Development of Catalyst for Hydrogenolysis of Glycerol to 1,3 - Propanediol

by

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CERTIFICATION OF APPROVAL

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September 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(NUR HIDAYAH BINTI MOHAMED OMAR)

ACKNOWLEDGEMENT

ABSTRACT

The main purpose of this project is to find the best bi-metallic catalyst that gives high conversion of glycerol together with high selectivity towards the production of 1,3-propanediol. However, the catalyst that is selective in the yield of 1,3-propanediol is still much to be developed, since most of the conventional glycerol hydrogenolysis catalysts preferred in producing 1,2-propanediol and ethylene glycol. An abundant amount of glycerol need to be further utilized, by converting this readily available bio-renewable source into valuable chemicals. There are three main steps required in conducting this project which are; i) development of supported bi - metallic catalysts via incipient wetness impregnation method, ii) perform catalysts characterization by using temperature program reduction (TPR), X-ray diffraction (XRD), Fourier Transformed Infrared (FTIR) and Field Emission Scanning Electron Microscopy (FESEM); and iii) perform catalytic testing and analysis where the hydrogenolysis reaction of glycerol is conducted. The analysis is done by using gas chromatography (GC). From the results obtained, Cu – Mn catalyst gives the highest glycerol conversion in the hydrogenolysis reaction with 11.08 % . Meanwhile, for the selectivity towards 1,3-propanediol, Cu – Ce catalyst shows the highest value with 9.70 %. Both conversion and selectivity results of Cu – Ag and Cu – Mn catalyst are comparable, with only a slight difference, and these two catalysts produce more 1,3 – propanediol instead of 1,2 – propanediol. It is believed that, Cu – Ag and Cu – Mn have a high potential to be developed as the catalysts for hydrogenolysis of glycerol to 1,3-propanediol.

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CHAPTER 1: INTRODUCTION

1.0 Background of Study.

1.1.1 Biodiesel production and availability of glycerol.

Nowadays, the global development of biodiesel is entering a period of rapid, and the future of this industry appears to be very promising. Sustainable development is a pattern of resource use that aims to meet human needs while preserving the environment. The growth of biodiesel industry is in-line with the sustainable development of the world, where the need for fuel is met while conserving the nature. World biodiesel production and capacity show a steady increment, and this pattern is believed to be continuously rising year after year.
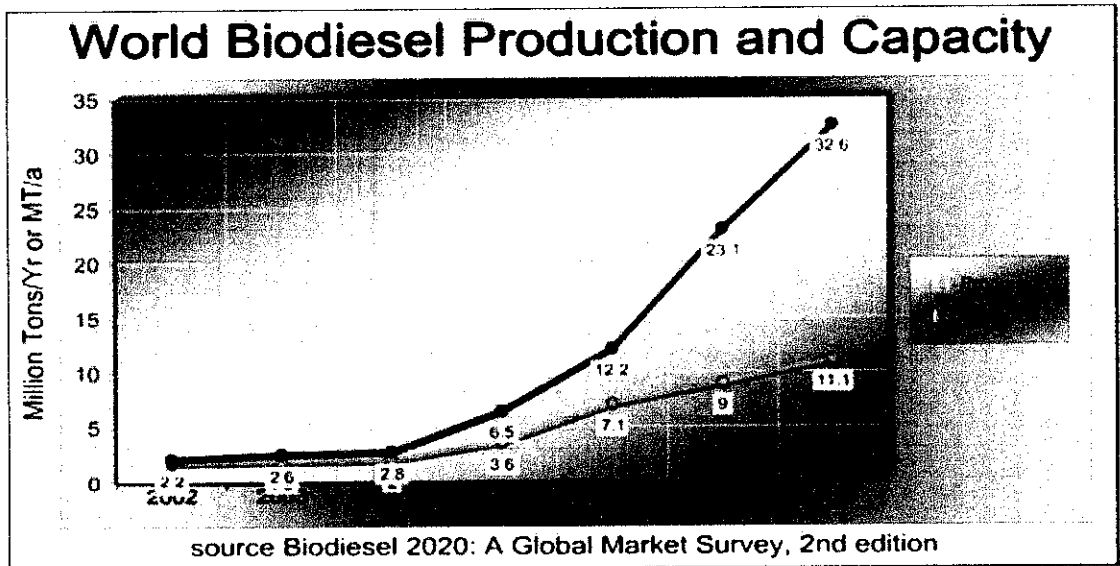
Figure 1: World Biodiesel Production and Capacity.
(Source: Biodiesel 2020: A Global Market Survey, 2ⁿᵈ Edition)

U. Schuchardt et. al., (1998) stated that, biodiesel is commonly produced by the transesterification of the vegetable oil or animal fat feedstock. In this process, a triglyceride will be reacting with an alcohol in the presence of a strong acid or base, and later on produces a mixture of fatty acids alkyl esters and glycerol
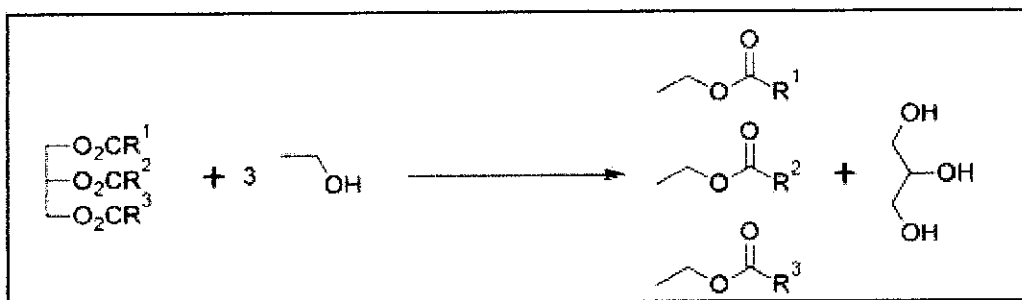
Figure 2: Transesterification of vegetable oil to methyl ester biodiesel
(U.Schuchardt et. al., 1998).

Due to the growth of biodiesel production globally, an abundant amount of bio-renewable glycerol is readily available as the reaction by-product. In fact, for every 9 kilograms of biodiesel produced, there will be about 1 kilogram of glycerol formed, which is the by-product of the reaction (M.A Dasari et. al., 2005). Therefore, it is obvious that there is a necessity for biodiesel production plants to develop methods that will add the values of glycerol, where the profit of the plants could be increased.

Glycerol is an outstanding material with many areas of application. The key to glycerol's technical versatility is a unique combination of physical and chemical properties, ready compatibility with many other substances, and easy handling. Glycerol is also nontoxic to human health and to the environment. Physically, glycerol is a water-soluble, clear, almost colourless, odourless, viscous, hygroscopic liquid with a high boiling point. Chemically, glycerol is a trihydric alcohol, capable of being reacted as an alcohol, yet stable under most conditions (American SDA).
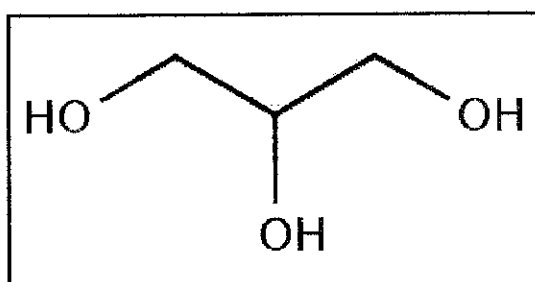
Figure 3: Molecular Structure of glycerol. (American SDA).

1.1.2 Hydrogenolysis of Glycerol to 1,3 – propanediol.

Hydrogenolysis can be defined as the splitting of hydroxyl bond of glycerol molecule with simultaneous addition of hydrogen atom to each of the fragment in producing 1,3 – propanediol (Rase H.F., 2000).
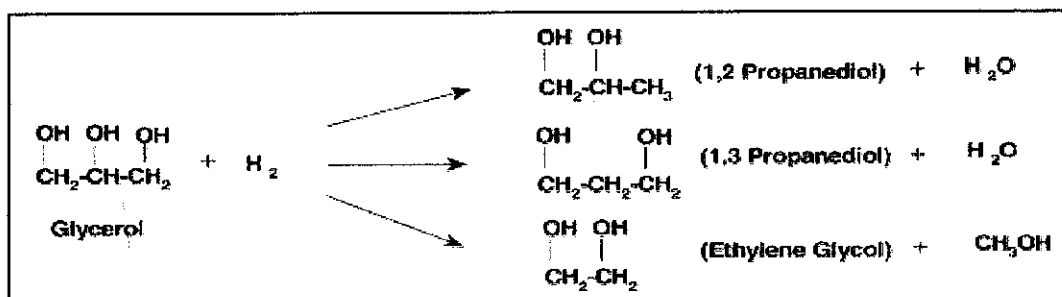
Figure 4: Summary of overall reaction of hydrogenolysis reaction of glycerol (M.A Dasari et. al., 2005).

J.Chaminand et. al., (2004) and R.D. Cortright et.al., (2002) say that: "1,3 – propanediol can also be produced from propylene (which is a petroleum-derived component) via the process that involve propylene or ethylene selective oxidation to propylene oxide, followed by subsequent hydrolysis". Somehow, the dependent on propylene as the raw material is not a good option since the petroleum source is diminishing. Recenly, DuPont reported that the fermentation process by using bacterial strains can also produce 1,3-propanediol from glycerol. However, the biological process has a low and poor metabolic efficiency, compared to the existing chemical plants (G. J. K. Acres, et. al., 1981). Therefore, the readily available glycerol is the best substitutes for propylene, where 1,3 – propanediol can be produced via hydrogenolysis process of glycerol.

According to Energetics Incorporated (2003), 1,3 – propanediol emerges as an important chemical, since it has a broad spectrum of uses such as solvent for thin film preparation, vinyl epoxide synthon, reagent for natural product synthesis and polymerization reaction. Copolymerization of 1,3 – propanediol with terephthalic acid will produce the polyester that possesses a unique properties, which are used in the textile and fabric industries

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1.1.3 Catalyst

Catalyst can simply be defined as a substance that increases the rate without being consumed in the reaction. A catalyst can make a reaction go faster and in a more selective manner (American Chemical Society (ACS)). Relating to the hydrogenolysis of glycerol, this process will yield polyol (which are 1,2 and 1,3-propanediols and ethylene glycol). The existing studies of catalysts for hydrogenolysis of glycerol are favoured in the production of 1,2 – propanediol compared to the other two. The typical catalysts used are – nickel, palladium, platinum, rhodium, copper and copper-chromite. However, in this study, the mechanism of catalyst reaction will not be discussed in detail.

1.1 Problem Statement

The abundant amount of glycerol need to be utilized, by converting this readily available bio-renewable source into valuable chemicals. The catalyst that is selective in the yield of 1,3-propanediol is still much to be developed, since most of the conventional glycerol hydrogenolysis catalysts preferred in producing 1,2-propanediol and ethylene glycol. Although many researches related to glycerol hydrogenolysis has been studied in recent years, the main product is not selective toward the production of 1,3-propanediol. As in the current market, the price of 1,3-propanediol is much higher compared 1,2-propanediol.

Table 1: Price comparison between 1,2-propanediol and 1,3-propanediol (Price quoted from Sigma-Aldrich).

Product	1,2-propanediol	1,3-propanediol
Price (RM/kg)	167.46	1565.00

Therefore, high market price of 1,3-propanediol added with its excellent properties (that is suitable for carpet and textile fabrication) would add the value to

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glycerol and increase the profit of the biodiesel production plant. The significant of this project are:

- Replace the petroleum – based process of producing 1,3 – propanediol. Glycerol appears to be the best raw material for this purpose, and it is a wise option since petroleum source is diminishing.
- Add value to the by – product of biodiesel industry by further utilize the glycerol.

1.2 Objective and Scope of Studies.

The main purpose of this project is to develop and find bi-metallic catalyst that favoured in the production of 1,3-propanediol, compared to the other products that are associated with the hydrogenolysis of glycerol process. The success output of this project would indirectly widen the textile fibres industries and add extra income to the biodiesel plant. The scopes of study for this project are listed as the following:

a) Development of bi – metallic catalysts on zeolite solid support, via incipient wetness impregnation method.
b) Perform catalysts characterization study in order to determine the physico – chemical properties of the catalysts.
c) Experimental study and analysis on the effect of the newly developed bi – metallic catalysts in the hydrogenolysis reaction of glycerol.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

The hydrogenolysis of glycerol to the desired product (which is 1,3 – propanediol) is an experimental work and analysis. Numerous aspects and parameters need to be taken into consideration along the way of conducting the experiment, and analysing the results which will be obtained. According to the literatures associated with this study, the features discussed are listed as the following, and details of each features will be explain further in the subsequent sections:

a) Metal used as the catalyst.

b) Reaction solution.

c) Reaction condition.

d) Catalyst reduction temperature.

e) Presence of second metal as catalyst.

The hydrogenolysis of glycerol can proceed by different pathways, depending on whether the primary or secondary hydroxyl is more easily reduced. Catalytic -OH cleavage with noble metals under reductive conditions usually favours reduction of primary hydroxyl groups over secondary. Tertiary hydroxyls are cleaved faster than secondary but likely because of different mechanisms (A.Perosa and P.Tundo. 2005). The conversion of glycerol proceeds by the combination of dehydration over acid catalyst with subsequent hydrogenation over metal catalyst (A. Marinoiu et. al., 2010).

Figure 5: Molecular Structure of glycerol.

