

## CHAPTER III

### METHODOLOGY

#### 3.1 Equipment

1. Isothermal fixed bed stainless steel U-tube reactor
2. Agilent Technologies 6890, Gas Chromatography (GC)
3. Varian CP-3800, Simulated Distillation Gas Chromatography (GC-Simdist)
4. Agilent 7890, Gas Chromatography-Mass Spectrometry, Time of Flight (GC-TOF)
5. X-Ray Fluorescence spectrophotometer (XRF)
6. Thermo Finnigan Sorptometric 1990, Surface Area Analyzer (SAA)
7. Hydraulic pellet machine
8. Sieves Mesh 20-40
9. Rigaku, X-ray Diffraction Spectroscopy (XRD)
10. Mass flow meter
11. Temperature program controller
12. Syringe pump
13. Tedlar bag

#### 3.2 Materials

1. Bio-ethanol concentration 99.5% (Sapthip Co.,Ltd)
2. SAPO-34 catalyst (Tianjin Chemist Scientific Ltd.)
3. Deionized water
4. Quartz Wool
5. Alumina ball
6. Helium gas (High purity)
7. Tin(II) oxide powder
8. Tin(IV) oxide powder
9. Antimony(III) oxide powder

10. Antimony(V) oxide powder
11. Tin(II) chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ )
12. Antimony Trichloride ( $\text{SbCl}_3$ )
13. Carbon disulfide ( $\text{CS}_2$ )

### 3.3 Experimental Procedures

#### 3.3.1 Catalyst Preparation

The catalyst preparation of this research work was divided into 2 parts. The first one was the oxides of Sn and Sb loaded on SAPO-34 catalyst by solid-solid interaction, and the second part was both of Sn and Sb oxides loaded on SAPO-34 at various concentrations.

For the first scope, a SAPO-34 catalyst, supplied from Tainjin Chemist Scientific Limited, was dried at  $110\text{ C}^\circ$  for 3 hours and calcined with the heating rate  $10\text{ C}^\circ/\text{min}$  to  $400\text{ C}^\circ$ . The catalyst was kept at this temperature for 2 hours to remove water and impurities from the catalyst. A calculated amount of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{SbCl}_3$  was individually mixed with SAPO-34 by using solid-solid interaction method to obtain elemental loading percentages of 5% and 7%. After that, the catalysts were calcined at different temperatures shown in Table 2.1. The catalysts were then pelletized by using a hydraulic pelletizer machine. The pellets were crushed and sieved in the range of 20-40 meshes.

For the second scope, the SAPO-34 catalyst supplied from Tainjin Chemist Scientific Limited was dried at  $110\text{ C}^\circ$  for 3 hours and calcined with the heating rate  $10\text{ C}^\circ/\text{min}$  to  $400\text{ C}^\circ$ . The catalyst was kept at this temperature for 2 hours to remove water and impurities from the catalyst. A calculated amount of metallic tin or metallic antimony was mixed with SAPO-34 by using solid-solid interaction method as shown in Table 2.2. After that, the catalysts were treated under hydrogen atmospheric pressure at  $400\text{ C}^\circ$  for 2 h. The catalysts were then pelletized by hydraulic pelletizer machine. The pellets were crushed and sieved in the range of 20-40 meshes before being loaded to the isothermal reactor.

### 3.3.2 Catalytic Reaction

The catalytic dehydration of bio-ethanol was carried out in an isothermal fixed-bed stainless steel reactor under atmospheric pressure. 3 grams of a catalyst was loaded into U-tube reactor with quartz wool as a support on the top of alumina balls. The reaction temperature was controlled at a desired temperature by temperature controllers. The bio-ethanol was fed by a syringe pump with helium gas as a carrier gas through the catalyst bed. The products coming out from U-tube reactor were condensed in a cooling condensing flask to collect the condensable products while the non-condensable ones were kept in the gas bag. The gaseous products were then injected to a gas chromatography in a flame ionization detector mode (FID). The liquid product was mixed with carbon disulfide ( $\text{CS}_2$ ) to separate extract oil from aqueous liquid since oil dissolves in  $\text{CS}_2$  layer. After that, the extracted oil was analyzed by using the SIMDIST GC and GC-TOF.

