

## **CHAPTER III**

### **EXPERIMENTAL**

#### **3.1 Materials and Chemicals**

1. Bisphenol A
2. Dioxane
3. Dimethylformamide (DMF)
4. Formaldehyde
5. Triethylenetetramine (TETA)
6. Silica suspension
7. Hydrofluoric acid (HF)
8. Surfactant cetyltrimethylammonium bromide (CTAB)
9. Tetraamminepalladium(II) chloride (Pd: 40.6%)
10. Potassium hydroxide (KOH)
11. Ethanol (EtOH)
12. Soybean oil
13. N-heptane 99.5%
14. Methanol (AR.)
15. Acetone, 99.9%

#### **3.2 Gases**

1. High purity (99.99%) oxygen, Thai Industrial Gases Public Co., Ltd.
2. High purity (99.99%) hydrogen, Thai Industrial Gases Public Co., Ltd.
3. High purity (99.99%) nitrogen, Thai Industrial Gases Public Co., Ltd.

#### **3.3 Equipment**

1. Fourier transform infrared spectrometer (FTIR) (Thermo Nicolet, Nexus 670)
2. Surface Area Analyzer (Autosorb-1MP)
3. Thermogravimetric analyzer (TG/DTA) (PerkinElmer, Pyris Diamond)
4. Gas chromatography (GC) (Pr 2100)
5. Field Emission Scanning Electron Microscopy (FE-SEM)
6. Transmission electron microscopy (TEM)

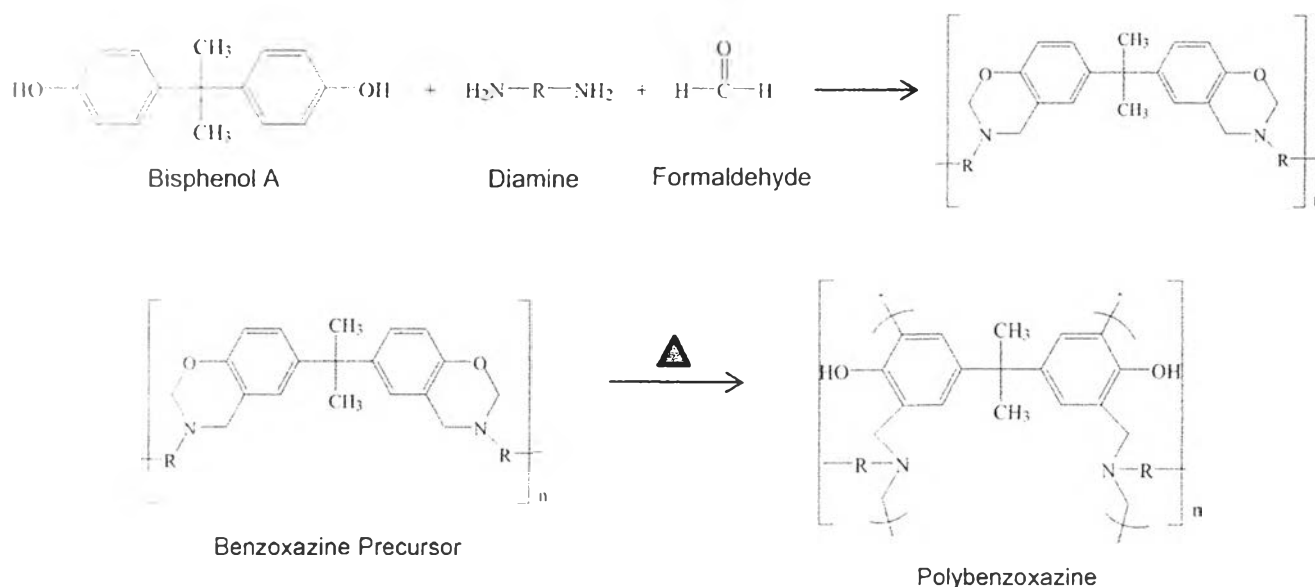
7. Surface Area Analyzer (SAA)
8. Condenser
9. Oil bath
10. Hot plate
11. Stirring plate
12. Thermometer
13. Temperature controller
14. Mass flow controller
15. Peristaltic pump
16. Magnetic bar
17. Water bath
18. Soxhlet extraction
19. Rotary evaporation
20. Filtration setup
21. Stainless steel semi-batch reactor
22. 500 ml three-necked round bottom flask
23. Furnace

