CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Feedstock

- Jatropha oil (PTT)

3.1.2 Chemicals

- Tetraammineplatinum (II) chloride hydrate (99.99 %, Aldrich)
- HY zeolite (SiO_2/Al_2O_3 ratio of 100, Tosoh Company)
- Palladium chloride ($PdCl_2$, 99.9%, Aldrich)
- Tetraisopropyl orthotitanate (TIPT, $Ti(OCH(CH_3)_2)_4$, 98%, Merck)
- Acetylacetone (ACA, $CH_3COCH_2COCH_3$, 99%, Merck)
- Laurylamine hydrochloride (LAHC, $CH_3(CH_2)_{11}NH_2HCl$, 98%, Merck)
- Ethanol (C_2H_6O, 99.9%, Labscan)
- Acetone (98% purity, Labscan)
- Distilled water

3.1.3 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

3.2.1 Preparation and Characterization of Core-shell Catalyst

- Oven
- Hot & stirrer plate (Cole Parmer)
- Bruker D8 Advance X-ray diffractmeter
- Bruker SRS3400 X-ray fluorescence spectrometer
- Scanning electron microscopy (Hitachi/S-4800)
- BET surface area analyzer (Quantachrome/Autosorb-1)
- Atomic absorption spectroscopy (SpectrAA,300)

3.2.2 Catalyst Performance Testing

- 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), ¾" 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
- Atomic absorption spectroscope (SpectrAA,300)
- Surface area analyzer (SAA, Quantachrome/Autosorb 1MP)
- Temperature programmed reduction (TPR) apparatus
- Temperature programmed oxidation (TPO) apparatus
- Temperature programmed desorption (TPD) apparatus
- Atomic absorption spectroscopy (SpectrAA,300)
- Hot & stirrer plate (Cole Parmer)
- Oven

3.3 Methodology

3.3.3 Catalyst Preparation

- *3.3.1.1 Preparation of 0.3 wt% Pt/HY Catalyst by Ion-exchange (IE)*

First, the HY zeolite was dried overnight at 110 °C. Then the dried zeolite was calcined at 500 °C for 3 h (heating rate 10 °C/min). Pt precursor solution was prepared by mixing 0.03133 g of $Pt(NH_3)_4C_{l2}$ with 180 mL of deionized water in the flask. Five gram HY zeolite was added into the Pt precursor solution. The flask was placed into an oil bath and stirred at 90 °C for 12 h. The precipitate of ion exchanged Pt/HY zeolite was thoroughly washed with deionized water until a pH of 7.5 was obtained. The particles were dried at 110 °C for 12 h (overnight). The dried particles were calcined for 3 h at 350 °C (heating rate of 10 °C/min).

3.3.1.2 Preparation of Pd/TiO_2 by Combined Single-step Sol-gel Process with Surtfactant-assisted Templating Method (SATM).

ACA was first introduced into the TIPT with the TIPT to ACA molar ratio equal to unity. The mixed solution was shaken until homogeneous mixing. Afterwards, a 0.1 M LAHC aqueous solution with pH of 4.2 was added to the ACA-modified TIPT solution, in which the molar ratio of TIPT to LAHC was tailored to a value of 4 in order to control the porosity of the TiO_2. The mixture was continuously stirred at 40 °C overnight to obtain transparent yellow sol. A required amount of palladium chloride solution for the desired Pd loading of 1 wt% was incorporated into the aged transparent sol solution. The resultant mixture was further aged at 40 °C for 1 h to acquire a homogeneous solution. The gel was then formed by placing the sol-containing solution in an oven at 80 °C for a week for complete gel formation. Afterwards, the gel was dried at 80 °C overnight. Finally, the dried gel was calcined at 500 °C for 4 h to remove the LAHC template, and subsequently the desired catalyst was achieved.

3.3.1.3 Preparation of Core-shell Catalysts

ACA was first introduced into the TIPT with the TIPT to ACA molar ratio equal to unity. The mixed solution was shaken until homogeneous mixing. Afterwards, a 0.1 M LAHC or CTAB aqueous solution with pH of 4.2 was added to the ACA-modified TIPT solution, in which the molar ratio of TIPT to LAHC or CTAB was tailored to a value of 4 in order to control the porosity of the TiO_2. The mixture was continuously stirred at 40 °C overnight to obtain transparent yellow sol. A required amount of palladium chloride solution for the desired Pd loading of 1 wt% was incorporated into the aged transparent sol solution. Then add desired amount of Pt/HY catalyst and stir until the solution is homogeneous. The resultant mixture was further aged at 40 °C for 1 h to acquire a homogeneous solution. The gel was then formed by placing the sol-containing solution in an oven at 80 °C for a week for complete gel formation. Afterwards, the gel was dried at 80 °C overnight. Finally, the dried gel was calcined at 500 °C for 4 h to remove the LAHC template, and subsequently the desired catalyst was achieved.

3.3.2 Catalyst Characterization

3.3.2.1 X-ray Diffraction (XRD)

The crystalline phase of prepared catalyst was analyzed by a Rigaku X-Ray Diffraction, RINT-2200 with Cu tube for generating CuKα radiation (1.5406 Å). The system consists of a voltage generator of 40 kV. The 2θ is in the range between 5 and 80 with a scanning rate of 5°/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.

3.3.2.2 Transmission Electron Microscopy (TEM)

TEM analysis was done on the JEM-2100 transmission electron microscope equipped with EDX operated at 200 kV. To prepare the sample for TEM, the catalysts were dispersed in absolute ethanol ultrasonically, and the solutions were dropped on the copper grids coated with a formvar film.

3.3.2.3 Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (SpectrAA, 300) was 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 syring filter. Finally, samples were transferred into a volumetric flask to make a desired volume using water.

