CHEPTER III
EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Equipment

- Gas Chromatograph (GC)
- X-ray Diffractometer (XRD)
- Surface Area Analyzer (SAA)
- Scanning electron microscope with energy dispersive spectrometer   (SEM-EDS)
- Temperature program desorption / temperature programmed reduction analyzer (TPD/R/O/-MS)
- Atomic absorption spectrometer (AAS)
- Fourier transform infrared spectrometer (FTIR)
- Furnace
- Temperature controller
- Stainless steel semi-batch reactor
- Mass flow controller
- Peristaltic pump

3.1.2 Chemicals

- Biodiesel, Veerasuwan Co., Ltd.
- Granule activated charcoal, Fluka
- Palladium (II) nitrate dihydrate (40% purum), Sigma Aldrich
- Bisphenol-A (99% purity), Aldrich
- Formaldehyde (37%wt. in water), Merck
- Triethylenetetramine (TETA) (98% purity), Fluka
- Dimethylformamide (DMF), Lab-Scan

3.1.3 Gases

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

3.2 Experimental

3.2.1 Catalysts Preparation

Pd loaded on carbon catalysts were prepared by impregnation method of the support with aqueous solution of $Pd(NO_3)_2.2H_2O$ precursor. Firstly, carbon aerogel was dried in an oven at 110°C for 24 h to remove the absorbed water on the surface. This dried carbon aerogel was stored in a silica gel desiccators prior to use. Secondly, to prepare 2 wt.% Pd loaded on carbon aerogel, the carbon aerogel was impregnated with an aqueous solution of Pd precursor for 24 h at room temperature to ensure that Pd diffuses and disperses thoroughly on the surface of activated carbon. Then, it was dried in an oven at 110°C for 24 h. Finally, the dried catalyst was calcined under N_2 gas at 500°C for 2 h.

3.2.2 Synthesis of Polybenzoxazine (carbon aerogel)

Polybenzoxazine was prepared by firstly dissolve bisphenol-A (2.283 g) in dimethylformamide (13.655 g) and then it was stirred for 10 minutes until clear solution was obtained. Then, formaldehyde solution (3.243 g) was added to bisphenol-A solvent and then it was stirred for 20 min in cooling bath, triethylenetetramine (1.827 g) was added into the mixture in the second step and then it was stirred for 1 h and transparent yellow viscous liquid was obtained. Then, the transparent yellow viscous liquid was brought to aging for 1 day and then the benzoxazine aerogel was obtained, benzoxazine aerogel was brought to oil bath at 80°C for 2 days in closed system and then the solid sample was obtained. Then, the solid benzoxazine aerogel was cut into a dish shape and placed into petri dish at room temperature for 4 day. Finally, the piece of solid benzoxazine aerogel was cure

in an oven as the following steps shown in Figure 3.1. After that, it was calcined under N_2 gas at 800°C for 23 h. Finally, it was calcined under CO_2 at 900°C for 12 h.
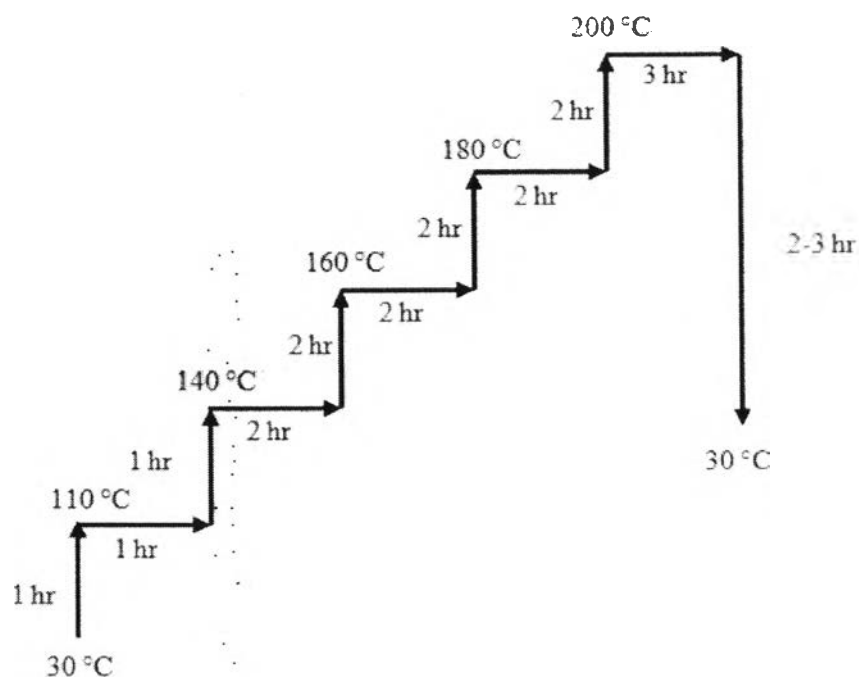

Figure 3.1 Schematic of curing step.

