Hydrogenolysis of Glycerol to Produce 1,3-Propanediol

By

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Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
Chemical Engineering

May 2013

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the Chemical Engineering Program

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In partial fulfillment of the requirements for the

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Approved by,

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A.P. Dr. Anita Ramli

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2013

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 acknowledgment, and the original work contained herein have not been undertaken or done by unspecified sources or persons.

NUR DIYANA BT SAAD

ACKNOWLEDGEMENTS

My deepest gratitude and appreciation are expressed to The Almighty God for his blessing through all the way of this final year project. The greatest appreciation to supervisor, A.P. Dr. Anita bt Ramli for her precious assistance and time, brilliant comments and guidance throughout the completion of this project. Not to forget, I would like to thank Pn Hashila for the help, explanation and the assistance in completing this project. I am really grateful for their efforts and contributions in helping me to overcome the difficulties throughout the period.

Millions of credits go to my beloved parents, *Abah* and *Mak*, who always bestow me with inundated love, patience, support and encouragement throughout this final year period. Not to forget to my lovely sisters, *Along*, *Angah*, *Ayu*, *Syida*, *Ahya*, *Aimi* and *Addah*, thank you so much for always being there for me. Your utmost support and understanding is my greatest strength. May Allah shower our family with His Blessings.

Deepest gratefulness I expressed to all lab technologists in Chemical Engineering Department for assistance and help that they gave to me in completing my project.

May God bless all of you and thank you very much.

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ABSTRACT

Currently the large surplus of glycerol formed as a by-product during the production of biodiesel offered an abundant and low cost feedstock. Researchers showed a surge of interest in using glycerol as renewable feedstock to produce functional chemicals. The main objective of this project is to find the most effective reaction temperature and pressure that gives highest high selectivity and good conversions and selectivity towards the production of 1,3-propanediol. This is because the product of glycerol hydrogenolysis conventionally preferred towards ethylene glycol and 1,2-propanediol. The effects of reaction temperature and hydrogen pressure on hydrogenolysis process were studied. There are few stages involved in completing this project which are; i) development of supported bi-metallic catalyst via incipient wetness impregnation method, ii) characterized the catalyst prepared by temperature program reduction (TPR), temperature program desorption (TPD), X-ray diffraction (XRD), and Fourier Transformed Infrared (FTIR), iii) perform catalytic testing and analysis of the results obtained. Hydrogenolysis of glycerol to propylene glycol was performed without using any support or catalyst, by using zeolite catalyst support, and copper-nickel catalysts at the optimum operating temperature and pressure obtained earlier.The analysis of the product is done by using gas chromatography (GC) technique. From the results obtained (test with bare zeolite), at the higher reaction temperature and pressure, the conversion of glycerol is high. The optimum temperature and pressure chosen are 200°C and 300 psi respectively. However, there is no selectivity towards 1,3-propanediol. For the reaction with Cu-Ni catalyst, the glycerol conversion is 3.23% And the selectivity towards 1,3-propanediol is 2.05%. While there is no conversion of glycerol for the reaction without any support or catalyst.

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INTRODUCTION

1.1. Background of Study

1.1.1. Biodiesel production and availability of glycerol

As the most viable alternative fuel, biodiesel has received an attractive attention during the past few years because of the dwindling petroleum reserves and the associated environmental impacts from the usage of fossil fuels. Although biodiesel represents a secure, renewable and environmentally safe alternative to fossil fuels, its economic viability is a major concern. At the same time, the increased production of biodiesel influenced remarkably the glycerol market due to the generation of a glut of crude glycerol, the by-product of biodiesel production via transestherification, which is yielded at about 10% (wt/wt) of biodiesel during the process of biodiesel production. The glycerol price has plummeted over the last few years due to the oversupply. Therefore, it is imperative to find alternative uses for glycerol. Glycerol has many uses in different industries, such as food, paint, pharmaceutical, cosmetic, soap, toothpaste, and many more, but its surplus is dramatically increasing, so new applications should be developed.

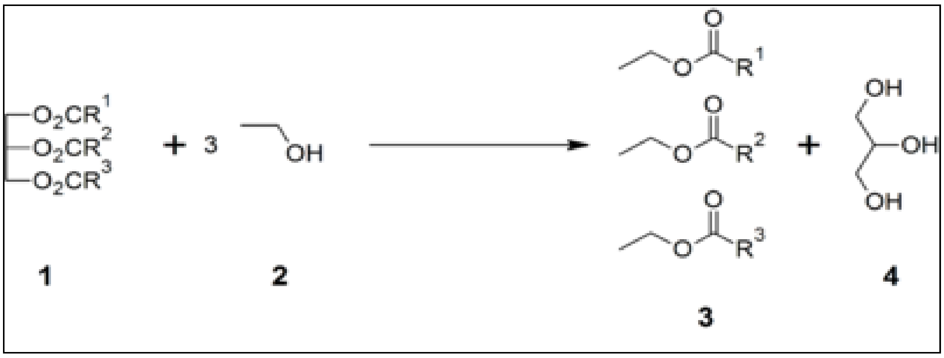

Figure 1 Byproduct of the production of biodiesel via transesterification: Triglycerides (1) are treated with an alcohol such as ethanol (2) with catalytic base to give ethyl esters of fatty acids (3) and glycerol (4)

Glycerol (or glycerine, glycerin) is a simple polyol compound. It is a colorless, odorless, viscous liquid that is widely used in pharmaceutical formulations. Glycerol has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. The glycerol backbone is central to all lipids known as triglycerides. Glycerol is sweet-tasting and of low toxicity. There are several ways to produce glycerol besides from byproduct of biodiesel production via transestherification.

Therefore, global research is focused on the effective conversion of glycerol to valuable chemicals to ameliorate the economy of the whole biodiesel production process. Recently, many studies have been dedicated to the transformation of this renewable polyol by various catalytic processes [1, 2].

1.1.2. Hydrogenolysis of glycerol to 1,3-propanediol

Hydrogenolysis is a chemical reaction whereby a carbon–carbon or carbon–heteroatom single bond is cleaved or undergoes "lysis" by hydrogen. The heteroatom may vary, but it usually is oxygen, nitrogen, or sulfur. A related reaction is hydrogenation, where hydrogen is added to the molecule, without cleaving bonds. Usually hydrogenolysis is conducted catalytically using hydrogen gas.

Direct hydrogenolysis of glycerol to 1,3-Propanediol (1,3-PDO), perfectly at mild conditions, represents a sustainable alternative with valuable potential applications.

1,3-PDO is a valuable chemical used in the synthesis of polymethylene terephthalates and in the manufacture of polyurethanes and cyclic compounds [1,2]. Polymers based on 1,3-PDO exhibit many special properties such as good light stability, biodegradability, and improved elasticity. 1,3-PDO is currently produced from petroleum derivatives such as ethylene oxide (Shell route) or acrolein (Degussa-DuPont route) by chemical catalytic routes.

1,3-propanediol is a simple organic chemical. The high cost and limited availability has restricted its commercial use. 1,3-propanediol has numerous uses. It can be formulated into composites, adhesives, laminates, powder and UV-cured coatings, mouldings, novel aliphatic polyesters, co-polyesters, solvents, 3 anti-freeze and other end uses (Shell Chemicals, 2006). One of the most successful applications has been in the formulation of corterra polymers. As the production is limited and costs are higher, glycerol has become an attractive feedstock for production of for 1,3-propanediol. Microbial fermentation is an important technology for the conversion of renewable resources to chemicals. It can be obtained by microbial fermentation of glycerol. Propanediol-based polymers exhibit better properties than those produced from 1,2-propanediol, butanediol or ethylene glycol.

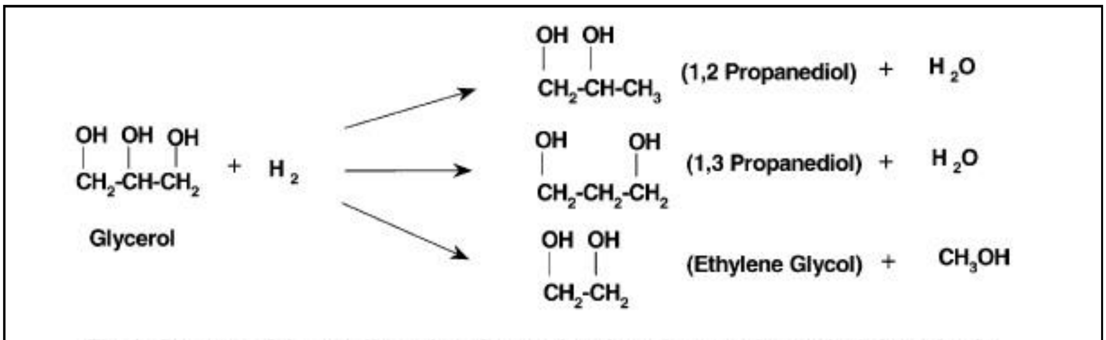

Fig. 1. Summary of the overall reaction of converting glycerol to propylene and ethylene glycols.

Figure 2 Reaction of converting glycerol to propylene and ethylene glycols (M.A. Dasari,2005)

1.2. Problem Statement

Biodiesel is a clean-burning diesel fuel produced from renewable resources (e.g. vegetable oils). Chemically, biodiesel is a mixture of methyl esters of fatty acids (FAMEs). As by product of biodiesel production via transesterification, one mole of glycerol is produced for every three moles of methyl esters, generally the reaction yields 90% methyl esters of fatty acids and 10% glycerol. As a result of the increased availability, the market price of glycerol has plummeted over the last few years due to the oversupply. Therefore, it is imperative to find alternative uses for glycerol.

Among the chemicals that can be derived from glycerol, 1,3-propanediol is a very promising target because of the high cost of conventional processes of 1,3-propanediol production and the large-scale production of polyester and polyurethane resin from 1,3-propanediol [4,5]. Therefore, the development of an efficient conversion process of glycerol into 1,3-propanediol will make the biodiesel process more profitable. However, selective hydrogenolysis of glycerol into 1,3-propanediol is not easy. Although glycerol hydrogenolysis has been heavily studied in recent years, the main products are less valuable such as 1,2-propanediol and propanols in most cases[4].

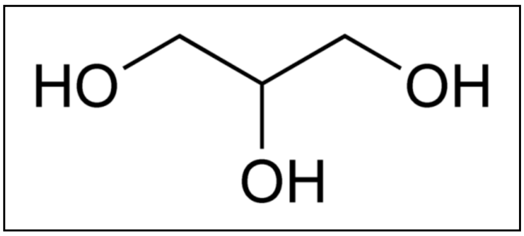

Figure 3 Glycerol structural formula

1.3. Objective and Scope of Study

The objectives of this project are:

1. To find the most effective reaction temperature and pressure that gives highest high selectivity and good conversions towards the production of 1,3-propanediol.
2. To develop bi-metallic catalyst on zeolite solid support, via wetness impregnation method.
3. To study the effect of bi-metallic catalyst on the hydrogenolysis reaction to produce 1,3-propanediol.
4. Perform catalyst characterization in order to determine the physical and chemical properties of the catalyst.

The scope of study for this project is hydrogenolysis process of glycerol to produce 1,3-propanediol. With the help of solid catalyst, the character of catalyst that is being tested will be studied and tabulated. The catalytic activity will be calculated in order to find the most suitable parameter in hydrogenolysis process of glycerol.

1.4. Relevancy and Feasibility of the Project

To achieve the objectives of this project will take time. However, the duration of the semester which is 14 weeks would definitely provide enough time to complete this project.

CHAPTER 2

LITERATURE REVIEW

Biodiesel is currently used as a valuable fuel for diesel engines. In spite of a slight power loss, exhausts contain less particulate matter. Biodiesel is becoming a key fuel in motor engines if blended in certain portions with petro diesel [6]. Biodiesel is a mixture of methyl esters of fatty acids (FAMEs) obtained by the transesterification reaction of vegetable oils with methanol in presence of a basic catalyst [7, 8]. Such a catalytic process converts raw triglycerides into FAMEs, but produces glycerol as side product. Besides, glycerol is an abundant carbon-neutral renewable resource for the production of biomaterials as well as source for a variety of chemical intermediates [1,9]. Unfortunately, biodiesel-derived glycerol is not biocompatible due to its contamination with toxic alcohol (methanol or ethanol).

Indeed, the inevitable formation of glycerol that accompanies the biodiesel production process is affecting the process economy [4,10]. Moreover, the growth of the biodiesel industry will result in overproduction of glycerol and create a superfluity of this impure product as its production is equivalent to 10% of the total biodiesel produced [11, 12].Current development of the production of biodiesel from vegetable oil leads to a dramatic increase of the availability of its co-product, glycerol. [7,8,13] In order to ensure the viability of the biodiesel activity there is the necessity not only to upgrade but also to find new large-scale uses of glycerol.

