

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Chemicals

All chemicals used in this work were analytical grade and they were used without any further purification. Palladium (II) chloride anhydrous ( $\text{PdCl}_2$ ; 60% purum, Sigma Aldrich), palladium (II) nitrate dihydrate ( $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ; 40% purum, Sigma Aldrich), and palladium (II) ammonium chloride ( $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot x\text{H}_2\text{O}$ ; N.E. Chemcat) were used as a Pd precursor. On the other hand, platinum (II) ammonium chloride ( $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot x\text{H}_2\text{O}$ ; N.E. Chemcat) and nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; Wako Chemicals) were used as a Pt and Ni precursor, respectively.

Activated carbon ( $\leq 40 \mu\text{m}$  particle size, Fluka), activated carbon (granule, Fluka), alumina ( $\text{Al}_2\text{O}_3$ ; JGC Catalysts and Chemicals), silica-alumina ( $\text{SiO}_2\text{-Al}_2\text{O}_3$ , 28 wt.%  $\text{Al}_2\text{O}_3$ , 72 wt.%  $\text{SiO}_2$ , JGC Catalysts and Chemicals) and four types of silica with an average pore diameter of 3 nm ( $\text{SiO}_2\text{-Q3}$ ), 10 nm ( $\text{SiO}_2\text{-Q10}$ ), 30 nm ( $\text{SiO}_2\text{-Q30}$ ), and 50 nm ( $\text{SiO}_2\text{-Q50}$ ) obtained from Fuji Silysia Chemical Company, were used as supports.

Bisphenol-A (99% purity, Aldrich), formaldehyde (37 wt.% in water, Merck), triethylenetetramine (TETA; 98% purity, Fluka), and dimethylformamide (DMF; Lab-Scan) were used for the preparation of carbon aerogel support.

Palm biodiesel obtained from Verasuwan Co., Ltd. was used as biodiesel feed for partial hydrogenation reaction in Parts 1 and 2. In addition, rapeseed oil (Yamakei Sangyo), potassium hydroxide (Wako Chemicals), and methanol (Wako Chemicals) were used as starting materials to prepare rapeseed biodiesel.

Moreover, n-heptane (99.5%, Fisher Scientific) and methyl heptadecanoate (99.7%, Fluka) were used as a solvent and standard for GC Agilent 5890, whereas tetrahydrofuran (stabilizer free, Wako Chemicals) was used as a solvent for GC Agilent 6890N. Furthermore, allyl isothiocyanate (Wako Chemicals) was used as a representative sulfur compound in rapeseed biodiesel.

Gases used in the partial hydrogenation experiment were high purity (99.99%) hydrogen and high purity (99.99%) nitrogen. Moreover, high purity (99.99%) oxygen and high purity (99.99%) carbon dioxide was used for the catalyst calcination, and preparation of carbon aerogel, respectively. All of them were purchased from Thai Industrial Gases Public Company Limited.

### **3.2 Synthesis of Carbon Aerogel**

Carbon aerogel or polybenzoxazine was prepared according to the method of Pekala (1989). Firstly, bisphenol-A was dissolved in dimethylformamide and stirred for 10 minutes until clear solution was obtained. Secondly, formaldehyde solution was added to bisphenol-A solvent and stirred for 20 minutes in a cooling bath. Thirdly, triethylenetetramine was added into the resulting mixture from the second step and stirred for 1 hour until obtaining a transparent yellow viscous liquid. Then, this liquid was aged for 1 day to obtain benzoxazine aerogel. After that, this aerogel was heated in an oil bath at 80°C for 2 days and a solid sample was obtained. Then, this solid sample was cut into a dish-shaped and kept in a petri dish at room temperature for 4 days. After that, the piece of solid benzoxazine aerogel was cured in an oven at 110°C. Finally, it was calcined under N<sub>2</sub> at 800°C for 23 hours and calcined under CO<sub>2</sub> at 900°C for 12 hours

### **3.3 Catalyst Preparation**

#### **3.3.1 Pd Supported on Carbon Materials**

The 2 wt.% Pd on the activated carbon and carbon aerogel catalysts were prepared by the incipient wetness impregnation (IWI) technique using PdCl<sub>2</sub> and Pd(NO<sub>3</sub>)<sub>2</sub>.2H<sub>2</sub>O precursor. Firstly, carbon supports were dried in an oven at 110°C for 24 h to remove the adsorbed water. Secondly, the carbon supports were impregnated with a solution of Pd precursor for 24 h at room temperature to ensure that Pd diffused and dispersed thoroughly onto the surface of the carbon support.

After that, it was dried in an oven at 110°C for 24 h. Finally, the dried catalyst was calcined at 500°C for 2 h under a nitrogen flow.

