



CHAPTER III EXPERIMENTAL

3.1 Materials

- Beef tallow from PTT Public Company Limited
- Dodecane (99.9 % purity, Merck)
- Tetraammineplatinum(II) nitrate (99.9 % purity, Aldrich)
- Iridium(III) chloride hydrate (99.9 % purity, Aldrich)
- Ruthenium(III) chloride (99.9 % purity, Aldrich)
- Rhodium(III) chloride hydrate (99.9 % purity, Aldrich)
- Ammonium heptamolybdate tetrahydrate (99.9 % purity, Aldrich)
- Palladium(II) nitrate hydrate (99.9 % purity, Aldrich)
- Nickel(II) nitrate hexahydrate (99.9 % purity, Aldrich)
- Cobalt(II) nitrate hexahydrate (99.9 % purity, Aldrich)
- Zinc chloride anhydrous (99.9 % purity, Aldrich)
- Copper(II) nitrate (99% purity, Univar)
- Ammonium(meta) tungstate hydrate(99% purity, Fluka)
- Gamma aluminum oxide (99 % purity, Saint-Gobain)
- Distilled water

3.2 Equipment

- Thermogravimetric/derivative thermogravimetric (TG-DTG, Perkin Elmer/Pyris Diamond)
- Surface area analyzer (SAA, Quantachrome/Autosorb-1)
- Temperature-programmed reduction apparatus
- High pressure continuous flow packed-bed reactor consisting of mass flow controllers (Brooks instrument 5850E), high pressure liquid pump (Waters 515), back pressure regulator (SIEMENS), and furnace

- Gas chromatograph (Agilent 7890)
- Hot & stirrer plate (Cole Parmer)

3.3 Methodology

3.3.1 Catalyst Preparation

Three series of Ni-based, Cu-based, and noble metal catalysts were prepared by incipient wetness impregnation method with sequential metal aqueous solution of desired concentrations. The metal aqueous solutions were prepared by mixing a desired amount of nickel, copper, and other metal precursor in distilled water. The alumina support material was ground and sieved in order to get the support with 400-814 microns. The impregnated catalysts were dried in air at 110 °C overnight, then calcined in air at 500 °C for 4 h. Table 3.1 shows list of catalysts and their composition. The second metal was impregnated to first metal to prevent the formation of spinel metal aluminates (Scheffer et al., 1987).

Table 3.1 List of prepared catalysts and their composition

Catalysts name	Composition	
	1 st metal (wt.%)	2 nd metal (wt.%)
Ni-based catalysts		
Ni/Al ₂ O ₃	10	-
Ni-Mo/Al ₂ O ₃	10	5
Ni-Co/Al ₂ O ₃	10	5
Ni-Cu/Al ₂ O ₃	10	5
Ni-Ru/Al ₂ O ₃	10	1
Ni-Rh/Al ₂ O ₃	10	1

Table 3.1 (Cont.) List of prepared catalysts and their composition

Catalysts name	Composition	
	1 st metal (wt.%)	2 nd metal (wt.%)
Ni-Ir/Al ₂ O ₃	10	1
Ni-W/Al ₂ O ₃	10	5
Cu-based catalysts		
Cu/Al ₂ O ₃	10	-
Cu-Mo/Al ₂ O ₃	10	5
Cu-Co/Al ₂ O ₃	10	5
Cu-W/Al ₂ O ₃	10	5
Cu-Zn/Al ₂ O ₃	10	5
Noble catalysts		
Pt/Al ₂ O ₃	1	-
Pd/Al ₂ O ₃	1	-

3.3.2 Catalyst Characterizations

3.3.2.1 *Temperature Programmed Reduction (TPR)*

Temperature-programmed reduction was employed for evaluating the number and quantity of the reducible species present in the prepared catalysts, 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 1/4" O.D. quartz tube reactor, heated (10 °C/min) under a He flow up to 550 °C, and held at this temperature for 1 h in order to remove moisture from the catalyst surface. The sample was then cooled to 30 °C. Then, the sample will be 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 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.

