

CHAPTER III EXPERIMENTAL



3.1 Equipment

- High pressure continuous flow packed-bed reactor system consisting of;
 - Mass flow controller (Brooks instrument 5850E)
 - High pressure liquid pump (Water 515 HPLC)
 - Back pressure regulator (SIEMENS)
 - ½" O.D stainless steel reactor
 - Tubular furnace with a temperature controller
- Agilent Technology 7890 gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID)
- X-ray diffractometer (Bruker AXS/D8 advance)
- Thermogravimetric/derivative thermogravimetric analyzer (TG-DTG, Perkin Elmer/Pyris Diamond)
- Temperature-programmed reduction apparatus (TPR)
- Temperature-programmed oxidation apparatus (TPO)
- Surface area analyzer (SAA, Quantachrom/Autosorb 1MP)
- Stirring hot plate (Cole Parmer)
- Oven (Cabolite CWE 1100)

3.2 Catalyst Supports

- Titanium dioxide (TiO₂ P25 Aeroxide, Degussa)
- Zirconium (IV) butoxide (Zr(O(CH₂)₃CH₃)₄, 80 wt. % in 1-butanol, Aldrich)
- Cerium(III) nitrate hexahydrate (Ce(NO₃)₃, 99.5 % purity, Acros)
- Aluminum oxide (γ-Al₂O₃, Saint-Gabain Norpro)
- Activated Charcoal (C, Sigma-Aldrich)
- Silicon dioxide (SiO₂, Hi-Sil 255)
- Zeolite L (KL, HSZ-500, Tosoh)

3.3 Chemicals

- Beef fat (from PTT public company limited)
- Nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2$, 99.9 % purity, Aldrich)
- Ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, 99.9 % purity, Aldrich)
- Ammonium hydrogen difluoride ($\text{NH}_4\text{F}\cdot\text{HF}$ 95 % purity, Unilab)
- Palladium(II) nitrate dehydrate ($\text{Pd}(\text{NO}_3)_2$, 99.9 % purity, Aldrich)
- Dodecane ($\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$, 99.9 % purity, Merck)
- Acetone (CH_3COCH_3 , 99 % purity, LabScan)
- Methanol (CH_4O , 99 % purity, Merck)
- Pyridine ($\text{C}_5\text{H}_5\text{N}$, 98 % purity, Carlo Erba reagente puro)
- N,O-bis(trimethylsilyl)-trifluoro acetamide (BSTFA, $\text{C}_8\text{H}_{18}\text{F}_3\text{NOSi}_2$, 99 % purity, ACROS)
- Eicosane ($\text{C}_{20}\text{H}_{42}$, 99 % purity, ACROS)

3.4 Gases

- Hydrogen (H_2 , HP grade, 99.99 % purity, TIG)
- Helium (He, HP grade, 99.99 % purity, TIG)
- Nitrogen (N_2 , HP grade, 99.99 % purity, TIG)
- Air (HP grade, 99.99 % purity, TIG)

3.5 Experimental Procedures

3.5.1 Catalyst Preparation

The catalysts were prepared by incipient wetness impregnation. $\text{CeO}_2\text{-ZrO}_2$ support was prepared by co-precipitation. The chemical precursors for each catalyst are shown in Table 3.1.

Table 3.1 List of investigated catalysts

Catalyst	Support	Chemical Precursor	Loading (wt.%)
<i>Pd metal</i>		Pd(NO ₃) ₂	Pd = 5
Pd/Al ₂ O ₃	Al ₂ O ₃	-	
Pd/F-Al ₂ O ₃	F-Al ₂ O ₃	NH ₄ F	F = 3
Pd/SiO ₂	SiO ₂	-	
Pd/TiO ₂	TiO ₂	-	
Pd/C	C	-	
Pd/KL	KL	-	
<i>NiMo metal</i>		Ni(NO ₃) ₂ (NH ₄) ₆ Mo ₇ O ₂₄	Ni = 3 Mo = 11
NiMo/Al ₂ O ₃	Al ₂ O ₃	-	
NiMo/F-Al ₂ O ₃	F-Al ₂ O ₃	NH ₄ F	F = 3
NiMo/SiO ₂	SiO ₂	-	
NiMo/TiO ₂	TiO ₂	-	
NiMo/C	C	-	
NiMo/CeO ₂ -ZrO ₂	CeO ₂ -ZrO ₂	Ce(NO ₃) ₃ Zr(O(CH ₂) ₃ CH ₃) ₄	Ce:Zr = 7:3

