



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Feedstock

- Crude jatropha oil, supplied by PTT Public Company Limited

3.1.2 Catalyst Support and Metal Precursors

- Palladium(II) nitrate hydrate (99.9% purity, Aldrich)
- Tetraammineplatinum(II) chloride hydrate (99.99%, Aldrich)
- Nickel(II) nitrate hexahydrate (99.9% purity, Aldrich)
- Ammonium molybdate hexahydrate ($\geq 99\%$ purity, Sigma-Aldrich)
- Cobalt(II) nitrate hexahydrate (98% purity, Sigma-Aldrich)
- Copper(II) nitrate hydrate (99% purity, Ajax Finechem Pty Ltd.)
- Gamma alumina oxide (Saint-Gobain NorPro Corporation)

3.1.3 Standard Chemicals

- 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, supplied by PTT Public Company Limited
- Palmitic acid, supplied by PTT Public Company Limited
- 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)
- Eicosane (99% purity, ACROS)

3.1.4 Other Chemicals

- Pyridine (99% purity, CARLO ERBA)
- N, O-bis(trimethyl)trifluoroacetamide (98% purity, ACROS)
- Acetone (98% purity, Labscan)
- Methanol (99.9% purity, Labscan)

3.1.5 Gases

- Hydrogen (99.999% purity, BIG)
- Nitrogen (99% purity, TIG)
- Helium (99% purity, TIG)
- Air zero (99% purity, TIG)

3.2 Equipments

- 3.2.1 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.x16" long stainless steel reactor, and a tubular furnace with a temperature controller.
- 3.2.2 Gas chromatograph (Agilent GC 7890 equipped with cool on-column inlet, FID, and TCD detectors)
- 3.2.3 X-ray diffractometer (XRD, Bruker AXS/Model D8 Advance)
- 3.2.4 Thermogravimetric-differential thermal analyzer (TG-DTA, Perkin Elmer/Pyris Diamond)
- 3.2.5 TPR equipped with an SRI model 110 thermal conductivity detector (TCD)

3.2.6 TPO equipped with an SRI model 110 flame ionization detector (FID)

3.2.7 Surface area analyzer (SAA, Quantachrome/Autosorb 1MP)

3.3 Methodology

3.3.1 Catalyst Preparation

Catalysts studied in this work are Al₂O₃-supported Pd, Pt, Cu, NiCu, NiMo, and CoMo catalysts. All catalysts were prepared by incipient wetness impregnation method. The Al₂O₃ support was first sieved to the size between 20 and 40 meshes (425-850 μm). Then, the support was impregnated with an aqueous solution of the desired metal precursors. The metal precursors and the metal content in the prepared catalysts are shown in Table 3.1. After the impregnation, the catalysts were dried at room temperature for 2 h and then at 110°C overnight. Subsequently, the catalysts were calcined at calcination temperature for each catalyst for 6 h (heating rate of 10 °C/min).

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

Catalyst	Metal precursor	Metal	Metal content (wt.%)
Pt/Al ₂ O ₃	Pt(NH ₃) ₄ Cl ₂ · xH ₂ O	Pt	1
Pd/Al ₂ O ₃	Pd(NO ₃) ₂ · xH ₂ O	Pd	5
Cu/Al ₂ O ₃	Cu(NO ₃) ₂ · 2.5H ₂ O	Cu	10
NiCu/Al ₂ O ₃	Ni(NO ₃) ₂ · 6H ₂ O	Ni	28
	Cu(NO ₃) ₂ · 2.5H ₂ O	Cu	10
NiMo/Al ₂ O ₃	Ni(NO ₃) ₂ · 6H ₂ O	Ni	3
	(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	Mo	11
CoMo/Al ₂ O ₃	Co(NO ₃) ₂ · 6H ₂ O	Co	3
	(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	Mo	11

3.3.2 Catalyst Characterization

The prepared catalysts were characterized by various methods described as follows.

3.3.2.1 *X-ray Diffraction (XRD)*

The crystalline phase of catalysts was analyzed by a Bruker AXS/Model D8 Advance X-Ray diffractometer with Cu tube for generating CuK α radiation (1.5406 Å). The system consists of a voltage generator of 40 kV. The 2θ is in the range between 10 and 80 with a scanning rate of 1°/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.

