CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Equipments

- Gas Chromatograph (GC)
- X-ray Diffractometer (XRD)
- Surface Area Analyzer (SAA)
- Scanning Electron Microscope with Energy Dispersive Spectrometer (SEM-EDS)
- Temperature Programmed Desorption / Reduction / Oxidation Analyzer (TPD/R/O/-MS)
- Atomic Absorption Spectrometer (AAS)
- Furnace
- Stirrer
- Stainless Steel Semi-Batch Reactor
- Temperature Controller
- Mass Flow Controller
- Pressure Controller
- Peristaltic Pump

3.1.2 Chemicals

- Biodiesel, Verasuwan Co., Ltd.
- Silicon Dioxide, Cariact Fuji Silysia Chemical Ltd.
- Palladium (II) Nitrate Dihydrate (40% Purum), Sigma Alorich
- n-Heptane (99.5% Purity), RCI Lab-Scan
- Acetone (99.5% Purity), RCI Lab-Scan

3.1.3 Gases

- 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 Catalyst Preparation

Pd supported on silica support catalyst was prepared by incipient wetness impregnation method. An aqueous solution containing the desired amount of palladium (II) nitrate dihydrate ($Pd(NO_3)_2.2H_2O$) precursor was prepared. The amount of aqueous solution required to the silica support (incipient wetness) was determined prior to the impregnation. Firstly, the silica support dried in an oven overnight at 110 °C to remove the absorbed water on the surface. Then, pore volume was found by slowly drop distillated water on silica support and stirred thoroughly until it is saturated. Secondly, Pd solution was prepared by dissolving $Pd(NO_3)_2.2H_2O$ with distillated water in equal amount of pore volume that we found in the first step. The Pd solution was added to the SiO_2 powder with stirring to wet the support, the impregnated catalyst was allowed to stand for 24 h in a cover beaker to ensure that Pd diffuses and disperses thoroughly on the surface of silica. Finally, the catalyst was dried in an oven overnight at 110 °C and then calcined in air at 500 °C for 2 h and reduce with hydrogen at 250 °C under atmospheric pressure for 3 h.

3.2.2 Partial Hydrogenation

The partial hydrogenation reaction of polyunsaturated FAMEs was carried out at 120 °C and 4 bar in a 300 ml stainless steel semi-batch reactor. Approximately 1.5 g of supported Pd catalyst was placed into the reactor. The system was purged with nitrogen to remove remaining air. Then 100 ml of biodiesel obtained from Verasuwan Co., Ltd. was fed into the reactor by peristaltic pump. After that, the partial hydrogenation occurred with hydrogen flow passing through at a rate of 50 ml/min. The temperature and pressure was increased until the desired point. In order to prevent external mass transfer limitation, oil, catalyst and hydrogen

will be mixed by using stirrer speed at 500 rpm. Samples were collected every 30 minutes and the product was analyzed by a Hewlett Packard gas chromatograph 5890 Series II equipped with a FID detector after addition of n-heptane a solvent. The schematic of the partial hydrogenation experiment is shown in Figure 3.1.
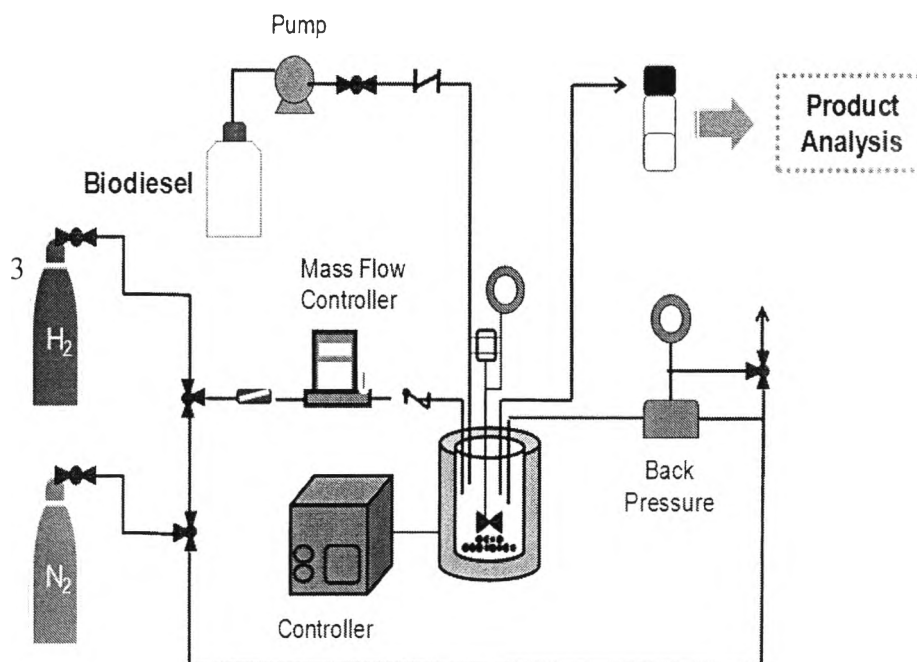

Figure 3.1 Schematic of the partial hydrogenation reaction.