However, it was found that the drying method for the preparation of Pd/C catalysts resulted in the low dispersion of Pd and the agglomeration of Pd particles. Therefore, the new catalyst preparation technique was developed, as follows.

### 3.3.2 Pd Supported on Amorphous Mesoporous Materials

Pd on amorphous mesoporous supports: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were prepared based on the new catalyst preparation and drying method. These catalysts were prepared by the incipient wetness impregnation using pore filling technique and Pd(NH<sub>3</sub>)<sub>4</sub>.Cl<sub>2</sub>.xH<sub>2</sub>O was used as a Pd precursor. The support was dried in an oven at 110°C for 24 h. An aqueous solution containing appropriate amounts of Pd(NH<sub>3</sub>)<sub>4</sub>.Cl<sub>2</sub>.xH<sub>2</sub>O was impregnated into the support under vacuum and kept for 24 h. The total amount of Pd loading was 1 wt.%. After impregnation, the catalyst was dried using a rotary evaporator at room temperature for 2 h, then at 60°C for 2 h, and finally using a vacuum pump at 60°C for 2 h. After that, it was calcined under an oxygen stream at 300°C with a heating rate of 0.5°C/min and 1 L/min oxygen flow rate. Finally, the catalyst was reduced at 300°C for 2 h with a heating rate of 5°C/min and 100 ml/min hydrogen flow rate before use in the partial hydrogenation reaction. In addition, Pt and Ni supported SiO<sub>2</sub> catalysts were prepared by the same method using Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>.xH<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O precursor, respectively. The Pt catalyst was calcined at 300°C, whereas; the Ni catalyst was calcined at 450°C. After that, the Pt catalyst was reduced at 300°C for 2 h, while; 400°C is a reduction temperature for the Ni catalyst.

## 3.4 Catalyst Characterization

Several characterization techniques were used to characterize the prepared catalysts including: X-ray Diffraction (XRD), surface area analysis, Field Emission-

Scanning Electron Microscopy (FE-SEM), Transmission Electron Microscopy (TEM), CO-pulse chemisorption, and NH<sub>3</sub>-adsorption technique.

#### 3.4.1 X-ray Diffraction (XRD) Technique

A Rigaku DMAX2200 X-ray diffractometer was used to characterize and identify the internal structure, bulk phase, crystallinity, and composition in crystalline phases of the support and catalysts. A 2.2 kW Cu anode long fine focus ceramic X-ray tube, which generates CuK<sub>α</sub> 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 30 mA. The sample was prepared and held in the X-ray beam. The detector scanned the intensity of diffracted radiation from the sample as a function of  $2\theta$  in the range of 5° to 90° with a scan speed of 5°/sec. Finally, the XRD patterns were compared to the standard file to identify crystalline phases.

#### 3.4.2 Surface Area Analysis

The specific surface area, pore volume, and pore size of the supports and catalysts were determined using Quantachrome Autosorb-1 MP surface area analyzer. 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; whereas, nitrogen gas was used as an adsorbate for analysis. And then, the specific surface area, pore volume, and pore size of the catalyst, were calculated by the software.

#### 3.4.3 Field Emission-Scanning Electron Microscopy (FE-SEM)

A Field Emission-Scanning Electron Microscope (FE-SEM), Hitachi Model S4800, was utilized to identify the microstructure and capture the micrograph of the support and catalyst morphology. The catalyst sample was placed on the stub and coated by platinum in a sputtering device before being placed in the sample holder in the FE-SEM machine.

#### 3.4.4 Transmission Electron Microscopy (TEM)

The catalyst morphology and dispersion of metal were examined using a Transmission Electron Microscope, JEOL, JEM-200CX. The catalyst sample was ultrasonically dispersed in 2-propanol solution. After that, this suspension was dropped onto a nickel microgrid.

#### 3.4.5 CO-Pulse Chemisorption Technique

Metal dispersion of the prepared catalysts was determined by pulse chemisorption of 10.1% CO/He, using a Temperature-Programmed Desorption/Oxidation/Reduction (TPD/R/O) Ohkura R6015. Prior to the measurements, the calcined sample was pretreated with hydrogen at 120°C (for Pd/C catalysts) or 300°C (for Pd/amorphous mesoporous materials) for 1 h and followed by purging with helium at the same temperature for 10 min. The Pd dispersion was measured at 50°C and calculated by assuming a stoichiometry of CO:Pd = 1:1.

#### 3.4.6 NH<sub>3</sub>-Adsorption Technique

Acidity of the amorphous SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supports was investigated by the NH<sub>3</sub>-adsorption technique using an NH<sub>3</sub> calorimeter (CSA-450G) manufactured by Tokyo Riko Co., Ltd. The sample was evacuated at 300°C for 1 h and cooled down to 50°C to measure the heat of adsorption of NH<sub>3</sub> on the acid sites.