As important commodity chemicals, propanediols are widely used as functional fluids such as de-icing reagents, antifreeze/ coolants, and as precursors for the syntheses of unsaturated polyester resins and pharmaceuticals.[11**]** Propanediols are currently produced from propylene via a process involving selective propylene oxidation to propylene oxide and subsequent hydrolysis[12,13]. The process is restricted by the supply of propylene derived from crude oil, and that stimulated a search for more economical and renewable alternative feeds. Readily available glycerol has made the catalytic hydrogenolysis of glycerol to propanediols a highly viable alternative route.[15,16]

Supported noble metals and transition metal oxides have been reported as catalysts for the hydrogenolysis of glycerol. Noble metal based catalysts are usually more active than transition metal oxide catalysts, but the selectivity to propanediols is lower[13].

Synthesis of propanediols, 1,2-Propanediol (1,2-PDO) and 1,3-Propanediol (1,3-PDO), from glycerol has attracted significant interest [13–18]. 1,2-PDO is an important commodity chemical, which finds use as antifreeze, aircraft deicer and lubricant. 1,3-PDO is copolymerised with terephthalic acid to produce polyesters, which are used for manufacturing carpet and textile fibres exhibiting strong chemical and light resistance [13]. 1,2-PDO and 1,3-PDO are currently produced from petroleum derivatives by chemical catalytic routes: 1,2-PDO from propylene oxide and 1,3-PDO from ethylene oxide or acrolein [19]. These diols can be produced by an alternative route involving hydrogenolysis of glycerol.

Propylene glycol is a three-carbon diol with a steriogenic center at the central carbon atom. Propylene glycol is a major commodity chemical with an annual production of over 1 billion pounds in the United States [15] and sells for about \$0.71 [16] per pound with a 4% growth in the market size annually. The commercial route to produce propylene glycol is by the hydration of propylene oxide derived from propylene by either the chlorohydrin process or the hydroperoxide process [17,18]. There are several routes to propylene glycol from renewable feedstock. The most common route of production is through hydrogenolysis of sugars or sugar alcohols at high temperatures and pressures in the presence of a metal catalyst producing propylene glycol and other lower polyols [19–24]. Some typical uses of propylene glycol are in unsaturated polyester resins, functional fluids (antifreeze, deicing, and heat transfer), pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants, flavors and fragrances, personal care, paints and animal feed. The antifreeze and deicing market is growing because of concern over the toxicity of ethylene glycol-based products to humans and animals as well.

1,3-PDO is an important chemical intermediate used mostly in the manufacture of polytrimethylene terephthalate (PTT) [21]. Based on petrochemicals, the industrial production of 1,3-PD begins with hydroformylation of ethylene oxide (Shell route) or hydration of acrolein (Degussa–DuPont route)[22]. With the decrease of petroleum resource, it is increasingly more imperative to develop an alternative route for the sustainable production of 1,3-PDO.

A number of patents and papers have disclosed the hydrogenolysis of glycerol in the presence of homogeneous and heterogeneous catalysts [13–18]. In the presence of metallic catalysts and hydrogen, glycerol can be hydrogenated to propylene glycol, 1,3-Propanediol, or ethylene glycol. Several publications and patents document multiple schemes for hydrogenating glycerol to propylene glycol. Casale and Gomez [10,11] described a method of hydrogenating glycerol using copper and zinc catalyst as well as sulfided ruthenium catalyst at a pressure of 2175 psi and temperature in the range of 240–270 °C. Ludvig and Manfred [12] described a method for the production of propanediols using a catalyst containing cobalt, copper, manganese, molybdenum, and an inorganic polyacid achieving a 95% yield of propylene glycol at pressures of 3625 psi and a temperature of 250 °C. Tessie [13] describes a method of production of propanediols over homogeneous catalyst containing tungsten and Group VIII transition metals at a pressure of 4600 psi and a temperature of 200 °C. Haas et al. [14] described a process of simultaneous production of propylene glycol and 1,3-Propanediol from gaseous glycerol solutions at a temperature of 300 °C using two stages. Cameron et al. proposed a biocatalytic fermentation technique for production of propanediol from glycerol and sugars [15,16].

CHAPTER 3

METHODOLOGY

3.1. Materials

Anhydrous glycerol (purity 99.99%), copper compound (Cu (NO3)2. 3H2O), nickel compound (Ni(NO3)2·3H2O), hydrogen, zeolite (CBV2134), Magnesium Sulfate ($MgSO_4$) need to be purchased to conduct this experiment. Some of these chemicals were used with further treatment.

3.2. Equipment and Tools

The equipment that will be used is the high pressure reactor, and some laboratory apparatus (500 ml of beaker, conical flask, 250 mL of measuring cylinder, 50 ml of volumetric flask and etc.). The equipment and apparatus needed is available in the laboratory.

3.3. Supported Metal Catalyst Preparation

There are several metals that are capable of performing hydrogenolysis; however, there is a not a clear consensus of the active species and reaction mechanisms involved. One of the generally accepted criteria for a catalyst is the ability to activate (i.e. dissociate) hydrogen for the reaction. Most metals that can perform this dissociation are also considered hydrogenation catalysts including: Pt, Pd, Rh, Ru, Ni, Fe, and Cu. Of these metals, copper has been shown to preferentially perform C-O hydrogenolysis over C-C hydrogenolysis and also minimize aromatic hydrogenation [13, 18-44]. The performance of supported copper catalyst can vary depending on the nature of the support and processing conditions [35-36].

Impregnation as a means of supported catalyst preparation is achieved by filling the pores of a support with a solution of the metal salt from which the solvent is subsequently evaporated. The catalyst is prepared either by spraying the support with a solution of the metal compound or by adding the support material to a solution of a suitable metal salt, such that the required weight of the active component is incorporated into the support without the use of excess of solution. This is then followed by drying and subsequent decomposition of the salt at an elevated temperature, either by thermal decomposition or reduction. With this method of preparation it is essential to have an understanding of both chemical and physical properties of the support and the chemistry of the impregnating solution in order to control the physical properties of the finished catalyst. When used for the preparation of mixed metal catalysts, care has to be taken to confirm that a component in an impregnating solution of metal salts is not selectively adsorbed, resulting in an unexpectedly different and undesirable concentration of metals in a mixed-metal catalyst.

1) Catalyst Preparation Procedure

In preparing the catalyst to be used in this project, the catalyst support which is Zeolite Socony Mobil-5 (ZSM-5) is chosen. The catalyst support was weighed by using electronic weighing balance. The fine powder form of zeolite was then transferred into a clay crucible to be calcined in the chamber furnace. It was calcined at the temperature of 500 °C for 8 hours. After 8 hours of calcination, the zeolite is let to be cooled to room temperature before being transferred into an air tight container.

For the preparation of bi-metallic catalyst, the catalyst support is mixed with two different aqueous solutions containing the components to be deposited on the surface. In this project, Copper has been chosen as the first metal of the catalyst and

Nickel as the second. The Cu-Ni catalyst was synthesized using an incipient wetness impregnation method between aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 3H_2O$. 10 wt% of metal loading on the catalyst support is chosen in preparing the catalyst which is 5 wt% for each metal.

The required mass of Copper, Nickel and catalyst support (zeolite) is weighed. Then, the copper and nickel compound is transferred into a small beaker (50ml) and dilute the metal with distilled water up until 50 ml. The three components were mixed in one beaker and stirred continuously using magnetic stirring bar for 4 hours. After impregnation, the catalyst was dried at 100 °C for 16 hours. After being cooled down to room temperature, the catalyst was grounded into fine powder. After that, the catalyst was put into a sample boat to be calcined in tube furnace for 6 hours at 500 °C with the flow of nitrogen. The final appearance of this catalyst is in powder form.

3.4. Catalyst characterization

There are a few methods that will be used in finding the surface characterization of the catalyst.

i) X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analysed material will be finely grounded, homogenized, and average bulk composition is determined. X-ray powder diffraction is most widely used for the identification of unknown crystalline materials.

ii) Temperature Programmed Reduction (TPR) is a technique for the characterization of solid materials and is often used in the field of heterogeneous catalysis to find the most efficient reduction conditions, an oxidized catalyst precursor is submitted to a programmed temperature rise while a reducing gas mixture is flowed over it.

iii) Temperature Programmed Desorption (TPD) is the method of observing desorbed molecules from a surface when the surface temperature is increased. When molecules or atoms come in contact with a surface, they adsorb onto it, minimizing their energy by forming a chemical bond with the surface. The binding energy varies with the combination of the adsorbate and surface. If the surface is heated, at one point, the energy transferred to the adsorbed species will cause it to desorb. The temperature at which this happens is known as the desorption temperature. Thus TPD shows information on the binding energy.

iv) Brunauer–Emmett–Teller (BET) is a method to 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 of a material.

v) Field Emission Scanning Electron Microscope (FESEM) is a scanning electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. FESEM can achieve resolution better than 1 nanometre. Specimens can be observed in high vacuum, in low vacuum, and in wet conditions.

vi) Fourier Transform Infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

3.5. Catalytic test

The hydrogenolysis of glycerol was carried out in a high pressure reactor (PARR) system with capacity of 1.8 L with mechanical stirring. An aqueous solution of glycerol (50 wt% concentration) prepared with pure glycerol (>99.9%) and distilled water was used as feed. In a typical run, 250 ml of the glycerol solution and a specified quantity of the catalyst were loaded into the reactor. The molar ratio of the active metal(s) on the catalyst to the glycerol (M:G) was 5 : 100 (5wt% of the glycerol used). With stirring at 200 RPM, the mixture of the glycerol and the catalyst was heated to 200 °C and maintained for 6 hours. The reactor was pressurized with H_2 to 200 psi when the temperatures reach desired temperature (200°C) at an interval of every 30 minutes for 6 hours. The stirring speed was selected to eliminate the influence of external mass transfer and to avoid creating splash inside the reactor which would make sampling and temperature control very difficult. Hydrogen was fed on demand so as to keep the total reaction pressure at 200 psi during the 6 hours period. After the reaction, the system was cooled to room temperature. Depressurized the gas left in the reactor system to a safe tube. For the liquid phase product, it was collected a put into an air-tight glass container.

Later, it will be separated from the catalyst by vacuum filtration. This product will be analysed by using a gas chromatograph (GC). The specification of GC that will be used is:

Table 1 Specification of GC to be used

Model	GC Shimadzu 2010
Column Type	SGE BP-20
Column Size	30mm×0.25mm×0.25µm
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

Standard solution of glycerol, 1,2-propanediol and 1,3-propanediol will be prepared and used for quantification of various glycerol-derived compounds in the products. Before all samples were tested in GC, the water contains in the samples were removed by adding Magnesium Sulphate ($MgSO_4$) into the samples. The mixture is stirred for 1 hour then filtered by filter paper.