3.3 Biodiesel Analysis

There are many characterization techniques to analyze the quantity and quality of biodiesel and partial hydrogenated biodiesel for example gas chromatography (GC), rancimat testing, and cold flow properties testing.

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 was helium (99.99%) with a flow

rate of 70 ml/min. The fatty acids were quantified by injecting 0.2 μl of each sample. The injector and detector temperatures were 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.

3.3.2 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 affect on vehicle system by increase the viscosity. Oxidative stability was analyzed according to European standard EN14112 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 L/h. The volatile compounds formed were 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 was performed in duplicate (Wadumesthrige *et al.*, 2009).

3.3.3 Cold Flow Properties Testing

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

3.3.3.1 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 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.

3.4 Catalysts Characterization

The characteristics of the catalysts before and after partial hydrogenation were obtained using various analysis techniques such as X-ray diffraction (XRD), surface area analysis (Brunauer-Emmet-Teller (BET) method), scanning electron microscopy (SEM), atomic absorption spectrometry (AAS), and temperature programmed desorption/reduction/oxidation analysis (TPD/R/O/-MS).

3.4.1 X-ray Diffraction (XRD)

X-ray diffraction shows primary metallic Pd crystallites on the reduced catalyst and the formation of Pd on the reacted catalyst. The X-ray diffraction data were acquired with a Bruker D8 Advance X-ray diffractometer system 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 fine focus ceramic X-ray tube, which generates CuK_α (λ = 1.5405 Å) monochromatic radiation was used as an X-ray source to obtain the XRD patterns. The sample was prepared and held in the X-ray beam. The X-ray diffraction profiles were recorded both in a continuous mode and in a step-by-step scanning mode in a range of 2θ value between 5° to 90° with a scanning speed of 5°/second at 40 kV and 30 mA. Finally, the XRD patterns were compared to standard file to identify crystalline phases.

3.4.2 Surface Area Analysis (SAA)

The specific surface area, pore volume and pore size distribution of catalyst were measured by Autosorb-1 analyzer. Prior to the analyses, each sample was degasses under vacuum for 24 h at 250 °C in order to eliminated the volatile

species that adsorbed on the catalyst surface. Helium gas and nitrogen gas were used as an adsorbate for blank analysis and for analysis, respectively. The pore characteristics of the catalyst were calculated from the adsorption curve according to the Brunauer-Emmet-Teller (BET) method.

3.4.3 Scanning Electron Microscopy (SEM)

SEM images were taken on a JSM-5800LV scanning electron microscope (SEM). This machine was utilized to identify the microstructure and capture the micrograph of catalyst morphology. Prior to analysis, samples will be placed on the stub and coated by platinum in sputtering device.

3.4.4 Atomic Absorption Spectrometry (AAS)

The actual amount of palladium in fresh and spent catalysts was determined using a atomic absorption spectrometer (AAS). Varian Model Spectra AA 30 equipped with a GTA 110 graphite furnace, a deuterium lamp as background correction system was used. Hollow cathode lamp of Pd was used as sources. A pneumatic nebulizer with a glass impact bead was used. The instrumental parameters of the spectrometer were as follow: wavelengths and width bands at 265.9 and 0.2 nm, respectively. Observation height was varied between 6 and 12 nm. A slot burner for air-acetylene flame was used. Acetylene flow rate was varied between 1.5 and 4.0 l/min and air flow was kept constant at 13.5 l/min. Peal of absorbance signals was measured by the AA instrument and the volume of the solution introduce into 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.

3.4.5 Temperature - Programmed Desorption/Oxidation/Reduction (TPD/R/O)

Temperature programmed characterizations, reduction (TPR) was carried out using Thermofinnigan 1100. This analysis used for observing desorbed molecules from a surface when the surface temperature is increased. In addition, the

reducibility and reduction temperature of catalyst will be determined by using the TPR.