3.5.1.1 Incipient Wetness Impregnation

The supports, which were initially sieved to the particle size 20/40 mesh and dried at 110 °C overnight, were impregnated with the aqueous solution of metal precursors. After impregnation, the catalysts were dried at 110 °C overnight and subsequently calcined at suitable temperature for 4 h.

In the case of NiMo/F-Al₂O₃, the support was dried at 110 °C overnight and subsequently calcined at 500 °C for 4 h after impregnating F to Al₂O₃. Then, the molybdenum precursor was impregnated to the support, and the catalyst was dried at 110 °C overnight. After that, the nickel precursor was impregnated to the support. The catalyst was dried overnight and calcined subsequently.

3.5.1.2 Co-precipitation

For CeO₂-ZrO₂ support, the precursors of ceria (Ce(NO₃)₃) and zirconia (Zr(O(CH₂)₃CH₃)₄) were dissolved with de-ionized water by the concentrations of 1 wt.%. Then, they were mixed and stirred at room temperature for

30 min. A NaOH solution (1N) was added dropwise as precipitator under vigorous stirring to the mixed solution at 70 °C. The pH of the solution was maintained at 10. The precipitates were aged for 3 h under the same conditions, filtered, washed repeatedly with de-ionized water and dried at 110 °C overnight. The dried samples were calcined at 500 °C for 4 h.

3.5.2 Catalyst Pretreatment

The 1 ml of prepared catalysts were placed in the reactor and reduced to activate before the reaction by flowing hydrogen of 20 ml/min at 200 psig for 3.5 h. The temperature was increased with a rate of 10 °C/min until reaching the reduction temperature, typically 650 °C for the NiMo-supported catalysts and 200 °C for the Pd-supported catalysts.

3.5.3 Catalyst Characterizations

3.5.3.1 *Temperature-programmed Reduction (TPR)*

The catalysts were characterized by temperature-programmed reduction (TPR) to evaluate the number of the reducing species and the reducibility of samples. For each run, the fresh catalyst was weighed for 10 mg. The samples were heated up to 900 °C with heating rate of 10 °C/min in a flow of 5 % H₂/Ar (30 ml/min).

3.5.3.2 *Thermogravimetry and Differential Thermal Analysis (TG-DTA)*

Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) was used to study the thermal decomposition behavior of the catalysts and to obtain their suitable calcination temperatures. The catalyst of 1-5 mg was heated from 50 °C to 900 °C with a heating rate of 10 °C/min in a static air atmosphere.

3.5.3.3 *Brunauer Emmett Teller (BET) Method*

The surface area of catalysts was measured by BET surface area analyzer. The catalyst samples were firstly outgassed to remove the moisture and volatile adsorbents adsorbed on surface under vacuum at 300 °C for about 10 h prior to the analysis. Then, N₂ was purged to adsorb on the surface, and the quantity

of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressures was measured 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 were used to calculate the specific surface area.

3.5.3.4 X-ray Diffraction (XRD)

X-ray diffraction (XRD) was used to identify crystalline phases present in the samples by using a Bruker AXS system (D8 Advance) with a copper tube for generating $\text{CuK}\alpha$ radiation (1.54056 Å) at 40 kV and 30 mA and a nickel filter. A catalyst was pressed into a hollow of glass holder and held in place by glass window. Then, it was scanned in the 2θ range of 20° to 90° in the continuous mode with the rate of $1^\circ/\text{min}$ with scan step of 0.02 (2θ). The XRD results show peak parameters, including the centroid 2θ , the full width at half the maximum of intensity (β), d-value, and intensity. The mean crystallite size was calculated from the XRD data using X-ray line broadening. The signal was sent to the online computer to record and analyze. The Scherrer equation as expressed in Equation 3.1 shows the relationship between the crystallite size (D) and the broadening (β) of the diffraction line corresponding to the Bragg angle (θ) and X-ray wavelength (λ).