The conversion of glycerol and the selectivity of propanediols were used to evaluate the performance of each catalyst. They were defined by the following equations. The amount of glycerol converted was calculated from the total amount of carbon based species formed in the product.

$$\text{Conversion \%} = \frac{moles\ of\ glycerol\ (in) - moles\ of\ glycerol\ (out)}{moles\ of\ glycerol\ (in)} \times 100\%$$

$$\text{Selectivity \%} = \frac{moles\ of\ product\ formed}{moles\ of\ glycerol\ consumed} \times 100\%$$

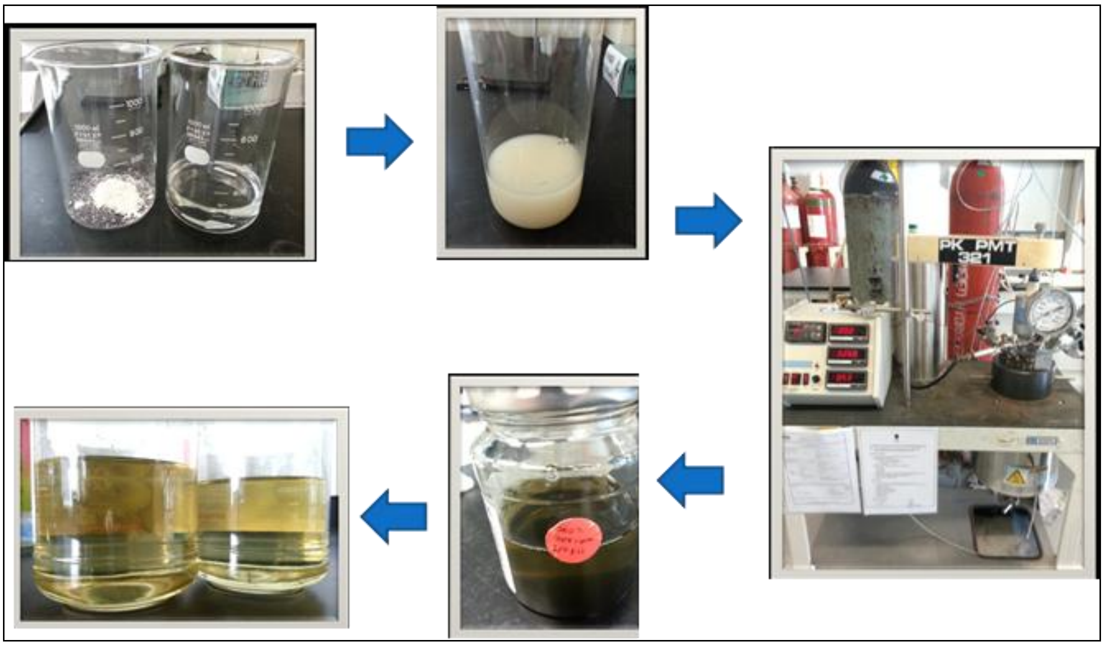

Figure 4 Step of catalytic test

CHAPTER 4

RESULT AND DISCUSSION

4.1. Catalyst Characterisation

1) X-ray diffraction (XRD)

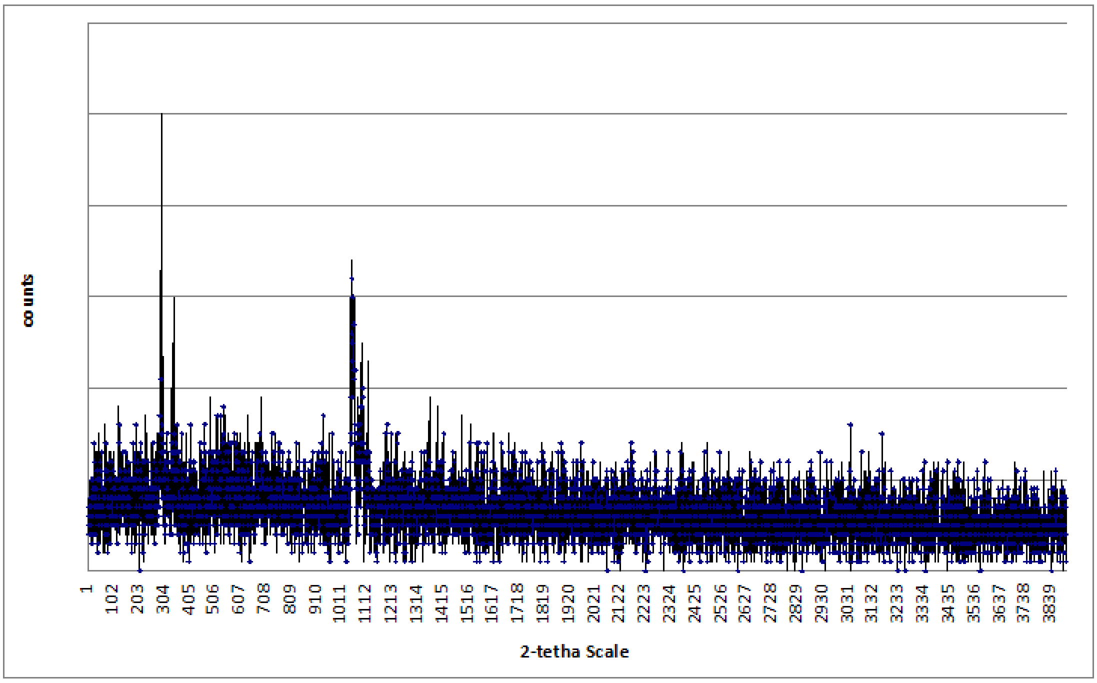

Figure 4 XRD pattern for Cu-Ni catalyst

For the prepared bi-metallic catalyst and bare zeolite, the X-ray diffraction (XRD) pattern observed with 2θ scale. For bare zeolite (black line), the peaks at 2θ = 303°, 345° and 1058° appeared in the graph. For Cu-Ni catalyst(blue line), the peaks at 2θ = 303°and 1058° appeared in the graph. As were mentioned before, the zeolite used in this project is zeolite (CBV 2134) with SiO_2/Al_2O_3 mole ratio of 23. Therefore, the pattern that is similar to SiO_2 was identified in the XRD pattern for bare zeolite. The pattern also was identified in the Cu-Ni catalyst XRD pattern as the catalyst support. Due to low metal loading of the metal impregnated on the support, the pattern cannot be clearly observed and identified. It may also due to crystalline structure of the metal itself.

2) Fourier Transform Infrared spectroscopy (FTIR)