3.2.3 Partial Hydrogenation Experiment

Partial hydrogenation reaction of polyunsaturated FAMEs was carried out in a 300 ml stainless steel semi-batch reactor at temperature and pressure of 120°C and 4 bar, respectively. Stirring speed was maintained at 500 rpm to prevent external mass transfer limitation. The flow rate of hydrogen gas was 50 ml/min and was controlled by a mass flow controller. Firstly, the supported-Pd catalyst was placed into the reactor. Then, the system was purged with nitrogen to remove the remaining air. After that, the feed biodiesel obtained from Veerasuwan Co., Ltd. was fed into the reactor by a peristaltic pump. The reaction will be started by increasing temperature and pressure to the desired point.

Finally, the liquid products was collected and analyzed by Hewlett Packard gas chromatography 5890 Series II equipped with a FID detector. The schematic of the partial hydrogenation experiment is shown in Figure 3.2.
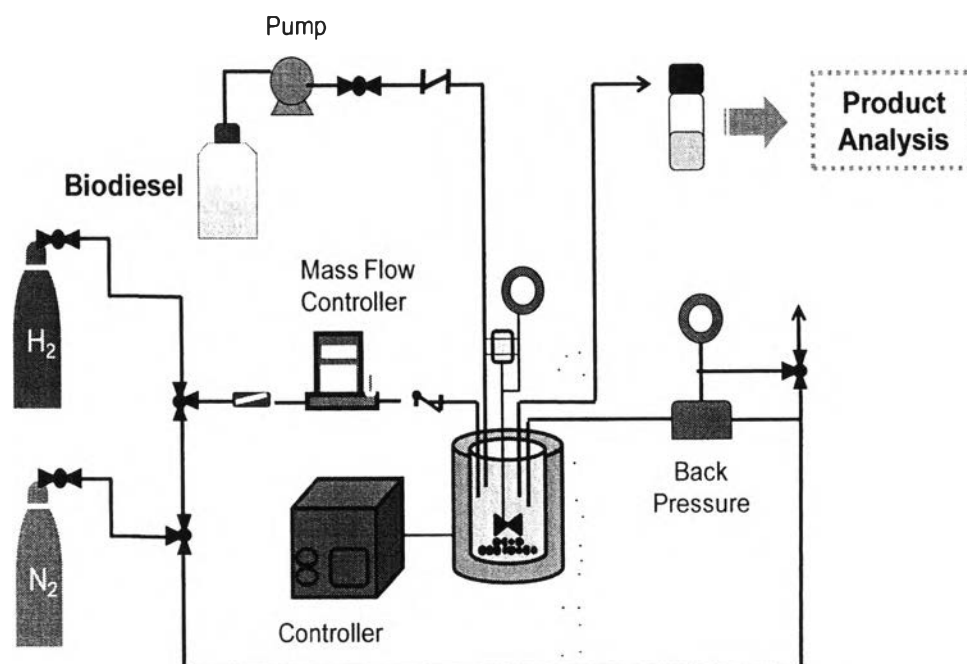
Figure 3.2 Schematic of the partial hydrogenation reaction.

3.3 Biodiesel Analysis

Biodiesel before and after partial hydrogenation reaction was analyzed by several characterization techniques including: Gas Chromatography (GC), Fourier Transform-Infrared Spectrometry (FT-IR), Rancimat, and cold flow properties testing.

3.3.1 Gas Chromatography (GC)

Biodiesel before and after partial hydrogenation reaction was analyzed by gas chromatography technique by using a Hewlett Packard gas chromatograph 5890 Series II equipped with a flame ionization detector (FID). A DB-WAX (30 m x 0.25 mm) fused-silica capillary column coated with a 0.1 μm film was used. Samples of 0.2 μl was injected under the following conditions: the carrier gas was helium with a flow rate of 70 ml/min, the injector temperature was 200°C with a split ratio of 75:1, and the detector temperature was 230°C. The sample was

injected at an oven temperature of 130°C. After an isothermal period of 2 min, the GC oven was heated to 220°C at a rate of 2°C/min and held for 15 min with the total running time of 62 min. Methyl heptadecanoate was used as an internal standard to determine the methyl ester content, as shown in Equation 3.1.

