

CHAPTER III

EXPERIMENTAL

3.1 Materials and Chemicals

- 3.1.1 Soybean oil, TVO Co., Ltd.
- 3.1.2 Potassium hydroxide 85% (AR.), RCI Labscan Limited
- 3.1.3 Nickel (II) nitrate hexahydrate (99.9%), Wako Pure Chemical Industries, Ltd.
- 3.1.4 Tetraammineplatinum (II) chloride (Pt:56.48%), N.E. Chemcat Corporation
- 3.1.5 Tetraamminepalladium (II) chloride (Pd:40.6%), N.E. Chemcat Corporation
- 3.1.6 Sodium sulfate anhydrous puriss, Riedel-de Haën
- 3.1.7 Silicon dioxide (SiO₂-Q30), Fuji Silysia Chemical Company Ltd.
- 3.1.8 n-heptane 99.5% purity, 2.5 L
- 3.1.9 Acetone, 99.9%, 20 L, RCI Labscan Limited
- 3.1.10 Methanol (AR.), 20 L, RCI Labscan Limited

3.2 Gases

- 3.2.1 High purity (99.99%) oxygen, Thai Industrial Gases Public Co., Ltd.
- 3.2.2 High purity (99.99%) hydrogen, Thai Industrial Gases Public Co., Ltd.
- 3.2.3 High purity (99.99%) nitrogen, Thai Industrial Gases Public Co., Ltd.

3.3 Equipment

- 3.3.1 Furnace
- 3.3.2 Hot plate
- 3.3.3 Stirring plate
- 3.3.4 Condenser

- 3.3.5 500 ml three-necked round bottom flask
- 3.3.6 Separatory funnel
- 3.3.7 Volumetric flask
- 3.3.8 Stainless steel semi-batch reactor
- 3.3.9 Fixed-bed reactor
- 3.3.10 Thermometer
- 3.3.11 Temperature controller
- 3.3.12 Mass flow controller
- 3.3.13 Pressure controller
- 3.3.14 Peristaltic pump
- 3.3.15 Magnetic bar

3.4 Instrument

- 3.4.1 Gas Chromatograph (GC)
- 3.4.2 X-ray Diffractometer (XRD)
- 3.4.3 Surface Area Analyzer (SAA)

3.5 Methodology

3.5.1 Transesterification of Soybean Oil

A 50 g of soybean oil is added to 500 ml three-necked round bottom flask and is heated on hot plate which is set to be 60 °C. Then the mixture of methanol and KOH catalyst is prepared by using 16.9 g methanol (9:1 methanol to oil molar ratio) and 0.5 g KOH (1 wt.% of soybean oil). The mixture is stirred until it is completely mixed. Heated soybean oil is observed until its temperature reaches 60 °C and then the solution mixture is added and stirred together at 300 rpm. Its container is connected to a condenser for 1 hour for transesterification of soybean oil. After that the container is taken off the condenser and hot plate and then it is left to cool down. Afterwards, the soybean oil solution is poured into a separatory funnel. The oil separates into 2 phases after leave it for 1 night; the lower glycerine phase will be removed, and the upper biodiesel phase will be kept in volumetric flask.

3.5.2 Biodiesel Cleaning

Biodiesel which is obtained after separation is contaminated by methanol, glycerol, and KOH. Therefore, biodiesel cleansing is an essential step in order to remove unwanted substances. Firstly, distilled water is heated until the temperature reaches 60 °C and then 50 ml of hot distilled water is poured into biodiesel. The mixture is stirred at 500 rpm for 30 minutes. After that, the mixture is poured back to separatory funnel and it is left again for 15 minutes. The mixture separates into 2 phases; the lower unwanted phase is removed, while the upper biodiesel phase is kept separately in a beaker. The procedure is repeated for 5 times. The pH values of the final batch of biodiesel and the final wash are measured using litmus paper, the pH values of both have to be neutral. Finally, biodiesel is kept in glass bottle that contains Na_2SO_4 (12.5 g/50 g of oil) in order to remove leftover water.