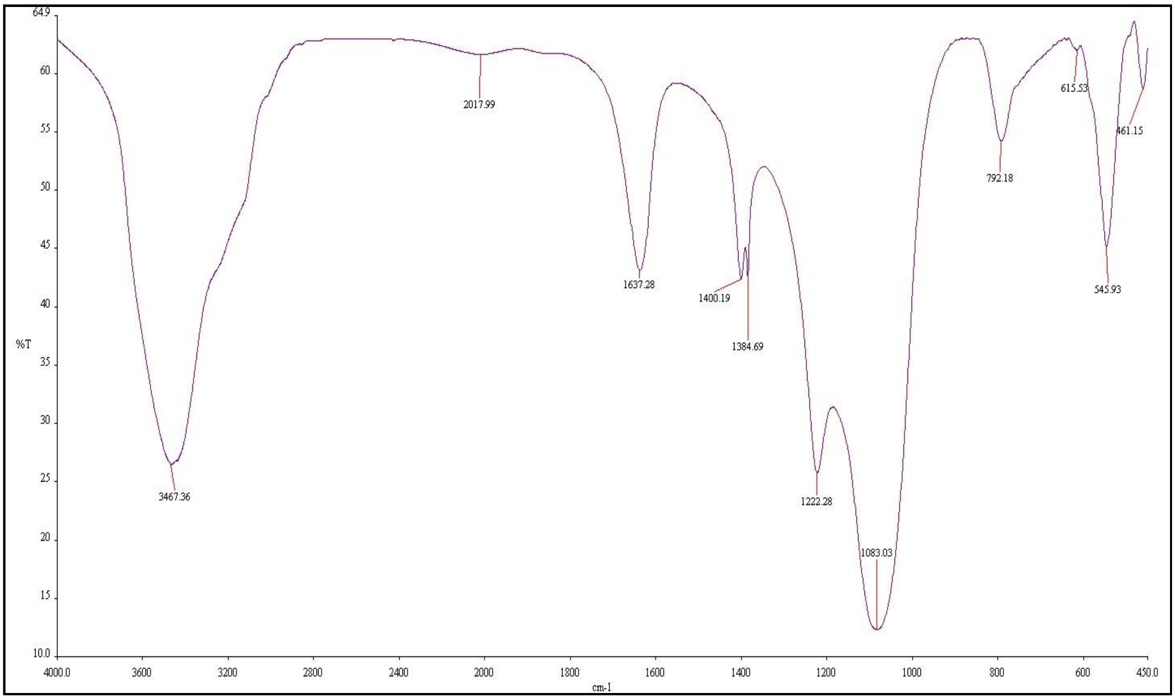

Figure 5 FTIR pattern for bare zeolite before calcination

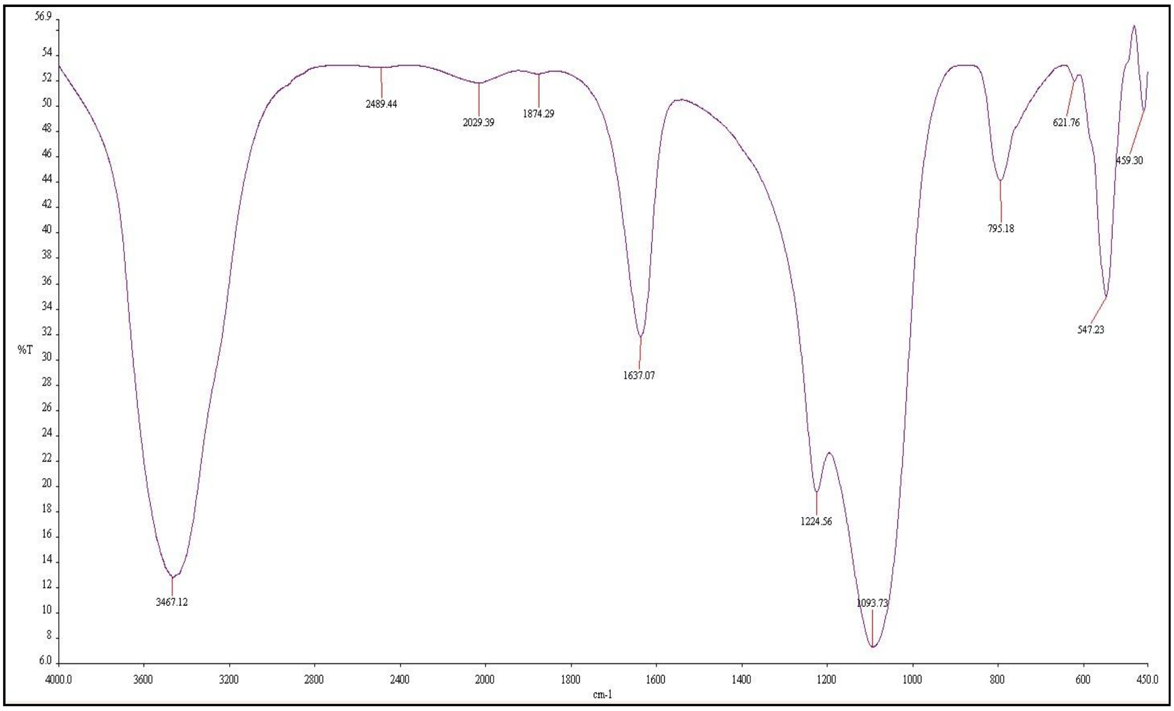

Figure 6 FTIR pattern for bare zeolite after calcination

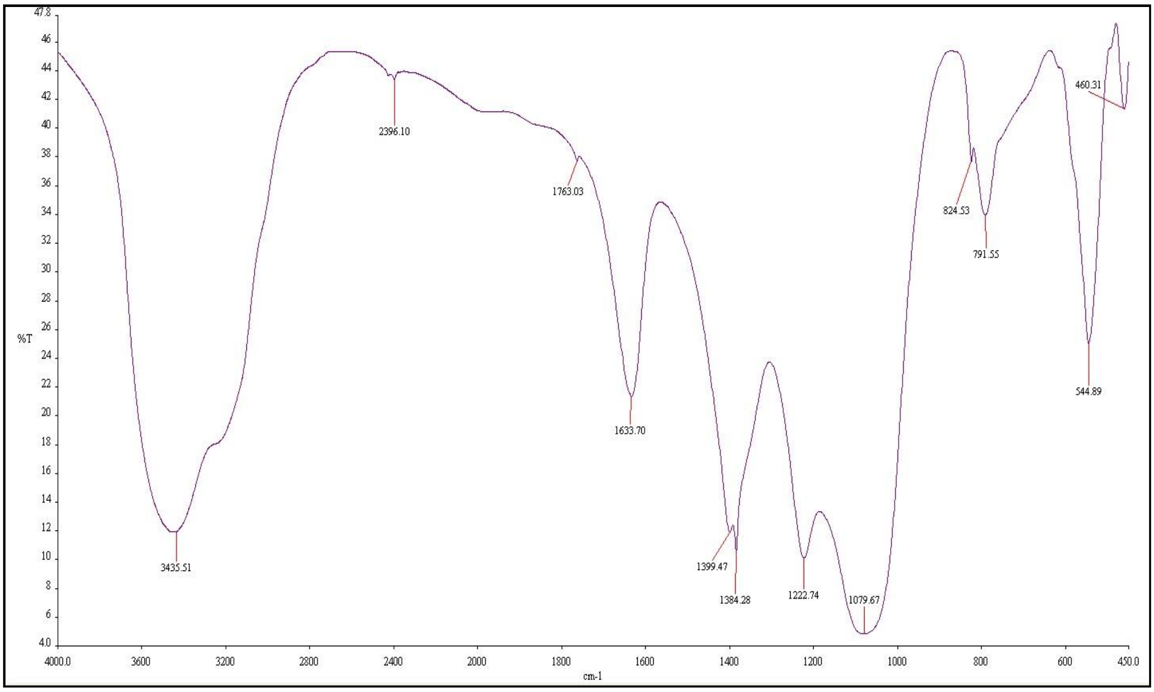

Figure 7 FTIR pattern for Cu-Ni catalyst before calcination

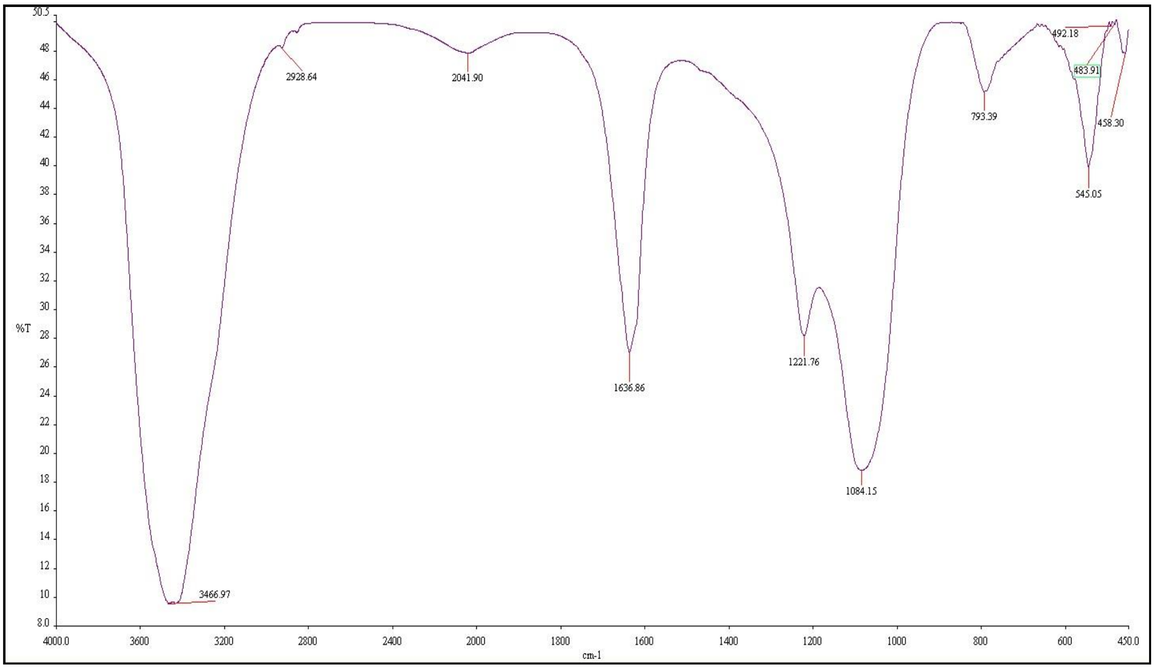

Figure 8 FTIR pattern for Cu-Ni catalyst after calcination

Based on the FTIR results obtained, the pattern appeared are to be almost familiar for both before and after calcination process due to low percentage of metal loading. FTIR is meant to detect the functional group of organic compound only. As from the Figure 6 and 7, the most significant different is at wavenumber 1400.19 and 1384.69 cm^{-1} that indicates the nitro stretch (N-O) functional group, with transmittance percentage of 42. From Figure 8 and 9, the most significant different is at wavenumber 1399.47 and 1384.28 cm^{-1} that indicates the nitro stretch (N-O) functional group, with transmittance percentage of 11. After calcination, where the catalyst and bare zeolite are treated with a high temperature, the nitro stretch is no longer available. Therefore, calcination process manages to remove the volatile constituents of the sample.

3) Temperature Programmed Desorption (TPD)

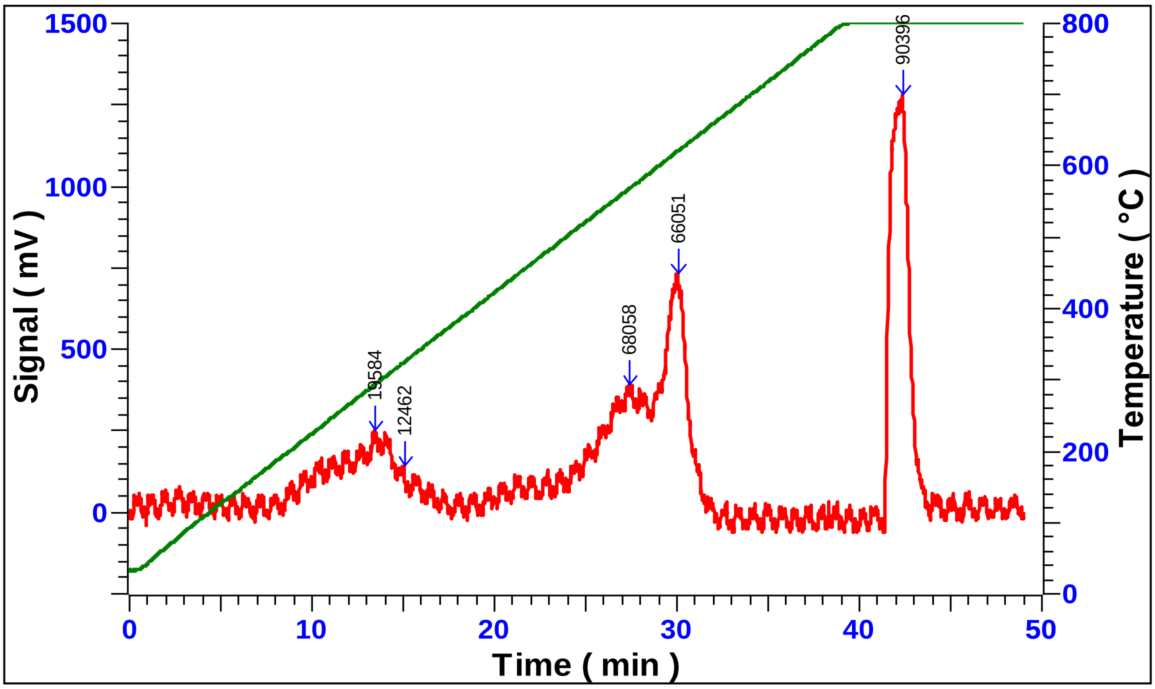

Figure 10 TPD pattern for Cu-Ni catalyst after calcination

Figure 10 shows the amount of desorbed species as a function of temperature. From this graph we can see the character of bind in adsorbate/substrate system which is carbon monoxide adsorbed into bi-metallic catalyst prepared. The highest peak is at 700°C.

4) Temperature Programmed Reduction (TPR)

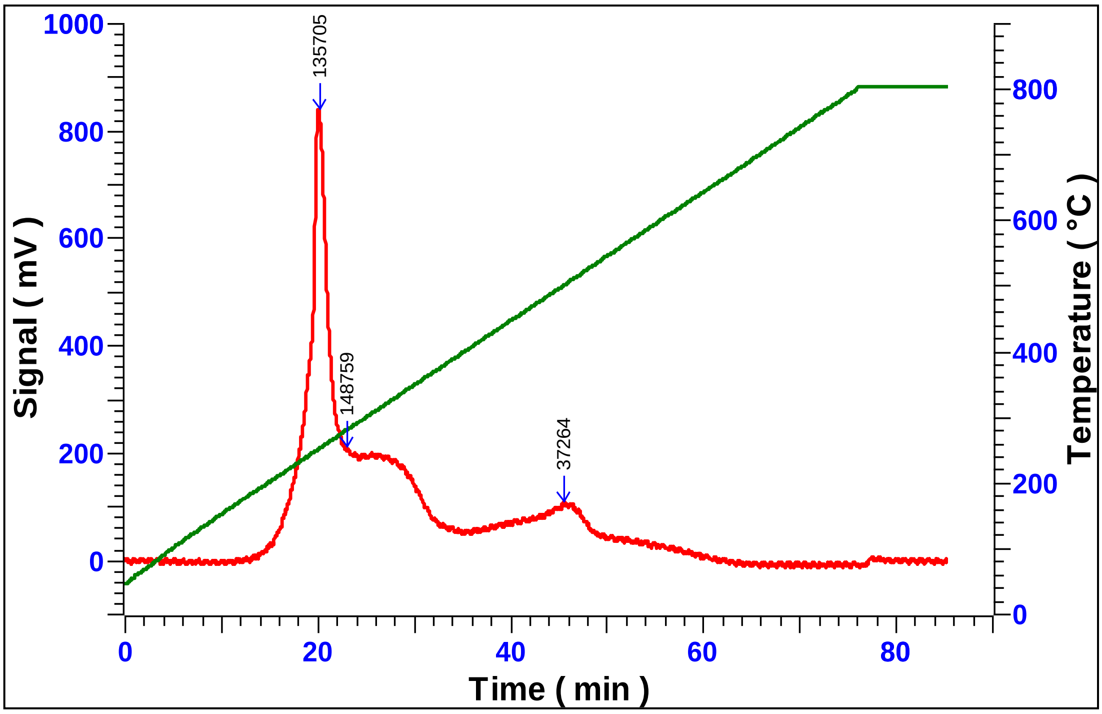

Figure 11 TPR pattern for Cu-Ni catalyst after calcination

TPR profile of the prepared catalyst (Cu-Ni) was observed. Figure 11 shows the TPR profile for bi-metallic catalyst prepared. Red-colored line indicates thermal conductivity detector (TCD) signal output as a function of time, while green-colored line indicates the temperature as a function of time of heating rate from 0°C up to 1000°C. The peak maximum (T_{max}) indicates the temperature that corresponds to the maximum rate of reduction.The area under the peak is equivalent to amount of hydrogen consumed in the reaction. Higher hydrogen consumption for the reduction of metal oxide result in better dispersion of metal species on the support. The T_R of the Cu-Ni catalyst prepared is 800°C.

5) Field Emission Scanning Electron Microscope (FESEM), and Brunauer–Emmett–Teller (BET)

For FESEM and BET, due to time constraints, the results cannot be obtained and included in this report and project. However, for BET, it is believed that the surface area of the catalyst would be lesser than bare zeolite support (425 m^2/g) due to the impregnation of metal particles on the support's surface.

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 retention times for the expected products are listed in Table below.

Table 2 Retention time for the expected products

Retention Time (min)	Component
2.290	2-Propanol
2.581	1-Butanol
7.092	1,2-Propanediol
7.529	1,3-Propanediol
9.333	Ethylene Glycol
14.715	Glycerol

The results obtained for each sample were compared with the retention times of the standard solutions. The standard solutions of the expected products were prepared at different concentrations of 5000 ppm, 7000 ppm, 10000 ppm.

4.3. Parametric studies

The effects of reaction temperature and hydrogen pressure by using solid support (zeolite) were determined in this project. After getting the optimum pressure and temperature, the experiment were run by using copper-nickel catalyst and also without any catalyst. This is to study the effect of the usage of catalyst, support only and .without any catalyst or support on the reaction of hydrogenolysis of glycerol to produce 1,3-propanediol.

1) Effect of Reaction Temperature

Temperature has a significant effect on the overall yield of the propylene glycol. Reactions were carried out at 180, 200, 230, and 250 °C and at a pressure of 200 psi of hydrogen in the presence of a catalyst support (zeolite). The selection of the reaction pressure (200 psi) is according to the literature. Table 3 shows the effect of temperature on the conversion, yield, and selectivity of the reaction.

Table 3 Effect of reaction temperature on formation of propylene glycol from glycerol

Temperature (°C)	% Conversion	% Selectivity
180	0.39	0
200	0.57	0
230	0.63	0
250	0.65	0

All the reactions were performed using 50% glycerol solution at 200 psi hydrogen pressure for 6 hours.

2) Effect of Reaction Pressure

Pressure has a significant effect on the overall yield of the propylene glycol. Reactions were carried out at 150, 200, 250 and 300 psi and at a temperature of 200 °C of hydrogen in the presence of a catalyst support (zeolite). The selection of the reaction temperature (200 °C) is according to the literature. Table 4 shows the effect of pressure on conversion, yield, and selectivity of the reaction.

Table 4 Effect of reaction pressure on formation of propylene glycol from glycerol

Pressure (psi)	% Conversion	% Selectivity
150	0.25	0
200	0.57	0
250	0.72	0
300	0.84	0

All the reactions were performed using 50% glycerol solution at 200 °C hydrogen pressure for 6 hours.

The results obtained are not really significant because the bare zeolite support were used. The overall conversions are much lower compared to the literatures that are related to this project. This is because the operating conditions used for this project are different. The glycerol was not converted to the desired product, which is 1,3-propanediol. After getting the most effective reaction temperature and pressure that gives highest selectivity and conversion, the test were run by using Cu-Ni catalyst and without using any support or catalyst. Based on the results obtained, the optimum temperature is 200 °C and the pressure is 300 psi.