Primary OH group

Secondary OH group

Tertiary OH group

Figure 6: Pathways for hydrogenolysis of glycerol (A. Marinoiu et. al., 2010)
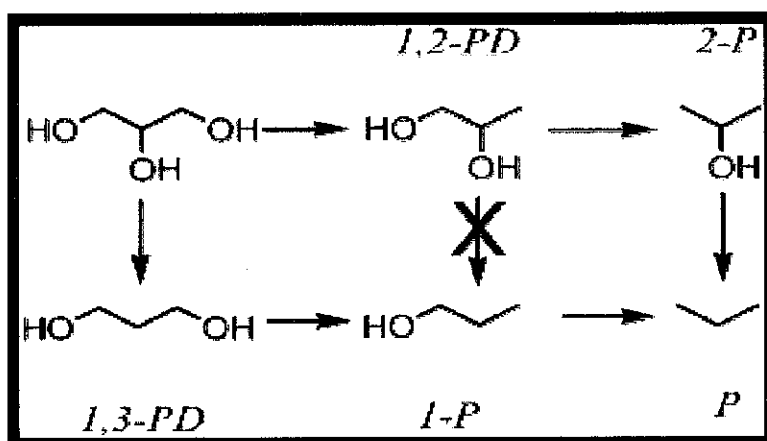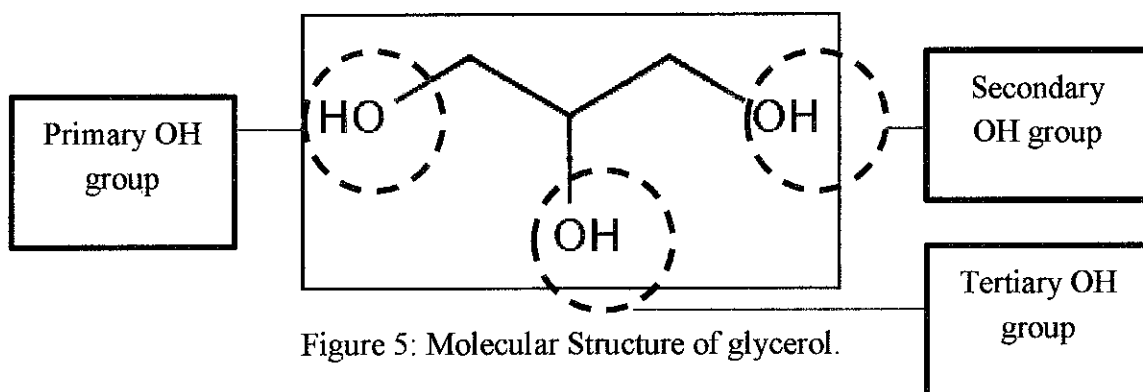
In the first case, the hydrogenolysis of the two primary hydroxyls yields 1,2 propanediol (1,2-PD), then 2 -propanol (2-P), and eventually propane (top pathway). In the second case, 1,3-propanediol (1,3-PD) is formed first, and then consecutive removal of the remaining OH's yields 1-propanol (1-P) and propane (bottom pathway) (A.Perosa and P.Tundo., 2005).

2.2 Metal used as the catalyst.

The conversion of glycerol proceeds by the combination of dehydration over acid catalyst with subsequent hydrogenation over metal catalyst. Selective hydrogenolysis of glycerol requires the cleavage of a C–O bond by hydrogen, without attacking C–C bonds from the glycerol molecule. The preferred catalysts seem to be copper – containing catalyst (A. Marinoiu et. al., 2010; Wang S. and Liu

H., 2007). Copper is potentially a good catalyst for alcohol hydrogenation. It is known for its poor hydrogenolytic activity towards C – C bond, and an efficient catalyst for C – O bond hydro-dehydrogenation. Copper based catalyst exhibited higher selectivity towards polyol (M.A Dasari et. al., 2005); J.Chaminand et. al., 2004). For bi-metallic catalysts (where copper is used as the first metal), higher copper content of the catalyst would lead to high selectivity towards the desired product, while the conversion decreases gradually. The correct amount of copper is important in obtaining the optimum conversion and selectivity (Wang S. and Liu H. 2007).

Catalyst like ruthenium and palladium showed low selectivities (less than 50%) due to competitive hydrogenolysis of C – C and C – O bonds, leading to excessive degradation of glycerol, to form lower alcohols and gases (M.A Dasari et. al., 2005).

Zirconia-based superacids can be a good catalyst for the selective hydrogenolysis of glycerol to 1,3-propanediol. superacids consisting of sulfated zirconia were used as a catalyst for the selective conversion of glycerol to 1,3-propanediol. Iron or Manganese sulfated zirconia generated only 1,3-propanediol. Aluminium sulfated zirconia was also quite active for glycerol conversion, producing similar amounts of 1,2- and 1,3-propanediol. This is due to the abundant Brønsted acid sites promoted the removal of the hydroxyl group from the secondary carbon of glycerol, preferentially generating 1,3-propanediol. (J.Oh et. al., 2011).

The highest yield reported so far is 38% using rhenium – iridum oxide (Re–IrOx) catalyst. Other catalysts such as Rh-ReO$_x$ /SiO$_2$, Pt/WO$_3$/ZrO$_2$, Pt/WO$_3$/TiO$_2$ /SiO$_2$ have been reported, but their yields are quite low, and 1,2-propanediol is often produced in greater quantities (J.Oh et. al., 2011; Y.Amada et. al., 2011).

Supplier	Description	Conversion	Yield	Selectivity
Johnson Matthey	5% Ru/C	43.7	17.5	40.0
Johnson Matthey	5% Ru/alumina	23.1	13.8	59.7
Degussa	5% Pd/C	5	3.6	72.0
Degussa	5% Pt/C	34.6	28.6	82.7
PMC Chemicals	10% Pd/C	8.9	4.3	48.3
PMC Chemicals	20% Pd/C	11.2	6.4	57.1
Grace Davision	Raney nickel	49.5	26.1	52.7
Grace Davision	Raney copper	48.9	33.8	69.1
Sud-Chemie	Copper	53	21.1	39.8
Sud-Chemie	Copper-chromite	54.8	46.6	85.0
Johnson Matthey	Ni/C	39.8	27.3	68.6
Alfa-Aesar	Ni/silica-alumina	45.1	29.1	64.5

Reactions were carried using 80% glycerol solution at 200 C and 200 psi hydrogen pressure for 24 h.

Figure 7: Summary of conversion of glycerol, yield and selectivity of propylene glycol from glycerol over various metal catalysts (M.A Dasari et. al., 2005).

2.3 Reaction Solution

Water is generated from this reaction, and it is always preferable to eliminate the water from the initial reaction mixture to drive the equilibrium in the forward direction. Some literatures used very dilute glycerol solution (10% – 30%) and the reason being unknown. Usage of diluted solution of glycerol (10 – 30% of glycerol) will reduce the average space – time yield of the reaction and increase the size and pressure ratings of the reactor. It is proven that, for copper – chromite (Cu – Cr) catalysts, lower initial water content in the reaction would increase the conversion of glycerol and selectivity of the product. At 10% initial water content of the reaction, the glycerol conversion is 58.8%, compared to 40% initial water content, where the conversion is at 48% (M.A Dasari et. al., 2005). This demonstrates that high conversion of glycerol can be achieved by using only 10% - 20% water in glycerol.

The nature of solvent had a dramatic effect on the rate and selectivity of the reaction. Sulfolane when used as the reaction solvent for rhodium (Rh) catalyst gives higher conversion of glycerol (32%), compared to water (21%) and dioxane (15%). However, the main product is 1-propanol (J.Chaminand et. al., 2004). It was also shown that heterogeneous catalytic hydrogenolysis of glycerol was possible in the

presence of tungstic acid. The acid can favour the dehydration route via protonation of the hydroxyl groups and loss of water (J.Chaminand et. al., 2004; Y.Amada et. al. (2011).
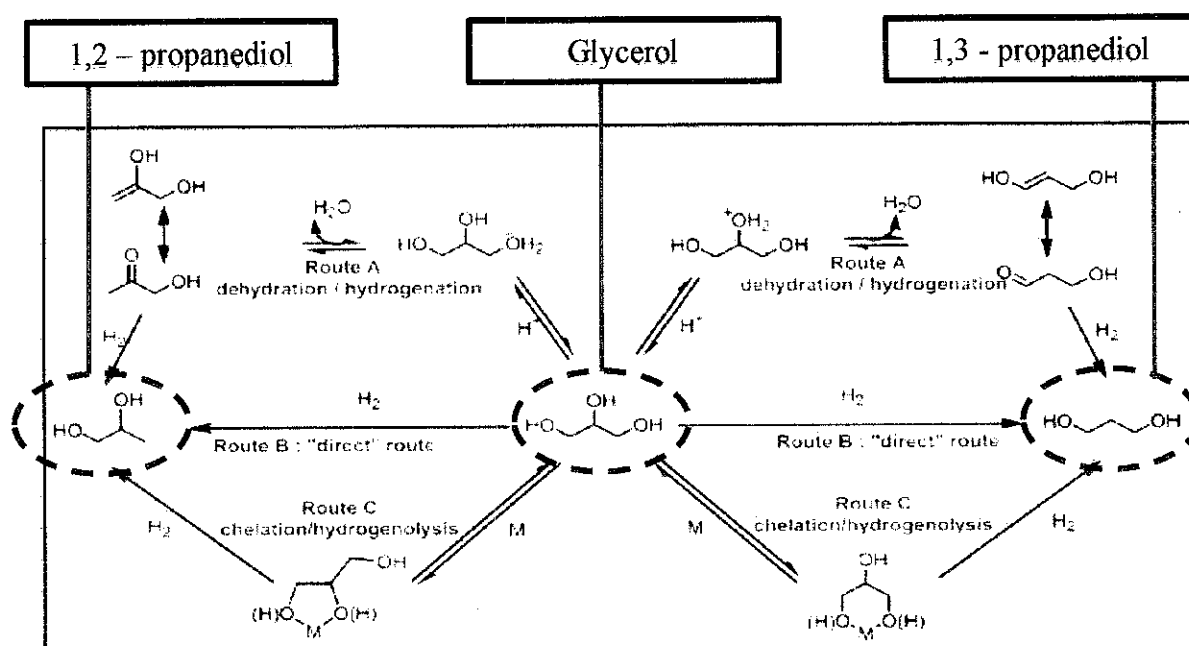
Figure 8: Detail hydrogenolysis process routes (J.Chaminand et. al., 2004).

2.4 Reaction Condition

For hydrogenolysis of glycerol, acetol formed has been identified as the intermediate of the reaction (M.A Dasari et. al., 2005; Wang S. and Liu H., 2007). Lower temperature favour strong adsorption of the intermediates, leading to high probability of their decomposition, while higher temperature favor their desorption and also breaking of their C – C bonds, leading to over-hydrogenolyzed products. For copper – zinc oxide (Cu – ZnO) catalyst, With an increasing temperature between 453K to 493K, the selectivity increases sharply from 16.5% to 81.4%, then declined to 59.0% at 513K (Wang S. and Liu H., 2007).

As for copper – chromite (Cu – Cr) catalyst, reaction temperature beyond 473K would increase the conversion of glycerol, but significantly reducing the yield and selectivity of the desired product (M.A Dasari et. al., 2005). Referring to copper

oxide – zinc oxide (CuO – ZnO) and rhodium (Rh) catalysts, when higher temperature was used (493K), the selectivity to diols was poor. volatile hydrocarbons were formed (J.Chaminand et. al., 2004). For Raney – nickel catalyst, the optimal tradeoff between the rate and selectivity is at 463K. At this temperature, selectivity is in the range of 70-80%, even after prolonged reaction (A.Perosa and P.Tundo., 2005). Thus, high selectivity requires optimal temperatures facilitating the selective conversion. From the literatures, it can be concluded that the reaction temperature should be between 453K to 493K.

Few studies were conducted on the effect of hydrogen pressure in hydrogenolysis reaction of glycerol. For copper – chromite (Cu – Cr) catalyst, conversion of glycerol increase as the hydrogen pressure increased from 3.4 atm to 20.4 atm (M.A Dasari et. al., 2005). However, lower pressure of hydrogenolysis can be important in maximizing the utility of existing equipment.

Pressure (psi)	%Conversion	%Yield	%Selectivity
50	25	9.1	36.4
100	37	15.7	42.4
150	44	22.3	50.7
200	54.8	46.6	85.0
300	65.3	58.5	89.6
All the reactions were performed using 80% glycerol solution at 200 C for 24 h.			

Figure 9: Effect of hydrogen pressure in hydrogenolysis reaction of glycerol
(M.A Dasari et. al., 2005).

As concentration of catalyst in the reaction medium increases, more surface area is available for the hydrogenolysis reaction to take place. The initial rates of conversion of glycerol, and formation of product have a proportional increase with the catalyst amount. However, as the excess catalyst promotes excessive hydrogenolysis reaction, producing lower alcohols. Thus, optimal amount of catalyst is important (M.A Dasari et. al., 2005).

The effect of reaction retention time was studied for Ni/Al$_2$O$_3$ –CuCr catalyst. As expected, the highest conversions are obtained at high reaction time, namely a growth from 20.61 to 46.54% being noticed while the time increasing from 4 to 20 h (A. Marinoiu et. al., 2010).

2.5 Presence of Second Metal

The significant amount of 1,3- propanediol is formed only in the cases where metal of group 6 or 7 is added as a co-catalyst. It is reported that the co-catalyst much enhances the glycerol conversion and 1,3-propanediol selectivity (Y.Nakagawa et. al., 2010). The presence of iron, nickel, and manganese could interact with the catalyst and/or the substrate, thus improving the selectivity of the reaction in favor of 1,3 – propanediol (J.Chaminand et. al., 2004). It was also reported that, addition to rhenium (Re) on the noble metal was effective in the hydrogenolysis of glycerol (Y.Amada et. al., 2011).