### **3.5 Transesterification of Rapeseed Oil**

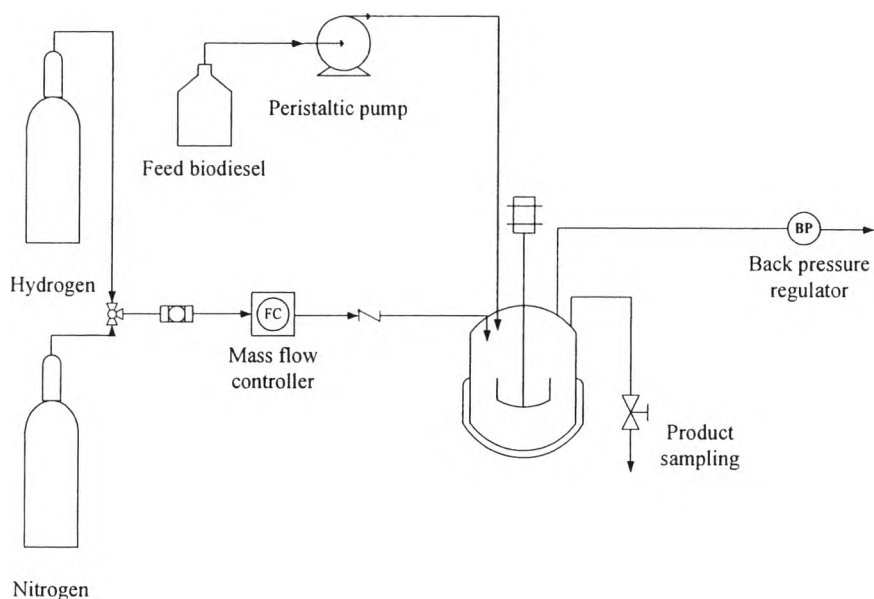
Commercial biodiesel or FAME derived from palm oil was obtained from Verasuwan Co., Ltd. On the other hand, the rapeseed oil-derived FAMEs were experimentally prepared by a typical transesterification reaction, where potassium hydroxide (KOH) was used as a catalyst. The reaction took place in a 2 L three-necked round-bottomed flask, equipped with a stirrer and a condenser. The amount of KOH catalyst used was 1 wt.% compared to the starting rapeseed oil, with 9:1 methanol to oil molar ratio. Firstly, KOH was dissolved in methanol and added into the rapeseed oil. After that, the mixture was stirred at 60°C for 2 h and cooled down.

A phase separation was followed; the lower glycerine phase was removed. The upper phase was washed with 60°C distilled water several times to remove remaining KOH, methanol, and possible soap. Finally, it was dried using a rotary evaporator at 60°C, to remove remaining washed water. The FAMES composition of the palm and rapeseed biodiesel fuel (BDF) was determined by gas chromatography (GC).

### **3.6 Partial Hydrogenation of Polyunsaturated FAMES**

#### **3.6.1 Batch-Type Reactor**

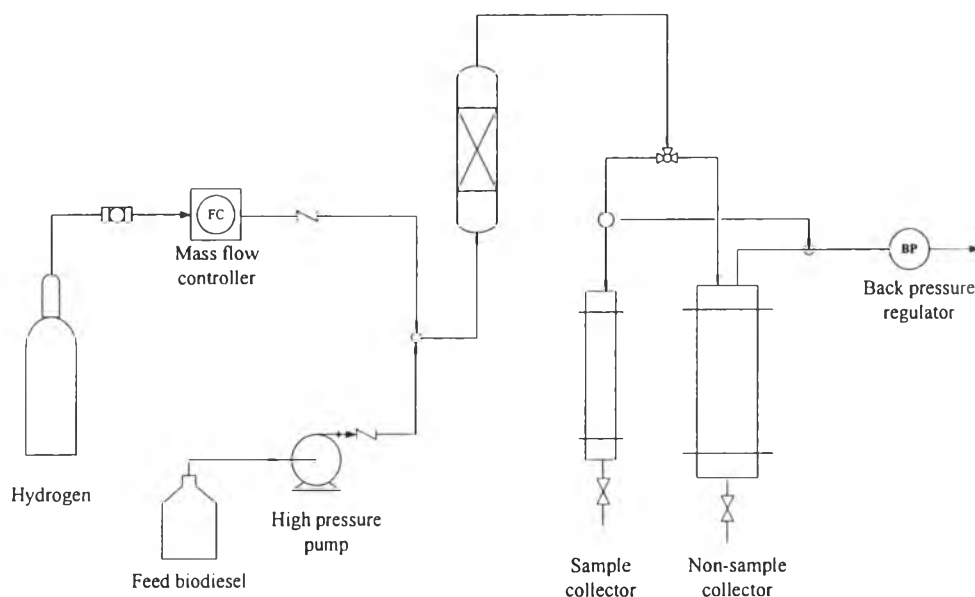
Partial hydrogenation of polyunsaturated FAMES was carried out in a 300 ml stainless steel semi-batch reactor at reaction conditions of 120°C, 0.4 MPa, 500 rpm stirring rate, 50 ml/min hydrogen flow rate, and 1.5 wt.% catalyst compared to starting BDF for Pd/C catalyst. On the other hand, the reaction conditions of 80°C, 0.3 MPa, 1,000 rpm stirring rate, 200 ml/min hydrogen flow rate, and 0.2 wt.% catalyst compared to starting BDF, were used for Pd/amorphous mesoporous material. First, the catalyst was transferred into the reactor containing BDF feed, in the box flowing with Ar, to prevent oxidizing of the reduced catalyst. Second, the reactor containing catalyst and BDF was connected to the reaction line and the system was purged with nitrogen three times to remove any remaining air. Third, the reaction was started by increasing the temperature and hydrogen partial pressure to the desired values. Finally, the liquid products were collected every 30 minutes. The total reaction time was 4 h for Pd/C catalyst, and 3 h for Pd/amorphous mesoporous material. The schematic of the partial hydrogenation experimental step with batch-type reactor is shown in Figure 3.1.



