CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Chemicals:

- Copper (II) nitrate, $(Cu(NO_3)_2 \cdot 2.5H_2O$, lab grade ≥ 99 % purity) was obtained from Ajax Finechem Pty Ltd.

- Zinc (II) nitrate, $(Zn(NO_3)_2 \cdot 6H_2O$, reagent grade, 98 % purity) was obtained from Ajax Finechem Pty Ltd.

- Aluminum oxide (γ-Al_2O_3, extrudate with 99% purity) was obtained by Saint-Gobain NorPro Corporation.

- Glycerol ($C_3H_5(OH)_3$, refined grade, 99% purity) was obtained from PTT Global Chemical Public Company Limited. The specification is shown in Appendix A.

- Glycerol ($C_3H_5(OH)_3$, yellow grade, 82 % purity) was obtained from PTT Global Chemical Public Company Limited. The specification is shown in Appendix A.

- Glycerol ($C_3H_5(OH)_3$, technical grade, 80 % purity) was obtained from PTT Global Chemical Public Company Limited. The specification is shown in Appendix A.

- Glycerol ($C_3H_5(OH)_3$, crude grade, 62% purity) was obtained from PTT Global Chemical Public Company Limited. The specification is shown in Appendix A.

3.1.2 Gases:

- Hydrogen (H_2, HP grade, 99.99 % purity) was supplied from Thai Industrial Gas Public Company Limited.

- Helium (He, HP grade, 99.99 % purity) was supplied from Thai Industrial Gas Public Company Limited.

- Nitrogen (N_2, HP grade, 99.99 % purity) was supplied from Thai Industrial Gas Public Company Limited.
- Air (HP grade, 99.99 % purity) was supplied from Thai Industrial Gas Public Company Limited.

3.1.3 Equipment:

- High pressure packed-bed continuous flow reactor system consist of:
  - Mass flow controller (Brooks Instrument 5850E)
  - High pressure liquid pump (TELEDYNE ISCO D-Series)
  - Back pressure regulator (Swagelok)
  - 16 mm I.D. × 40 mm long stainless steel reactor (Swagelok)
- Gas chromatograph (Agilent Technology model 6890N network gas chromatograph equipped with a Stabilwax® capillary column (0.53mm×30m) and flame ionization detector)
- Surface area analyzer (SAA, Quantachrome/Autosorb1)
- Temperature programmed reduction equipment (TPR)
- Temperature programmed oxidation equipment (TPO)
- Atomic absorption spectroscopy (AAS, Avanta GBC)
- Inductively coupled plasma optical emission spectrometry (ICP-OES, Parkin Elmer, Optima 4300DV)
- Stirring hot plate (Cole Parmer)
- Oven (Carbolite CWE 1100)

3.2 Experimental Procedure

3.2.1 Catalyst Preparation

The Cu-ZnO/Al$_2$O$_3$ catalyst was prepared by incipient wetness impregnation methods. The Cu-ZnO/Al$_2$O$_3$ catalyst was prepared using γ-Al$_2$O$_3$as a support. The γ-Al$_2$O$_3$was first ground and sieved to the size between 20 and 40 mesh (425-850 μm). The copper and zinc oxide were deposited by impregnation of γ-Al$_2$O$_3$ support with aqueous solution of copper nitrate and zinc nitrate. After impregnation, the catalysts was dried at 383 K overnight and subsequently calcined at 773 K for 6 h.

3.2.2 Catalyst Characterizations

The prepared catalysts were characterized by various methods described as follows.

3.2.2.1 Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (GBC, Avanta PM) was used to determine the concentration of a particular element in a sample. Chemical elements will absorb ultraviolet light when they are excited by heat. Each element has a characteristic wavelength that will be absorbed. The AAS instrument seeks for a particular element by focusing a beam of UV light at a specific wavelength through a flame and into a detector. The sample of interesting element is aspirated into the flame. If the element is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance. As a concentration increases, an absorbance increases. A standard calibration curve is constructed by standard solutions at various concentrations

3.2.2.2 TemperatureProgrammed Reduction (TPR)

Temperature programmed reduction (TPR) was employed for evaluating the number and quantity of the reducible species present in the prepared catalyst and the temperature, at which the reduction itself takes place as a function of temperature. A 50 mg of catalyst was placed in a quartz reactor, and heated (10

K/min) under a He flow up to 823 K, and held at the temperature for 1 h in order to remove moisture from the catalyst surface. The sample was then cooled down to 303 K. Then, the sample was exposed to a stream of 5% H_2/Ar with a flow rate of 20 ml/min. After that, the sample was heated to 873 K with a ramping rate of 10 K/min. The consumption of hydrogen consumed was monitored on-line by an SRI model 110 FID detector as a function of temperature.