2.6 Effect of Catalyst Reduction Temperature

Usually, catalyst will be reduced in an atmosphere of hydrogen at different temperatures, ranging from 150 °C to 400°C for 4 hours. There will be an optimum reduction temperature of the catalyst, and different combinations of catalysts have different reduction temperature. As for copper – chromite, it was reported to be at 300°C (M.A Dasari et. al., 2005), while for Ir–ReOx /SiO$_2$, it was 200°C (Y.Amada et. al., 2011).

CHAPTER 3: METHODOLOGY

Basically, this chapter will briefly explain on the experimental procedures, materials and equipment that are going to be used in this study. The reactants will undergo the hydrogenolysis process with the presence of catalyst, and the final product will be analysed in order to find the details on composition of liquid product produced. There are three main steps required in conducting this project which are:

a) Preparation of supported metal catalysts.

b) Catalysts characterization.

c) Catalytic tests and analysis.

3.1 Preparation of supported metal catalyst

The predominance of alumina and zeolites are reflected in the literature on the preparation of supported catalysts (G. J. K. Acres, et. al., 1981). Hence, zeolite is used as the catalyst support for this study. Supports are in general porous materials, so as to allow a high loading of highly dispersed metal particles, while the particles of the active phase usually need to be synthesized in such a way that they are as small as possible (Guido Mul and Jacob A. Moulijn).

Zeolite Socony Mobil – 5 (ZSM – 5) is an aluminosilicate zeolite mineral belonging to the pentasil family of zeolites. Its chemical formula is $Na_nAl_nSi_{96-n}O_{192} \cdot 16H_2O$ ($0<n<27$). ZSM – 5 (CBV 2314) supplied by Zeolyst International is used as the catalyst support for this project. Details of this material are described as the following:

Table 2: Details of ZSM – 5 catalyst support.

Zeolyst Products	SiO2 / Al2O3 mole ratio	Nominal Cation Form	Na2O weight percent (%)	Surface Area (m^2/g)
CBV 2314	23	Ammonium	0.02	452

Several procedures exist in order to attach the active phase to the support (to prepare supported catalysts). In the catalyst manufacturing industry, impregnation is usually employed for practical and economic reasons. Impregnation allows the use of pre-shaped or structured supports (Guido Mul and Jacob A. Moulijn).

Impregnation is a preparation technique in which a solution of the precursor of the active phase is brought in contact with the support. Co – impregnation consists in contacting a solid (support) with two or several liquids containing the components to be deposited on the surface (J. Haber et. al., 1995). To be specific, incipient wetness impregnation method is used in preparing the catalyst in this project. In wet impregnation, the support is dipped into an excess quantity of solution containing the precursor(s) of the active phase. In the first step of impregnation, three processes occur:

- Transport of solute to the pore system of the support bodies;
- Diffusion of solute within the pore system; and
- Uptake of solute by the pore wall.
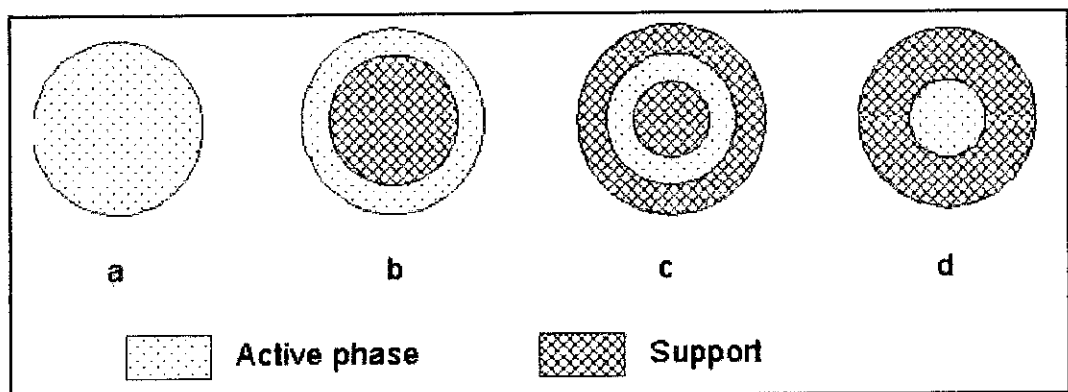
Figure 10: Four types of active-phase distribution. (a) uniform; (b) egg-shell; (c) egg white; and (d) egg-yolk. (J. Haber et. al., 1995)

The drying step, which follows the impregnation step, also affects the distribution of the active phase. In drying, the solution in the pores will become oversaturated and precipitation takes place. In principle, rapid evaporation is

favourable because it causes rapid supersaturation, and associated with that, a high dispersion (J. Haber et. al., 1995). The drying process usually takes place at 100°C to remove the water content of the prepared catalyst. Later on, the catalyst will be calcined at the temperature ranging from 400 °C to 600 °C. Calcination is a further heat-treatment beyond drying. The calcination process is important in determining the physico – chemical properties of the catalyst.
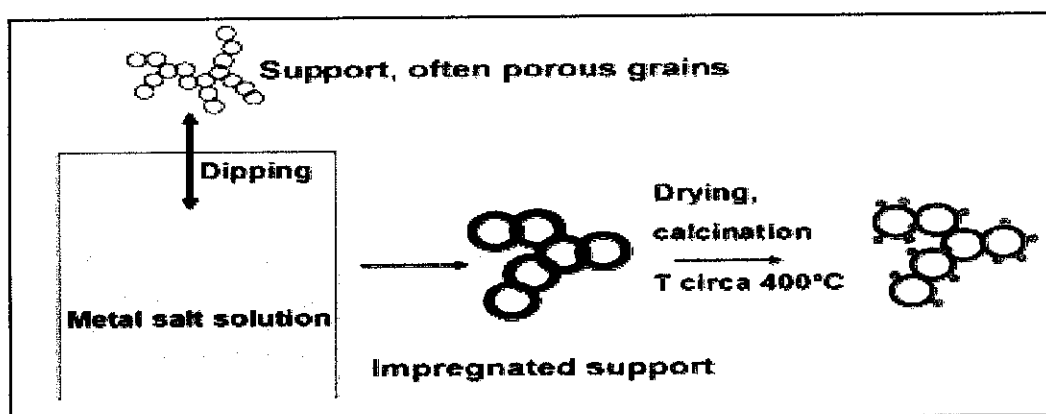
Figure 11: Impregnation method for catalyst preparation
(R.D. Cortright et. al., 2002).

3.1.1 Catalysts Preparation Procedures

To prepare the catalyst, the catalyst support (Zeolite CBV 2314 supplied by Zeolyst International) was weighed by using the electronic balance. Later on, the zeolite which is in the form of fine powder is transferred into the glass chamber of the rotary furnace. The zeolite was then calcined at the temperature of 500°C for eight (8) hours in a rotary furnace. The main purpose of this calcination process is to remove the impurities in the zeolite powder. The rotating action will enhance the impurities removal process where the contacting surface area is maximized and the heat along the glass chamber can be assumed as uniform. After 8 hours, the calcined zeolite powder is cooled to room temperature and stored in an air – tight glass container.
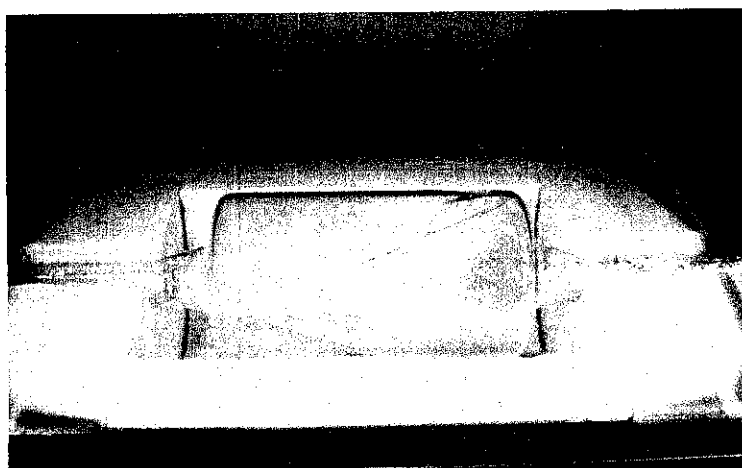
Figure 12: Glass chamber in the rotary furnace.

List of the metals used in preparing the catalysts are as the following:

Table 3: List of metal salts used to prepare the catalysts.

Metal	Chemicals	Molecular Formula	Molecular weight (g/mol)	Manufacturer
Copper	Copper Nitrate Trihydrate (99%)	$Cu(NO_3)_2.3H_2O$	241.60	Merck
Silver	Silver Nitrate (99.8%)	$AgNO_3$	169.87	Bendosen Laboratory Chemicals
Manganese	Manganese Sulphate Monohydrate (99%)	$MnSO_4.H_2O$	169.01	R&M Chemicals
Cerium	Cerium (III) Nitrate Hexahydrate (99.5%)	$CeN_3O_9.6H_2O$	434.22	Acros Organics
Cobalt	Cobalt (II) Chloride (99%)	$CoCl_2$	129.83	Fisher Chemicals
Barium	Barium Chloride Dihydrate (99%)	$BaCl_2.2H_2O$	244.28	R&M Chemicals
Titanium	Titanium (IV) Oxide (99%)	TiO_2	79.9	R&M Chemicals

In preparing bi – metallic catalysts, the solid (support) is contacted with two different liquids containing the components to be deposited on the surface. Copper (from Copper (II) Nitrate trihydrate) is the first metal of the catalyst. Overall, six combinations of copper – based catalysts are prepared. They are:

i.   Copper – Barium (Cu – Ba)

ii.   Copper – Silver (Cu – Ag)

iii.   Copper – Manganese (Cu – Mn)

iv.   Copper – Cerium (Cu – Ce)

v.   Copper – Cobalt (Cu – Co)

vi.   Copper – Titanium (Cu – Ti)

10 weight percent (wt %) of metal loading on the solid (support) is chosen in preparing all catalysts for this study (which is 5 wt % for each metal).

The required mass of Copper, second metal and zeolite powder are weighed. Then, the zeolite powder was transferred into a 1L beaker and approximately 50 mL of distilled water was added. The mixture was stirred continuously using the glass rod and mass of Cu and Mn were added. The formed solution is left for 4 hours, allowing the impregnation of the metals on the zeolite's surface. Then, the liquid mixture was place in an oven at the temperature of 100°C, and again left for 16 hours for drying. Eventually, the sample was cooled to room temperature, grounded into fine powder and transferred into labelled air – tight glass containers.

Figure 13: Weighing and preparing solution for catalyst impregnation method.

Calcination conditions can be varied in temperature, pressure, duration, and gas-phase composition which affect the surface area, oxidation state, and catalytic activity – which are the physico – chemical properties of the catalysts. Therefore, the temperature of 500 °C and the duration of 16 hours are chosen for calcination process of all catalysts used in this study. All prepared catalysts are put inside the ceramic crucibles, and later on are placed inside the box furnace. The calcination process is basically similar to thermal gravimetric analysis (TGA), where certain components of the catalysts will be decomposed, and leaving only metal oxide on the catalyst support – to be reacted with the glycerol solution. It is highly recommended to perform TGA at the first place in order to determine the calcination temperature for different combination of the prepared catalyst. For this study, 500°C and 16 hours of temperature and pressure are chosen for calcination process.
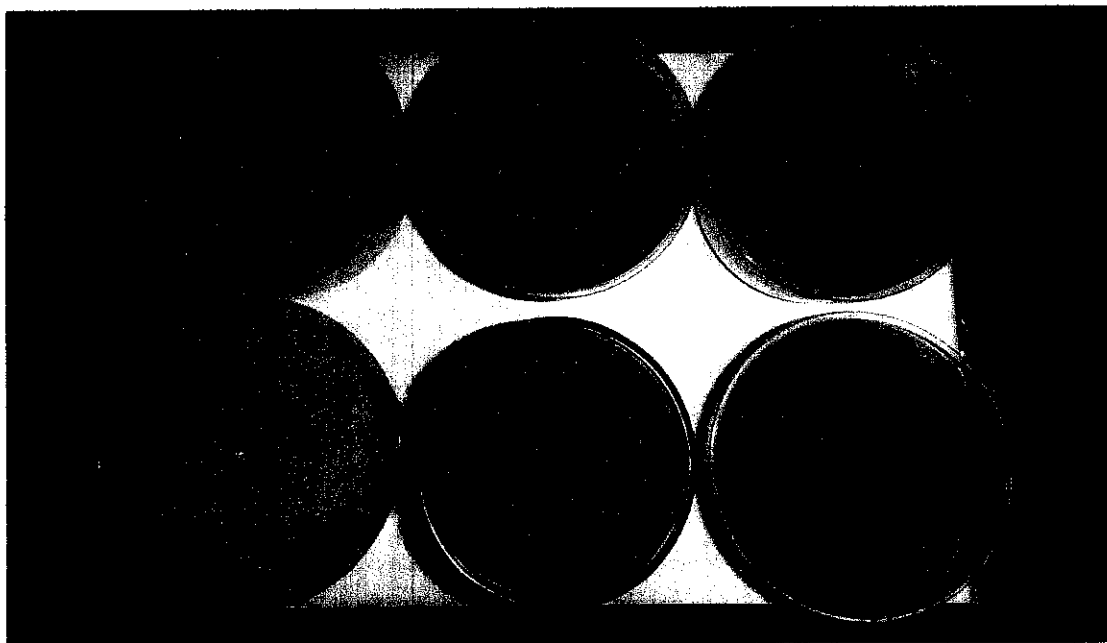
Figure 14: Prepared and calcined catalysts
Top, from left to right: i) Cu – Ti, ii) Cu – Ce, iii) Cu - Mn
Bottom, from left to right: i) Cu – Ba, ii) Cu – Ag, iii) Cu - Co