**Software:**

1. Omnic
2. Sigma plot

**3.4 Methodology****3.4.1 Polybenzoxazine Preparation**

Bisphenol-A was dissolved in dioxane and magnetically stirred for 20 min before mixed with formaldehyde, silica colloids, CTAB (cetyltrimethylammonium bromide) and hexamethylenediamine (HAD), respectively. The mixture was then continuously stirred for 1 h before putting in a closed system and heating at 80°C for 2 days in an oil bath to let the gel set. After that, CTAB and solvent were removed by ambient pressure drying (Soxhlet Extraction). The resulting organogel was cured at 160°C and 180°C for 3 h at each temperature, and 200°C for 1 h to obtain the fully-cured polybenzoxazine.



**Figure 3.1:** Reaction of Polybenzoxazine Preparation.

### 3.4.2 Pyrolysis Process

Fully-cured polybenzoxazine xerogels were pyrolyzed under nitrogen flow at 800°C, followed by cooling to room temperature.

### 3.4.3 Silica Removal

Silica colloids were removed from carbon xerogels (CX) by immersing in 15% wt hydrofluoric acid for 24 h.

#### Preparation of 15% wt of HF

Mixed solvents = EtOH 50:50 H<sub>2</sub>O (mass ratio)

Total weight of mixed solvent = 200 g (From EtOH 100 g and H<sub>2</sub>O 100 g)

*Calculation*

$$\frac{\text{HF}}{200 \text{ g of mixed solvents} + \text{HF}} \times 100 = 15\% \text{ wt of HF solution}$$

$$\text{HF} = 35.29 \text{ g}$$

However, the commercial HF solution bought is 48% wt in water.

Therefore, 35.29 g HF can be calculated from the following equation:

$$\frac{35.29 \times 100}{48} = 73.52 \text{ g}$$

In addition, the amount of water in 73.52 g of 48% wt HF solution is  $73.52 - 35.29 = 38.23$  g.

Therefore, the amount of water added is  $100.00 - 38.23 = 61.77$  g

The preparation of 15 % wt of HF aqueous solution can be prepared as the following formula:

100 g EtOH : 61.77 g Water : 73.52 g of 48% wt HF solution

After that, the solution of 15% HF will be weighted for etching PBZ-Silica composite. The amount of 15% wt HF solution used, comparing to amount of PBZ-Silica, can be calculated by the following mass ratio:

$$\frac{\text{Weight of mixed solvent}}{\text{Weight of PBZ-Silica}} = 100$$

- The 48% of HF solution shows the density of 1.16 g/cc.
- 73.52 g of 48% wt HF solution can be calculated in term of volume by

$$\frac{73.52 \text{ g}}{1.16 \text{ g/cc}} = 63.38 \text{ cc}$$

#### 3.4.4 Catalyst Preparation

Commercial activated carbon (AC) with an average pore diameter of 3.64 nm, carbon xerogels (CX) with an average pore diameter of 29.95 nm and commercial silica (SiO<sub>2</sub>) with an average pore diameter of 43.09 nm were used as supports to study the effect of pore size on the catalytic activity. The sample was prepared by incipient wetness impregnation with an aqueous solution containing appropriate amounts of Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>. The total amount of Pd loading was 1 wt%. After impregnation, the catalyst was dried by a rotary evaporator and calcined at 300°C under nitrogen flow. In case of SiO<sub>2</sub>, it was reduced under hydrogen stream at 300°C before the catalytic activity test. The prepared Pd supported on AC, CX and SiO<sub>2</sub> catalysts are abbreviated as Pd/AC, Pd/CX and Pd/SiO<sub>2</sub> respectively.