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} * \frac{C_{EI} * V_{EI}}{m} * 100 \qquad \text{Eq (3.1)}$$

C   Methyl ester contentation

$\sum A$ The overall area of methyl ester from C12:0 to C22:0

A_{EI} The peak area which is assigned to methyl heptadecanoate solution

C_{EI} Concentration in mg/ml of methyl heptadecanoate solution

V_{EI} Volume of methyl heptadecanoate solution

m Weight in mg of biodiesel sample

3.3.2 Fourier Transform Infrared Spectrometry (FT-IR)

Thermo Nicolet Fourier Transform-Infrared spectrometer (FT-IR) Nexus 670 was used to identify the chemical functional groups of biodiesel before and after partial hydrogenation reaction, in order to confirm with the results obtained from GC that the characteristic peak, which represents C=C disappeared after biodiesel was partially hydrogenated. The liquid sample was placed on the zinc-selenide sample holder and then this sample holder was assembled in the module that was finally put into sample chamber of FT-IR. 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. In addition, the size of the peaks in the spectrum directly indicates the amount of material present.

3.3.3 Rancimat Testing

Oxidative stability is one of the major issues affecting the use of biodiesel because of its content of polyunsaturated methyl esters. The oxidative stability of biodiesel after partial hydrogenation reaction will be tested by Metrohm 743 Rancimat. Biodiesel will be aged at 110°C under a constant air stream. The oxidative stability corresponds to the period of time passing before fatty acid methyl esters are degraded to such an extent that the formation of volatile acids can be recorded through an increasing of conductivity. This procedure was developed according to EN 14112 (Ramos *et al.*, 2009).

3.3.4 Cold Flow Properties Testing

The cold flow properties of biodiesel after partial hydrogenation reaction including cloud point and pour point will be investigated. The details on each property are described below.

3.3.4.1 Pour Point

According to the ASTM D97, 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.

3.3.4.2 Cloud Point

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 40mm in thickness. The cloud point is the temperature at which the milky cloud crystals first appear.

3.4 Catalyst Characterization

Several characterization techniques was used to characterize the fresh and spent catalysts including: X-ray Diffraction (XRD), Brunauer-Emmet-Teller (BET) surface area measurement, Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDS), Atomic Absorption Spectrometry (AAS), and Temperature - Programmed Desorption / Temperature - Programmed Reduction analyzer (TPD/R/O/-MS).

3.4.1 X-ray Diffraction (XRD) Technique

A Bruker D8 Advance X-ray diffractometer system was 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 fine focus ceramic X-ray tube which generates CuK_α radiation (1.5405 Å) was used as an X-ray source to obtain the XRD patterns at running conditions for the X-Ray tube of 40 kV and 40 mA. The sample was prepared and held in the X-ray beam. The detector was 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 of 5°/second. Finally, the XRD patterns was compared to standard file to identify crystalline phases.

3.4.2 BET Surface Area Measurement

The specific surface area and pore size distribution was determined by Brunauer-Emmet-Teller (BET) method Autosorp-1-MP. Before analyzing, the volatile species that adsorbed on the catalyst surface was eliminated by heating the catalyst under vacuum atmosphere at 250°C overnight. Helium gas was used as an adsorbate for blank analysis and nitrogen gas was used as an adsorbate for analysis. And then, the software was calculated the specific surface area and pore size distribution of the catalyst.

3.4.3 Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDS)

Scanning Electron Microscope (SEM), Model JSM-5800LV, was utilized to identify the microstructure and capture the micrograph of catalyst morphology. And Energy Dispersive Spectrometer (EDS) was utilized to identify the presence of elements (from characteristic X-ray) in the catalyst region being examined. The catalyst sample was placed on the stub and coated by platinum in sputtering device before place in the sample holder in the SEM machine.

3.4.4 Atomic Absorption Spectrometry (AAS)

In order to determine the actual amount of palladium in the fresh catalyst and spent catalyst, Atomic Absorption Spectrometer (AAS), Varian Model Spectra AA 30 was used. This technique uses the absorption of light to measure the concentration of gas-phase atoms. Concentration measurements will be 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 Desorption / Oxidation / Reduction Thermofinnigan 1100 will be used for observing desorbed molecules from a surface when the surface temperature is increased. The Pd dispersion will be determined using the TPD of CO, which is used as the probe molecule. A 50-mg sample will be degassed by heating in a flow of helium at a rate of 8°C/min from room temperature to 250°C and will be kept at this temperature for 2 h. And then, adsorption of CO gas will occur at 100°C. After that, the physical adsorbed CO gas will be purged by flow of helium gas at 25°C for 2 h. CO-TPD was performed at the rate of 10°C/min up to 400°C.