CHAPTER III
EXPERIMENTAL

3.1 Materials

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

3.1.2 Catalyst Supports and Metal Precursors
- Tetraammineplatinum (II) chloride hydrate (99.99 %, Aldrich)
- HY zeolite (SiO_2/Al_2O_3 ratio of 100, Tosoh Company)

3.1.3 Binder and Binder Solution
- Pseudo boehmite binder Pural SB1 (Sasol)
- Glacial acetic
- NH_4NO_3

3.1.4 Standard Chemicals and Others
- Pentadecane (99 % purity, Aldrich)
- Hexadecane (99 % purity, Aldrich)
- Heptadecane (99 % purity, Aldrich)
- Octadecane (99 % purity, Aldrich)
- Dodecane (99 % purity, Merck)
- Carbon disulphide (99.5 % PS, Panreac)
- Acetone (98 % purity, Labscan)
- Methanol (99.9 % purity, Labscan)
- Deionized water

3.1.5 Gases
- Hydrogen (99.99 % purity. BIG)

- Nitrogen (99.99 % purity, TIG)
- Helium (99.995 % purity, TIG)
- Air zero (99.99 % purity, TIG)

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), ¼" O.D.x16" long stainless steel reactor, and a three-zone tubular furnace with a temperature controller (Cabolite).

- Gas chromatograph (Agilent GC 7890 equipped with injector, DB-5 column , and FID)

- Gas chromatograph-Simulated Distillation (Varian/ CP-3800)

- Shimadzu GC-17A gas chromatograph equipped with a capillary HP-PLOT/Al_2O_3 "S" deactivated column and FID detector

- Surface area analyzer (SAA, Quantachrome/Autosorb 1MP)
- Atomic absorption spectroscopy (SpectrAA,300)
- Bulk density testing equipment (ASTM D4164)
- Attrition lost testing equipment
- Single pellet radial crushing strength testing machine
- Bulk crushing strength equipment
- Hot plate & stirrer (Cole Parmer)
- Oven
- Stainless die for trilobe extrusion forming

3.3 Methodology

3.3.1 HY Catalyst Formulation

HY zeolite was mixed with pseudo boehmite binder with 20, 40, 60, and 80 wt% of extruded catalysts. The 3 vol% of glacial acetic acid was added for peptization. Next, the mixture was kneaded homogeneously. After that, the dough was extruded using the extrusion die. Then, the extrudates were cooled down to room temperature at 25 °C overnight, dried at 110 °C for 7 h. Finally, it was calcined at 500 °C for 4 h.

3.3.2 Catalyst Treatment with Ammonium Nitrate

The extruded HY zeolite was added by 0.5M of NH_4NO_3 aqueous solution. After that the mixture was heated at 80 °C for 3 h. Then the powder was washed by distilled water to remove nitrate ions and repeated it several times. The last step, sample was dried overnight in an oven at 110 °C. Finally, the catalyst was heated in an air stream at 550 °C for 5 h with a heating rate of 10 °C/min. After the extruded catalyst was cooled down, it was stored in a bottle in desiccators.

3.3.3 Pt Loading on HY Extrudate.

The zeolite was loaded with Pt by ion-exchange method. Firstly, the extrudates of HY zeolite were suspended in 150 mL solution of $Pt(NH_3)_4Cl_2$ in a beaker. Secondly, the beaker was placed into an oil bath and stirred at 90 °C for 12 h. Thirdly, the precipitate of ion-exchanged Pt/HY zeolite was thoroughly washed with deionized water. Finally, the extrudates were dried at 110 °C for 12 h, and calcined for 3 h at 350 °C (heating rate 10 °C/min). Then, a bifunctional catalyst was obtained in metal oxide forms.

3.3.4 Catalyst Characterization

3.3.4.1 Crystalline Phase Determination

X-ray diffractometer model D8-Advanced, Bruker was used for determination of crystalline phases in fired samples. Prior to the analysis, fired samples were ground and mounted in a sample holder and investigated a diffraction patterns using Cu-Kα radiation with scanning speed of 0.02 degree per minute from 5-50 degree of 2 theta.

3.3.4.2 Brunauer-Emmett-Tellet Method (BET)

The surface area of the fresh and spent 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.

3.3.4.3 Temperature Programmed Reduction (TPR)

Temperature programmed reduction was 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 ¼ " O.D. quartz tubular 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 be exposed to a stream of 5% H_2/Ar with a flow rate of 20 mL/min. After that, the sample was heated to 800 °C with a ramping 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.

3.3.4.4 Temperature Programmed Desorption (TPD) of
Isopropylamine

The acidity of prepared catalysts was tested by the amine TPD technique. First, 50 mg of sample was reduced at 500 °C in a flow of H_2 for 3 h. After reduction, the sample was cooled in H_2 to room temperature and then isoproplyamine was injected in to the 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.