Pd (1 wt%) was loaded on the supports(carbon xerogel and activated carbon) by incipient wetness impregnation, wherein a calculated amount of palladium(IV)nitrate dissolved in a minimum amount of water was added dropwise

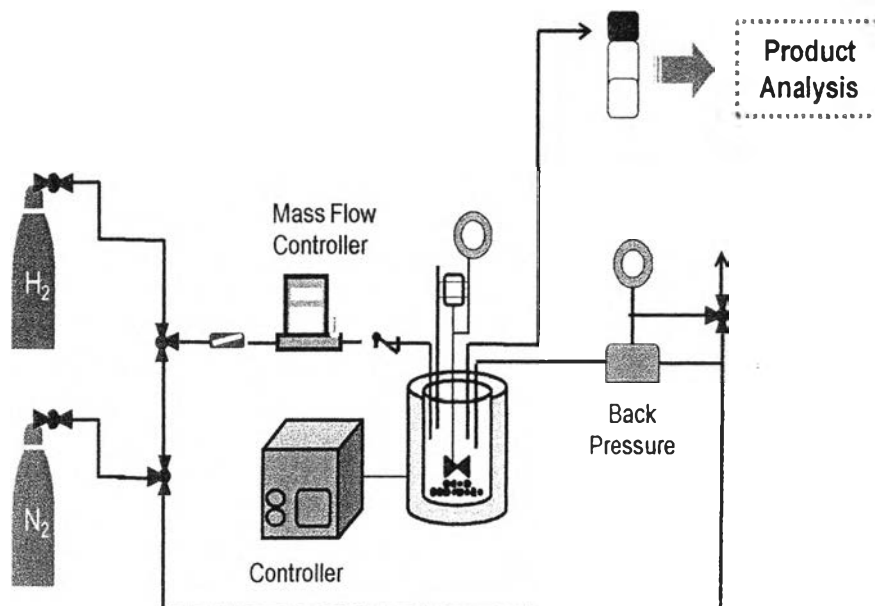
before mixing with the supports. The Pd-loaded supports were then dried overnight before calcining at 500°C for 2 hr to remove the organic moieties.

#### 3.4.5 Tranesterification of Soybean Oil

Fatty acid methyl esters (FAMES) of soybean oil were prepared by a typical transesterification reaction catalyzed by potassium hydroxide (KOH). The reaction took place in a three-necked round-bottomed flask. The amount of catalyst used was 1 wt.% compared to the starting soybean oil with 9:1 methanol to oil molar ratio. KOH was dissolved in methanol and added into the oil. 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, soybean biodiesel fuel (SBD) was dried by using sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) to remove the remaining washed water.

#### 3.4.6 Partial Hydrogenation of FAMES

The partial hydrogenation reaction was carried out in a stainless steel semi-batch reactor at a temperature and hydrogen partial pressure of 120 °C and 4 bar, respectively. The stirring rate was maintained at 1000 rpm and the flow rate of hydrogen gas was 150 ml/min. The reactor was charged with approximately 180 ml of SDF feed and 1 wt% of Pd/AC, Pd/CX and Pd/SiO<sub>2</sub> catalyst. The reactor was connected to the reaction line and the system was purged with nitrogen. The reaction proceeded under the desired conditions. Finally, the liquid products were collected every 30 min. The total reaction time was 4 h. followed the diagram in Figure 3.2.



**Figure 3.2:** Schematic of the partial hydrogenation reaction.

### 3.4.7 Biodiesel Analysis

#### 3.4.7.1 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  $\mu\text{m}$  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  $\mu\text{l}$  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.

#### 3.4.7.2 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 °C with the temperature correction factor ( $\Delta T$ ) of 0.98 °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).

#### *3.4.7.3 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.

##### *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.

##### *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.