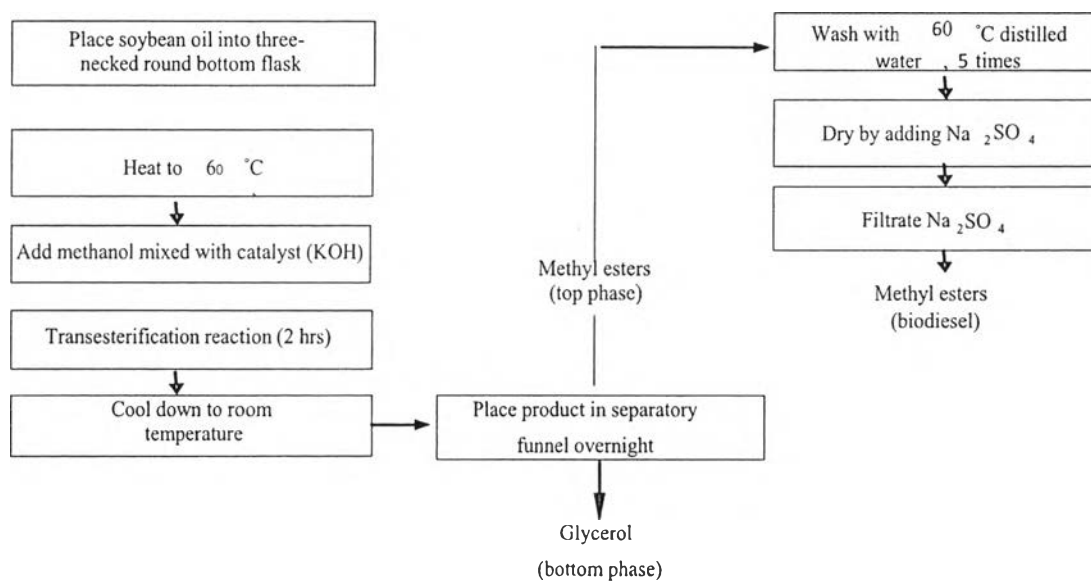


Figure 3.1 Schematic diagram of biodiesel production by homogeneous catalytic transesterification.

3.5.3 Catalyst Preparation

The main method used for preparing catalysts used in this experiment is incipient wetness impregnation. Three types of metals that are Ni, Pd, and Pt were used. At the beginning, Pd on SiO₂ catalysts were impregnated with an aqueous solution containing appropriate amounts of Pd(NH₃)₄.Cl₂. The total amount of Pd loading was 1 wt.%. After impregnation, the catalyst was dried by a rotary evaporator at room temperature for 2 hours, then at 60 °C for 2 hours, and finally by a vacuum pump at 60 °C for 2 hours. Then, the catalyst is calcined under an oxygen stream at 300 °C with a heating rate of 0.5 °C/min and 1 L/min of oxygen flow rate. Lastly, the catalyst is reduced by heating it to 300 °C for 2 hours with a heating rate of 5 °C/min and 100 ml/min hydrogen flow rate prior to using in partial hydrogenation reaction. The same procedure is applied for preparation of Ni catalyst (loading 10 wt.%) and also Pt catalyst (loading 1.82 wt.%). The precursors which were used for both catalysts are Ni(NO₃)₂.6H₂O and Pt(NH₃)₄.Cl₂.

3.5.4 Partial Hydrogenation

The reaction is carried out in a 300 ml stainless steel semi-batch reactor with operating conditions of 120 °C and 4 bar. For the procedure, it starts with the approximately 1.304 g of supported Pd catalyst (1 wt.% of Pd/SiO₂) is placed in the reactor and the system is purged with nitrogen to remove remaining air. And then 150 ml of prepared biodiesel is fed into the reactor by peristaltic pump. Hydrogen is then flowed into the reactor with the flow rate of 150 ml/min controlled by a mass flow controller and the partial hydrogenation reaction occurs. After that, the temperature and pressure is increased up to a desired point. During partial hydrogenation step, the stirrer is used at 1000 rpm to mix the biodiesel, catalyst, and hydrogen thoroughly to prevent external mass transfer. In addition, the sample is collected at every 30 minutes and Hewlett Packard gas chromatography 5890 Series II equipped with a FID detector is applied to analyze the product by using n-heptane as a solvent.

