were set to the desired value in a flowing H<sub>2</sub>. Then, the stream of hydrogenated biodiesel derived from jatropha oil was fed into the reactor by using a high-pressure liquid pump. The flow of carrier 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/Al<sub>2</sub>O<sub>3</sub> "S" deactivated column and FID detector. Amount of gas product was measured by using a wet test gas meter (Ritter TG 05/2). The liquid product was analyzed by another gas chromatograph, Agilent 7890 equipped with a DB-5HT column and FID detector. Both gas and liquid products were collected and analyzed hourly.



**Figure 3.1** Schematic of the reactor system.

The hydrocracking of hydrogenated biodiesel derived from jatropha oil is conducted at temperature, pressure, LHSV, and H<sub>2</sub>/Feed ratio as shown in Table 3.1.

**Table 3.1** The reaction conditions for hydrocracking of hydrogenated biodiesel derived from jatropha oil

Parameter	Condition
Reaction temperature	310 °C
Reaction pressure	500 psig
LHSV	1.0 h <sup>-1</sup>
H <sub>2</sub> /feed molar ratio	30.0

### 3.5.1 Liquid Product Analysis

The liquid products were analyzed by a gas chromatograph (Agilent 7890) equipped with FID detector. The liquid products from the hydrocracking of hydrogenated biodiesel derived from jatropha contain non-polar hydrocarbons. 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)

The following chromatographic temperature program was used for liquid product analysis.



**Table 3.2** 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 7890) were converted to gram unit by Equation 3.1 because the each peak of products detected by FID detector can be varied from area unit to gram unit directly.

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

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

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

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

### 3.5.2 Gas Product Analysis

The composition of gas product was analyzed qualitatively on-line 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 <sub>2</sub> O <sub>3</sub> "S" deactivated column

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

**Table 3.3** The chromatographic temperature program for gas-phase product analysis

Step	Temperature (°C)	Rate (°C/min)	Hold time (min)
1	40	-	10
2	150	5	5
3	175	2	2

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 comparing with the area of methane from gas standard by mol % (equal to vol %), as shown in Equations 3.4 and 3.5.

$$\text{Volume of product i (ml)} = \frac{(\text{areas of product i}) \times (\text{volume of gas product}) \times (\text{mol \% of methane})}{(\text{mol of carbon atom}) \times (\text{reference area of methane})} \quad (3.4)$$

$$\text{Weight of product i (g)} = \frac{(\text{volume of product i}) \times (\text{molecular weight i})}{(22.4) \times (1000)} \quad (3.5)$$

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

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

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

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