3.2 Catalyst Characterization

These are the methods that will be used in finding the surface characterization of the catalysts (Niemantsverdriet J.W, 2007):

a) Temperature program desorption (TPD) technique is used to determine the amount of desorbed species as a function of temperature. The provided information is also related to the binding character of the adsorbate/substrate system. It aids in giving the information of the catalyst reactivity.
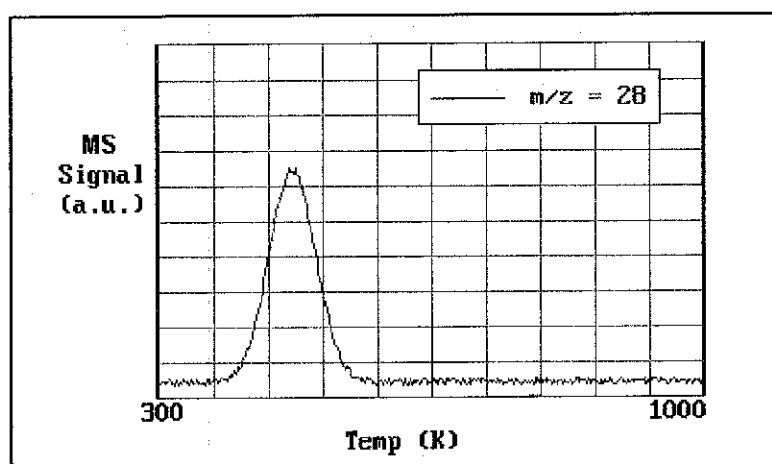
Figure 15: Example of TPD of carbon monoxide adsorbed onto palladium crystal (Temperature-Programmed Techniques. From http://www.chem.qmul.ac.uk/surfaces/scc/scat5_6.htm)

b) Temperature program reduction (TPR) technique is used to determine the required catalyst reduction temperature. TPR is widely used for the characterization of metal oxides, mixed metal oxides and metal oxides dispersed on a support. The TPR method yields quantitative information of the reducibility of the oxide's surface, as well as the heterogeneity of the reducible surface. The appropriate catalyst TPR is important in obtaining better catalytic performance in the reaction.

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c) X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit dimensions. The analysed material will be finely ground, homogenized, and average bulk composition is determined. This technique is important in determining the elemental composition, crystal structure and crystal particle size, where it can detects crystals larger than 3 – 5 nm in quantities higher than 1%.

d) Brunauer, Emmett and Teller (BET) method explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area and pore size of the prepared catalysts.

$$y = \frac{x}{V(1-x)}$$

$$m = \frac{(c-1)}{cV_m}$$
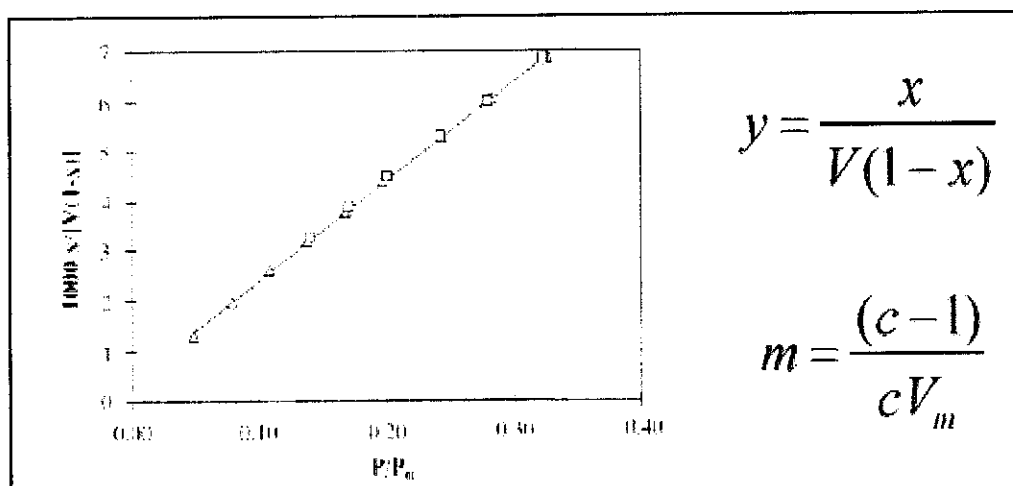
Figure 16: BET plot (Niemantsverdriet J.W, 2007)

e) Field Emission Scanning Electron Microscopy (FESEM) is basically a microscope that uses electrons instead of light to form an image. It provides the information about the sample's surface morphology and the composition of metals adsorbed on the catalyst support.

f) Fourier Transformed Infrared (FTIR) spectrometer is subjected to an infrared source, which is scanned from 4000 cm^{-1} to 400 cm^{-1}. It is use to analyse the

organic molecules by causing molecular rotation and molecular vibrations (stretching or bending of bonds) in the molecules. The resultant spectrum shows the absorption due to various distinctive functional groups, giving a molecular fingerprint of the studied compound. For this project, the prepared solid catalysts are tested using FTIR for both before and after calcination process.

3.3 Catalytic Test and Analysis

The prepared bi – metallic catalysts are tested in the hydrogenolysis process of glycerol, where the reaction is carried out in 1.80 Litre of stainless steel autoclave (by Parr Instrument Company) conducted at the temperature of $200^{\circ}C$ and pressure of 15 bar. The reactor is equipped with a stirrer, heater and a sample ports for both liquid and gas samplings.

The reactor is flushed several times with nitrogen. The system is then heated to $200^{\circ}C$. The prepared reacting solution (250 mL solution of 50 wt % of glycerol) together with the catalyst (5.0 weight percent (wt %) with respect to glycerol weight) is immediately transferred into the reactor without further delay. The reactor is then pressurized with hydrogen up to 15 bar, stirrer speed is set at 200 rpm, and the reaction is carried out for 8 hours.

The collected samples (both liquid and gas) are cooled to room temperature. For liquid sample, the centrifugal (with 3000 rpm for 15 minutes) is used to separate the liquid product from the solid catalyst. Later on, the analysis of the product is done by using gas chromatography device (Shimadzu GC - 2010). The resulting analysis of GC shows the products that are formed in the reaction. The obtained data are recorded accordingly.

For each data of reaction obtained, conversion of glycerol, and selectivity of 1,3 – propanediol are calculated.

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a) $\text{Conversion} = \dfrac{\text{concentration of glycerol consumed}}{\text{Initial concentration of glycerol}} \times 100$

b) $\text{Selectivity} = \dfrac{\text{Concentration of 1,3-propanediol formed}}{\text{Concentration of glycerol consumed}} \times 100$
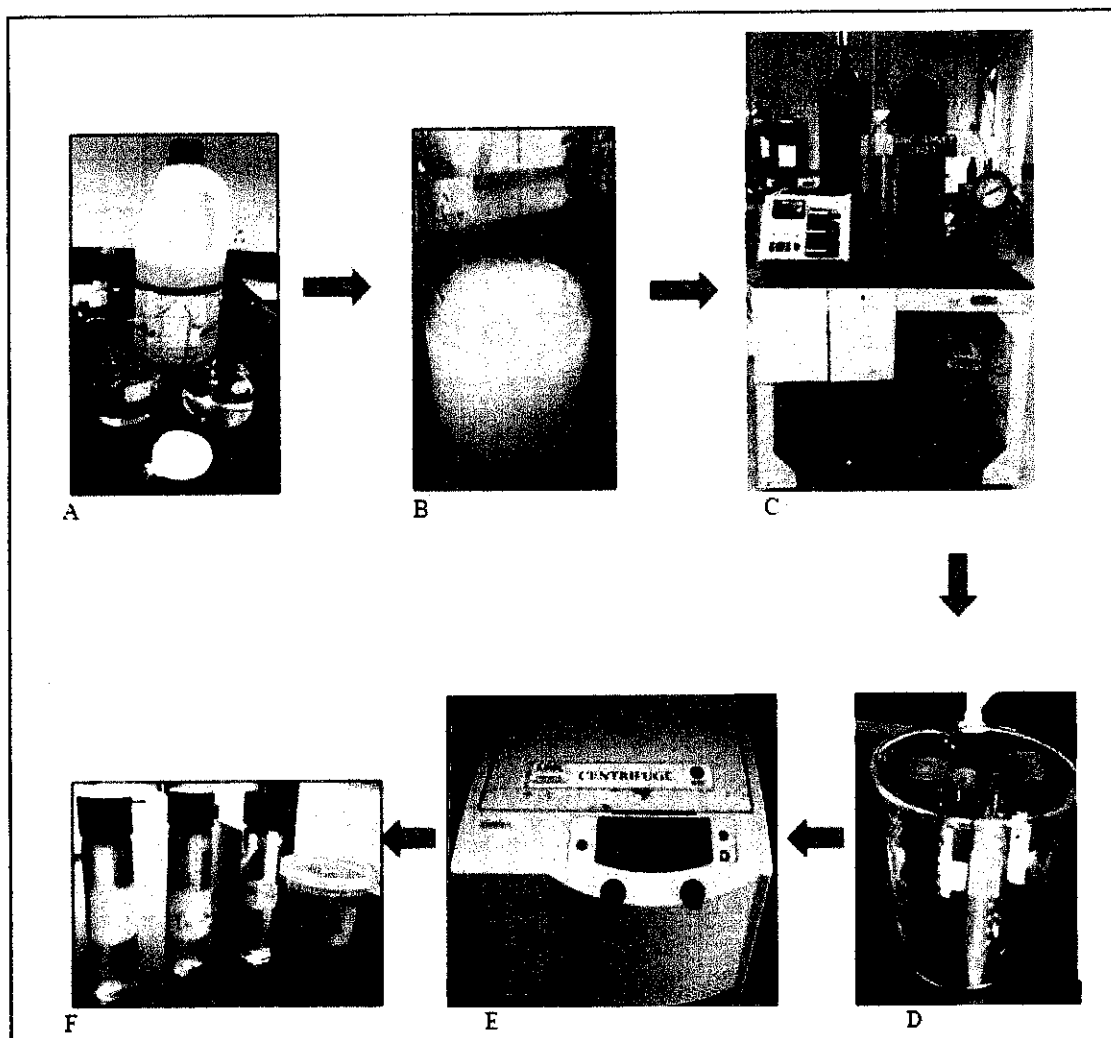
Figure 17: Flow chart of the catalytic test and analysis activities. A: Reacting solution preparation. B: The reacting solution. C: Reaction in pressure reactor D: Raw liquid samples E: Refined liquid samples.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Catalyst Characterization