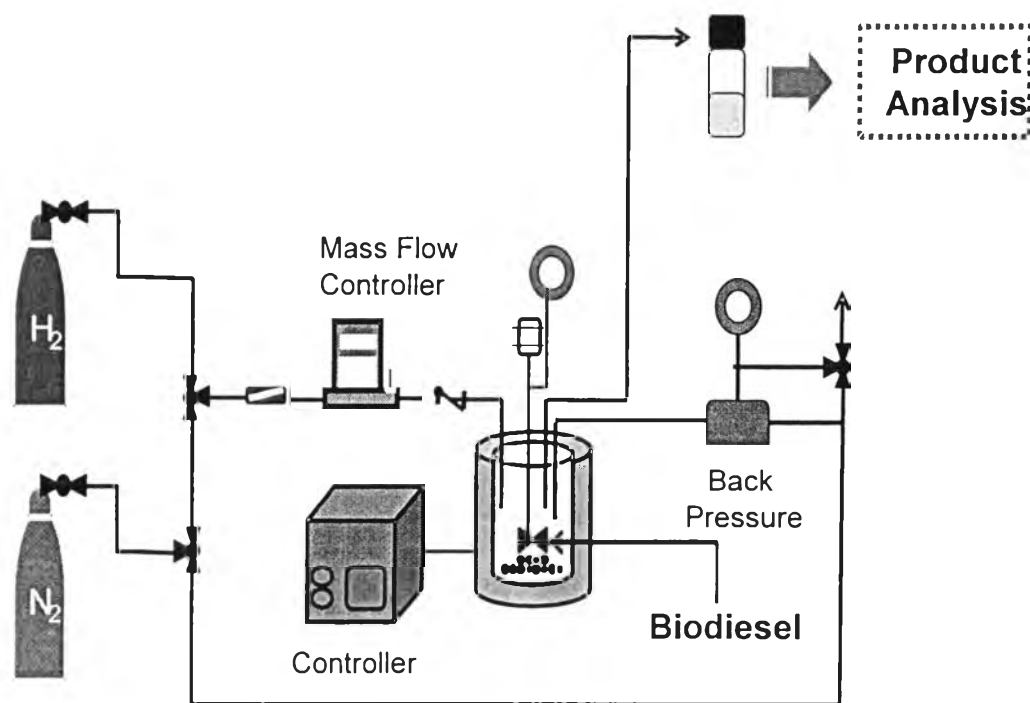


Figure 3.2 Schematic of the partial hydrogenation reaction.

3.5.5 Sulfur Tolerance

Allyl Isothiocyanate is added into biodiesel before partial hydrogenation reaction in order to observe sulfur tolerance of each catalyst. Prior to study sulfur tolerance, soybean oil based-biodiesel is tested for sulfur concentration. The initial sulfur concentration is 0.64 ppm. For this study, the sulfur concentration is doubled to be 1.28 ppm. Since, the study in terms of both catalytic activity and selectivity before and after adding additional sulfur compound is concerned, doubled sulfur concentration of original biodiesel is only applied for this work.

3.6 Biodiesel Analysis

3.6.1 Gas Chromatography (GC)

Biodiesel and partial hydrogenated biodiesel will be identified the composition of C12:0, C14:0, C16:0, C18:0, C18:1, C18:2 and C22:0 by Hewlett

Packard gas chromatograph 5890 Series II. The GC equipped with a flame ionization detector (FID) and a DB-WAX (30 m x 0.25 mm) fused-silica capillary column coated with a 0.1 μm film will be used. A carrier gas will be helium (99.99%) with a flow rate of 70 ml/min. The fatty acids will be quantified by injecting 0.2 μl of each sample. The injector and detector temperatures will be set at 200 $^{\circ}\text{C}$ with a split ratio of 75:1 and 230 $^{\circ}\text{C}$, respectively. The oven temperature will be initially at 130 $^{\circ}\text{C}$ after an isothermal period of 2 min, then increased to 220 $^{\circ}\text{C}$ with a rate of 2 $^{\circ}\text{C}/\text{min}$ and held for 15 min with the total analysis time of 62 min. FAME composition will be identified from the fraction of the area under the peak at different retention times.