3.3.4.5 Temperature Programmed Desorption (TPD) of Ammonia

Acidity properties of the catalysts were determined by ammonia temperature programmed desorption, NH_3-TPD. The NH_3-TPD was performed in a homemade flow apparatus using a quarter inch quartz tube reactor. Sample was first reduced at 400 °C in H_2 flow of 30 mL/min for 1 h. And then the reactor was cooled to 50 °C in He, exposed to 10 % NH_3/He for 30 min, purged by He for 1 h at 50 °C in order to eliminate the physical adsorbed NH, Temperature programmed desorption was conducted by ramping to 800 °C at 10 °C/min and NH, (m/e = 17) in effluent was detected and recorded as a function of temperature by an online MS detector (MKS Cirrus).

3.3.5 Mechanical Catalyst Characterization

3.3.5.1 Diameter and Length

After firing, the sample's diameter and length were measured by a venire caliper.

Figure 3.1 Picture of samples illustrating the diameter and length.

3.3.5.2 Bulk Density

First of all, the sample was dried at 150 °C for 4 h. After heating, the sample was cooled in a desiccator to eliminate the possibility of moisture adsorption prior to the test. The 100 mL of the specimen was poured carefully into the graduated cylinder using a funnel. Then, the sample was tapped with 1000 times using a tapping device showed in Figure 3.2. When the tapping stop had

completed, the tapped volume was read by estimating the average level of the catalyst in the cylinder followed a standard test method ASTM D4164.
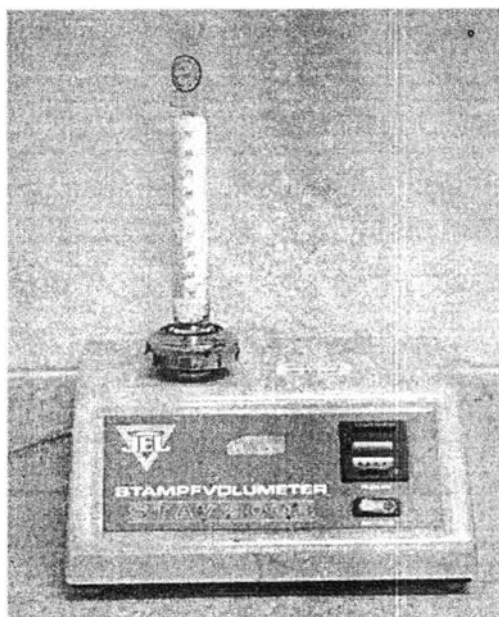

Figure 3.2 Picture of bulk density testing equipment.

3.3.5.3 Attrition Loss

First, 100 g of the prepared sample (*A*) was poured into the cylindrical drum with inside dimensions of 10 in. diameter and 6 in. length with a single radial baffle 2 in. A lid secured to the container with Allen-head screws, wing nuts or other suitable means as to assure that no fines escape during the test. Secondly, the test cylinder was carefully closed and sealed before rotation. The ball mill roller was used to rotate the cylindrical drum at 1800 revolutions with a rate of 60 rpm. Figure 3.3 shows specimen in the cylindrical drum laid on the ball mill roller. When the ball mill roller was rotating, the test cylinder was tapped with a rubber mallet several times to roll the specimen within the test cylinder. Thirdly, the No. 20 (850-μm) sieve was used to sieve the fined particle separated from the specimen. The weight of specimen remaining on the sieve was recorded as *B*. The percentage of attrition loss was calculated as % = (*A* −*B*)/*A* x 100 followed ASTM D4058.
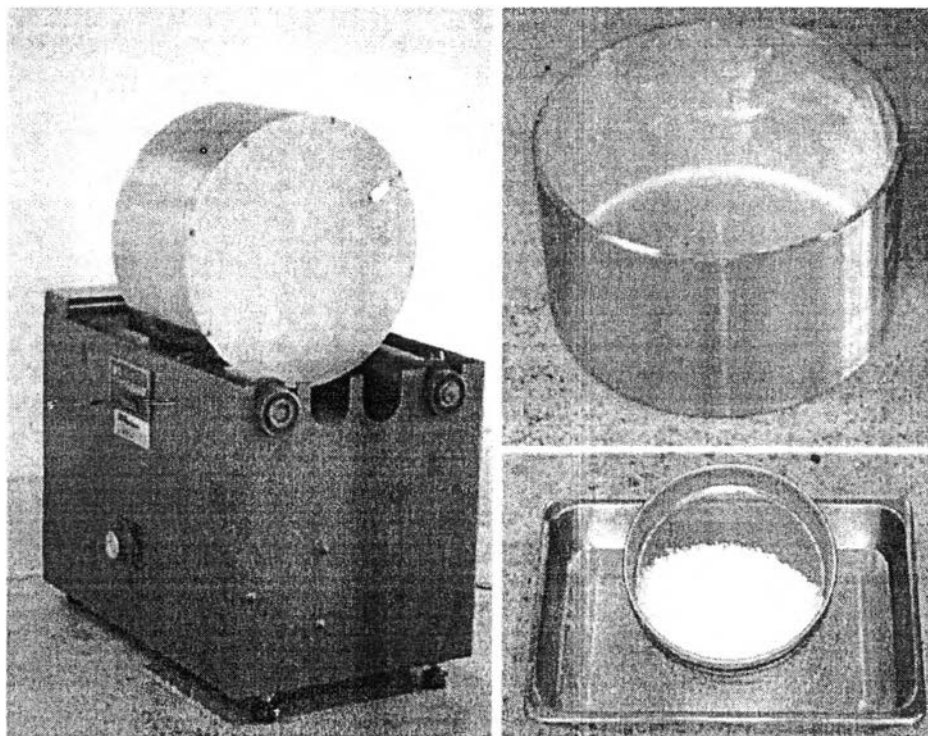
Figure 3.3 Picture of attrition lost testing equipment.

