

CERTIFICATION OF APPROVAL

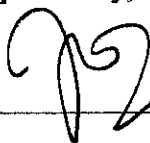
Feasibility Study of Bimetallic Catalysts for Hydrogenolysis Process of Solid Biomass to 1,3-Propanediol

By

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



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ABSTRACT

1,3-propanediol promotes high market value as a result of its versatility as intermediate for the synthesis of heterocycles and as a monomer for the production of improvised polyester, Polytrimethylene Terephthalate (PTT) (Silvia Casali, 2011). Sugarcane bagasse will act as raw material and react with bimetallic catalysts in Parr Reactor and undergo Hydrogenolysis Process. There will be three main products by the end of this reaction, which are 1,2-propanediol, 1,3-propanediol and Ethylene Glycol (Mohanprasad A. Dasari, 2005).

Hydrogenolysis catalytic process is performed using the combination of two metals, with copper as a based with the present of Zeolite as a carrier. Cerium, Manganese, Nickel, Zinc, Titanium and Cobalt are the perfect chosen metals based on their compatibility in electro negativity will combined with copper and tested its catalytic reaction during hydrogenolysis process. Besides the choice of catalyst, the effects of temperature, hydrogen pressure, carriers, initial water content and type of solid biomass are important features that needed to be monitored in order to generate high selectivity and yield of 1,3-propanediol.

CHAPTER 1 - INTRODUCTION

1.1 BACKGROUND

In recent years, more attractive processes have been developed for the production of commercial high quality 1,3-propanediol derived from renewable resources with low cost. Polymers based on 1,3-Propanediol are more resistant to strains and has better wash-fastness. 1,3-Propanediol based polyesters are expected to be different from 1,4-butandiol, because of different interaction between the diol and dibasic acid. Polyesters based on 1,3-propanediol are most promising in terms of biodegradability due to the presence of odd number of methylene units. Besides that, the production of new polyester, Polytrimethylene Terephthalate (PTT) has caused a drastic rise in the demand of 1,3-Propanediol due to its superior stretching and stretch recovery characteristics. Since this type of polymer is biodegradable, it makes the demand become incredibly high (Saxena *et al.*, 2009). In recent years, more attractive processes have been developed for the production of commercial high quality 1,3-Propanediol derived from renewable resources with low cost. Polyesters based on 1,3-Propanediol are most promising in terms of biodegradability due to the presence of odd number of methylene units (Umare *et al.*, 2007). One of the methods that widely used to produce 1,3-Propanediol is Hydrogenolysis.

1.2 PROBLEM STATEMENT

With the increasing demand in polymer industry recently, the market value of 1,3-Propanediol has reach to the top. It has become one of the most highly demand commodity chemicals in the whole world (Kurosaka *et al.*, 2008). Unfortunately, the production of 1,3-Propanediol is limited compared to propylene glycol. Catalyst used in hydrogenolysis process in current technology unable to comprehend 1,3-Propanediol over propylene glycol. Thus, it is essential to study on the catalytic properties that favour more 1,3-Propanediol as the main product.

1.3 OBJECTIVE

This project is focusing mainly on studying the feasibility of bimetallic catalysts for hydrogenolysis process from solid biomass that favour high selectivity and yield of 1,3-Propanediol as the product. For designing appropriate catalyst formulations, the combination of these metals; Cerium, Manganese, Nickel, Zinc, Titanium and Cobalt, will be tested in hydrogenolysis process. With the abundant source of solid biomass, this project will be going to use solid biomass instead of glycerol. Thus, sugarcane bagasse will act as the raw material replacing the glycerol. The raw material will then react with the combination of suitable bimetallic catalysts to determine the result desired. The appropriate operating temperature, hydrogen pressure as well as type of support used will also be controlled and varied in order to achieve as high as possible 1,3-propanediol by the end of the project.