4.1.1 Fourier Transformed Infrared (FTIR)
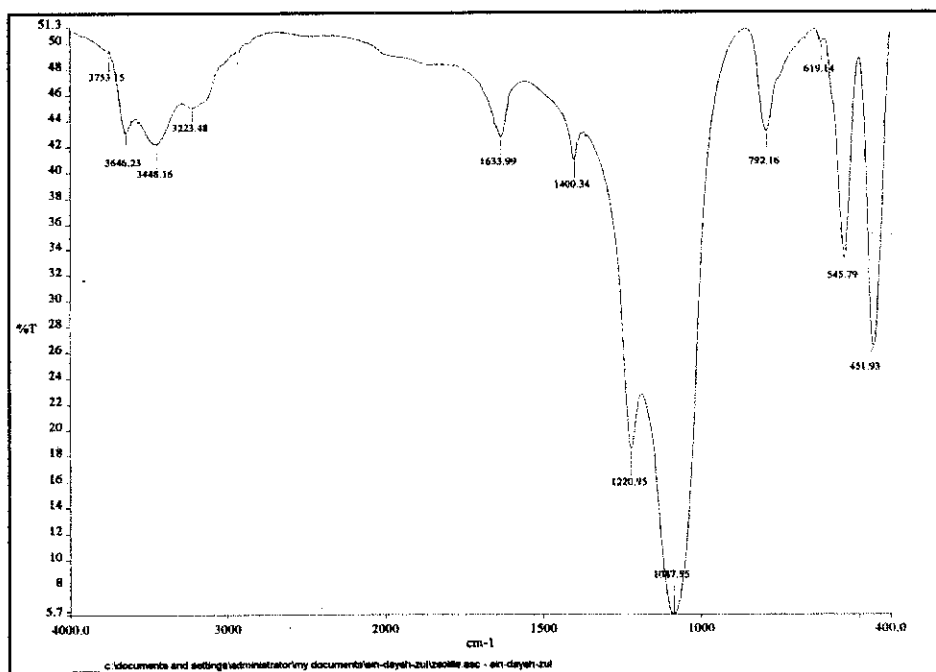
Figure 18: FTIR pattern for bare zeolite powder
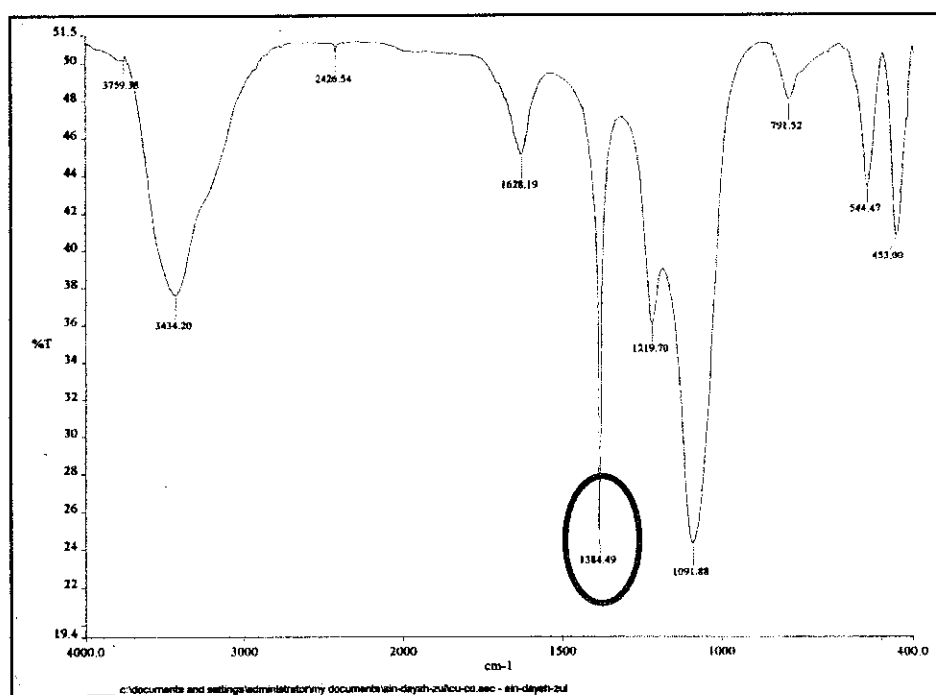
Figure 19: FTIR pattern for Cu – Co catalyst (before calcination).
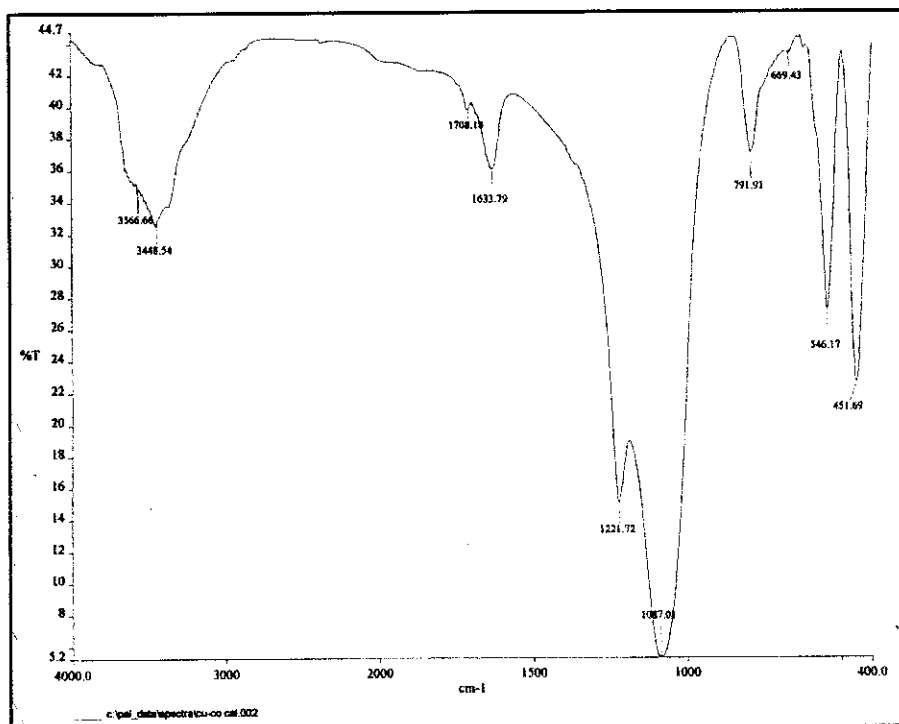
Figure 20: FTIR pattern for Cu – Co catalyst (after calcination)

Based on the FTIR results obtained, for all six catalysts prepared, the pattern appeared to be almost similar for both before and after calcination process. This is due to the low percentage of metal loading on the zeolite, and FTIR is meant for detecting the functional group of organic compound only. The most significant different is at wavenumber 1384.50 cm^{-1} that indicates the nitro stretch (N – O) functional group, with transmittance percentage of 24. After calcination, where the catalyst is treated with a high temperature, the nitro stretch is no longer available. Therefore, calcination process manages to remove the volatile constituents of the sample.

4.1.2 Temperature Program Reduction (TPR)

Six different TPR profiles of the prepared catalysts were observed. These figures illustrate the TPR profiles for different combination of bi – metallic catalysts prepared. Red-coloured line displays thermal conductivity detector (TCD) signal output as a function of time, while green-coloured line displays the temperature as a function of time of heating rate from 0°C up to 700°C. The peak maximum (T_{max})

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indicates the temperature that corresponds to the maximum rate of reduction. The area under the peak is equivalent to amount of hydrogen (H_2) consumed. Higher H_2 consumption for reduction of metal oxide (M_xO) results in better dispersion of metal species on the support. Theoretically, shoulder or small peak at lower reduction temperature indicates the reduction of small metal M_xO with lesser interaction with the support. On the other hand, the dominant reduction peak at high temperature observed in all samples prepared is due to the large particle formation of bulk M_xO having stronger interaction with the support.
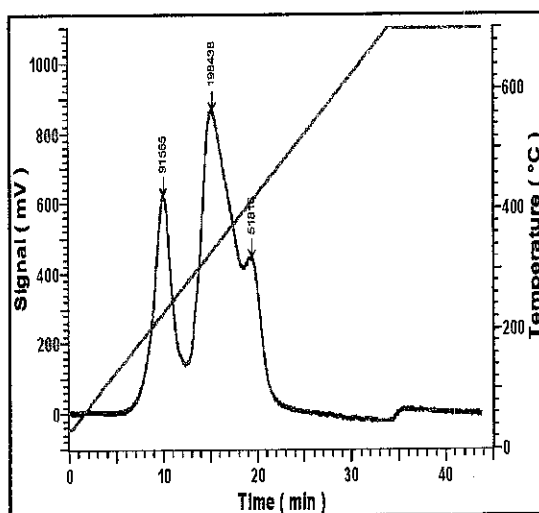
a) Cu – Ag (T_R : 560 °C)
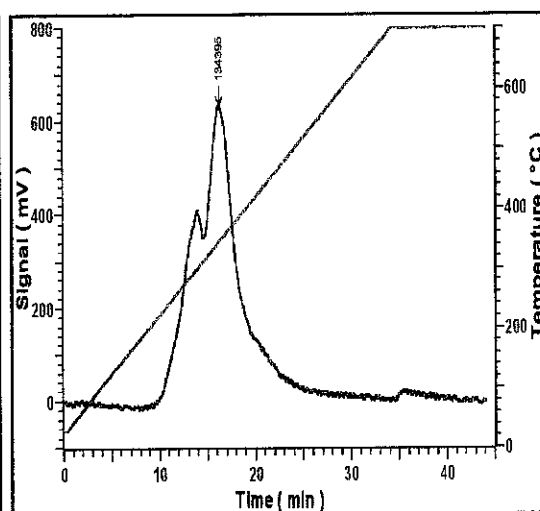
b) Cu – Ba (T_R : 570 °C)
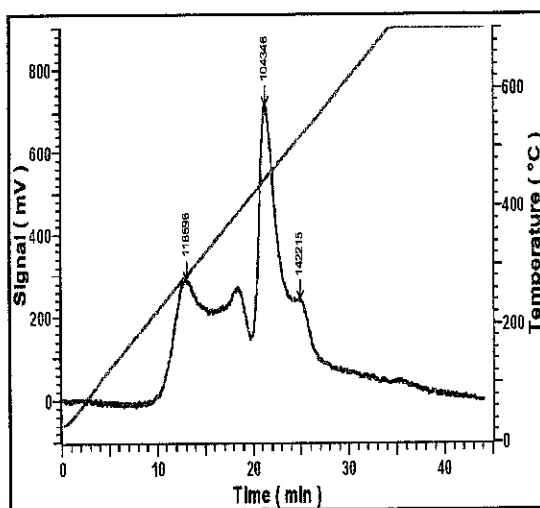
c) Cu – Ce (T_R : 580 °C)

d) Cu – Co (T_R : 580 °C)
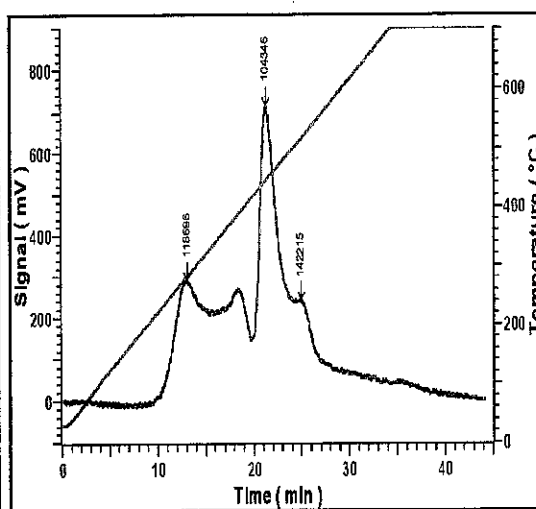
e) Cu – Mn (T$_R$: 560 °C)   f) Cu – Ti (T$_R$: 570 °C)
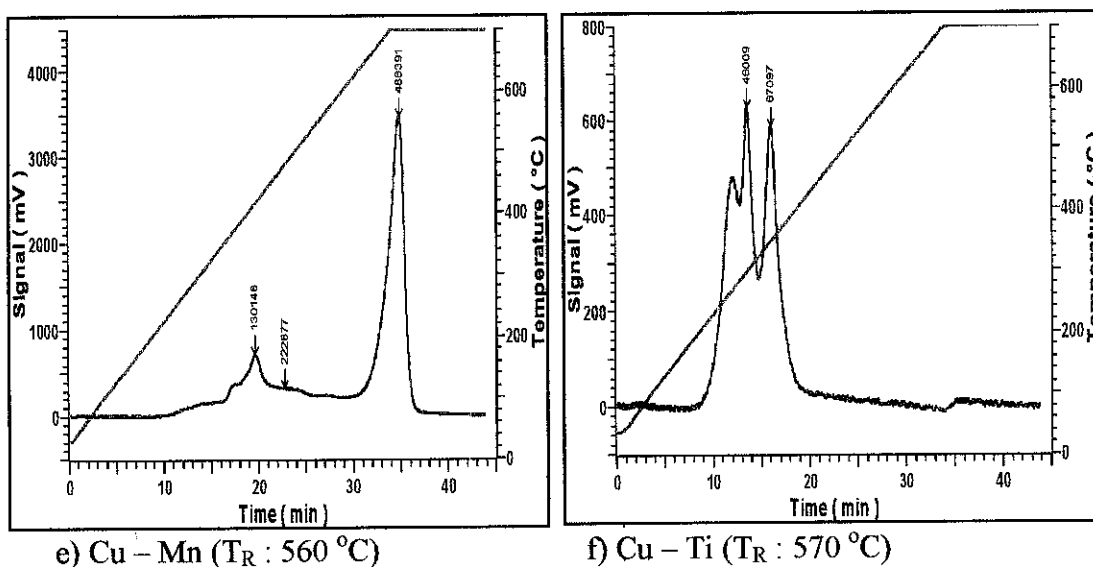
Figure 21: TPR profile of prepared catalyst with reduction temperature (T$_R$)

4.1.3 X – Ray Diffraction (XRD)

For all prepared bi – metallic catalyst, the X – Ray diffraction (XRD) patterns observed are very similar to one another. The peaks at 2θ = $8°$, $9°$, and $24°$ appear in all samples. The black-coloured line represents the XRD pattern of the tested catalyst, while the red-coloured line indicates the pattern of component that suits the pattern of the tested catalyst. From the databank provided by the software, Tetrakis (tetrapropylammonium) silicate hydroxide pattern is shown by red-coloured line. As mentioned in the earlier chapter, zeolite with $SiO_2/Al2O3$ mole ratio of 23 is used in this study as the catalyst support. Therefore, tetrakis (tetrapropylammonium) silicate hydroxide that behaves similar to SiO_2 was identified from the XRD pattern of the tested catalyst. Due to the low metal loading of the metals impregnated on the support, the pattern could not be observed and identified. It may also due to crystalline structure of the metal itself. Example of the XRD pattern for Cu–Ag catalyst is shown below.