3.3.5.4 Radial Crushing Strength

The sample was dried at 150 °C for 4 h. After heating, the sample was cooled in a desiccator. The prepared sample of individual pieces was place between the anvils of the compressing device. Each of pellets was orient in the radial orientation before crushing. Figure 3.4 shows pellets in radial orientations. Then, the sample was applied with increasing force until the pellet crushed or collapsed. The force was detected at the instant collapse. After that, the strength of each pellet was calculated by following ASTM D4179.
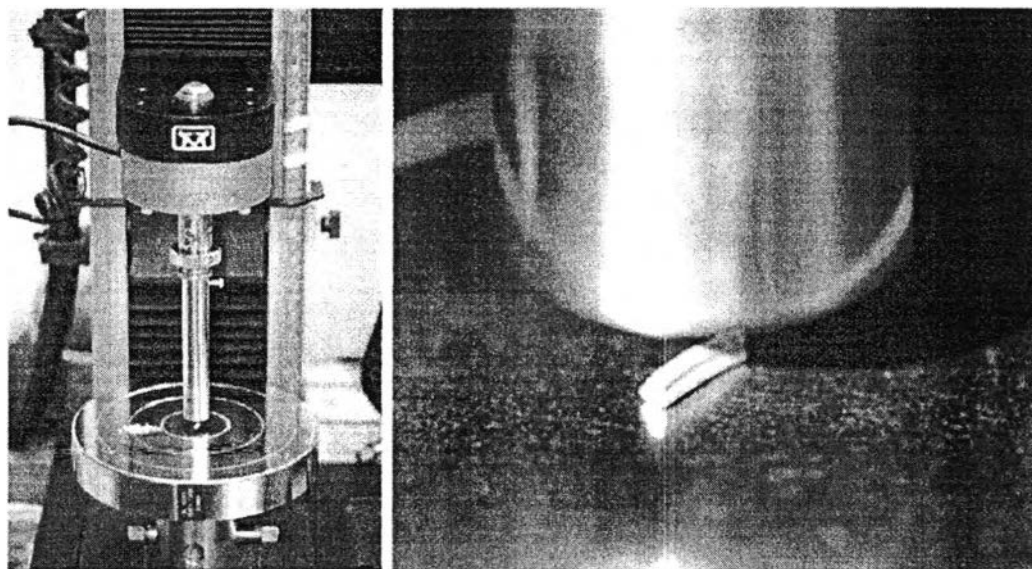
Figure 3.4 Picture of single pellet radial crushing strength testing machine.