3.3.2.2 *Thermogravimetric 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 flow (100 mL/min flow-rate) in order to remove moisture content then temperature was increased to 800 °C with a heating rate of 10 °C/min up to 800 °C).

3.3.2.3 *Temperature Programmed Reduction (TPR)*

Temperature programmed reduction was employed for evaluating the type 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 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% H₂/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.

3.3.2.4 Brunauer-Emmett-Tellet Method (BET)

The surface area of the fresh catalysts was measured by BET surface area analyzer (Quantachrome/Autosorb-IMP). 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 introduced 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 was established. This volume-pressure data was used to calculate the BET surface area.

3.3.2.5 Temperature Programmed Oxidation (TPO)

This technique was employed to analyze the amount and characteristics of the coke deposited on the spent catalysts. 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.

3.3.3 Hydrodeoxygenation Experiments

The catalytic deoxygenation of crude jatropha oils was carried out in a 3/4 inch 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, respectively. The catalyst was firstly reduced for 3.5 h under flowing H₂ 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 H₂. Then, the stream of vegetable oil is 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 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).

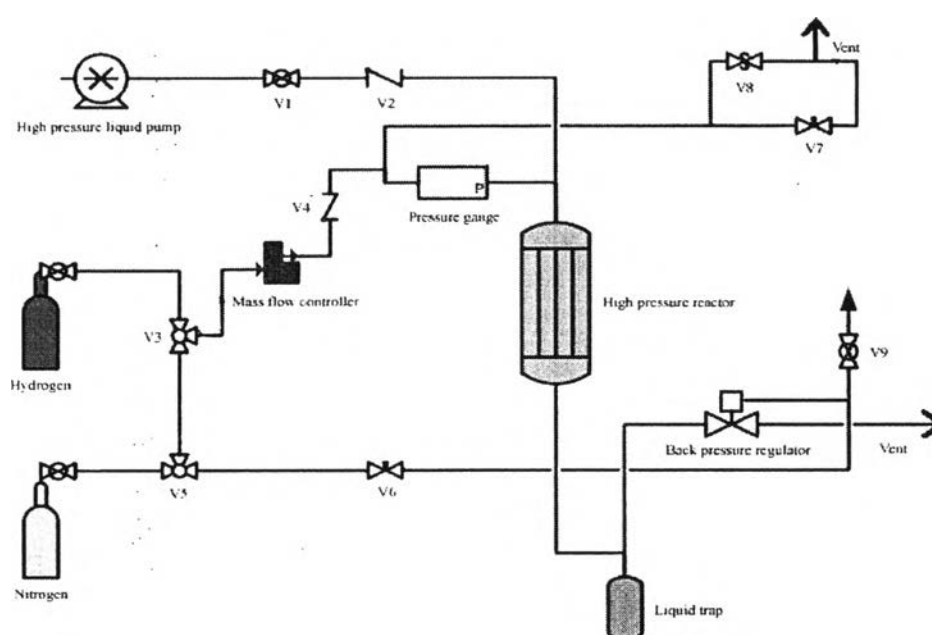


Figure 3.1 Schematic of reactor system.

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 H₂/Feed ratio as shown in Table 3.3.

Table 3.3 The reaction condition for deoxygenation of crude jatropha oil

Parameters	Condition
Reaction temperature	325 °C
Reaction pressure	500 psig
LHSV	0.5, 1, 2, 3, 4 h ⁻¹
H ₂ /feed molar ratio	30

3.3.4 Products Analysis

In this work, the liquid product was analyzed by GC/FID (Agilent 7890). In order to analyze in GC, liquid-phase samples had to be dissolved in pyridine and silylated with N,O-bis(trimethyl)trifluoroacetamide, BSTFA. The

internal standard eicosane, $C_{20}H_{42}$ was added for quantitative calculations. 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 as shown in equation 3.1:

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

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:

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

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 product selectivity of each product are calculated by equations 3.3 and 3.4:

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

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

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 was 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