1.4 SCOPE OF STUDY

As indicated in the objective, scope of study will be centred on the development of the catalyst. From the catalyst preparation until the catalytic testing, this project is purposely conduct in order to determine the best combination of two metal catalysts that can maximize the production of 1,3-Propanediol over other by-products. For the catalyst preparation, the process will include the impregnation, calcinations and drying. Throughout the process, the parameters such as temperature during calcination process for both support and metal catalysts, hydrogen pressure during hydrogenolysis process and also the temperature during drying process will be monitored really closely as it will be affecting the result of the whole process.

Then this report will also discuss on the catalytic testing, which is hydrogenolysis process. The suitable parameters and operating condition such as temperature and pressure for inert gas, hydrogen are the most important parts for this process. Other than that, the preparation process of solid biomass must also be taken into account. Even though the process is not as complicated as the process mentioned above, but it must be prepared carefully for getting the desired result.

CHAPTER 2 - LITERATURE REVIEW

2.1. HYDROGENOLYSIS

Hydrogenolysis reaction has huge applications in many key industrial sectors, including the petrochemical, pharmaceutical, food and agricultural industries. According to The American Heritage® Dictionary of the English Language, Hydrogenolysis can be define as the breaking of a chemical bond in an organic molecule with the simultaneous addition of a hydrogen atom to each of the resulting molecular fragments. The reaction consists of process which inert gas causes a chemical change that is similar to the role of water in hydrolysis (Munslow, 2008). The chemical reaction happens when the carbon-carbon or carbon-heteroatom single bond is cleaved or undergoes "lysis" by hydrogen. This process usually conducted with the presence of catalyst and hydrogen gas passing through the reactor (Smith & Notheisz *et al.*, 1999).

Also known as batch autoclave system, Hydrogenolysis process is believed to accelerate the reaction rate of any process with the help of catalysts. Usually, hydrogenolysis is conducted in the presence of hydrogen gas throughout the reaction. The range of operating pressure and temperature is depending on the type of reaction itself. For example the reaction of hydrogenolysis process from solid biomass to 1,3 propanediol requires temperature within the range 200°C, meanwhile for the pressure it varies from 260psi to 290psi.

2.2. SOLID BIOMASS (SUGARCANE BAGASSE)

Generally, the biodiesel transesterification reaction of triglycerides to fatty acid methyl esters with methanol yields glycerol as a by-product. Since biomass is the source of biodiesel, hence the mechanism of reaction for biomass and glycerol considered as similar (M. Pagliaro, 2008). Based on this literature, some modification will be applied for this project. Instead of using glycerol, solid biomass will be replaced this substance. Since there is abundance source of solid biomass nowadays, this project can manoeuvre the usage of biomass and if it's a success, it will become reference for future used. Since there are plenty sources of biomass, the one that has been chosen is sugarcane bagasse. Sugarcane bagasse is still considered as fresh source as compared to palm shell kernel and it is easily obtained and

processed. Figure 1 below shows the basic schematic diagram for the mechanism of hydrogenolysis process of glycerol.

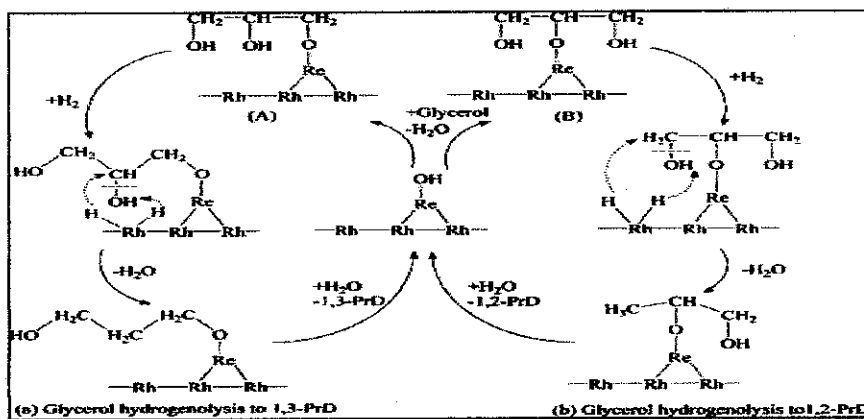


Figure 1. Mechanism of Hydrogenolysis

Based on the research and literature regarding the development of catalyst for hydrogenolysis process of solid biomass as raw material to 1,3-propanediol, this project is considered as early discovery as compared to the hydrogenolysis process of glycerol (Seung-Hwan Lee, 2011). Even though the sources and references is quite limited but the possibility of getting positive result is still high.

