CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Feedstocks

- Crude jatropha oil (obtained from PTT PLC)
- Tetraammineplatinum(II) chloride hydrate (99.99%, Aldrich)

3.1.2 Catalyst Supports and Metal Precursors

- Iridium(III) chloride hydrate (99.9% purity, Aldrich)
- Ruthenium(III) chloride, Ru content 45-55% (Aldrich)
- Y zeolite (SiO_2/Al_2O_3 ratio of 5.5, Tosoh Company)
- Ammonium Fluoride(99% purity, LabScan)
- Gamma alumina oxide (99% purity)

3.1.3 Standard Chemicals and Others

- Triolein (99% purity, Sigma)
- Trilinolein (99% purity, NU-CHEK PREP)
- Tristearin (99% purity, NU-CHEK PREP)
- Tripalmitin (99% purity, NU-CHEK PREP)
- 1,3 Diolein (99% purity, Sigma)
- 1,3 Dilinolein (99% purity, NU-CHEK PREP)
- 1,3 Distearin (99% purity, NU-CHEK PREP)
- Dipalmitin (99% purity, NU-CHEK PREP)
- Monoolein (99% purity, Sigma)
- Monolinolein (99% purity, NU-CHEK PREP)
- Monostearin (99% purity, NU-CHEK PREP)
- Monopalmitin (99% purity, NU-CHEK PREP)
- Stearic acid (99.5%, Fluka)
- Oleic acid (99.5%, Fluka)

- Palmitic acid (99.5%, Fluka)
- Octadecanol (95% purity, ACROS)
- Hexadecanol (96% purity, ACROS)
- Pentadecane (99% purity, Aldrich)
- Hexadecane (99% purity, Aldrich)
- Heptadecane (99% purity, Aldrich)
- Octadecane (99% purity, Aldrich)
- Dodecane (99% purity, Merck)
- Pyridine (99% purity, CARLO ERBA)
- N, O-bis(trimethyl)trifloroacetamide (98% purity, ACROS)
- Acetone (98% purity, Labscan)
- Methanol (99.9% purity, Labscan)
- Distilled water

3.1.4 Gases

- Hydrogen (99% purity, BIG)
- Nitrogen (99% purity, TIG)
- Helium (99% purity, TIG)
- Air zero (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), 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 cool-on column injection FID/TCD)
- Gas chromatograph-simulated distillation (Varian/ CP-3800)

- LECO Pegasus two-dimensional gas chromatograph with time-of-flight mass spectrometer (4D GCxGC TOFMS)
- Bruker D8 Advance X-ray diffractometer
- Bruker SRS3400 X-ray fluorescence spectrometer
- Gas chromatograph (GC, Perkin Elmer/ARNEL)
- Micromeritic TPR 2900 equipped with thermal conductivity detector
- Thermo Finnigan TPDRO 1100 equipped with flame ionization detector
- Surface area analyzer (SAA, Quantachrome/Autosorb 1)
- Hot & stirrer plate (Cole Parmer)
- Oven

3.3 Methodology

3.3.1 Catalysts Preparation

3.3.1.1 Preparation of Pt/H-Y, Ru/H-Y and Ir-H-Y Catalysts

Y zeolite was 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 technique consisting of 4 steps. Firstly, a desired amount of $Pt(NH_3)_4Cl_2$ compounds was dissolved in deionized water. Secondly, the $Pt(NH_3)_4Cl_2$ solution was added on the zeolite drop wise using a micro syringe. 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 the heating rate of 10°C/min. Then, a bifunctional catalyst was obtained in metal oxide forms.

Before catalytic activity test, the bifunctional catalyst was reduced in-situ with H_2 in order to convert metal oxide to metal.

The Ru/H-Y and Ir/H-Y catalysts was prepared by the same method as Pt/H-Y catalyst. The metal precursor that use were $RuCl_3$ and $IrCl_3$ respectively.

3.3.1.2 Preparation of Pt/Al_2O_3 and $Pt/F\text{-}Al_2O_3$ Catalysts

The catalysts were prepared by incipient wetness impregnation method. The Al_2O_3 support was first sieved to the size between 20 and

40 meshes (425-850 μm). The platinum was deposited by impregnation of γ-Al_2O_3 support with aqueous solution of $Pt(NH_3)_4Cl_2$. After impregnation, the catalysts was dried at 110 °C overnight and subsequently calcined at 500 °C for 4 h.