3.3.2.2 Brunauer-Emmett-Tellett(BET) Surface Area Analysis

The surface area of the fresh and spent catalysts was measured by BET surface area analyzer (Quantachrome/Autosorb 1). First the sample was 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 purged to adsorb on surface, and the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method was measured. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium was established. This volume-pressure data used to calculate the BET surface area.

3.3.2.3 Temperature Programmed Oxidation (TPO)

Temperature-programmed oxidation (TPO) was carried out to determine the amount and characteristics of coke formed on the spent catalysts. TPO of the spent catalysts was performed in a continuous flow of 2% O₂/He while the temperature linearly ramped to 800 °C with a heating rate of 10 °C/min. The sample (30 mg) was placed in a ¼ inch quartz fixed bed reactor. The CO₂ produced by the oxidation of coke was further converted to methane over 15% Ni/Al₂O₃ catalyst in the presence of hydrogen at 400 °C. The methane obtained will be analyzed online by an FID detector. The amount of oxidized coke was calibrated using a 100 µl pulses of pure CO₂.

3.3.3 Catalytic Activity Testing

The experiments were carried out in a high pressure fixed bed reactor, as shown in Figure 3.1, and the description of flow diagram is shown in Table 3.2. A stream of 10% animal fat in dodecane was fed to the reactor using a high pressure 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 collected in a condenser immersed in an ice bath at the bottom of reactor and analyzed by a gas chromatograph equipped with a FID detector. As the liquid products from the hydrodeoxygenation contained both non polar and polar hydrocarbons, the polar oxygenated compounds were silylated with N, O-

bis(trimethylsilyl)trifluoroacetamide and pyridine to improve the chromatographic behavior.

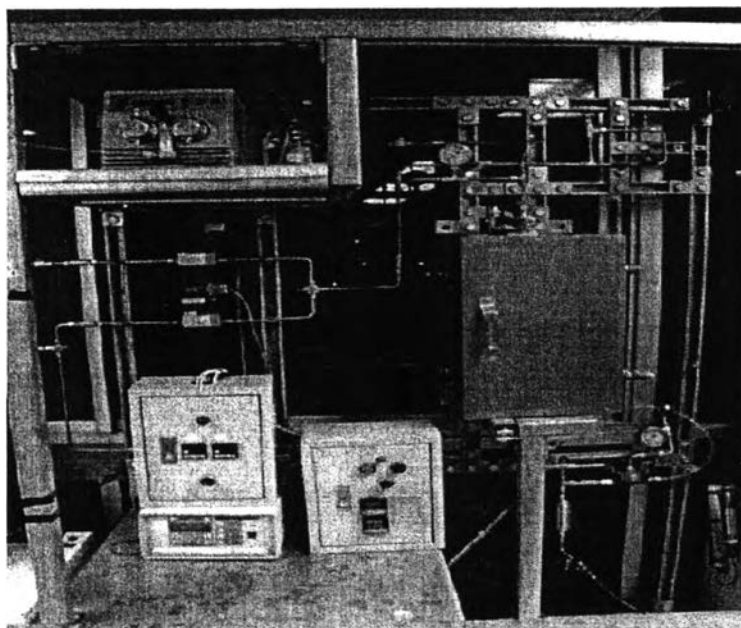


Figure 3.1 A photograph of the catalyst testing unit.