3.3.2.4 Brunauer-Emmett-Teller (BET)

The surface areas of the fresh and spent catalysts were 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.

3.3.2.5 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 would 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.

3.3.2.6 Temperature Programmed Desorption (TPD)

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 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.

3.3.2.7 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_2 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_2 in He for 30

min to stabilize the signal before starting a run. The CO_2 produced by the oxidation of the coke species was converted to methane using a methanizer filled with 15% Ni/Al_2O_3 and operated at 400 °C in the presence of H_2. The evolution of methane was analyzed using an FID detector.

3.3.3 Catalytic Activity Testing

The hydrocracking of jatropha oils 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 3.1. The catalyst was firstly reduced for 3 h under flowing H_2 at the reduction temperature of 500 °C. 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 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 liquid trap 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.

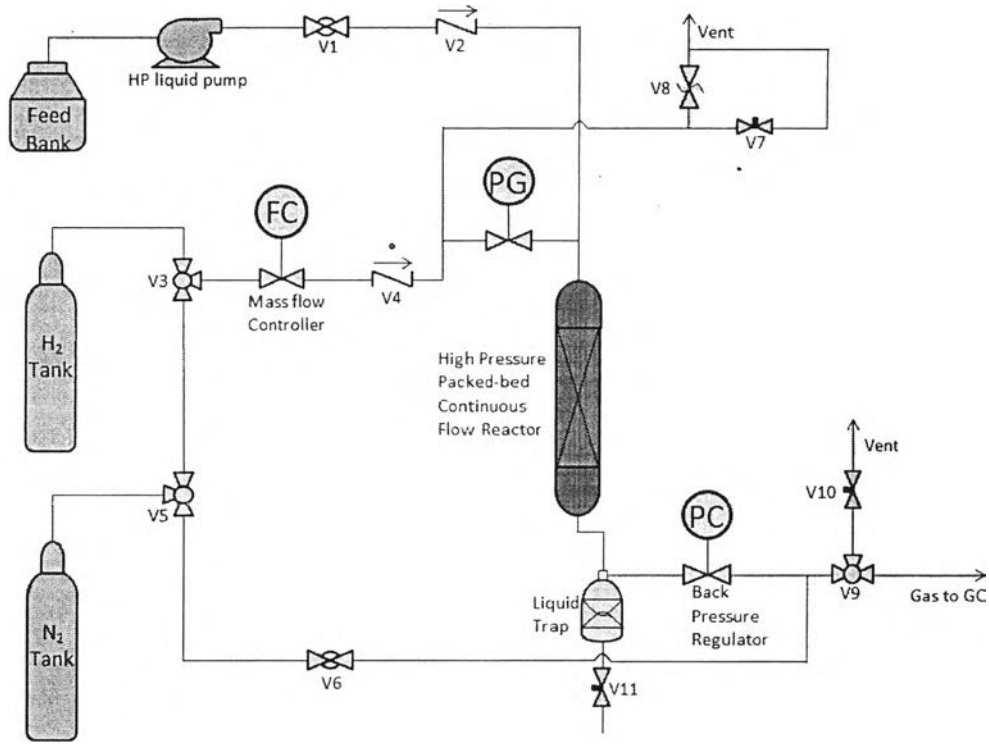

Figure 3.1 Schematic of the reactor system.

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.	Item	Function
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 N_2 and H_2 gas flow
4	V4	Checking valve for avoiding the backward flow of N_2 and H_2 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

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

No.	Item	Function
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 reaction conditions for one-pot reaction of jatropha oil over prepared catalysts are shown in Table 3.2.

Table 3.2 The reaction conditions for one-pot reaction of jatropha oil

Parameter	Condition
Reaction temperature	310 °C
Reaction pressure	500 psig
LHSV	0.5, 0.9 h^{-1}
H_2/feed molar ratio	60

3.3.4 Product Analysis

3.3.4.1 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 3.3 The chromatographic temperature program for liquid product analysis

Step	Temperature (°C)	Rate (°C/min)	Holding Time (min)
1	50	-	5
2	169	10	10
3	380	20	10

The conversion and products selectivity of each product were calculated by Equations 3.1 and 3.2:

$$\text{Conversion (\%)} = \frac{(\text{moles of feed converted}) \times (100)}{\text{moles of feed input}} \quad (3.1)$$

$$\text{Selectivity to product i (\%)} = \frac{(\text{moles of product i}) \times (100)}{\text{moles of overall products}} \quad (3.2)$$

3.3.4.2 Gas Products 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_2O_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 comparing with the area of methane from gas standard by mol % (equal to vol %), as shown in Equations 3.3 and 3.4.

$$\text{Volume of product i (ml)} = \frac{(\text{areas of product i}) \times (\text{volume of gas product}) \times (\text{mol \% of methane})}{(\text{reference area of methane}) \times (\text{carbon atom})} \quad (3.3)$$

$$\text{Weight of product i (g)} = \frac{(\text{volume of product i (ml)}) \times \left(\text{molecular weight i } \left(\frac{g}{mol}\right)\right)}{\left(22{,}400 \left(\frac{mL}{mol}\right)\right)} \quad (3.4)$$

The calculations of conversion, selectivity and yield of product are defined as shown in Equations 3.5, 3.6 and 3.7, respectively.

$$\text{Conversion (\%)} = \frac{(\text{weight of total products}) \times 100}{\text{weight of (total products + remainning feed)}} \quad (3.5)$$

$$\text{Selectivity of product i (\%)} = \frac{(\text{weight of product i}) \times 100}{\text{weight of total products}} \quad (3.6)$$

$$\text{Yield of product i (\%)} = (\text{conversion}) \times (\text{selectivity of product i}) \quad (3.7)$$