For the promotion with F^- ions, F^- ions was deposited on γ-Al_2O_3 support with an aqueous solution of ammonium fluoride (NH_4F) by impregnation method. After impregnation, the F-Al_2O_3 was dried at 110 °C overnight and subsequently calcined at 450 °C for 3 h. The platinum was deposited by impregnation of γ-Al_2O_3 support with aqueous solution of $Pt(NH_3)_4Cl_2$. After impregnation, the catalyst was dried at 110 °C overnight and subsequently calcined at 500 °C for 4 h.

Table 3.1 The metal precursors and the metal content of prepared catalysts

Catalyst	Metal precursors	Metal	Metal content (wt.%)
Pt/Al_2O_3	$Pt(NH_3)_4Cl_2 \cdot xH_2O$	Pt	0.5
$Pt/F\text{-}Al_2O_3$	$Pt(NH_3)_4Cl_2 \cdot xH_2O$	Pt	0.5
Pt/HY	$Pt(NH_3)_4Cl_2 \cdot xH_2O$	Pt	0.5
Ir/HY	$IrCl_3 \cdot xH_2O$	Ir	0.5
Ru/HY	$RuCl_3 \cdot xH_2O$	Ru	0.5

3.3.2 Catalyst Characterization

The prepared catalysts will be characterized by various methods described as follows.

3.3.2.1 X-ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence spectroscopy was used to determine the actual metal content in the catalysts. With a primary X-ray excitation source from an X-ray tube, the X-ray can be absorbed by the atom and its energy are transferred to an innermost electron. During this process, if the primary X-ray has sufficient energy, electrons are ejected from the inner shells, 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 this

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.

3.3.2.2 Temperature Programmed Reduction (TPR)

Temperature programmed reduction was employed for evaluating the number and 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. fifty mg of catalyst was placed in a quartz reactor, and heated (10°C/min) under a He flow up to 550°C, and held at the temperature for 1 h in order to remove moisture from the catalyst surface. The sample was then cooled down to 30°C. Then, the sample was exposed to a stream of 5% H_2/Ar with a flow rate of 20 ml/min. After that, the sample was heated to 600°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 Thermal Gravimetric Analysis (TGA)

Thermogravimetric-differential thermal analyzer (TG-DTA) was used to study thermal decomposition of catalyst precursor in order to evaluate the calcination temperature of prepared catalysts. Each catalyst was previously heated to 100 °C for 5 minutes in N2 (100 mL/min flow-rate) in order to remove moisture content then temperature was increased to 800 °C with ramp rate of 10 °C/min up to 800 °C.

3.3.2.4 Brunauer-Emmett-Tellet Method (BET)

The surface area of the prepared 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 was used to calculate the BET surface area.

3.3.2.5 Temperature Programmed Deposition (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 cool in H_2 to room temperature and then isoproplyamine was bubbled in to sample for 4h. After removing the excess isopropylamine, the sample was linearly heat to 800 °C at a heating rate of 10 °C/min. Mass 44, 41, and 17 were monitored to determine the evolution of isopropylamine, propylene, and ammonia, respectively.

3.3.2.6 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_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" O.D. 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 catalytic deoxygenation of crude jatropha oils is 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 and Table 3.2. The catalyst is 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 are set to the desired value in a flowing H_2. Then, the stream of jatropha oil is fed into the reactor by using a high-pressure liquid pump. The flow

of carrier gas and the reaction pressure are 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 sent directly to sample loop of 10-port valve. Both gas product and liquid product were collected and analyzed hourly. The liquid product was analyzed by a gas chromatograph, Agilent 7890 equipped with a flame ionization detector (FID). The gas product was injected automatically to a gas chromatograph, Agilent 7890 equipped with a thermal conductivity detector (TCD).