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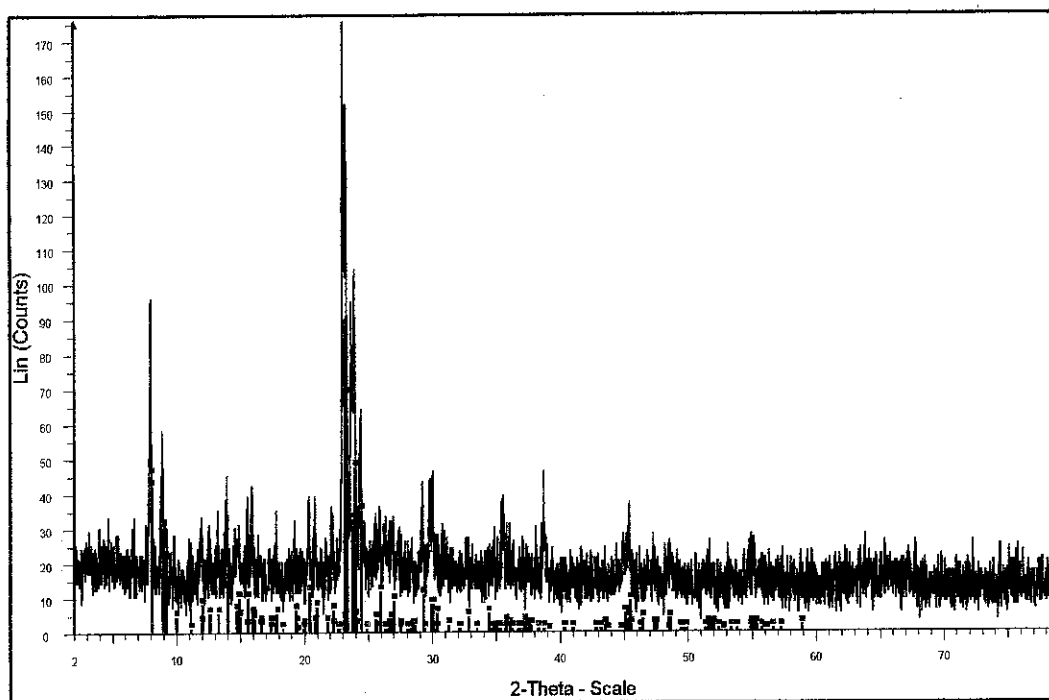
Figure 22: XRD pattern for Cu – Ag catalyst

4.1.4 Field Emission Scanning Electron Microscope (FESEM)

FESEM offers high-resolution surface observation of particles, where it is used in this study as a method to obtain internal morphology, and the intra-particle distribution (known as Energy Dispersive X-ray Analysis – EDX) of the prepared supported catalysts. For the morphology of the bi – metallic catalysts tested, the FESEM images show prismatic and cubic units that represent the structure of the catalysts support used (ZSM-5 zeolite). The average particle size between 0.4 μm – 0.8 μm was observed. As for EDX, the analysis reveals carbon (C), Oxygen (O), Aluminium (Al), and Silicon (Si) as the significant elements. The graphs obtained show the presence of metals used to prepare the catalysts. However, the resulting weight percentage (wt %) of certain metals on the support does not correlate well with the actual amount of metal used (5 wt % of each metal) for catalyst preparation. The deviation occurred maybe due to some factors such as the penetration depth of the electron beam (because of layer thickness), the cluster size, surface coverage, and also preparation performance.

a) Cu – Ag   b) Cu - Ba
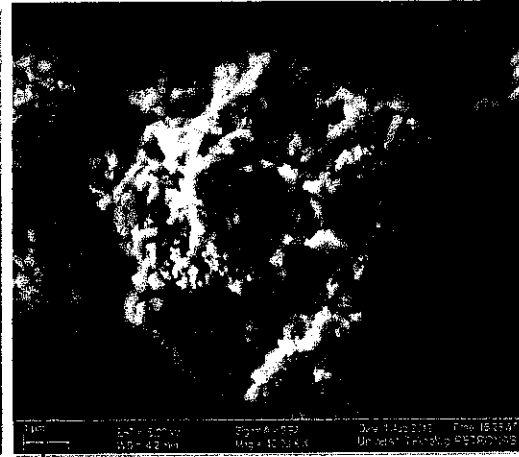
c) Cu – Ce   d) Cu - Ti
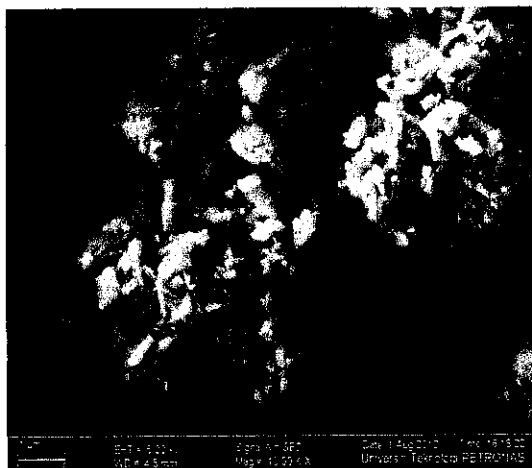
e) Cu – Co   f) Cu – Mn

Figure 23: FESEM images of prepared catalysts at 10,000 magnifications
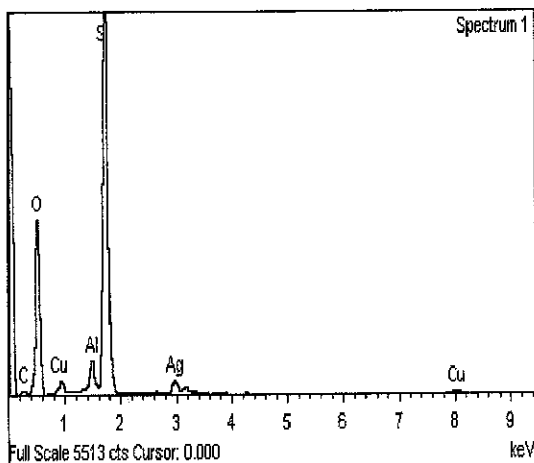
a) Cu: 1.86 wt%, Ag: 3.36 wt%
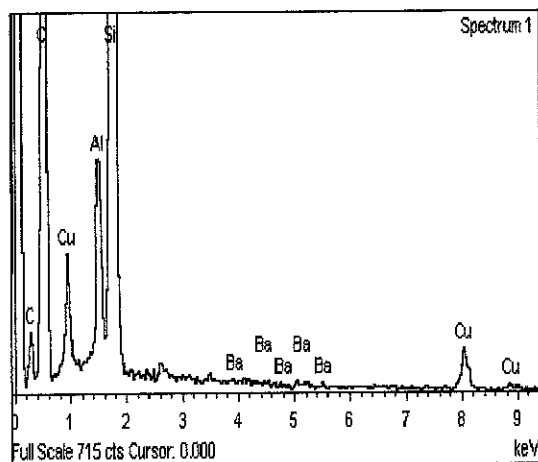
b) Cu: 3.26 wt%, Ba: 0.07 wt%
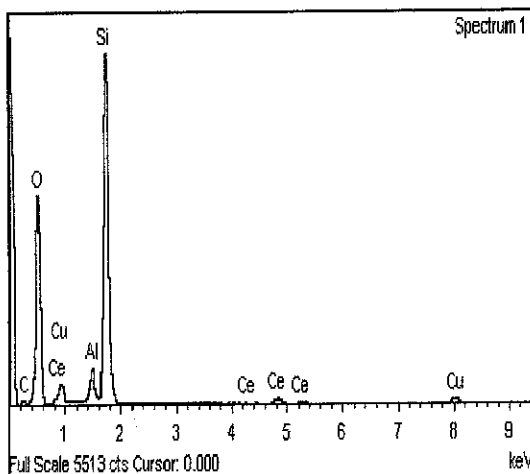
c) Cu: 3.41 wt %, Ce: 2.96 wt %
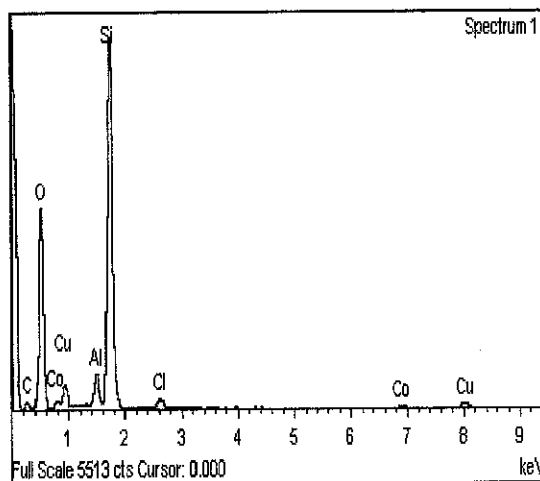
d) Cu: 3.04 wt %, Co: 1.34 wt %
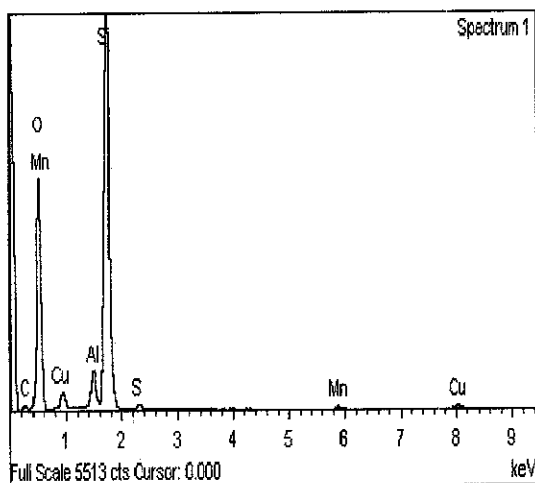
e) Cu: 2.21 wt %, Mn: 0.82 wt %
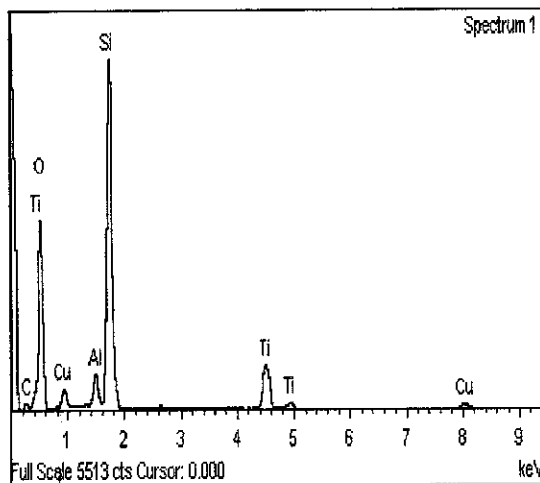
f) Cu: 2.77 wt %, Ti: 6.72 wt %

Figure 24: EDX analysis with weight percentage of metals on support.

4.1.5 Temperature Program Desorption (TPD) and Brunauer, Emmett and Teller (BET).

Due to the time constraint, the results for both TPD and BET could not be included in this report and project. However for BET, it is believed that the surface area of the catalysts would be lesser than the bare zeolite support (425 m^2/g) due to the attachment of metal particles on the support's surface.

In summary, the catalyst characterization provides the necessary information on the distinctive functional groups, reduction temperature, crystalline structure, morphology and mapping of the catalysts prepared.

4.2 Experimental Analysis

The refined liquid products of the experiment were sent for GC – FID tests, where the results can be analysed qualitative and quantitatively. All samples were diluted 10 times with 1 – butanol, in order to avoid peak overshoot and to ensure that the peaks that are obtained are between the ranges. The specifications of GC – FID used are stated as the following:

Table 4: Specifications of GC – FID used.

Model	GC Shimadzu 2010
Column Type	SGE BP – 20
Column Size	30m x 0.25 mm x 0.25 μm
Column Temperature	100°C
Heating Rate	10°C / min
Final Temperature	240 °C, hold 5 minutes
Injection Temperature	250 °C
Detection Temperature	260 °C
Column Flow Rate	0.9 mL/min
Linear Velocity	26.1 cm/s
Pressure	87 kPa
Carrier Gas	Helium

The retention times for the expected products are listed in Table 5 below:

Table 5 : Retention time for the expected reaction products.

Retention Time (tr) (min)	Component
2.212	2 – Propanol
2.858	1 – Butanol
7.092	1,2 – Propanediol
7.528	Ethylene Glycol
9.329	1,3 – Propanediol
14.714	Glycerol

The results obtained for each catalyst were compared with the retention times of the standard solutions. The standard solutions of the expected experiment products were prepared at different concentrations of 3000 ppm, 5000 ppm and 7000 ppm. Later on, the standard calibration curves were produced, where the actual concentrations of products can be calculated.

Based on the GC results obtained, the peaks of the expected experiment products which are 1,3 – propanediol and 1,2 – propanediol were not noticeable. Only the solvent (1 – butanol) and glycerol peaks were observed clearly. Some unidentified components with a small peak areas appeared in the results. The conversions of glycerol are calculated and simplified in Table 6:

Table 6: Conversion of glycerol

Catalyst	Conversion (%)
Bare Zeolite	0.89
Cu – Ag	3.63
Cu – Ba	2.87
Cu – Co	2.56
Cu – Mn	3.81

From the obtained results, the conversions of glycerol are in the range of 0.89 % to 3.81 %. Bare zeolite support that is tested in the reaction shows no significant effect to the conversion of glycerol. The overall conversions are much lower compared to the literatures that are related to this project. The gas samples of the reactions were tested, and a significant amount of methane (around 97 %) and traces of carbon dioxide ($\geq$ 3 %) were detected. The glycerol was not converted to the desired product, which is 1,3 propanediol. The reaction between hydrogen and glycerol with the presence of the catalysts produced gases instead of the aimed product. It is believed that the insufficient amount of hydrogen throughout the reaction is the main contributor to this finding. Cu – Ce and Cu – Ti catalysts are not tested yet since it is predicted that the conversions would also be in the range as stated above, due to the insufficient of hydrogen for the reaction to occur effectively. Therefore, a slight modification was made to the experimental procedures, where the reactions are repeated in order to improve the results. The repeated reactions are named as '**batch 2**', while the previous conducted reactions are named as '**batch 1**'.

Batch 1	**Batch 2**

Operating Condition:
• Temperature: 200 °C
• Pressure: 15 bar (The system is pressurized once and the pressure is maintained at 15 bar)
• Duration: 6 hours
• Stirrer speed: 200 rpm
• Tested catalysts:
  o Bare Zeolite, Cu – Ba, Cu – Mn, Cu – Co, Cu – Ag.
	Operating Condition:
	• Temperature: 200 °C
	• Pressure: 15 bar (The system is pressurized and de-pressurized continuously, at an interval of 30 minutes)
	• Duration: 6 hours
	• Stirrer speed: 200 rpm
	• Tested catalysts:
	  o Cu – Ag, Cu – Ce, Cu - Mn

Figure 25: Difference in terms of operating condition for batch 1 and batch 2

As shown in Figure 26, the only difference between the two batches of experiments is the pressure of the system. In Batch 2, the system is pressurized and de-pressurized continuously at an interval of 30 minutes. It is assumed that, within 30 minutes of reaction, the supplied hydrogen gas was fully consumed. Therefore, at an interval of 30 minutes, the gas in the system was purged out to a safe location, and then the system was pressurized with hydrogen again up to 15 bar. The flow of hydrogen into the reactor could not be made continuous, due to some limitations that are stated as the following:

a) Limited availability of hydrogen gas for this project.

b) The system is not suitable to have a continuous gas flow since the liquid reactants would be carried over due to high pressure condition.

