CHAPTER III
EXPERIMENTALS

3.1 Materials and Equipment

3.1.1 Equipment
- Gas Chromatography (GC)
- X-ray Diffractometer (XRD)
- Surface Area Analyzer (SAA)
- Atomic Absorption Spectrometer (AAS)
- Fourier Transformed Infrared Spectrometer (FTIR)
- Furnace
- Hot plate
- Stirring plate
- Condenser
- 500 ml three-necked round bottom flask
- Separatory funnel
- Volumetric flask
- Stainless steel semi-batch reactor
- Fixed-bed reactor
- Thermometer
- Temperature controller
- Mass flow controller
- Pressure controller
- Magnetic stirrer

3.1.2 Chemicals
- Soybean oil, TVO Co., Ltd.
- Potassium hydroxide 85% (AR.), RCI Labscan Limited
- Nickel (II) nitrate hexahydrate (99.9%), Wako Pure Chemical Industries, Ltd.

- Tetraammineplatinum (II) chloride (Pt:56.48%), N.E. Chemcat Corparation

- Tetraamminepalladium (II) chloride (Pd:40.16%), N.E. Chemcat Corparation

- Sodium sulfate anhydrous puriss, RCI Labscan Limited

- Silicon dioxide (SiO_2-Q30), Fuji Silysia Chemical Company Ltd.

- Magnesium nitrate hexahydrate (ACS reagent, 99%), Sigma-Aldrich Pte Ltd.

- n-heptane 99.5% purity, 2.5 L

- Acetone, 99.9%, 20 L, RCI Labscan Limited

- Methanol (AR.), 20 L, RCI Labscan Limited

3.1.3 Gases

- High purity (99.70%) oxygen, Thai Industrial Gases Public Co., Ltd.

- High purity (99.99%) hydrogen, Thai Industrial Gases Public Co., Ltd.

- High purity (99.99%) nitrogen, Thai Industrial Gases Public Co., Ltd.

3.2 Methodology

3.2.1 Transesterification of Soybean Oil

A 50 g of soybean oil is added to 500 ml three-necked round bottom flask and is heated to 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 h 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 (Thunyaratchatanon, 2012).

3.2.2 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 min. After that, the mixture is poured back to a separatory funnel and it is left again for 15 min. 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 (Thunyaratchatanon, 2012).

3.2.3 Catalyst Preparation

The main method used for preparing catalysts used in this experiment is incipient wetness impregnation. Three types of metals, Ni, Pd, and Pt were used. At the beginning, SiO_2 supports were impregnated with an aqueous solution containing appropriate amounts of $Pd(NH_3)_4.Cl_2$. The total amount of Pd loading was 1 wt.%. After impregnation, the catalyst was dried by a rotary evaporator at room temperature for 2 h, then at 60 °C for 2 h, and finally by a vacuum pump at 60 °C for 2 h. Then, the catalyst is calcined under an oxygen stream at 300 °C with a heating rate of 0.5 °C/min and 1,000 ml/min of oxygen flow rate for 3 h. Lastly, the catalyst is reduced by heating it to 300 °C for 2 h with a heating rate of 5 °C/min and 100 ml/min hydrogen flow rate prior to catalytic testing in partial hydrogenation reaction. The same procedure is applied for preparation of Pt catalyst (loading 1.82 wt.%) and also Ni catalyst (loading 10 wt.%) (Thunyaratchatanon, 2012).

For the Pd-Mg/SiO$_2$ catalyst, SiO$_2$ supports were impregnated with an aqueous solution containing appropriate amounts of Pd(NH$_3$)$_4$.Cl$_2$. The total amount of Pd loading was 1 wt.%. After impregnation, the catalyst was dried by a rotary evaporator at room temperature for 2 h, then at 60 °C for 2 h, and finally by a vacuum pump at 60 °C for 2 h. Then, the catalyst is calcined under an oxygen stream at 300 °C with a heating rate of 0.5 °C/min and 1,000 ml/min of oxygen flow rate for 3 h. After that the Pd/SiO$_2$ sample was impregnated with an aqueous solution containing appropriate amounts of Mg(NO$_3$)$_2$.6H$_2$O. The total amount of Mg loading was 4 wt.% (Tonetto *et al.*, 2009). After impregnation, the catalyst was dried by a rotary evaporator at room temperature for 2 h, then at 60 °C for 2 h, and finally by a vacuum pump at 60 °C for 2 h. Then, the catalyst is calcined under an oxygen stream at 500 °C with a heating rate of 0.5 °C/min and 1,000 ml/min of oxygen flow rate for 4 h. Lastly, the catalyst is reduced by heating it to 100 °C for 30 min with a heating rate of 5 °C/min and 100 ml/min hydrogen flow rate prior to catalytic testing in partial hydrogenation reaction. The same procedure is applied for preparation of Pt-Mg/SiO$_2$ catalyst (Pt loading 1.82 wt.%) and also Ni-Mg/SiO$_2$ catalyst (Ni loading 10 wt.%).