$$D_b = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \quad (3.1)$$

where:

D_b = Crystallite size (Å)

K = Scherrer constant, 0.9

λ = X-ray wavelength (Å)

β = Full width at half maximum of peak at 2θ (radian)

θ = Bragg angle of the reflection (radian)

The dispersions of Pd were also calculated from the XRD results. The relationship between crystallite size (d_{va}) and dispersion (D) are shown in Equation 3.2.

$$D = 6 \left(\frac{v_m}{a_m d_{va}} \right) \cdot 100 \quad (3.2)$$

where:

D = Percent metal dispersion

v_m = Volume occupied by metal one atom (\AA^3), 14.7

a_m = Area occupied by metal one atom (\AA^2), 7.93

d_{va} = Crystallite size (\AA)

3.5.3.5 Hydrogen Chemisorption

This technique was used to determine the dispersion of Pd and NiMo on the surface of catalysts. It was performed in a conventionally made-up system connected to a thermal conductivity detector (TCD) with 20- μl pulses of the purified H_2 . Prior to the pulse chemisorption, the sample was reduced in H_2 atmosphere at reduction temperature for 1 h. Consecutively, it was heated up to 400 $^\circ\text{C}$ to purged with N_2 for 1 h and cooled down to room temperature by flowing N_2 . H_2 pulses were injected onto the sample at room temperature until the saturation was observed. The result was detected with the TCD to determine the bound chemisorbed H_2 , which corresponded to H_2 adsorbed on the Pd and NiMo surface. To calculate the Pd dispersion, it was supposed that the adsorption stoichiometry was one H atom for one surface Pd atom.

3.5.3.6 Temperature-programmed Oxidation (TPO)

The spent catalysts were analyzed for the amount and characteristics of coke by temperature-programmed oxidation (TPO). TPO of the spent catalysts was performed in a continuous flow of 2 % O_2 in He, and the temperature was linearly increased with a heating rate of 12 $^\circ\text{C}/\text{min}$. The oxidation reaction was conducted in a $\frac{1}{4}$ " quartz fixed-bed reactor. The spent catalyst was placed between the layers of quartz wool. The sample was flushed by flowing 2 % O_2 in He for 30 min before the TPO is performed. CO_2 produced by the oxidation of coke species will be further converted to methane using a methanizer filled with 15 % Ni/ Al_2O_3 catalyst and operated at 420 $^\circ\text{C}$ in the presence of hydrogen flow. The methane will be then analyzed as a function of temperature using an FID detector.

3.5.4 Hydrodeoxygenation Experiments

The experiments were carried out in a high pressure $\frac{1}{2}$ " O.D. fixed bed reactor, as shown in Figure 3.1. The description of flow diagram is shown in

Table 3.2. The prepared catalyst was placed in the reactor and reduced by flowing hydrogen at 200 psig for 3.5 h at the reduction temperature of each catalyst. The hydrodeoxygenation was conducted at temperature, pressure, and H₂/feed ratio as shown in Table 3.3.

