



CHAPTER III EXPERIMENTAL

3.1 Materials

Catalysts used in this research were impregnated CaO/SBA-15, impregnated BaO/SBA-15, impregnated CaO/Al₂O₃, impregnated BaO/Al₂O₃, SILD CaO/Al₂O₃, and SILD BaO/Al₂O₃. Barium nitrate (99.5%), calcium nitrate tetrahydrate ($\geq 99.0\%$ (KT)), ammonium hydroxide solution 28.0-30.0% NH₃ basis, aluminum oxide pellets, tetraethyl orthosilicate (TEOS) (99.999%), γ -Al₂O₃, and pluronic P123 (EO₂₀PO₇₀EO₂₀) were used in these syntheses. All of them were obtained from SIGMA-ALDRICH.

3.2 Preparation of the Catalysts

3.2.1 Synthesis of SBA-15 support

Firstly, 2 g of P123 (EO₂₀PO₇₀EO₂₀) as a template was dissolved in 60 ml HCl solution at room temperature. Then, 4.25 g tetraethyl orthosilicate (TEOS) was added dropwise under stirring at 40 °C for 24 h. Subsequently, the resulting mixture was aged at 40 °C for 24 h without stirring. The final aqueous solution was transferred into a Teflon-lined stainless steel autoclave, sealed tightly, and treated hydrothermally at 100 °C for 24 h. The autoclave was cooled down naturally. The product was filtered and then washed with deionized water. After that, the product was dried at 80 °C overnight. In order to obtain the pure mesoporous silica SBA-15, the surfactant template was removed by calcination at 550 °C for 5h.

3.2.2 Impregnation of CaO or BaO

For impregnation method, 1g of SBA-15 or Al_2O_3 support was impregnated by calculated amount of barium nitrate or calcium nitrate tetrahydrate aqueous solutions. The amount of barium oxide or calcium oxide incorporated to the support, after drying in air at 80 °C and calcination at 520 °C (or 550 °C for calcium oxide) for 5 h.

3.2.3 SILD of CaO or BaO on Al_2O_3

The 1st SILD solution containing the desired hydroxyl species was comprised of 4.3% \pm 0.2% NH_4OH , pH=11.0 (Sigma-Aldrich), 25% ethanol, and 70.7% water by volume. And the 2nd SILD solutions containing the desired cationic complex were comprised of 0.01 M $\text{Ca}(\text{NO}_3)_2$ or $\text{Ba}(\text{NO}_3)_2$ (Aldrich) in 25% ethanol and 75% DI water by volume. The rinse solution in the SILD of barium oxide or calcium oxide was 75% DI water with 25% ethanol by volume.

Firstly, 3 g of Al_2O_3 was placed in 120 ml of rinse solution. After 1 h, the rinse solution was replaced with 120 ml of 1st SILD solution. Then, left Al_2O_3 in the 1st SILD solution for 1 h. Next, 1st SILD solution was substituted with 2nd SILD solution and Al_2O_3 was left again for 1h. Repeat the previous procedure for 5 cycles. Then, SILD Al_2O_3 was dried at 80 °C for 24h. Finally, the catalyst was calcined at 450 °C to form BaO or 550 °C to form CaO.

3.3 Equipment

3.3.1 Reactor

A 250 ml three-necked flask equipped with a reflux condenser, a thermometer and a sampling port were used in this experiment. The heating mantle which suit with the three-necked flask was used to provide heat and the temperature was digitally controlled by a temperature controller equipped with a thermo couple. The nitrogen gas was uninterruptedly fed into the system to provide the inert atmosphere during reaction and to carry the water that formed during the reaction out from the system. The magnetic stirrer was used to provide agitation. The experimental set-up was shown in Figure 3.1

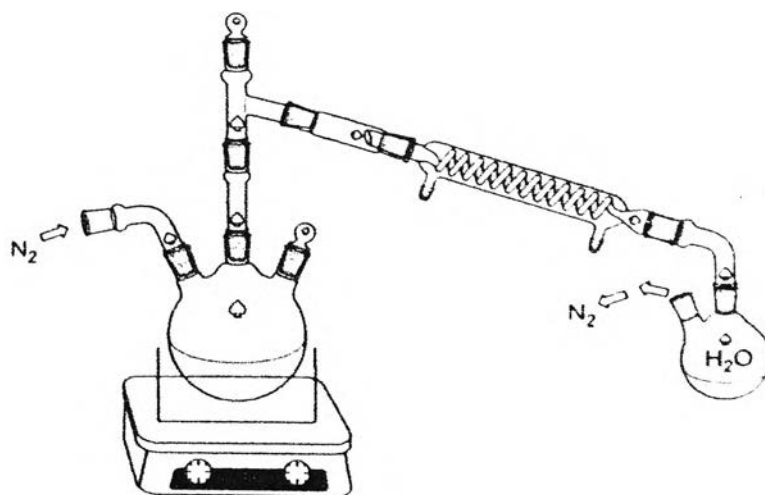


Figure 3.1 Experimental set-up used for etherification of glycerol.