3.2.4 Partial Hydrogenation

The reaction is carried out in a 300 ml stainless steel semi-batch reactor with operating conditions of 120 °C and 0.4 MPa. For the procedure, it starts with the approximately 1.304 g of supported Pd catalyst (1 wt.% of Pd/SiO$_2$) 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. 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 1,000 rpm to mix biodiesel, catalyst, and hydrogen thoroughly to prevent external mass transfer. In addition, the sample is collected every 30 min and Hewlett Packard gas chromatograph 5890 Series II equipped with a FID detector is

applied to analyze the product by using n-heptane as a solvent (Thunyaratchatanon, 2012). The schematic of the partial hydrogenation experiment is shown in Figure 3.1.
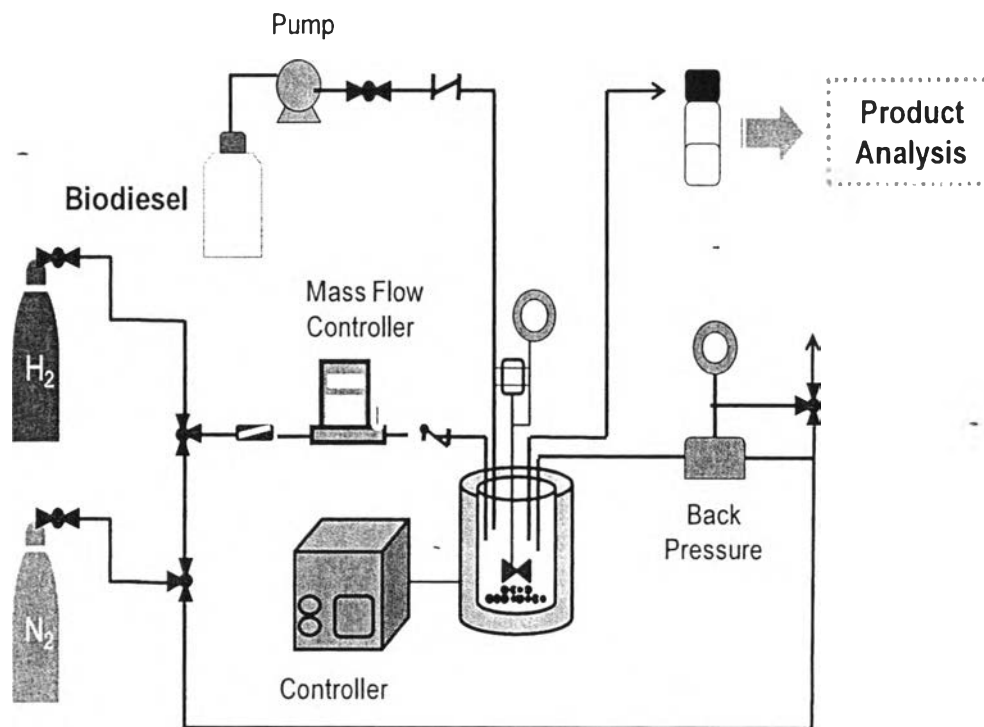
Figure 3.1 Schematic of the partial hydrogenation reaction.

3.3 Biodiesel Analysis

3.3.1 Gas Chromatography (GC)

Biodiesel and partial hydrogenated biodiesel was 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 was 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 temperature was set at 200 °C with a split ratio of 75:1 and 230 °C, respectively. The oven temperature was initially at 130 °C after an isothermal period of 2 min, then increased to 220 °C with a rate of 2 °C/min and held

for 15 min with the total analysis time of 62 min. FAME composition was identified from the fraction of the area under the peak at different retention times (Thunyaratchatanon, 2012).