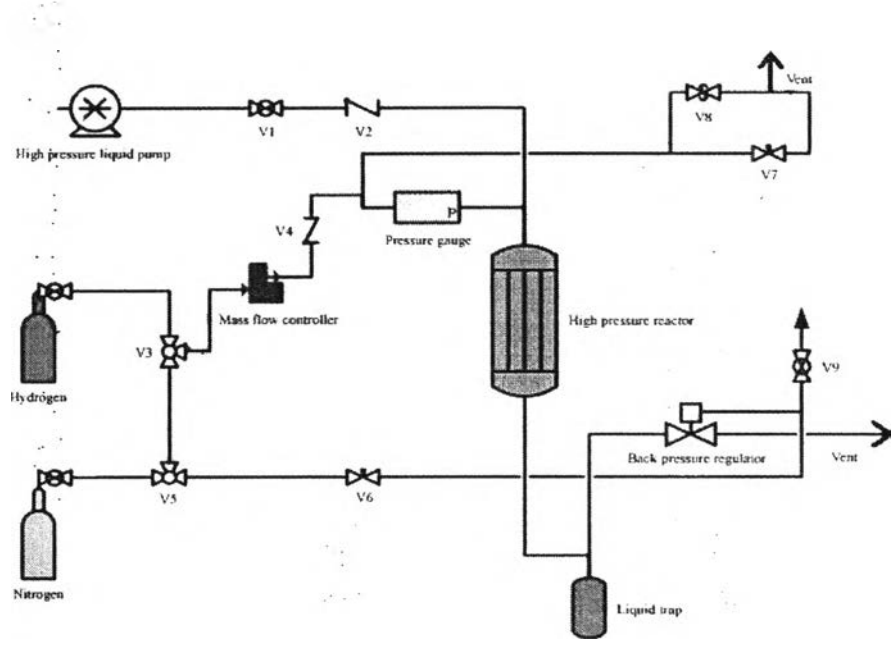

Figure 3.1 Schematic of reactor system.

Table 3.2 Description of flow diagram

No.	Items	Functions
1	V1	On-off valve for liquid from high pressure liquid pump
2	V2	Checking valve for avoiding the backward flow of liquid from high pressure pump
3	V3	Three ways valve for switching nitrogen gas to hydrogen gas
4	V4	Checking valve for avoiding the backward flow of hydrogen or nitrogen gas
5	V5	Three valve for switching direction of nitrogen 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 to release to pressure overload in the system
9	V9	On-off valve for releasing the pressure from back pressure regulator
10	V10	Metering valve for releasing the product from condenser

The catalytic deoxygenation of crude jatropha oil is conducted at temperature, pressure, LHSV, and H_2/Feed ratio as shown in Table 3.3.

Table 3.3 The reaction condition for deoxygenation of crude jatropha oil

Parameters	Condition
Reaction temperature	375 °C
Reaction pressure	600 psig
LHSV	0.5 h^{-1}
H_2/feed molar ratio	38.5

3.3.4 Product Analysis

3.3.4.1 GC/FID

The liquid products were analyzed by a gas chromatograph equipped with FID detector. The liquid products from the hydrodeoxygenation

contain non-polar and polar hydrocarbons. The non-polar hydrocarbon can be determined by using DB-5 column (non-polar column), whereas, the polar hydrocarbon cannot be analyzed by using the HP-5 column. Therefore, to improve the chromatographic behavior, these substances have to be silylated with N, O-bis(trimethyl)trifloroacetamide (BSTFA) and pyridine before injection into GC. The GC operating condition is 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 is used for liquid product analysis.

Table 3.4 The chromatographic temperature program for liquid product analysis

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

For the 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 3.1:

$$R_x = \left(\frac{m_{is}}{m_x}\right) \times \left(\frac{A_x}{A_{is}}\right) \qquad (3.1)$$

Where R_x is response factor of reference substance x

m_{is} is mass in g of internal standard

m_x is mass in g of reference substance x

A_x is peak area of reference substance x

A_{is} is peak area of internal standard

The composition of each product is calculated following formula, as shown in equation 3.2:

$$m'_x = \left(\frac{1}{R_x}\right) \times \left(\frac{m'_{is}}{m'_x}\right) \times \left(\frac{A'_x}{A'_{is}}\right) \qquad (3.2)$$

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 are calculated by equations 3.3 and 3.4:

$$\text{Conversion (\%)} = \frac{\text{moles of feed converted}}{\text{moles of feed input}} \times 100 \qquad (3.3)$$

$$\text{Selectivity to product i (\%)} = \frac{\text{moles of product i}}{\text{moles of overall products}} \times 100 \qquad (3.4)$$

The composition of gas product was analyzed qualitatively on-line in interval of 1 h by GC/TCD (Agilent 7890). The GC operating condition is summarized as follows:

Injection temperature :	200 °C
Detector temperature :	300 °C
Carrier gas :	N_2
Column type :	Packed column (Hyasep Q)

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

Table 3.5 The chromatographic temperature program for gas-phase product analysis

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

3.3.4.2 Simulated Distillation Gas Chromatography (SIMDIST GC)

SIMDIST GC was used to analyzed 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

3.3.4.3 4D GCxGC TOFMS

The liquid products were sent to perform the analysis at TOP by using ASTM D 2622 method. The GC operating condition:

Injection Temperature:	250 °C
Detector Temperature:	250 °C
Carrier gas:	He, N_2
Column	DB-1 capillary column and Porapak-Q packed column

Table 3.6 summarizes chromatographic temperature program used in the product analysis:

Table 3.6 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