3.3.6 Catalytic Activity Testing

The hydrocracking and hydroisomerization of hydrogenated biodiesel derived from jatropha oil was carried out in a 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 3.5. The catalyst was firstly reduced for 3 h under flowing H_2 at the reduction temperature of each catalyst. After the reduction, the temperature and pressure of the reactor were set to the desired value in a flowing H_2. Then, the stream of hydrogenated biodiesel 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_2O_3 "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 7890 equipped with a DB-5HT column and FID detector. Both gas product and liquid product were collected and analyzed hourly.
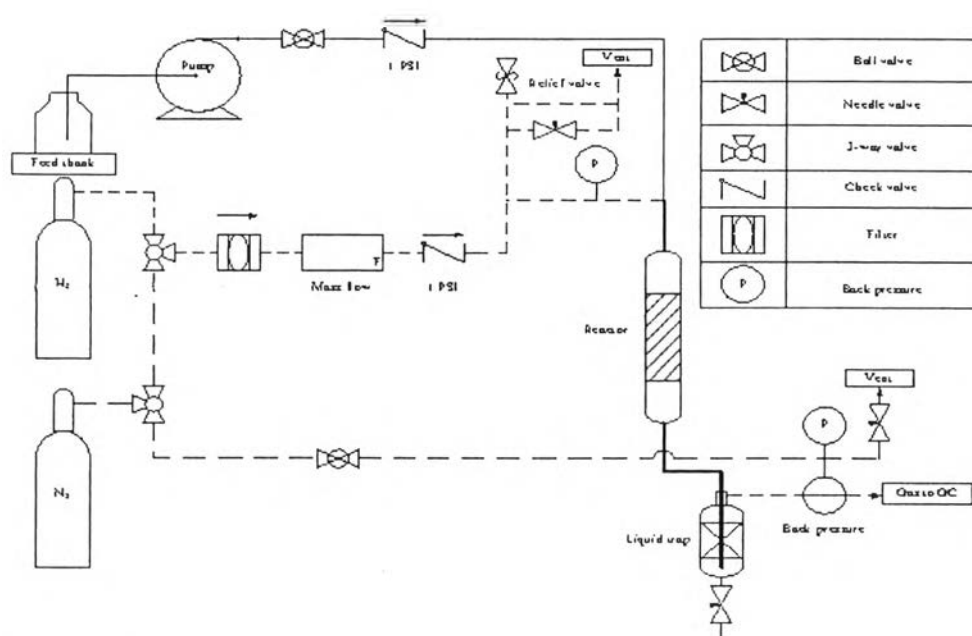

Figure 3.5 Schematic diagram of the reactor system.

The hydrocracking of hydrogenated biodiesel derived from jatropha oil is conducted at temperature, pressure, LHSV, and H_2/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^{-1}
H_2/feed Molar Ratio	30.0

3.3.7 Product Analysis

3.3.7.1 GC/FID

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. Each peak detected by the FID detector can be varied from area unit to gram unit directly.

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

For another quantitative calculations of liquid product, eicosane ($C_{20}H_{42}$) was used as the internal standard. The response factors of each product are calculated based on the following formula (Bruschweiler and Hautfenne, 1990) as shown in Equation 3.2:

$$R_x = \left(\frac{m_{is}}{m_x}\right) \times \left(\frac{A_x}{A_{is}}\right) \qquad 3.2)$$

where

R_x is the response factor of reference substance x

m_{is} is the mass in g of internal standard

m_x is the mass in g of reference substance x

A_x is the peak area of reference substance x

A_{is} is the peak area of internal standard

The composition of each product was calculated following formula, as shown in Equation 3.3:

$$R_x = \frac{1}{R_x} \times \left(\frac{m'_{is}}{m'_x}\right) \times \left(\frac{A'_x}{A'_{is}}\right) \qquad (3.3)$$

where

m'_x is percentage of mass of component x in sample

R_x is response factor of component x in sample

m'_{is} is mass in g of internal standard in sample

m'_x is mass in g of sample

A'_x is peak area of component x in sample

A'_{is} is peak area of internal standard in sample

The conversion and products selectivity of each product were calculated by Equations 3.4 and 3.5:

$$\text{Conversion (\%)} = \frac{(\text{moles of feed converted}) \times (100)}{(\text{moles of feed input})} \qquad (3.4)$$

$$\text{Selectivity to product i (\%)} = \frac{(\text{moles of product i}) \times (100)}{(\text{moles of overall products})} \qquad (3.5)$$

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$_2$O$_3$ "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 3.6 and 3.7.

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

(3.6)

$$\text{Weight of product i (g)} = \frac{(\text{volume of product i (ml)})\times(\text{molecular weight i(g/mol)})}{(22.4(\text{L/mol}))\times(1000)}$$

(3.7)

The calculations of conversion, products selectivity, and yield of product are defined as shown in Equations 3.8, 3.9, and 3.10 respectively.

$$\text{Conversion (\%)} = \frac{(\text{weight of total products(g)}) \times (100)}{\text{weight of (total products(g) + remaining feed(g))}} \quad (3.8)$$

$$\text{Selectivity of product i (\%)} = \frac{(\text{weight of products i(g)}) \times (100)}{\text{weight of total products(g)}} \quad (3.9)$$

$$\text{Yield of product i (\%)} = (\text{conversion}) \times (\text{selectivity of product i}) \quad (3.10)$$

3.3.7.2 Simulated Distillation Gas Chromatography

SIMDIST GC was used to analyze boiling point of liquid product by using ASTM D2887 at the following condition;

Initial temperature	30	°C
Time at initial temperature	0.01	min
Heating rate	20	°C
Final temperature	320	°C
Holding time	8.50	min