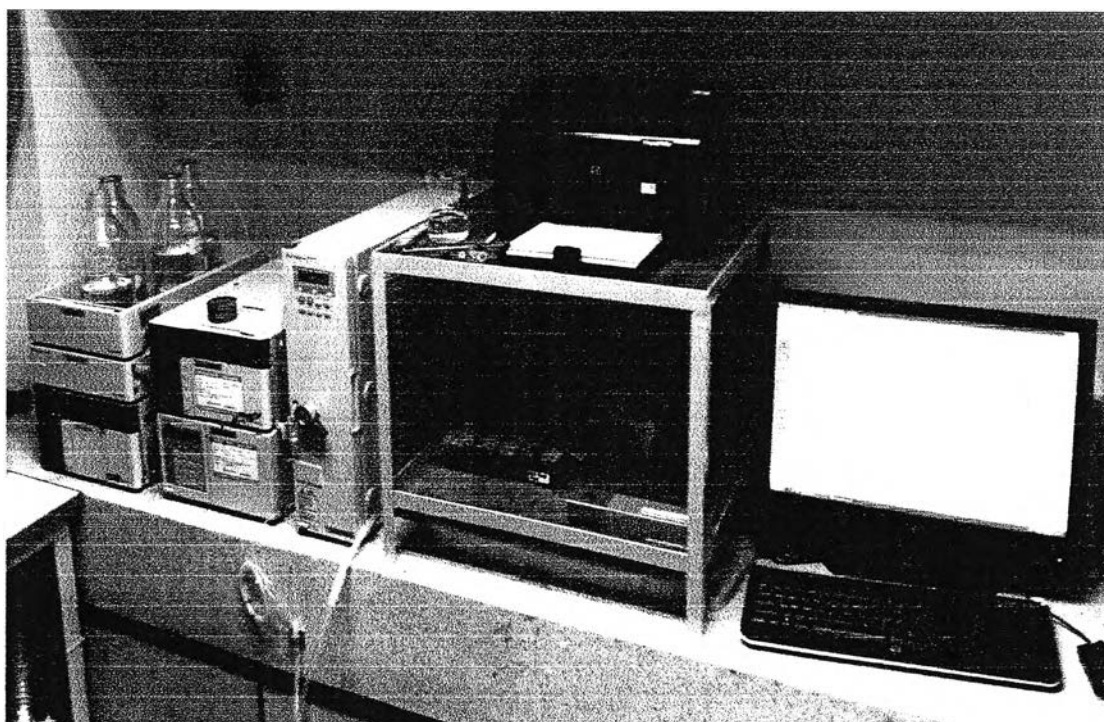


Figure 3.2 High Performance Liquid Chromatography (HPLC).

3.3.2 High Performance Liquid Chromatography (HPLC)

The Shimadzu high pressure liquid chromatography with RID-10A refractive detector was used to analyze diglycerol product samples. The size of chromatographic was 4.6 mm×150 mm×5 μm. The mobile phase was acetonitrile/water mixture (85:15 vol/vol) at a flow rate of 0.2 ml/min. High Performance Liquid Chromatography (HPLC) was shown in Figure 3.2

3.4 Methodology

3.4.1 Reaction

Fifty grams of glycerol was weighed and placed in a 3-neck flask. Then, the flask was heated to 150 °C for 30 minutes under nitrogen atmosphere. After that, the flask was heated to 250 °C and 2 wt% of catalyst was added into the reactor. The reaction was performed under nitrogen atmosphere and stirring condition. Sample was taken out every hour and the reaction time is 8 h. Then, the reactor was cooled down to room temperature.

3.4.2 Products quantification

Analysis of the products was done by using HPLC. The temperature of column was 40 °C, and 0.1 g of product was diluted with mobile phase in 25 ml volumetric flask before injected to HPLC and the injection volume is 20 μl.

The glycerol and diglycerol were quantified by comparing the RID signal for each glycerol and diglycerol of the HPLC chromatogram of polyglycerols products with the RID signal of each glycerol and diglycerol standard.

The glycerol conversion was defined as a portion of weight of glycerol used, which was calculated from the approximate fifty grams of sample (from experimental section) deduct with the remaining of glycerol that was calculated from HPLC chromatogram (from peak area convert to amount of glycerol in grams), to weight of starting glycerol (fifty grams) as shown in Equation (3.1).

$$\text{Glycerol conversion (wt\%)} = \frac{\text{Weight of glycerol used}}{\text{Weight of starting glycerol}} \times 100 \quad (3.1)$$

The diglycerol selectivity was defined as a portion of weight of diglycerol, which was determined by using HPLC, to weight of product (exclude remaining glycerol) as shown in Equation (3.2).

$$\text{Diglycerol Selectivity (wt\%)} = \frac{\text{Weight of diglycerol}}{\text{Weight of product}} \times 100 \quad (3.2)$$

The diglycerol Yield was defined as a portion of weight of diglycerol, which was determined by using HPLC, to weight of starting glycerol as shown in Equation (3.3).

$$\text{Diglycerol Yield (wt\%)} = \frac{\text{Weight of diglycerol}}{\text{Weight of starting glycerol}} \times 100 \quad (3.3)$$