Table 5 Effect of Cu-Ni catalyst on formation of propylene glycol from glycerol

Temperature (°C)	Pressure (psi)	% Conversion	% Selectivity
200	**300**	3.23	2.05

The reaction was performed using 50% glycerol solution for 6 hours.

Based on the result obtained, the reaction with catalyst gives the conversion and selectivity towards 1,3-Propanediol of 3.23 % and 2.1 % respectively.

Table 6 Formation of propylene glycol from glycerol without any support or catalyst

Temperature (°C)	Pressure (psi)	% Conversion	% Selectivity
200	**300**	0	0

The reaction was performed using 50% glycerol solution for 6 hours.

CHAPTER 5

CONCLUSION

The main purpose of this project is to find the most effective reaction temperature and pressure that gives highest high selectivity and good conversions towards the production of 1,3-Propanediol. With the selected temperature and pressure, the tests were run by using the Cu-Ni catalyst and also without any support or catalyst. 1,3-Propanediol emerges as an important chemical, since 1,3-PD is a valuable chemical used in the synthesis of polymethylene terephthalates and in the manufacture of polyurethanes and cyclic compounds [1,2]. Polymers based on 1,3-Propanediol exhibit many special properties such as good light stability, biodegradability, and improved elasticity. 1,3- Propanediol is currently produced from petroleum derivatives.

By performing the catalyst characterization in order to determine the physical and chemical properties of the catalyst, it will give useful information regarding the reduction temperature of the catalyst used, strength of metal bonding on the catalyst support, crystalline structure and morphology of the catalyst. The average particle size and intra particle distribution also can be obtained.

From the support (zeolite) testing conducted, the optimum temperature and pressure are 200°C and 300 psi. No selectivity towards 1, 3-propanediol is obtained. For the experiment with Cu-Ni catalyst, the glycerol conversion achieved is 3.23% with selectivity of 2.05%. The experiment without any support or catalyst does not have any conversion and selectivity.

In conclusion, it is believed that the increases in temperature and pressure will increase the conversion of glycerol. Further studies and researches need to be done by considering various factors

CHAPTER 6

RECOMMENDATION

Based on the experiments conducted, some modification and improvement could be done in order to enhance the results of this study in the future. The modifications are listed as the following:

1) The initial water content should be lower. This is because according to literature, as the initial water contents increases, the glycerol conversion decreased. Moreover, for glycerol solution with concentration >80% a decrease in selectivity was observed due to the degradation of reaction product due to polymerization. Hence, it is essential need to to have at least 10–20% of solvent (water, methanol) to minimize the degradation.be increased.

2) The contact time between zeolite solid support ant the metal solution should be made longer in order to allow more metal to get into the pores of the support.

3) The weight percent of metal loading should be increase. As the concentration of the catalyst increases, more surface area is available for the hydrogenolysis reaction to take place. The initial rates of conversion of glycerol and formation of propylene glycol have a proportional increase with the catalyst amount.

4) Longer reaction time can be applied in the future testing. To get a good conversion of glycerol with high selectivity to propylene glycol an optimal amount of catalyst should be used depending on the reaction time. As reported from the literature, the reaction needs to be carried out for 24 hours.

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GANTT CHART/STUDY PLAN

Project activities	Week No./Date													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of project title	🟨	🟨												
Prelim Research Work		🟧	🟧	🟧	🟧									
Submission of Extended Proposal						○								
Proposal Defence								🟩	🟩					
Project Work Continues										🟦	🟦	🟦		
Submission of Interim Draft Report													○	
Submission of Interim Report														○

Work Progress: 🟨🟧🟩🟦

Suggested Milestones: ○

GANTT CHART/STUDY PLAN

Project activities	**Week No./Date**														
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**15**	**30th September**
Project Work Continues	🟨	🟨	🟨	🟨	🟨	🟨	🟨								
Submission of Progress Report							○								
Project Work Continues								🟨	🟨	🟨	🟨	🟨			
Pre-SEDEX										○					
Submission of Draft Report											○				
Submission of Dissertation (soft bound)													○		
Submission of Technical Paper													○		
Oral presentation														○	
Submission of Project Dissertation (hard bound)															○

Work Progress: 🟨

Suggested Milestones: ○

APPENDIX C: SAMPLE CALCULATION FOR CATALYST PREPARATION

Copper- nickel catalyst

5 weight percent (5 wt%) of each metal loading is considered for this catalyst preparation. Total of 10% metal loading.

Catalyst – 50 grams :- 45 grams of zeolite, 5 grams of metals

5grams of metal= 2.5 grams of Cu, 2.5 grams of Ni

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 grams of Cu:

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

For Ni:

Molecular weight of $Ni(NO_3)_2 \cdot 3H_2O$ = 182.7 g/mol

Molecular weight of Ni= 58.69 g/mol

In order to have 2.5 grams of Ni:

$\frac{182.7 g/mol}{58.69 g/mol} \times 2.5 gNi$ = 7.9 g $Ni(NO_3)_2 \cdot 3H_2O$ is needed.

APPENDIX D: PREPARATION OF THE REACTION SOLUTION

The solution of two components which are

i. Distilled water (mass fraction of water, xa=0.5)
ii. Glycerol (mass fraction of glycerol, xa=0.5)

For the preparation of solution, let x_a=125 mL=125g

Therefore mass of glycerol:

$$\frac{125 g water}{0.5 water} \times 0.5 glycerol = 125 \text{ g}$$

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

Converting mass of glycerol to volume:

$$\frac{0.125 kg glycerol}{1257 kg/m^3} = 9.94\times10^{-5} \text{ m}^3$$

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

$$= 9.94\times10^{-5} \text{ m}^3 \text{ x } \frac{1000L}{1m^3}$$

= 0.9944 L glycerol = 99.4 mL glycerol

Total volume of solution:

250 mL= Volume of water + volume of glycerol

Volume of water=250 mL-99.4 mL

=150.6 mL

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

Amount of catalyst required:

$$\frac{5.0}{100} \times 99.4g$$

= 4.97g

APPENDIX E: SAMPLE CALCULATION FOR GLYCEROL CONVERSION

Concentration of glycerol in ppm at 50 wt % = 44075.29ppm

Equation from glycerol standard calibration curve: y= 29.042x- 105534.48

Where y = peak area

x= concentration in ppm

Let glycerol concentration in ppm for 150 °C = 44073.13 ppm

$$\text{Conversion \%} = \frac{moles\ of\ glycerol\ (in) - moles\ of\ glycerol\ (out)}{moles\ of\ glycerol\ (in)} \times 100\%$$

$$= \frac{(44075.29\text{-}43963.13)}{44075.29} \times 100$$

$$= 0.254\ \%$$

APPENDIX F: SAMPLE CALCULATION FOR 1, 3-PROPANEDIOL SELECTIVITY

Concentration of 1,3-propanediol in ppm = 29.18 ppm

Equation from 1,3-propanediol standard calibration curve: $y= 14.129x+89857.29$

Where y = peak area

x= concentration in ppm

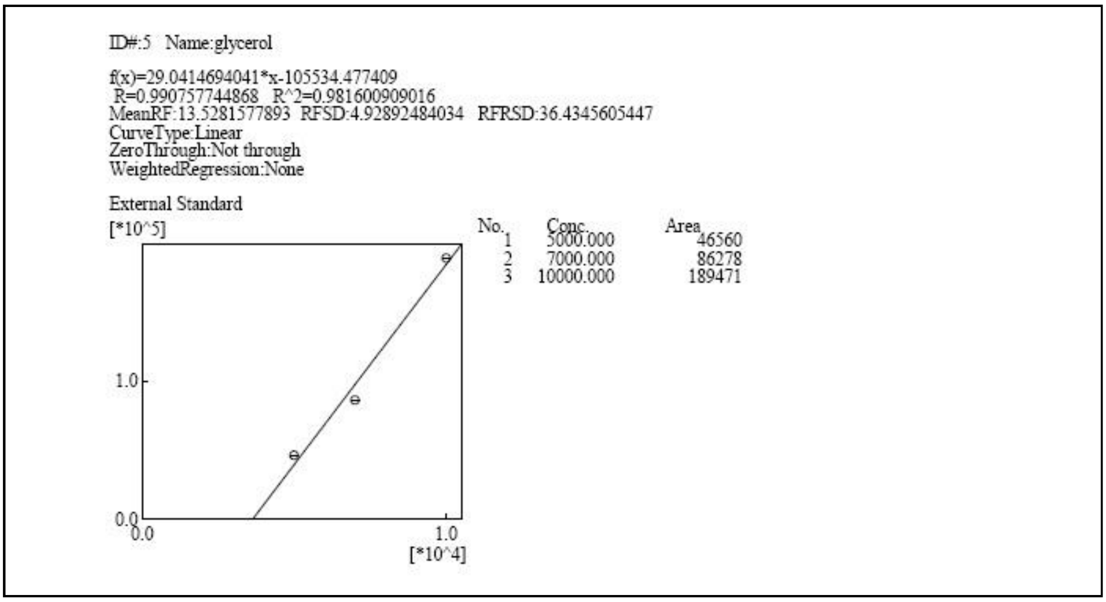
Initial concentration of glycerol concentration in ppm = 44075.29 ppm

$$\text{Selectivity \%} = \frac{moles\ of\ product\ formed}{moles\ of\ glycerol\ consumed} \times 100\%$$

$$= \frac{28.18}{(44075.29-42651.66)} \times 100$$

$$= 2.01\ \%$$

APPENDIX G: STANDARD CALIBRATION CURVE FOR GLYCEROL

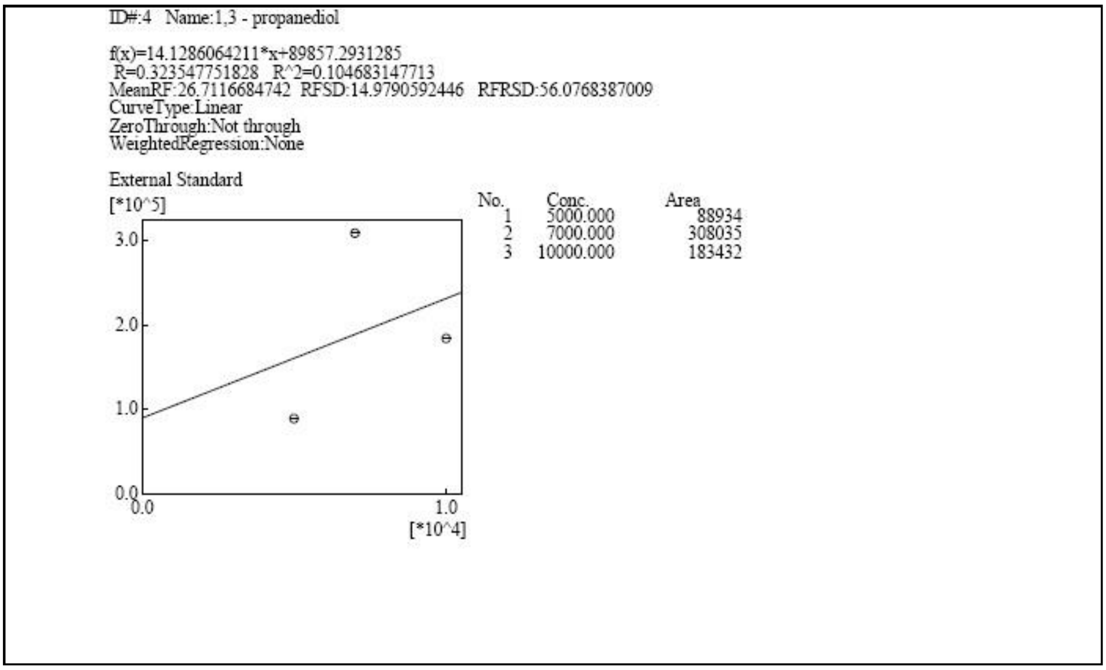


```
ID#:5   Name:glycerol

f(x)=29.0414694041*x-105534.477409
 R=0.990757744868   R^2=0.981600909016
MeanRF:13.5281577893  RFSD:4.92892484034   RFRSD:36.4345605447
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard
                                     No.     Conc.            Area
                                       1      5000.000        46560
                                       2      7000.000        86278
                                       3     10000.000       189471
```