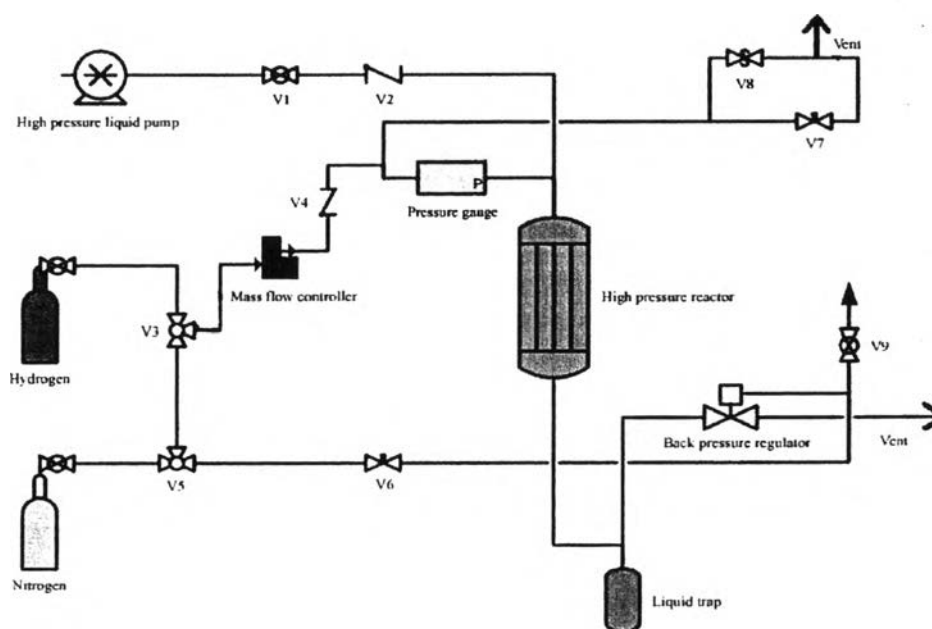


Figure 3.2 A schematic flow diagram of catalyst testing unit.

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 way 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 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

Production of the renewable diesel by the hydrodeoxygenation of animal fat for engine test will be conducted at 325 °C, 500 psig, and H₂/feed molar ratio of 30.

3.3.4 Feed and Product Analysis

3.3.4.1 *AOAC 966.06 (AOAC int. (2001))*

Fat and fatty acids were extracted from food by hydrolytic methods (acidic hydrolysis for most products, alkaline hydrolysis for dairy products, and combination for cheese). Pyogallic acid was added to minimize oxidative degradation of fatty acids during analysis. Triglyceride, triundecanoin (C₁₁₀), is added as internal standard. Fat is extracted into ether, then methylated to fatty acid methyl esters (FAMES) using BF₃ in methanol. FAMES are quantitatively measured by capillary gas chromatography (GC) against C₁₁₀ internal standard. Total fat is calculated as sum of individual fatty acids expressed as triglyceride equivalents.

saturated and monounsaturated fats are calculated as sum of respective fatty acids. Monounsaturated fat includes only *cis* form.

The main apparatus are gas chromatograph (GC) and capillary column.

- Gas chromatograph (GC) – Equipped with hydrogen flame ionization detector, capillary column, split mode injector, oven temperature programming sufficient to implement a hold-ramp-hold sequence. Operating conditions: temperature (°C): injector, 225; detector, 285; initial temp, 100 (hold 4 min); ramp, 3 °C/min; final temp 240; hold 15 min; carrier gas, helium; flow rate, 0.75 mL/min; linear velocity, 18 cm/s; split ratio, 200:1.

- Capillary column – Separating the FAME pair of adjacent peaks of C_{18:3} and C_{20:1} and the FAME trio of adjacent peaks of C_{22:1}, C_{20:3} and C_{20:4} with a resolution of 1.0 or greater: SP2560 100 m × 0.25 mm with 0.20 μm film was suitable.

3.3.4.2 Gas Chromatography

Feed and liquid products were analyzed by a gas chromatograph equipped with an FID detector. The liquid products from the hydrodeoxygenation contained both non polar and polar hydrocarbons. To improve the chromatographic behavior, polar substances were silylated with N, O - bis(trimethylsilyl)trifluoroacetamide and pyridene before injection into GC.

The GC operating conditions are as follows:

Injection 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 will be used for 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 calculations of conversion and products selectivity are defined as shown in Equations 3.1 and 3.2, respectively. Conversion of feed is defined as the mole ratio of feed consumed to the feed input, as shown in Equation 3.1. Selectivity is defined as the ratio of the number of moles of the products formed to that of the feed consumed in the reaction, as shown in Equation 3.2.

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

$$\text{Selectivity to product i (\%)} = \frac{\text{weight of product i obtained}}{\text{weight of feed converted}} \times 100 \quad (3.2)$$