4.2.1 Conversion of Glycerol in Batch 2.

The conversion of glycerol in the reactions for Batch 2 is simplified in Table 7:

Table 7: Conversion of glycerol in Batch 2

Catalyst	Conversion (%)
Cu – Ag	10.47
Cu – Mn	11.08
Cu – Ce	8.21

Based on the results obtained, Cu – Mn catalyst gives the highest conversion of glycerol compared to the other catalysts used with 11.08 % of conversion. This finding is in line with Y.Nakagawa et. al.,(2010) where the presence of metal of group 6 or 7 as a co – catalyst will enhance the glycerol conversion. It is also observed that the conversion of glycerol shows a slight increment, compared to the conversion results in Batch 1. It is somehow proves that the conversion of glycerol is proportional to the availability of hydrogen gas provided to the system.

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4.2.2 Selectivity Toward 1,3 – propanediol in Batch 2.

The selectivity towards 1,3 - propanediol for Batch 2 is simplified in Table 8:

Table 8: Selectivity towards 1,3 - propanediol in batch 2

Catalyst	Selectivity (%)
Cu – Ag	8.35
Cu – Mn	7.64
Cu – Ce	9.70

The results show that Cu – Ce catalyst gives the highest selectivity towards the production of 1,3-propanediol compared to the other two, with the percentage of 9.70 %. Compared to the literatures related to this study, the selectivity towards the desired product of the prepared catalysts in this project is quite low. This is because the reactions were conducted only for eight (8) hours (due to the purpose of catalyst initial screening only), while the literatures reported that the reaction was done for 24 hours. It can simply be said that glycerol conversion and selectivity are proportional to the reaction time (A. Marinoiu et. al., 2010).

Unfortunately, the catalytic testing and analysis of other catalysts could not be done due to sudden mechanical failure of the high pressure reactor used in this project. Therefore, no results can be discussed in this study regarding the conversion and also the selectivity of those catalysts towards 1,3 – propanediol. The presence of 2-propanol in all results is remain unknown.

The experiment results in Batch 2 also show the presence of 1,2 – propanediol as the reaction product. For both Cu – Ag and Cu – Mn catalysts, the production of 1,3-propanediol is slightly higher compared to 1,2-propanediol. As for Cu – Ce catalyst, 1,2-propanediol is produced more compared to 1,3-propanediol. The ratio of 1,3-propanediol to 1,2-propanediol produced for each catalyst is simplified in Table 9 below:

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Table 9: Ratio of products for hydrogenolysis of glycerol

Catalyst	1,3-propanediol : 1,2-propanediol
Cu – Ag	1.080
Cu – Mn	1.224
Cu – Ce	0.6161

In summary, the experimental results obtained from this project illustrate that Cu – Mn catalyst gives the highest conversion of glycerol in the hydrogenolysis reaction with the percentage of 11.08 % while Cu – Ce catalyst has the highest selectivity of 9.70 %. The conversion and selectivity of Cu – Ag and Cu – Mn catalysts are comparable to one another since the differences are not very significant. In fact, they produces more 1,3-propanediol instead of 1,2-propanediol based on the results shown in Table 9. It is believed that, Cu – Ag and Cu – Mn have a high potential to be developed as the catalysts for hydrogenolysis of glycerol to 1,3-propanediol.

CHAPTER 5: CONCLUSION

The purpose of this project is to find the best bi-metallic catalyst that gives high conversion of glycerol together with high selectivity towards the production of 1,3-propanediol. 1,3 – propanediol emerges as an important chemical, since it has a broad spectrum of uses. The readily available glycerol is the best substitutes for propylene, where 1,3 – propanediol can be produced via hydrogenolysis process of glycerol. Glycerol appears to be the best raw material for this purpose, and it is a wise option since petroleum source is diminishing.

From the characterizations of the prepared catalysts provide useful information regarding the reduction temperature of the catalyst, strength of metal bonding on the catalyst support, crystalline structure and morphology of the catalysts. Intra-particle distribution and average particle size can also be obtained.

From the catalytic testing conducted, Cu – Mn catalyst gives the highest glycerol conversion in the hydrogenolysis reaction with 11.08 % followed by Cu – Ag with 10.47 % and Cu – Ce at 8.21 %. For the selectivity towards 1,3-propanediol production, Cu – Ce catalyst shows the highest value with 9.70 %, compare to Cu – Mn and Cu – Ag with the percentage of 7.64 % and 8.35 % respectively. Both conversion and selectivity results of Cu – Ag and Cu – Mn catalyst are comparable, with only a slight difference. On the other hand, Cu – Ce catalyst is more selective towards the production of 1,2-propanediol, where the ratio of 1,3-propanediol to 1,2-propanediol is calculated as 0.6161.

In conclusion, it is believed that, Cu – Ag and Cu – Mn have a high potential to be developed as the catalysts for hydrogenolysis of glycerol to 1,3-propanediol. Further studies and researches need to be done by considering various factors such as catalyst reduction temperature and the reaction operating condition in order to make this study as a success.

CHAPTER 6: RECOMMENDATION

Based on the experiments conducted, some modifications could be done in order to improve the result of this study in the future. The recommendations are listed as the following:

1. The contact time between zeolite solid support and the metal salt solutions should be made longer, which is more than 4 hours, in order to allow more metal to get into the pores of the support.

2. The weight percent of metal loading for the catalyst preparation should be increase and tested since the most recent literature shows that 20 wt % of metals appear to be an optimum content.

3. Use Inductively-Coupled Plasma Mass Spectra (ICP – MS) to replace XRD for catalyst characterization. ICP-MS is an accurate analytical technique used for elemental determinations compared to XRD.

4. In order to obtain better results in the future, different parameters can be studied in the catalytic test. The parameters include:

   • Reaction temperature for the hydrogenolysis of glycerol.
   • Reaction pressure for the hydrogenolysis of glycerol.
   • Reduce the catalyst first (according to the catalyst reduction temperature) before performing the reaction.
   • Catalyst weight percent (wt %) used in the hydrogenolysis reaction should be vary, tested and analysed. (In this project, 5 wt % of catalyst with respect to glycerol weight is used in the reaction)

5. It would be beneficial for the department to purchase another high pressure high temperature reactor with a smaller working volume. Currently, only one reactor available with a volume of 1.8 litres. The sudden failure of the reactor would affect the studies. Furthermore, 1.8 litres of capacity is large for such a laboratory scale experiment.

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APPENDIX A: GANTT CHART FOR FYP I

Detail / Week	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14
1. Selection of Project Topic	▓	▓												
2. Preliminary research work a) Literature review. Production of 1.3 - Propanediol from hydrogenolysis of glycerol			▓	▓	▓									
3. Submission of extended proposal						●								
4. Proposal defense														
5. Project work continues a) further discuss on project methodology							▓	▓	▓	▓				
b) Preparation of catalysts											▓	▓		
6. Submission of Interim Draft Report													●	
7. Submission of Interim Report														●

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APPENDIX B: GANTT CHART FOR FYP II

Detail/week	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15
1. Project work continues															
a) Catalyst characterization															
b) Catalytic test															
2. submission of progress report								●							
3. Project work continues															
a) Catalytic test															
b) report and documentation															
4. Pre - EDX											●				
5. Submission of draft report												●			
6. Submission of dissertation (soft bound)													●		
7. Submission of technical paper													●		
8. Oral presentation														●	
9. Submission of project dissertation (hard bound)															●

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APPENDIX C: SAMPLE CALCULATION FOR CATALYST PREPARATION.

Copper – manganese catalyst

i. 5 weight percent (5 wt%) of each metal loading is considered for this catalyst preparation. Total of 10% metals loading.
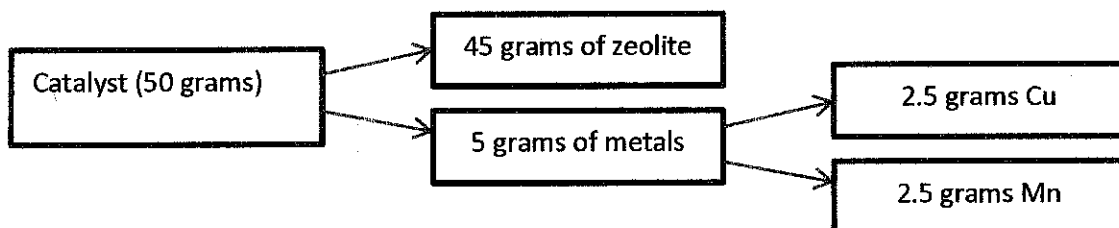
ii. For Cu:

Molecular weight of $Cu(NO_3)_2 . 3H_2O = 241.6$ g/mol

Molecular weight of $Cu = 63.55$ g/mol

In order to have 2.5 g of Cu:

$$\frac{241.6 \text{ g/mol}}{63.55 \text{ g/mol}} \times 2.5 \text{ g Cu} = \underline{9.5 \text{ g } Cu(NO_3)_2 . 3H_2O \text{ is required.}}$$

iii. For Mn:

Molecular weight of $H_2MnO_5S = 169.02$ g/mol

Molecular weight of $Mn = 54.94$ g/mol

In order to have 2.5 g of Mn:

$$\frac{169.02 \text{ g/mol}}{54.94 \text{ g/mol}} \times 2.5 \text{ g Mn} = \underline{7.69 \text{ g } H_2MnO_5S \text{ is required.}}$$

APPENDIX D : PREPARATION OF THE REACTION SOLUTION

The solution consists of two components which are:

a) Distilled water (mass fraction of water, $x_a = 0.5$)

b) Glycerol (mass fraction of glycerol, $x_b = 0.5$)

For the preparation of solution, let $x_a = \underline{150 \text{ mL}} = 150 \text{ g}$

Therefore, mass of glycerol:

$$= \frac{150 \text{ } g \text{ of water}}{0.5 \text{ } (water)} \times 0.5 \text{ (glycerol)} = 150 \text{ g glycerol}$$

Given that the density of glycerol = 1257 kg/ m^3

Converting mass of glycerol to volume:

$$= 0.150 \text{ kg glycerol} \times \frac{1 \text{ } m^3}{1257 \text{ } kg} = 1.193 \times 10^{-4} \text{ m}^3$$

Converting volume (m^3) to volume in Liter:

$$= 1.193 \times 10^{-4} \text{ m}^3 \times \frac{1000 \text{ } L}{1 \text{ } m^3}$$

$$= 0.1193 \text{ L glycerol} = \underline{119.3 \text{ mL of glycerol.}}$$

Total volume of solution:

$$= \text{volume of water} + \text{volume of glycerol}$$

$$= 150 \text{ mL} + 119.3 \text{ mL}$$

$$= \underline{269.3 \text{ mL}}$$

For this study, 5.0 wt % of catalyst with respect to glycerol is used.

Amount of catalyst required:

$$= \frac{5.0}{100} \times 150 \text{ g}$$

$$= \underline{7.5 \text{ g catalyst}}$$

APPENDIX E: STANDARD SOLUTION OF PRODUCT MIXTURE AT 3000 PPM

Sample Information

Analysis Date & Time : 30/07/2012 12:57:11 PM

Sample Name : standard 3000ppm
Sample ID :

Data Name : C:\GCsolution\Data\2012\hidayah\standard 2.gcd
Method Name : C:\GCsolution\Data\2012\hidayah\curve.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.214	67967.72	34254.27	2866.8253	ppm	2 - Propanol
2	2.866	28000375.62	11558391.65	0.0000		
3	7.050	43709.66	6815.90	2739.8256	ppm	1, 2 - Propanediol
4	7.459	33074.61	8872.01	2946.4905	ppm	Ethylene glycol
5	9.337	44625.09	2022.48	2982.0297	ppm	1, 3 - Propanediol
6	14.885	14906.43	856.93	2993.0929	ppm	Glycerol
7	16.511	4617.54	791.46	0.0000		
Total		28209276.67		14528.2639		

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APPENDIX F: STANDARD SOLUTION OF PRODUCT MIXTURE AT 5000 PPM

Sample Information

Analysis Date & Time	: 30/07/2012 1:23:52 PM
Sample Name	: standard 5000ppm
Sample ID	:
Data Name	: C:\GCsolution\Data\2012\hidayah\standard 3.gcd
Method Name	: C:\GCsolution\Data\2012\hidayah\curve.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.214	118338.48	62596.52	5058.6149	ppm	2 - Propanol
2	2.866	27845249.83	11470841.48	0.0000		
3	4.569	1370.15	474.93	0.0000		
4	7.040	78742.11	16804.94	4448.8602	ppm	1, 2 - Propanediol
5	7.455	58448.57	17290.42	5059.9722	ppm	Ethylene glycol
6	9.260	82798.29	8436.53	5035.9406	ppm	1, 3 - Propanediol
7	14.758	30803.77	1917.97	5013.8143	ppm	Glycerol
Total		28215751.20		24617.2022		

APPENDIX G: STANDARD SOLUTION OF PRODUCT MIXTURE AT 7000 PPM

Sample Information

Analysis Date & Time : 01/08/2012 3:05:06 PM

Sample Name   : standard 7000ppm
Sample ID   :

Data Name   : C:\GCsolution\Data\2012\hidayah\standard 7000.gcd
Method Name   : C:\GCsolution\Data\2012\hidayah\curve.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.216	163076.70	88329.57	7005.3150	ppm	2 - Propanol
2	2.871	28286637.19	11010775.66	0.0000		
3	7.043	140345.72	41881.14	7454.1513	ppm	1, 2 - Propanediol
4	7.458	81474.21	26661.11	6977.8550	ppm	Ethylene glycol
5	9.257	118967.55	24022.56	6982.0297	ppm	1, 3 - Propanediol
6	12.361	6737.80	384.87	0.0000		
7	14.677	46375.07	5307.63	6993.0929	ppm	Glycerol
8	15.168	7117.22	822.18	0.0000		
Total		28850731.46		35412.4439		