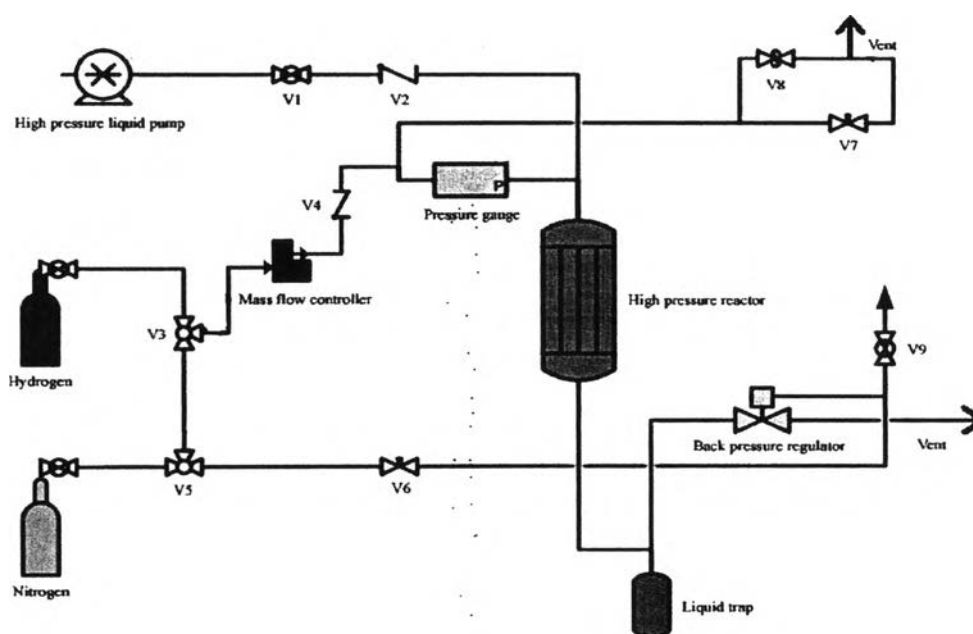


Figure 3.1 A schematic flow diagram of high pressure experimental setup.

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 backward flow of liquid from high pressure pump
3	V3	Three-way valve for switching nitrogen gas to hydrogen gas
4	V4	Checking valve for avoiding backward flow of hydrogen or nitrogen gas
5	V5	Three-way 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

Table 3.3 The reaction conditions for producing the hydrogenated biodiesel

Parameters	Condition
Reaction temperature	325 °C
Reaction pressure	500 psig
H ₂ /feed molar ratio	30

The stream of 10 vol% beef fat in n-dodecane was fed to the reactor using a high pressure pump. The flow of hydrogen and the reaction pressure were controlled by a mass flow controller and a back pressure regulator, respectively. The liquid product was collected in a stainless steel cylinder trap at the bottom of reactor.

3.5.5 Feed and Product Analysis

3.5.5.1 *Feed Analysis*

Feed, which is 10 vol.% beef fat in n-dodecane, was analyzed for fatty acids composition following AOAC 996.06 (Association of official analytical chemists) method, which is the recommended method for the determination of total fat and fatty acids in various foods under the current nutrition labeling regulations. Feed was also analyzed by an Agilent Technology 7890A gas chromatograph equipped with flame ionization detector (FID) and cool-on column injector, similar to the liquid products.

3.5.5.2 *Product Analysis*

In this research, GC/FID (Agilent 7890A) with cool-on column injector was used as liquid product analyzer. The liquid products from the hydrodeoxygenation contain non-polar and polar hydrocarbon. Therefore, to improve the chromatographic behavior, polar substances were silylated with N,O-bis(trimethylsilyl)-trifluoro acetamide (BSTFA, C₈H₁₈F₃NOSi₂) in the presence of pyridine (C₅H₅N) before injecting into GC. The GC operating conditions are 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 product analysis:

Table 3.4 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

For the quantitative calculations of liquid products, 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 3.3:

$$R_x = \left(\frac{m_{is}}{m_x} \right) \times \left(\frac{A_x}{A_{is}} \right) \quad (3.3)$$

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 compositions of each product are calculated following formula:

$$m'_x = \left(\frac{1}{R_x} \right) \times \left(\frac{m'_{is}}{m'_x} \right) \times \left(\frac{A'_x}{A'_{is}} \right) \quad (3.4)$$

Where

- m'_x is percentage of mass of component x in sample
- m'_{is} is mass in g of internal standard in sample
- m'_s 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 calculations of conversion and product selectivity are defined as shown in equation 3.5 and 3.6, respectively. Conversion of feed is defined as the weight ratio of feed consumed to the feed input, as shown in Equation 3.5. Selectivity is defined as the weight ratio of the products formed to that of the feed consumed in the reaction, as shown in Equation 3.6.

$$\text{Conversion (\%)} = \frac{\text{weight of feed converted}}{\text{weight of feed input}} \times 100 \quad (3.5)$$

$$\text{Selectivity to product i (\%)} = \frac{\text{weight of product i obtained}}{\text{weight of feed converted}} \times 100 \quad (3.6)$$