3.3.2. Fourier Transform Infrared Spectrometry (FTIR)

It is a technique used to identify the chemical functional group of the biodiesel. The model used in this experiment is Thermo Nicolet Fourier Transform Infrared spectrometer (FTIR) Nexus 670 model. The liquid sample was placed on the Zn-Se sample holder and the holder was assembled in a module that was finally put into a sample chamber of FTIR. The HATR mode is selected. The IR spectra at 2 cm^{-1} resolution with 32 scans were collected in the range of 3600-650 cm^{-1}. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the vibration frequencies between the bonds of the atoms making up the material. Additionally, the size of the peaks in the spectrum is a direct guide that indicates of the amount of material present.

3.3.3 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 was analyzed according to European standard UNE-EN 14212:2003 method using a Metrohm 743 Rancimat instrument (Herisau, Switzerland). Sample of 3 g was analyzed at a heating block temperature of 110 °C with the temperature correction factor (ΔT) of 0.98 °C, and a constant air flow of 10,000 ml/h. The volatile compound formed was 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 was reported as the induction period (IP, h). All the measurements were performed in duplicate (Wadumesthrige et al., 2009).

3.3.4 Cold Flow Properties Testing

Two major problems associated with the use of biodiesel are its oxidation stability and its cold flow properties. The cold flow properties can be indi-

cated by cloud points (CP) and cold filter plugging points (CFPP), which are important indices related to low-temperature operability of diesel fuels.

3.3.4.1 Cloud Point

The cloud point is the temperature at which fuel become cloudy due to formation of crystals and solidification of saturates. Biodiesel sample was first poured into a test jar to a level approximately half full. Then, the entire test subject was placed in a constant temperature cooling bath. At every 1 °C, the sample was 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 (Thunyaratchatanon, 2012).

3.3.4.2 Cold Filter Plugging Point

The cold filter plugging point of a liquid biodiesel, which usually occurs at a higher temperature than the pour point and lower temperature than could point. The cold filter plugging point is the lowest operating temperature in which a vehicle will operate. This procedure was developed according to ASTM D6371-05.

3.4 Catalyst Characterization

The catalysts were characterized by several techniques. Those techniques are X-ray Diffraction (XRD), Brunauer-Emmet-Teller (BET) surface area measurement, Atomic Absorption Spectrometry (AAS), CO pulse adsorption method (Model R6015, Ohkura), and Fourier Transform Infrared spectrometry (FT-IR).

3.4.1 X-ray Diffraction (XRD)

A Rigaku 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 CuKα 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

10° to 80° and a scan speed used is 5°/s. Finally, the obtained XRD patterns were compared to the standard file to identify the crystalline phases of the catalysts (Thunyaratchatanon, 2012).

3.4.2 Autosorb-1 MP Surface Area Measurement

The method used for measuring the specific surface area and pore size distribution by Brunauer-Emmet-Teller (BET) method Autosorb-1 MP. Prior to performing the test, the volatile species that are adsorbed on the catalyst surface was degasses under vacuum 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 was calculated by the software (Thunyaratchatanon, 2012).

3.4.3 CO Pulse Adsorption

CO pulse adsorption (Model R6015, Ohkura) is used for measuring metal dispersion and particle size of the catalysts. Prior to measurements, Pd/SiO_2, Pt/SiO_2, $Pd-Mg/SiO_2$, and $Pt-Mg/SiO_2$ catalyst was reduced with hydrogen at 300 °C for 1 h. Whereas Ni/SiO_2 and $Ni-Mg/SiO_2$ was reduced with hydrogen at 400 °C for 1 h.

3.4.4 Atomic Absorption Spectrometry (AAS)

The actual amount of metal loading was determined using a atomic absorption spectrometer (AAS), Varian Model SpectraAA 30 equipped with a GTA 110 graphite furnace, a deuterium lamp as background correction system was used. Hollow cathode lamp of metal was used as a source. A pneumatic nebulizer with a glass impact bead was used. Peal of absorbance signals was measured by the AA instrument and the volume of the solution introduce in to the graphite tube was 20 µl. The concentration of gas-phase atoms was measured by absorption light of atomic absorption spectrometer (AAS). The concentration was determined from a working curve after calibrating the instrument with standards of known concentration.