**Figure 3.1** Schematic of partial hydrogenation in batch-type reactor

### 3.6.2 Continuous Flow-Type Reactor

The experiments were performed using a stainless steel up-flow reactor (Figure 3.2) in the temperature range of 80–120°C and hydrogen partial pressure of 0.1–0.4 MPa. The flow rate of hydrogen was fixed at 200 ml/min and was controlled using a mass flow controller. First, the Pd/C catalyst (0.2 g) was mixed with methyl cellulose and silica diluents. After that, the mixture was pressed and sieved to 600  $\mu\text{m}$ –150  $\mu\text{m}$ , and packed inside the reactor. Blank tests using methyl cellulose and silica diluents were run. It was confirmed that almost no hydrogenation reactions occurred within the experimental conditions. Second, the reactor was assembled to the system and pressurized to the desired pressure. After that, the temperature was increased to the desired point and was controlled using a temperature controller. Then, the biodiesel feed was passed through the catalyst bed using a high pressure pump with flow rate ranging 20–180 g/h. Finally, the liquid products were collected every hour for 5 h of reaction.



**Figure 3.2** Schematic of partial hydrogenation in continuous flow-type reactor

### 3.7 Biodiesel Analysis

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

#### 3.7.1 Gas Chromatography (GC)

FAME composition in the biodiesel before and after the partial hydrogenation reaction was determined using a Hewlett Packard gas chromatograph 6890N equipped with a flame ionization detector (GC-FID). An HP-88 (100 m x 250  $\mu\text{m}$  x 0.2  $\mu\text{m}$ ) capillary column was used. Samples of 1  $\mu\text{l}$  were injected under the following conditions: the carrier gas was helium with a flow rate of 2.4 ml/min, an injector temperature was 200°C with a split ratio of 75:1, and a detector temperature was 230°C. The sample was injected at an oven temperature of 155°C. After an isothermal period of 20 min, the GC oven was heated to 230°C at a rate of 2°C/min



and held for 2.5 min with a total running time of 60 min. The FAME composition was identified by reference to the retention time. Methyl heptadecanoate (C17:0) was used as an internal standard to determine the methyl ester content, as shown in Equation 3.1 (Iangthanarat, 2008).

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

$C$	Fatty acid methyl ester (FAME) content
$\sum A$	The overall area of FAME from C12:0 to C22:0
$A_{EI}$	The peak area which is assigned to methyl heptadecanoate
$C_{EI}$	Concentration in mg/ml of methyl heptadecanoate solution
$V_{EI}$	Volume of methyl heptadecanoate solution
$m$	Weight in mg of biodiesel sample

### 3.7.2 Fourier Transform-Infrared Spectrometry (FT-IR)

A 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, 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 into a Zn-Se sample holder. The IR spectra at  $2 \text{ cm}^{-1}$  resolution with 32 scans were collected in the range of  $3,600$  to  $650 \text{ cm}^{-1}$ .

### 3.7.3 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 before and after partial hydrogenation was tested by Metrohm 743 Rancimat. The sample was aged at  $110^\circ\text{C}$  under a constant air stream of 10 l/min. The oxidative stability corresponds to the period of time passing before FAMEs are degraded to such an extent that the formation of volatile acids can be

recorded through an increasing conductivity. This procedure was developed according to EN 14112 (Ramos *et al.*, 2009).

#### 3.7.4 Cold Flow Properties Testing

The cold flow properties of biodiesel before and after partial hydrogenation including cloud point and pour point were investigated by using a Tanaka mini pour/cloud point tester Series MCP-102 that was developed according to ASTM D6749.