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

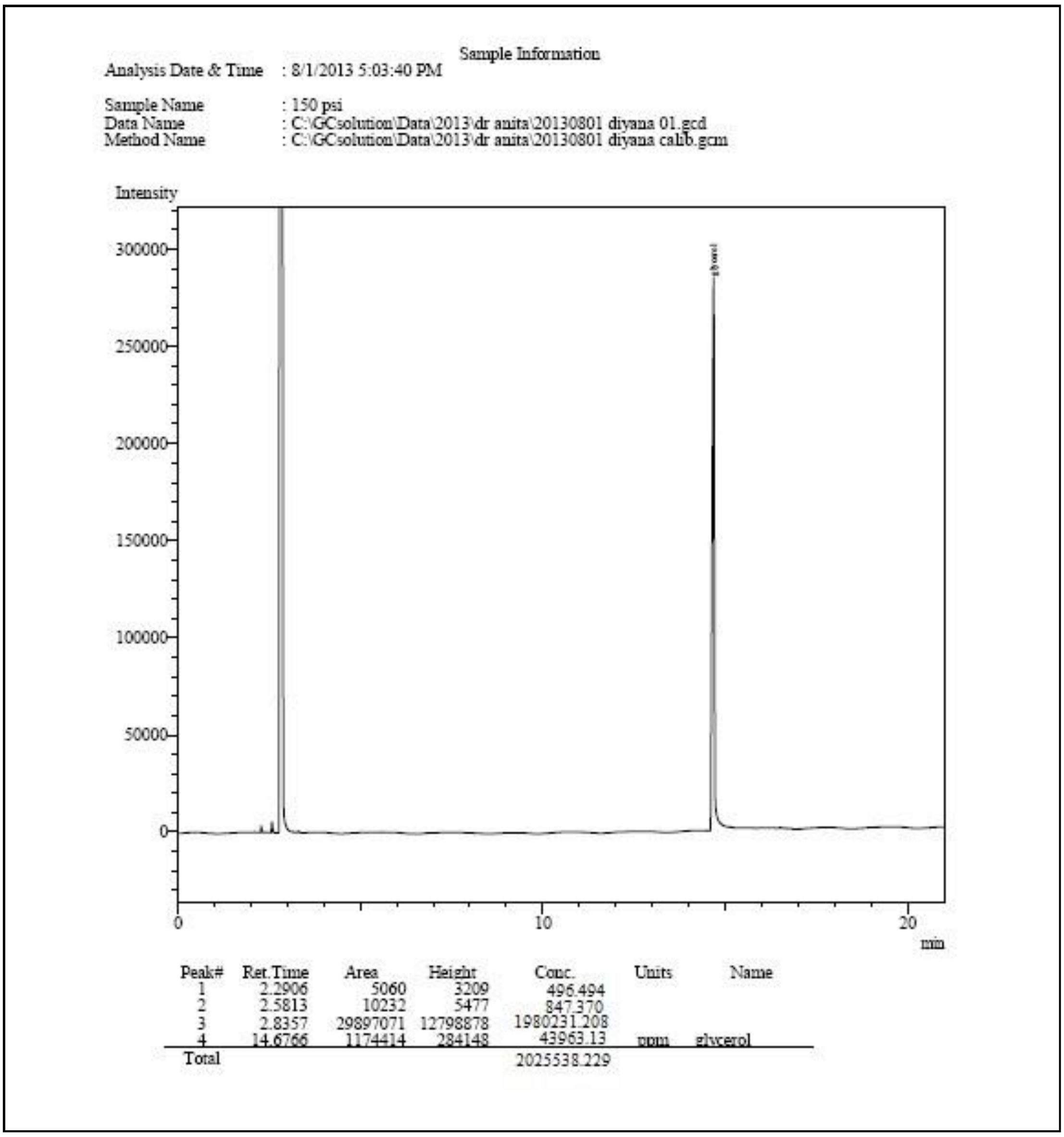


```
ID#:4   Name:1,3 - propanediol

f(x)=14.1286064211*x+89857.2931285
 R=0.323547751828   R^2=0.104683147713
MeanRF:26.7116684742  RFSD:14.9790592446   RFRSD:56.0768387009
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard
                                     No.     Conc.            Area
                                       1      5000.000        88934
                                       2      7000.000       308035
                                       3     10000.000       183432
```

APPENDIX I: RESULT FOR 150 PSI



Sample Information

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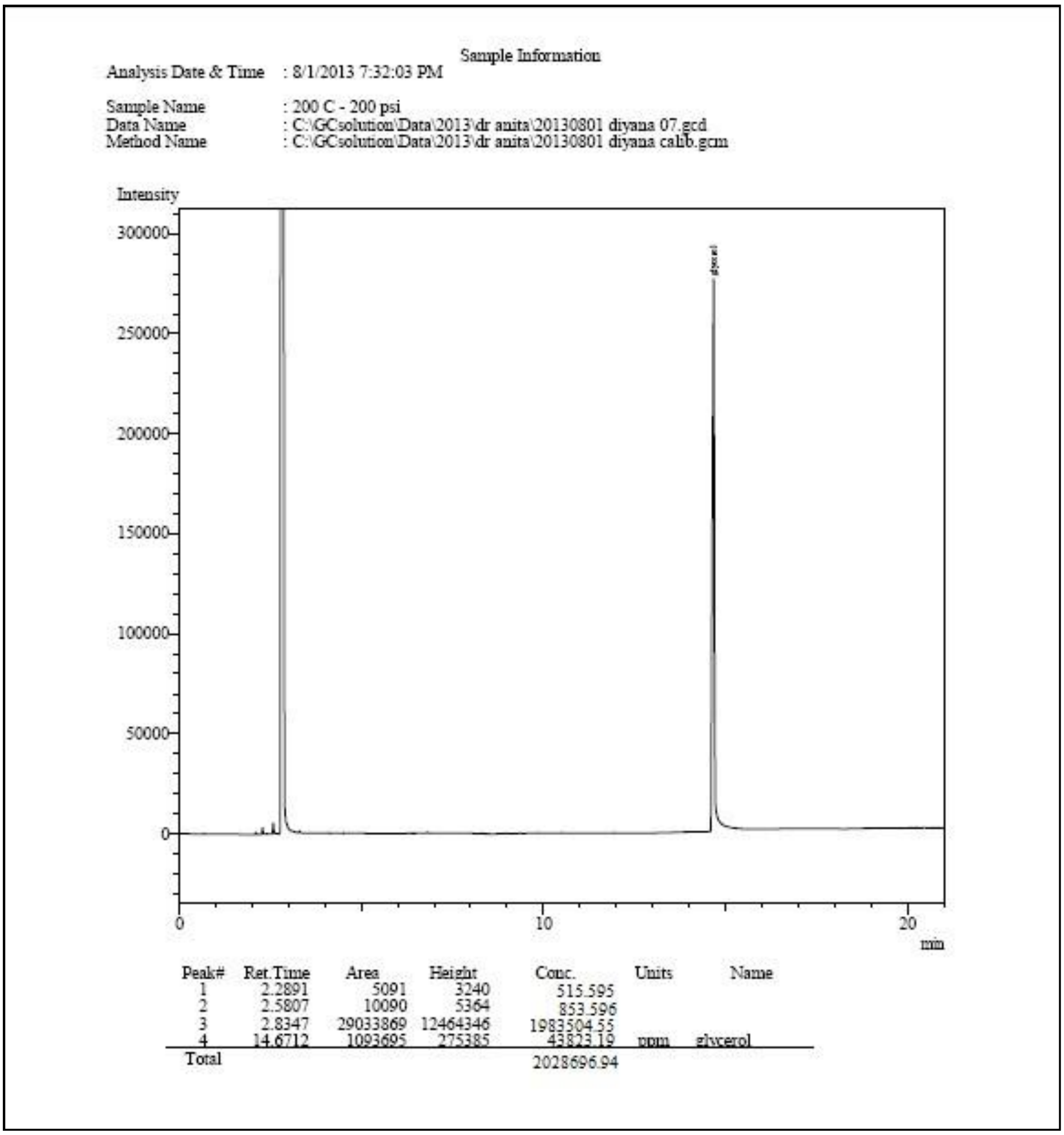
Sample Name : 150 psi
Data Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana 01.gcd
Method Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana calib.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.2906	5060	3209	496.494		
2	2.5813	10232	5477	847.370		
3	2.8357	29897071	12798878	1980231.208		
4	14.6766	1174414	284148	43963.13	ppm	glycerol
Total				2025538.229		

APPENDIX J: RESULT FOR 200 PSI & 200 °C



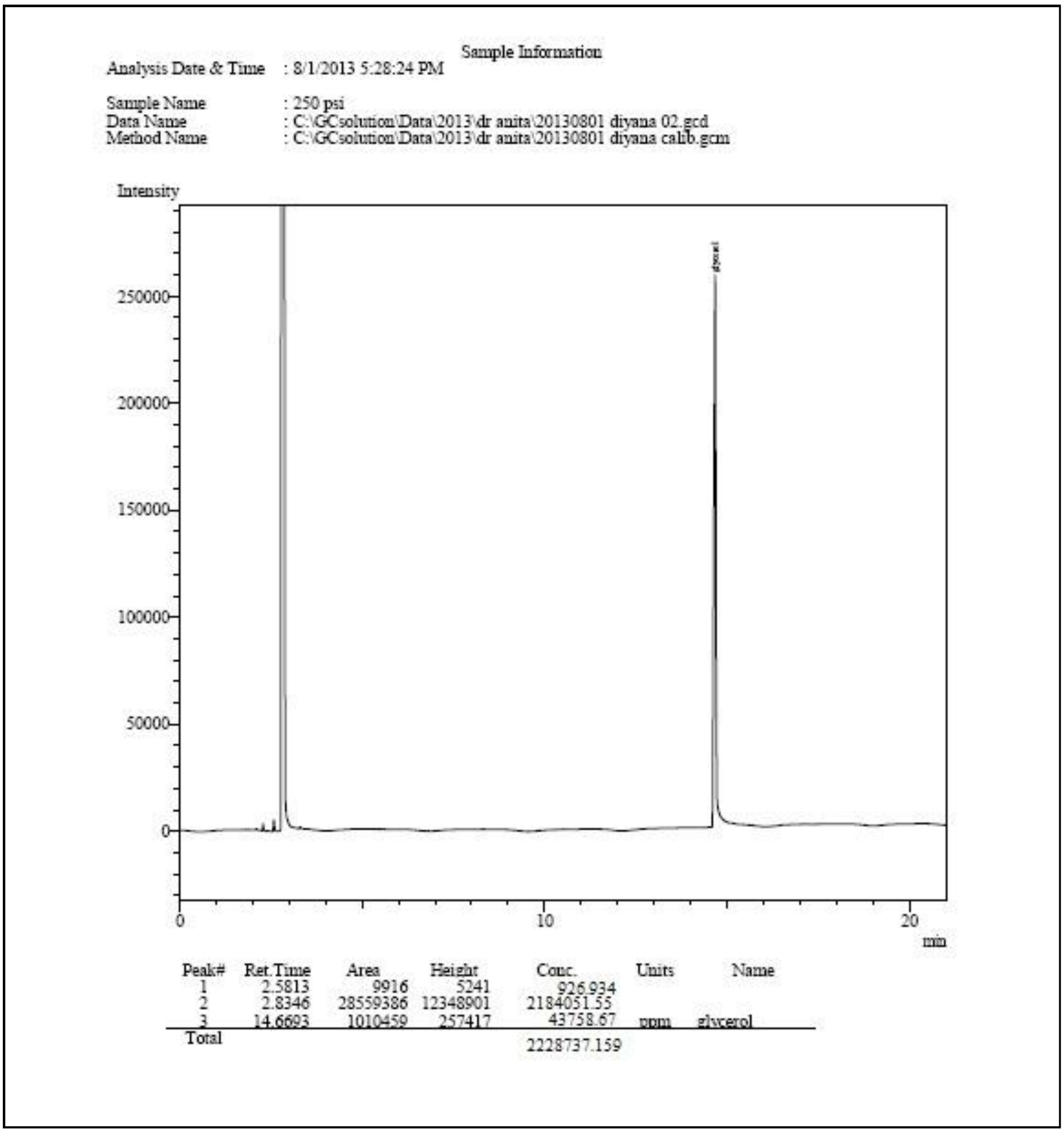
Sample Information

Analysis Date & Time : 8/1/2013 7:32:03 PM

Sample Name : 200 C - 200 psi
Data Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana 07.gcd
Method Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana calib.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.2891	5091	3240	515.595		
2	2.5807	10090	5364	853.596		
3	2.8347	29033869	12464346	1983504.55		
4	14.6712	1093695	275385	43823.19	ppm	glycerol
Total				2028696.94		