3.2.2.3 Temperature Programmed Oxidation (TPO)

Temperatureprogrammed oxidation (TPO) was employed to analyze the amount and characteristics of coke deposited on the catalyst surface after the course of reaction. The oxidation of coke was performed in a 4 mm I.D. quartz tube reactor. A 30 mg of spent catalyst was placed in the reactor between two layers of quartz wool. The sample was purged at room temperature by flowing 2% O_2 in He for 30 min to stabilize the signal before ramping the temperature linearly to 1073 K (10 K/min). The CO_2/CO produced by the oxidation of the coke species was converted to methane using a methanator filled with 15% Ni/Al_2O_3 and operated at 673 K in the presence of H_2. The evolution of methane was analyzed by an FID detector.

3.2.2.4 Brunauer-Emmett-Tellet Method (BET) Surface Area Analysis

The surface area of the fresh and spent catalysts was measured by BET surface area analyzer (Quantachrome/Autosorb 1). The sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 423 K for 4 h prior to the analysis. Then, $N_2$was purged to adsorb on surface, measuring the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium is established. This volume-pressure data was used to calculate the BET surface area.

3.2.2.5 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Inductively coupled plasma optical emission spectrometry (ICP-OES) is an analytical system used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited

atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. The ICP-AES is composed of two parts: the ICP and the optical spectrometer. The ICP torch consists of 3 concentric quartz glass tubes and a coil of the radio frequency (RF) generator which surrounds part of this torch. Argon gas is typically used to create the plasma.
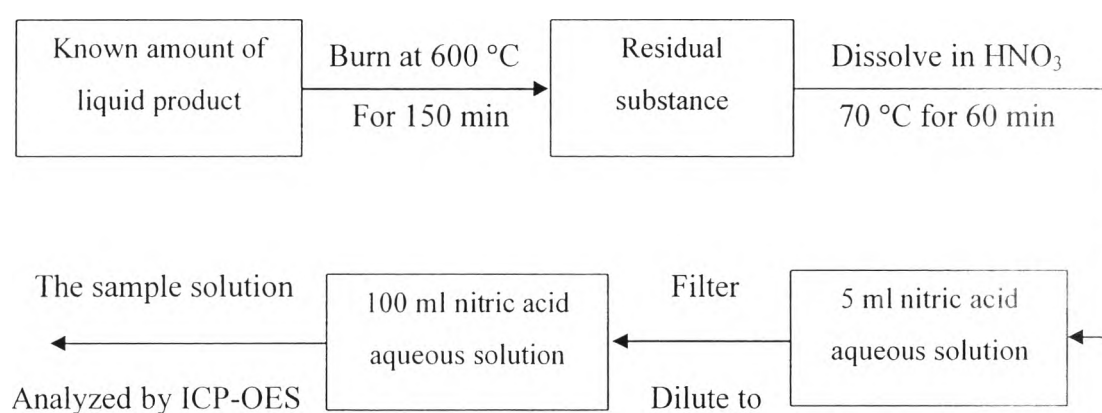

Figure 3.1 Flow chart to prepare the sample for ICP-OES analysis.

3.3 Feedstock Characterization

3.3.1 Gas Chromatography with Flame Ionization Detector (GC/FID)

All feedstock obtained from the reaction were analyzed by an Agilent model 6890N gas chromatograph equipped with a flame ionization detector to find amount of glycerol. A Stabilwax® capillary column (diameter, 0.53 mm; length, 30 m) was used for product separation.

3.3.2 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Inductively coupled plasma optical emission spectrometry (ICP-OES) is an analytical system used for the detection of trace metals. The sample was

prepared follow the flow chart as shown in Figure 3.1. This analysis is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. The ICP-OES is composed of two parts: the ICP and the optical spectrometer. The ICP torch consists of 3 concentric quartz glass tubes and a coil of the radio frequency (RF) generator which surrounds part of this torch. Argon gas is typically used to create the plasma.

3.4 Catalytic Activity Measurement

The performance and stability of Cu-ZnO/Al$_2$O$_3$ catalysts were evaluated by the glycerol dehydroxylation reaction.