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APPENDIX H: GC RESULT FOR 50 WT % GLYCEROL SOLUTION

Sample Information

Analysis Date & Time : 01/08/2012 3:31:47 PM

Sample Name : standard glycerol
Sample ID :

Data Name : C:\GCsolution\Data\2012\hidayah\standard glycerol.gcd
Method Name : C:\GCsolution\Data\2012\hidayah\curve.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.195	5774.07	2865.16	160.5847	ppm	2 - Propanol
2	2.866	25583558.22	10674336.68	0.0000		
3	4.572	1350.29	461.31	0.0000		
4	14.680	652991.69	173508.20	84100.5605	ppm	Glycerol
5	16.570	4897.54	743.30	0.0000		
6	19.412	1673.59	254.91	0.0000		
Total		26250245.40		84261.1452		

APPENDIX I: STANDARD CALIBRATION CURVE FOR GLYCEROL

Calibration curve of glycerol

$y = 7.8672x - 8640.7$
$R^2 = 1$

APPENDIX J: STANDARD CALIBRATION CURVE FOR 1,3-PROPANEDIOL

Calibration Curve for 1,3-Propanediol

$y = 18.586x - 10798$
$R^2 = 0.9998$

APPENDIX K: SAMPLE CALCULATION FOR GLYCEROL CONVERSION

Peak area of glycerol at 50 wt % = 652991.69

Equation from glycerol standard calibration curve: **y = 7.8672 x - 8640.7**

Where y = peak area,

     x = concentration in ppm

Therefore, concentration of glycerol in 50 wt % : x = (y + 8640.7) / 7.8672

$$x = (652991.69 + 8640.7) / 7.8672$$

$$x = 84100.11 \text{ ppm}$$

Let glycerol peak area for Cu – Mn catalyst for Batch 2 = 579682.81

Concentration in ppm = 74781.81 ppm

$$\text{Conversion} = \frac{\text{concentration of glycerol consumed}}{\text{Initial concentration of glycerol}} \times 100$$

$$= \frac{(84100.11 - 74781.81)}{84100.11} \times 100$$

$$= 11.08 \%$$

APPENDIX L: SAMPLE CALCULATION FOR SELECTIVITY OF 1,3-PROPANEDIOL

Peak area of 1,3-propanediol for Cu – Mn catalyst in Batch 2 = 2433.21

Equation from 1,3-propanediol standard calibration curve: $y = 18.586x - 10798$

Where y = peak area,

x = concentration in ppm

Therefore, concentration of 1,3-propanediol: $x = (y + 10798) / 18.586$

$$x = (2433.21 + 10798) / 18.586$$

$$x = 711.89 \text{ ppm}$$

From Appendix J, initial concentration of glycerol = 84100.11 ppm

Final concentration of glycerol = 74781.81 ppm (peak area = 579682.81)

$$\text{Selectivity} = \frac{\text{Concentration of 1,3-propanediol formed}}{\text{Concentration of glycerol consumed}} \times 100$$

$$= \frac{(711.89)}{(84100.11 - 74781.81)} \times 100$$

$$= 7.64 \%$$

APPENDIX M: GC RESULT FOR ZEOLITE (BATCH 1)

Sample Information

Analysis Date & Time : 17/07/2012 12:27:33 PM

Sample Name : Zeolite

Data Name : E:\gc\hidayah 105.gcd
Method Name : C:\GCsolution\method\bp20\BP20-FID-alcohol-glycerol.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.197	6110.49	2882.83	0.0226		2 - propanol
2	2.870	26355575.98	11386486.71	97.5772		butanol
3	4.573	1193.49	418.81	0.0044		
4	14.704	647103.16	256289.07	2.3958		glycerol
Total		27009983.12		100.0000		
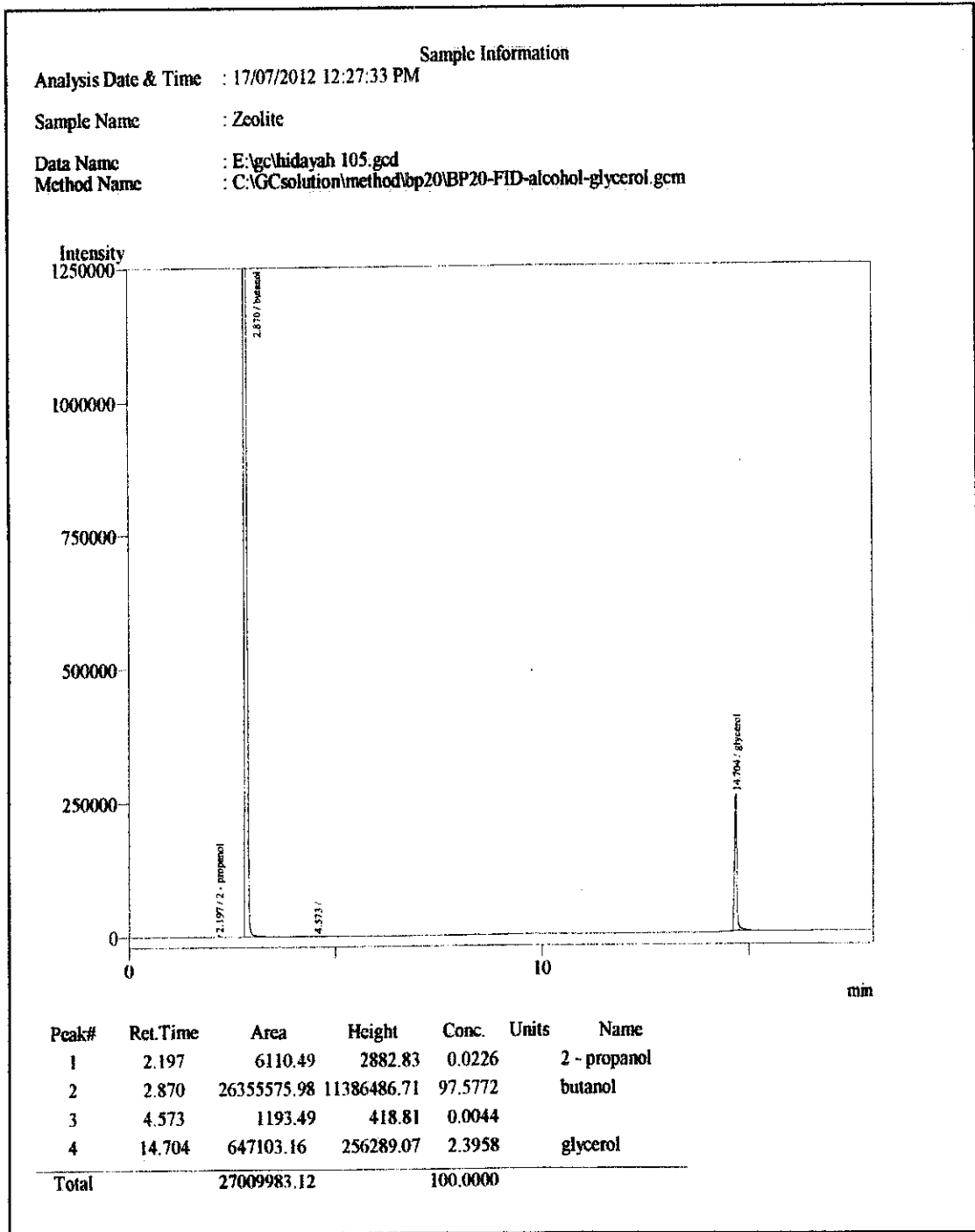
APPENDIX N: GC RESULT FOR Cu-Ag CATALYST (BATCH 1)

Sample Information

Analysis Date & Time : 23/07/2012 10:43:06 AM

Sample Name : Cu - Ag

Data Name : E:\gc\hidayah 101.gcd
Method Name : C:\GCsolution\method\bp20\BP20-FID-alcohol-glycerol.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.193	5168.78	2827.22	0.0214		2 - propanol
2	2.864	23445310.22	10426014.80	97.3573		1 - butanol
3	4.092	1250.91	533.71	0.0052		
4	4.568	1014.12	391.56	0.0042		
5	14.697	628974.43	257322.53	2.6118		glycerol
Total		24081718.46		100.0000		

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APPENDIX O: GC RESULT FOR Cu-Co CATALYST (BATCH 1)

Sample Information

Analysis Date & Time   : 17/07/2012 11:34:17 PM

Sample Name   : Cu - Co

Data Name   : E:\gc\hidayah 103.gcd
Method Name   : C:\GCsolution\method\bp20\BP20-FID-alcohol-glycerol.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.196	6495.10	2987.28	0.0238		2 - propanol
2	2.870	26557768.79	11444462.94	97.6281		1 - butanol
3	4.573	1232.89	438.40	0.0045		
4	9.975	1433.27	524.65	0.0052		
5	14.699	636053.89	233671.18	2.3382		glycerol
Total		27202983.95		100.0000		

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APPENDIX P: GC RESULT FOR Cu-Mn CATALYST (BATCH 1)

Sample Information

Analysis Date & Time : 17/07/2012 12:01:03 PM

Sample Name : Cu - Mn
Sample ID :

Data Name : C:\GCsolution\Data\2012\hidayah\hidayah 104.gcd
Method Name : C:\GCsolution\Data\2012\hidayah\curve.gcm

Intensity

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.196	5231.93	2589.43	0.01943		2 - Propanol
2	2.868	26281695.39	10711937.70	97.6541		1-Butanol
3	4.574	2727.71	910.24	0.01013		
4	6.880	1756.45	647.13	0.00652		
5	14.703	627783.49	255162.47	2.3321		Glycerol
Total		26919194.97		100.00000		

APPENDIX Q: GC RESULT FOR Cu-Ba CATALYST (BATCH 1)

Sample Information

Analysis Date & Time : 17/07/2012 11:10:01 AM

Sample Name : Cu - Ba

Data Name : E:\gc\hidayah 102.gcd
Method Name : C:\GCsolution\method\bp20\BP20-FID-alcohol-glycerol.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.194	5656.65	2935.91	0.0210		2 - propanol
2	2.872	26231059.91	11301591.53	97.6148		1 - butanol
3	4.580	1272.98	455.87	0.0047		
4	14.698	634002.84	214270.26	2.3593		glycerol
Total		26871992.38		100.0000		

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Sample Information

Analysis Date & Time : 1/08/2012 10:57:41 AM

Sample Name   : Cu - Mn

Data Name   : E:\gc\hidayah 402.gcd
Method Name   : C:\GCsolution\method\bp20\BP20-FID-alcohol-glycerol.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.195	5194.48	2649.30	0.0190		2 - propanol
2	2.870	26277965.56	11374986.96	97.7967		butanol
3	4.573	2720.99	1357.0	0.0101		
4	7.086	1987.52	925.47	0.0074		1, 2 -propanediol
5	9.312	2433.21	1128.4	0.0091		1,3-propanediol
6	14.704	579682.81	257865.18	2.1573		glycerol
Total		26869984.57		100.0000		

APPENDIX S: GC RESULT FOR Cu-Ce CATALYST (BATCH 2)

Sample Information

Analysis Date & Time : 1/08/2012 11:23:17 AM

Sample Name : Cu - Ce
Sample ID :

Data Name : C:\GCsolution\Data\2012\hidayah\hidayah 403.gcd
Method Name : C:\GCsolution\Data\2012\hidayah\curve.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.195	5523.95	2839.07	0.02110		2 - Propanol
2	2.865	25566188.18	10829972.52	97.6760		
3	4.570	1230.16	427.67	0.0047		
4	7.079	2713.11	393.02	0.0104		
5	9.314	1671.44	551.25	0.0064		
6	14.686	598671.66	213132.09	2.2872		Glycerol
Total		26174768.34		100.0000		

APPENDIX T: GC RESULT FOR Cu-Ag CATALYST (BATCH 2)

Sample Information

Analysis Date & Time   : 1/08/2012 11:31:08 AM

Sample Name   : Cu - Ag

Data Name   : E:\gc\hidayah 401.gcd
Method Name   : C:\GCsolution\method\bp20\BP20-FID-alcohol-glycerol.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.192	5107.84	2814.04	0.0214		2 - propanol
2	2.864	23046823.55	10259611.99	97.4796		butanol
3	4.092	1567.91	637.35	0.0066		
4	7.083	2646.24	650.60	0.0111		1,2-propanediol
5	9.319	2857.96	1166.8	0.0120		1,3-propanediol
6	14.685	583718.77	200385.58	2.4689		glycerol
Total		23642722.27		100.0000		

APPENDIX U: GC FOR HDROGENOLYSED GLYCEROL GAS

Sample Information

Analysis Date & Time : 11/07/2012 12:37:32 PM

Sample Name : hydrogenolysed glycerol gas
Sample ID :

Data Name : C:\GCsolution\Data\2012\hidayah\sample 03 0711.gcd
Method Name : C:\GCsolution\Data\2012\hidayah\identify.gcm

Peak#	Ret.Time	Area	Area%	Height	Height%	Name
1	1.622	4165660.93	95.3817	1438618.58	97.5799	Methane
2	1.966	8115.50	0.1858	4298.99	0.2916	Carbon Dioxide
3	5.728	80769.40	1.8494	7329.87	0.4972	
4	6.607	3040.58	0.0696	890.87	0.0604	Isobutane
5	8.244	86228.53	1.9744	17279.91	1.1721	
6	8.426	21653.90	0.4958	5248.52	0.3560	
7	9.605	1891.61	0.0433	630.63	0.0428	
Total		4367360.45	100.0000			