### 3.3.3 Product Analysis

#### 3.3.3.1 *Gas Chromatography (GC)*

The gaseous product leaving from the reactor was kept in a gas sampling bag and then analyzed by a gas chromatography (Agilent Technologies 6890 Network GC system) using an HP-PLOT Q column (30 m x 0.32 mm ID and 20  $\mu\text{m}$  film thicknesses) equipped with a flame ionization detector (FID) to determine hydrocarbon gases; namely,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ , and  $\text{C}_4\text{H}_8$ . A DBWAX column installed in parallel and also equipped with the FID was employed to determine oxygenate components.

#### 3.3.3.2 *Simulated Distillation Gas Chromatography (SIMDIST GC)*

All maltenes and their petroleum fractions (gasoline, kerosene, gas oil, light vacuum gasoil, and heavy vacuum gas oil) were analyzed by a Varian CP-3800 simulated distillation gas chromatography (SIMDIST GC) conformed to ASTM D2887 method for true boiling point curves. A liquid sample was injected to the SIMDIST GC after dilution with carbon disulphide ( $\text{CS}_2$ ). The conditions were set as follows: initial temperature of 320  $^\circ\text{C}$ , time at initial temperature of 0.01 min, heating rate of 20  $^\circ\text{C}/\text{min}$ , final temperature of 320  $^\circ\text{C}$ , and 8.50 minute holding time.

### 3.3.3.3 *Gas Chromatography-Mass Spectrometry, Time of Flight (CG×GC-TOF)*

The oils and aqueous products from the catalytic dehydration were identified for their compositions using a Gas Chromatography equipped with a Mass Spectrometry of Time of Flight type (CG×GC-TOF), Agilent 7890 with 2D dimension mode. Helium was used as the carried gas, and nitrogen was used in the cooling system. The conditions were set as follows: initial temperature of 80 °C, time at initial temperature of 2 minutes, 4°C/min heating rate, final temperature of 270 °C hold for 5 minutes, and split ratio at 1:50.

### 3.3.4 Catalyst Characterization

#### 3.3.4.1 *Surface area analyzer (SAA)*

The Brunauer-Emmett-Teller (BET) technique was performed to determine the specific surface area, the total pore volume, and the pore size of catalyst by using a Thermo Finnigan/Sorptomatic 1990 surface area analyzer, which was based on the physical adsorption of nitrogen gas. A sample was initially out-gassed to remove the humidity and volatile components adsorbed on the catalyst surface under vacuum at 300 °C for at least 18 hours prior to analysis. The specific surface area and the pore size of catalyst were obtained from the twenty-two-point nitrogen adsorption and desorption isotherm plot. The pore size distribution was calculated using the Horvath Kawazoe (HK) method.

#### 3.3.4.2 *X-ray Diffraction Spectroscopy (XRD)*

The oxide forms of catalysts were examined by using a Bruker X-Ray diffractometer system (D8 Advance) equipped with a 2.2 kW Cu anode long fine focus ceramic X-ray tube for generating a CuK $\alpha$  radiation (1.5405 Å). The detector scans the peak position from the sample as a function of  $2\theta$  by starting at the 10° to 50° ( $2\theta$ ) range and a scan speed of 0.02° ( $2\theta$ )/0.6 second. The data from XRD were analyzed and recorded by an on-line computer.

#### 3.3.4.3 *X-Ray Fluorescence (XRF)*

X-ray fluorescence spectrometry (AXIOS PW4400) was a non-destructive analytical technique used to identify and determine the concentrations of elements present in the solid and powder samples. XRF was

capable of measuring all elements from beryllium to uranium and beyond, at trace levels often below one part per million and up to 100 %. A little amount of ground samples was generally 1/min, external flow of 2.49 l/min, cabinet temperature of 29.97 °C, primary temperature of 19.00 °C, vacuum of 10.10 Pa, x-ray generation of 50 kV (60 mA), 150 mm of collimator, angle of 10.0002 degree, gas flow 0.90 l/h, and gas pressure of 1020.8 hPa

#### 3.3.4.5 *X-ray Photoelectron Spectroscopy (XPS)*

XPS spectra were carried out using a AXIS ULTRA<sup>DLD</sup> to determine the oxidation state of a metal oxide before and after catalytic testing. The system was equipped with a monochromatic Al X-ray source and a hemispherical analyzer. The spectrometer was operated with the pass energy of 160 eV and 40 eV when recording wide scan and core level spectra, respectively. All peaks were calibrated from referring C1s spectra located at 284.6 eV.