APPENDIX K: RESULT FOR 250 PSI



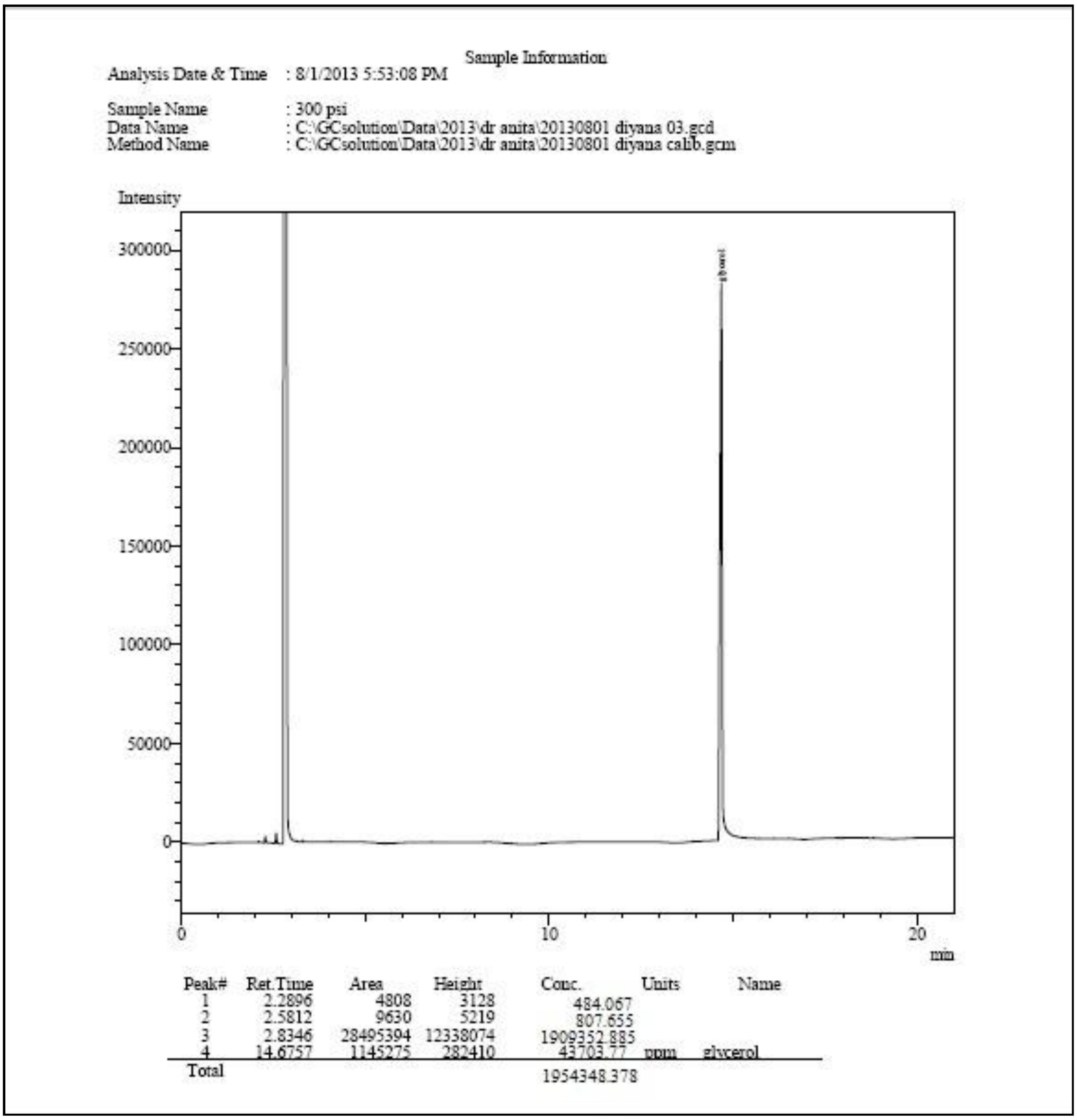
Sample Information

Analysis Date & Time : 8/1/2013 5:28:24 PM

Sample Name : 250 psi
Data Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana 02.gcd
Method Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana calib.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.5813	9916	5241	926.934		
2	2.8346	28559386	12348901	2184051.55		
3	14.6693	1010459	257417	43758.67	ppm	glycerol
Total				2228737.159		

APPENDIX L: RESULT FOR 300 PSI



Sample Information

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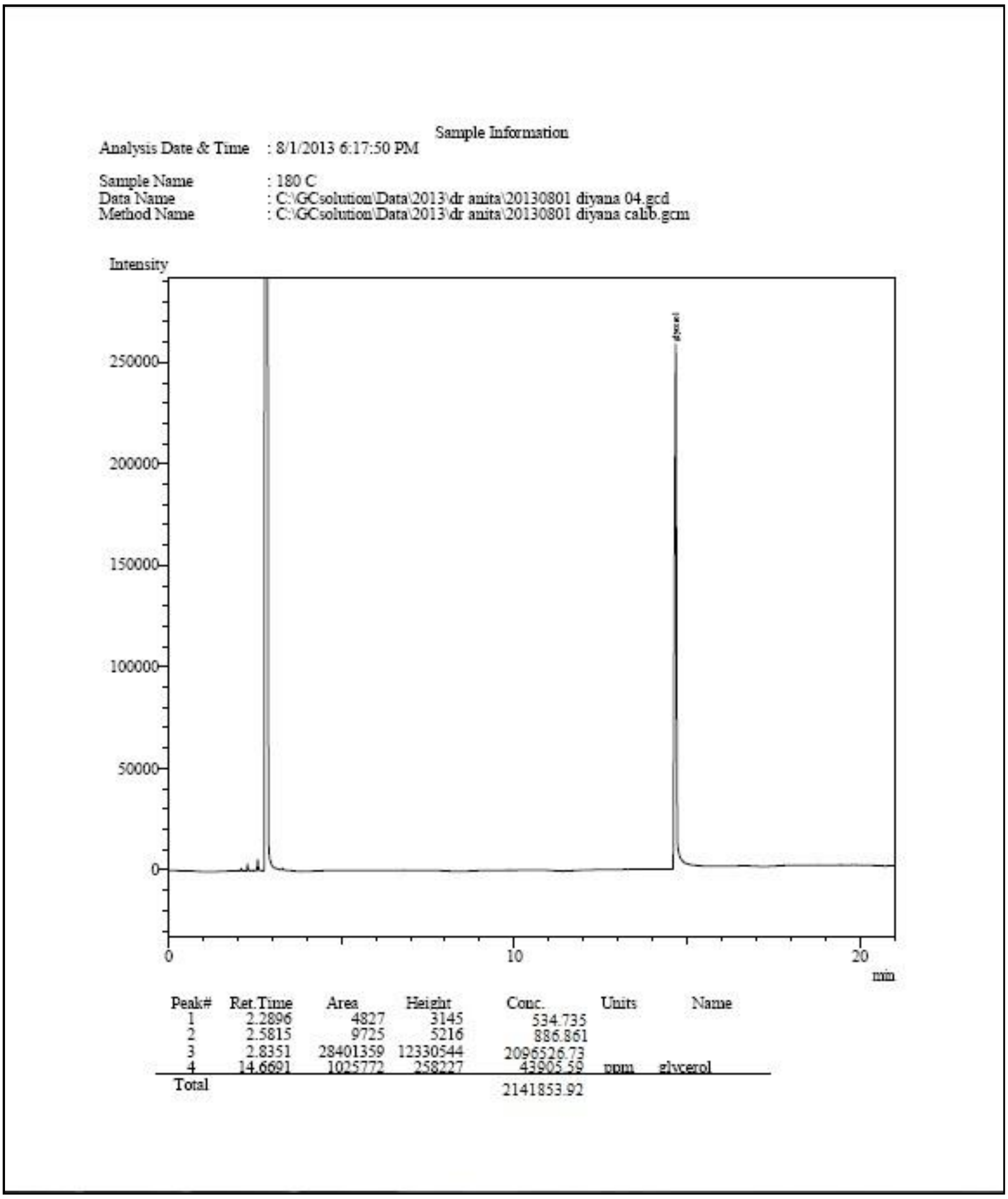
Data Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana 03.gcd
Method Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana calib.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.2896	4808	3128	484.067		
2	2.5812	9630	5219	807.655		
3	2.8346	28495394	12338074	1909352.885		
4	14.6757	1145275	282410	43703.77	ppm	glycerol
Total				1954348.378		

APPENDIX M: RESULT FOR 180 °C



Sample Information

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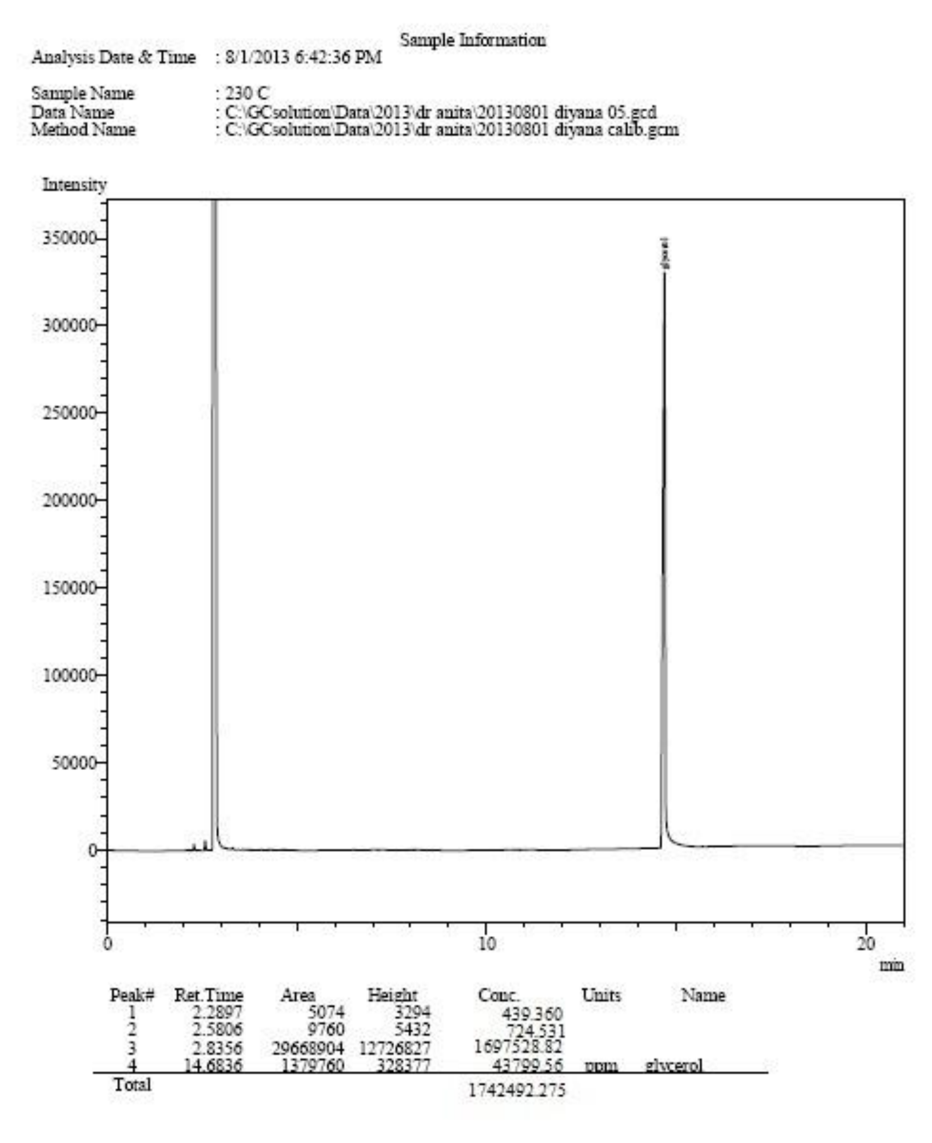
Data Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana 04.gcd
Method Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana calib.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.2896	4827	3145	534.735		
2	2.5815	9725	5216	886.861		
3	2.8351	28401359	12330544	2096526.73		
4	14.6691	1025772	258227	43905.59	ppm	glycerol
Total				2141853.92		