3.4.1 Dehydroxylation of Glycerol

The catalytic activity was examined using a 16mm O.D. continuous flow stainless steel packed bed reactor. In each test, 2 gram of catalyst was placed at the center of reactor between two layers of glass bead and glass wool. Thermocouples were placed concentrically in the reactor to measure the temperature in the catalyst bed. The reactor was pressurized by hydrogen to a reduction pressure. All catalysts were reduced at 673 K for 1 h in hydrogen flow prior to the activity evaluation. After that, the reactor was cooled to the working temperature (623 K), and the hydrogen pressure was adjusted to 500 psig. An aqueous solution of 80 wt.% glycerol continuously supplied to the reactor via a high pressure pump together with a flow of hydrogen controlled by a mass flow controller. The WHSV (WHSV is given as the ratio between the hourly mass flow of liquid and the weight of the catalyst) 3 h^{-1}. After the reaction, the products were collected in a stainless steel cylinder trap immersed in an ice bath. The flow diagram of the system used for dehydroxylation of glycerol is shown in Figure 3.2.
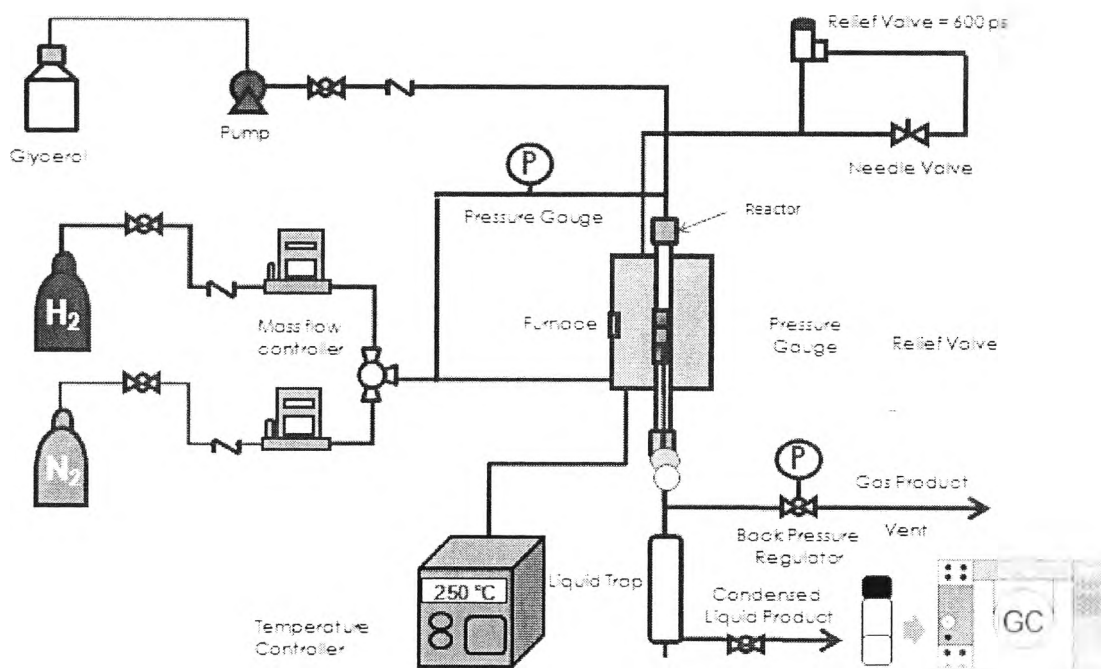
Figure 3.2 Flow diagram of the system used for dehydroxylation of glycerol.

3.4.2 Product Analysis

The products obtained from the reaction were analyzed by an Agilent model 6890N gas chromatograph equipped with a flame ionization detector. A Stibilwax® capillary column (diameter, 0.53 mm; length, 30 m) will be used for product separation. The GC operating conditions are summarized as follows:

Injection temperature:	493 K
Oven temperature:	353 to 473K held 10 min
	(heating rate 10 K/min)
Carrier gas:	High purity helium
Carrier gas flow rate:	7 mL/min
Carrier gas velocity:	52 cm/s
Column type:	Capillary column (Stabilwax®)
Detector temperature:	523 K

For each data point, selectivity of product, conversion of glycerol, and yield of product were calculated. Conversion of glycerol is defined as the ratio of number of moles of glycerol consumed in the reaction to the total moles of glycerol initially present, as shown in Equation 4.1.

$$\text{Glycerol conversion (\%)} = \frac{\text{moles of glycerol used}}{\text{moles of glycerol input}} \times 100 \qquad (4.1)$$

Selectivity is defined as the ratio of the number of moles of the product formed to that of the glycerol consumed in the reaction, taking into account the stoichiometric coefficient, as shown in Equation 4.2.

$$\text{Selectivity (\%)} = \frac{\text{moles of product obtained}}{\text{moles of glycerol used}} \times 100 \qquad (4.2)$$