3.6.2 Rancimat Testing

Oxidative stability is an important criterion for evaluating biodiesel quality. Because of its content of polyunsaturated methyl esters (FAME), which have several double bonds and oxidize easily so it effects on vehicle system. Oxidative stability will be analyzed according to European standard UNE-EN 14212:2003 method using a Metrohm 743 Rancimat instrument (Herisau, Switzerland). Sample of 3 g will be analyzed at a heating block temperature of 110 $^{\circ}\text{C}$ with the temperature correction factor (ΔT) of 0.98 $^{\circ}\text{C}$, and a constant air flow of 10 L/h. The volatile compounds formed will be collected in the conductivity cell of 50 ml of DI water. The inflection point of the derivative curve of conductivity as a function of time will be reported as the induction period (IP, h). All the measurements will be performed in duplicate (Wadumesthrige et al., 2009).

3.6.3 Cold Flow Properties Testing

Two of major problems associated with the use of biodiesel are its oxidation stability and its cold flow properties, which can be indicated by cloud points (CP) and pour points (PP), which are important indices related to low-temperature operability of diesel fuels.

3.6.3.1 *Pour Point*

Pour point is the temperature at which a fuel can no longer be poured due to gel formation, while the cold filter plugging point is the temperature at

which a fuel jams the filter due to the formation of agglomerates of crystals. The pour point measurement will be done as ASTM D97-D96a, biodiesel sample will be cooled inside a cooling bath to allow the formation of paraffin wax crystals. At about 9 °C above the expected pour point, and for every subsequent 3 °C, the test jar will be removed and tilted to check for surface movement. When the biodiesel sample does not flow when tilted, the jar will be held horizontally for 5 s. After that, if it does not flow, 3 °C will be added to the corresponding temperature and the result is the pour point temperature.

3.6.3.2 Cloud Point

The cloud point of a liquid FAME mixture, which usually occurs at a higher temperature than the pour point. The cloud point is the temperature at which fuel become cloudy due to formation of crystals and solidification of saturates. Biodiesel sample will be first poured into a test jar to a level approximately half full. Then, the entire test subject will be placed in a constant temperature cooling bath. At every 1 °C, the sample will be taken out and inspected for cloud. In accordance with ASTM D2500, the oil is required to be transparent in layers 40 mm in thickness. The cloud point is the temperature at which the milky cloud crystals first appear.

3.6.4 Sulfur Concentration

Most biodiesel fuels are inherently composed of little or no sulfur compound which is a potential catalyst poison. The specification is important to represent that biodiesel will not negatively affect catalyst systems. In ASTM D6751, biodiesel fuels will be determined by D5453 which is applied for sulfur content determination. The sample is tested by using UV fluorescence during its combustion. SO₂ which is produced during sample combustion is then converted to excited SO₂*. After that, the excited SO₂* try itself to return to the stable SO₂ state which cause the fluorescence emission. This emission is detected with the signal indicating the amount of sulfur in the sample (Knothe, 2006) .

3.7 Catalyst Characterization

Catalysts are characterized by several techniques. Those techniques include X-ray Diffraction (XRD), and Brunauer-Emmet-Teller (BET) surface area measurement.

3.7.1 X-ray Diffraction (XRD)

A Bruker D8 Advance X-ray diffractometer system is used to characterize and identify the internal structure, bulk phase, crystallinity and composition in crystalline phases of the catalysts. A 2.2 kW Cu anode long with fine focus ceramic X-ray tube which generates CuK α radiation (1.5405 Å) is used as an X-ray source to obtain the XRD patterns at running conditions for the X-Ray tube of 40 kV and 30 mA. The prepared sample will be held in the X-ray beam and the detector will scan the intensity of diffracted radiation from the sample as a function of 2θ in the range of 5° to 90° and a scan speed used is 5°/second. Finally, the obtained XRD patterns will be compared to the standard file to identify the crystalline phases of the catalysts.

3.7.2 Autosorb-1 MP Surface Area Measurement

The method used for measuring the specific surface area and pore size distribution is Quantachrome Autosorb-1 MP surface area analyzer. Prior to performing the test, the volatile species that are adsorbed on the catalyst surface must be eliminated by heating the catalyst under vacuum atmosphere at 250 °C overnight. Helium gas is used as an adsorbate for blank analysis and nitrogen gas is used as an adsorbate for actual analysis. The specific surface area and pore size distribution of the catalyst will be calculated by the software.