APPENDIX N: RESULT FOR 230 °C



Sample Information

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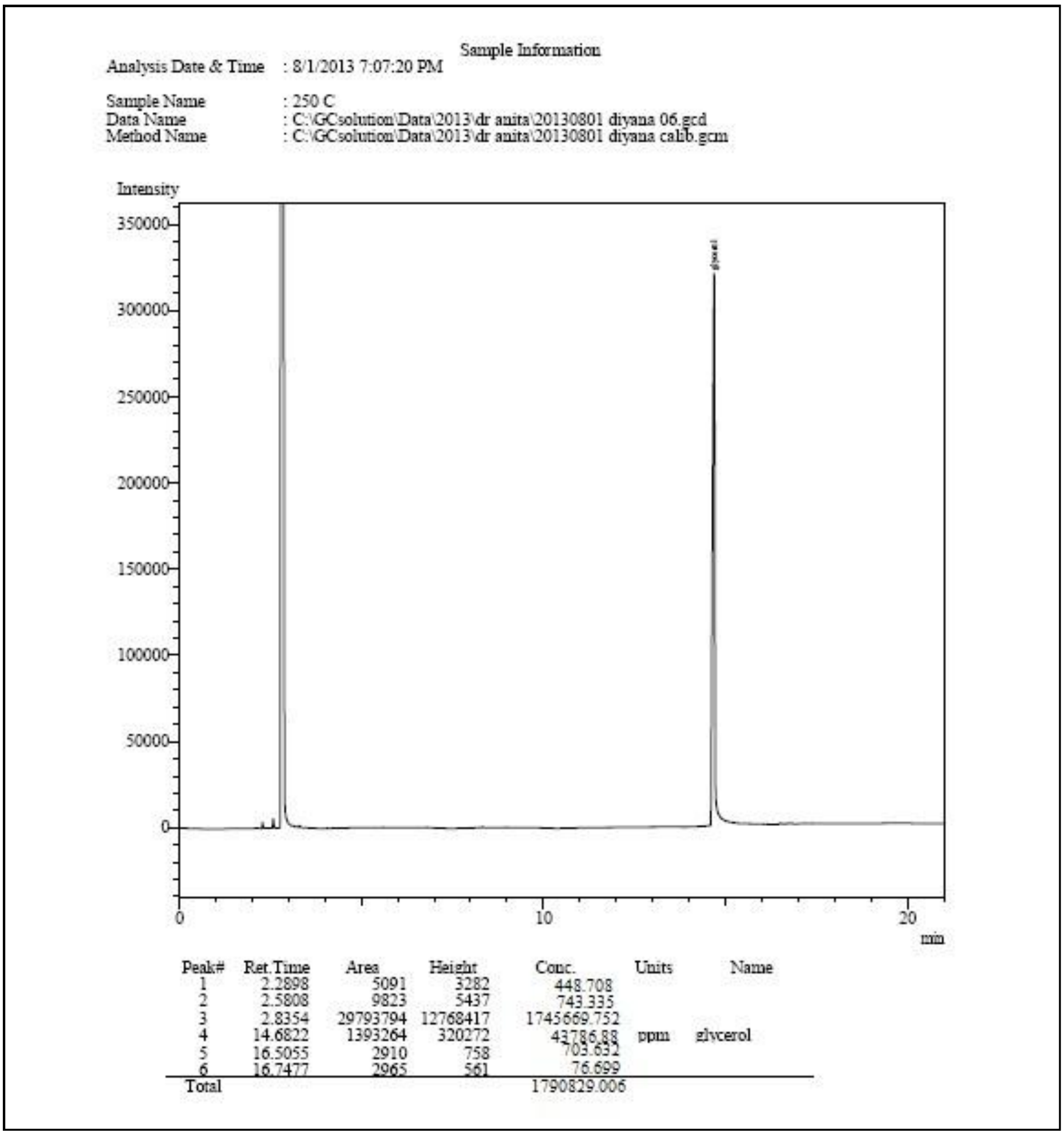
Method Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana calib.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.2897	5074	3294	439.360		
2	2.5806	9760	5432	724.531		
3	2.8356	29668904	12726827	1697528.82		
4	14.6836	1379760	328377	43799.56	ppm	glycerol
Total				1742492.275		

APPENDIX O: RESULT FOR 250 °C



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                                        Sample Information
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Method Name            : C:\GCsolution\Data\2013\dr anita\20130801 diyana calib.gcm
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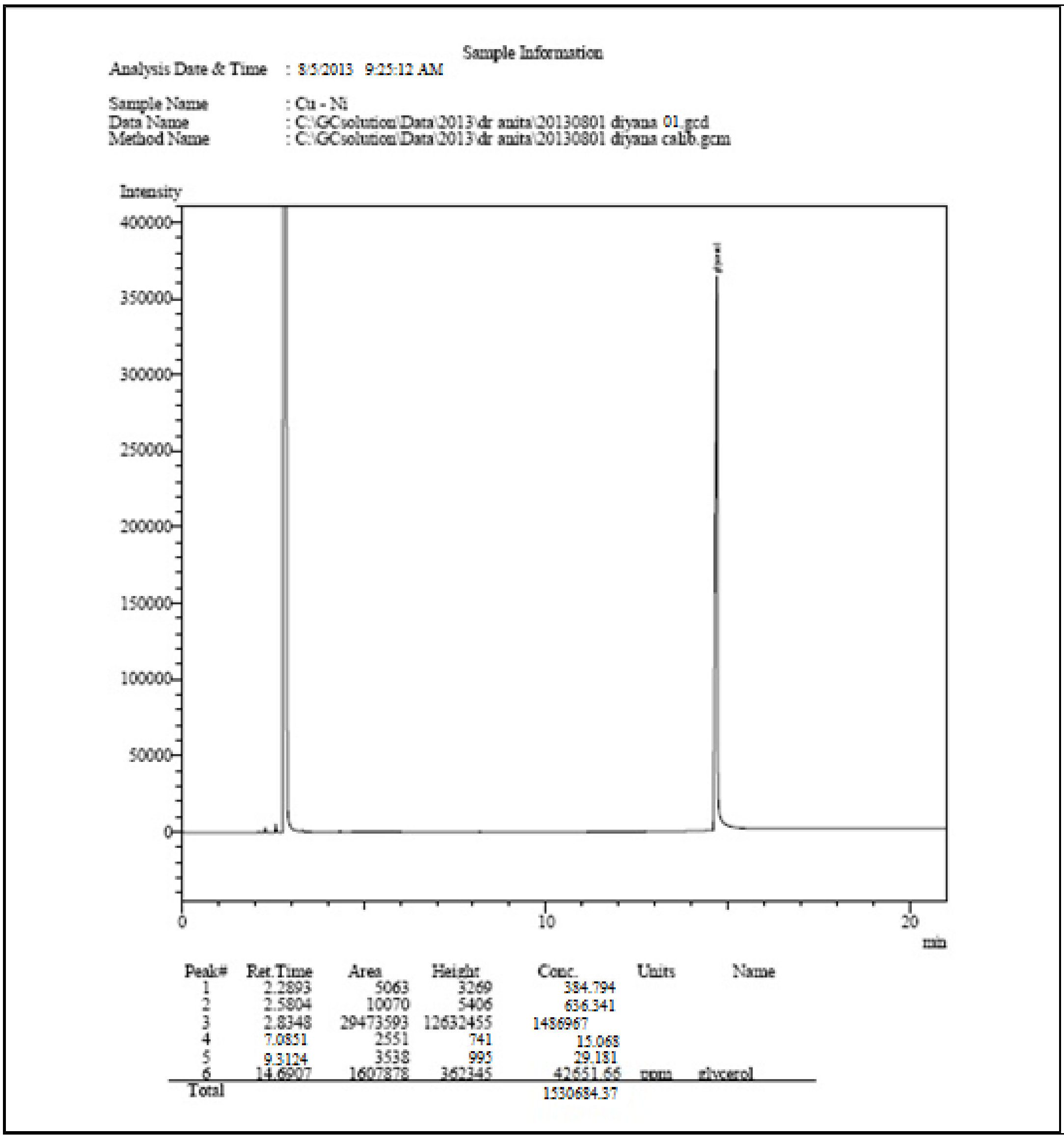
```
Peak#  Ret.Time      Area     Height        Conc.   Units    Name
  1     2.2898       5091       3282      448.708
  2     2.5808       9823       5437      743.335
  3     2.8354   29793794   12768417  1745669.752
  4    14.6822    1393264     320272    43786.88   ppm    glycerol
  5    16.5055       2910        758      703.632
  6    16.7477       2965        561       76.699
Total                                  1790829.006
```

APPENDIX P: RESULT FOR Cu-Ni Catalyst



Sample Information

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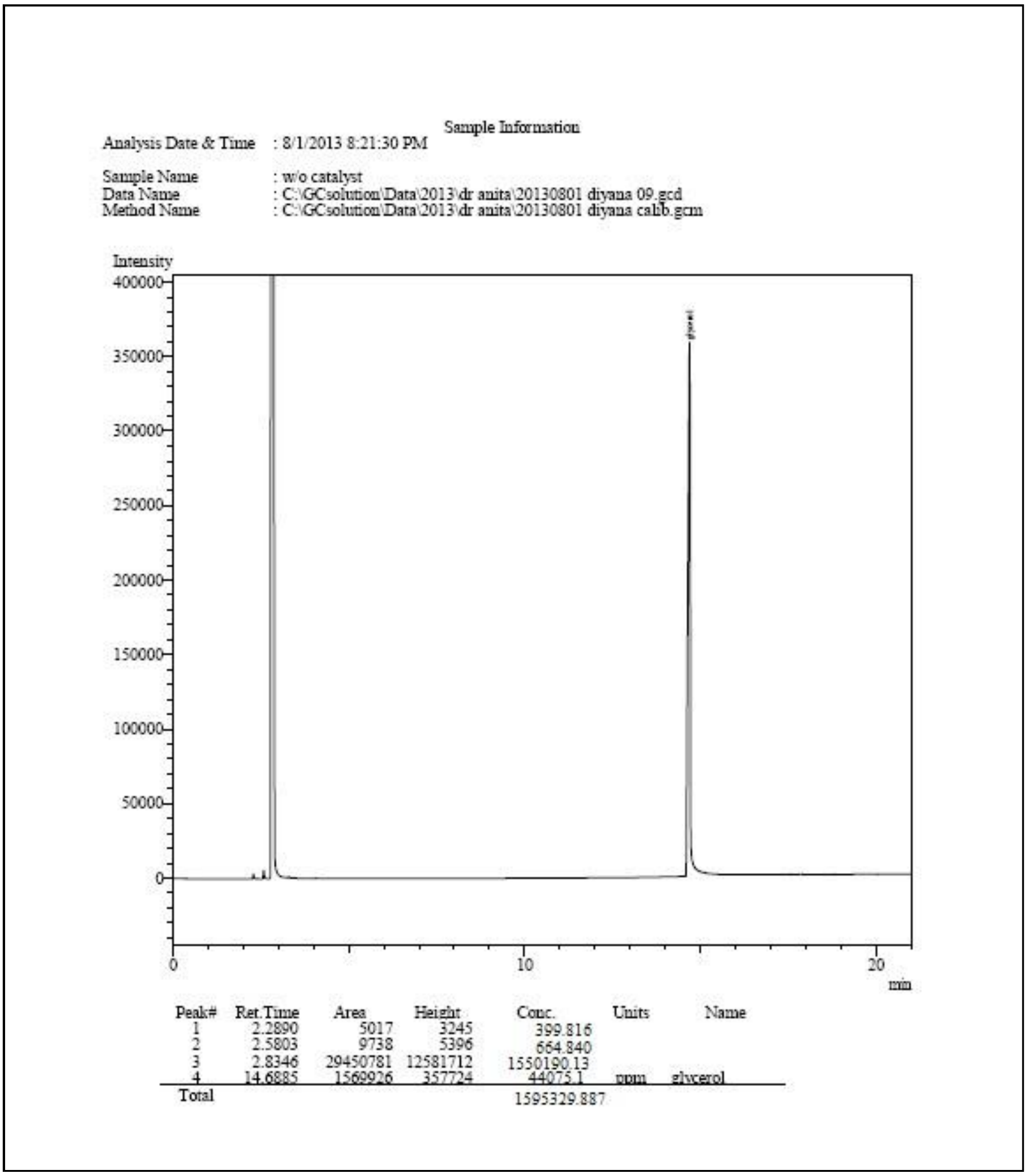
Sample Name : Cu - Ni
Data Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana 01.gcd
Method Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana calib.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.2893	5063	3269	384.794		
2	2.5804	10070	5406	636.341		
3	2.8348	29473593	12632455	1486967		
4	7.0851	2551	741	15.068		
5	9.3124	3538	995	29.181		
6	14.6907	1607878	362345	42651.66	ppm	glycerol
Total				1530684.37		

APPENDIX Q: RESULT FOR WITHOUT SUPPORT/CATALYST



Sample Information

Analysis Date & Time : 8/1/2013 8:21:30 PM

Sample Name : w/o catalyst
Data Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana 09.gcd
Method Name : C:\GCsolution\Data\2013\dr anita\20130801 diyana calib.gcm

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.2890	5017	3245	399.816		
2	2.5803	9738	5396	664.840		
3	2.8346	29450781	12581712	1550190.13		
4	14.6885	1569926	357724	44075.1	ppm	glycerol
Total				1595329.887		