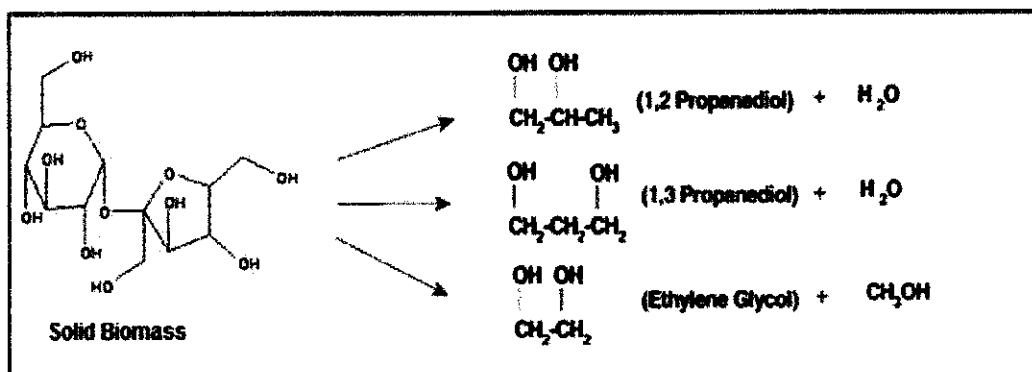


Figure 2. Conversion of Hydrogenolysis Process of Solid Biomass

Meanwhile figure 2 above shows the common products produced as the result from hydrogenolysis process of solid biomass. Even though it shows that the process produce varies products, the current technology that has been well established world wide mainly favour 1,2-propanediol as the main product. The conversion of hydrogenolysis process from raw material to the product ranges in the parameters of 15 bar, temperature between 240–270 °C along with the presence of platinum(Pt),

palladium(Pd), nickel(Ni), copper (Cu), ruthenium (Ru) and zinc (Zn) as catalysts (B. Casale, 1994).

2.3. 1,3-PROPANEDIOL

With the presence of two hydroxylic groups at position 1 and 3 as in figure 3 below, this differs between 1,3-Propanediol to propylene glycol (1,2-Propanediol).

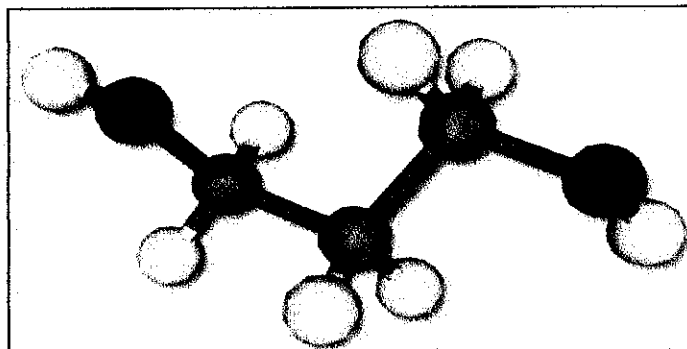


Figure 3. 3D Model of 1,3-Propanediol

Apparently the applications for both products are definitely diverse. 1,3-Propanediol has a large range of potential utilizations. It is a versatile intermediate for the synthesis of heterocycles. Given its chemical structure displaying two hydroxylic groups at mentioned position above, it is a monomer for the production of polyesters for example polytrimethylene terephthalate (PTT). It has better properties as compared to conventional polyesters like polyethylene terephthalate (Kurian, 2005).

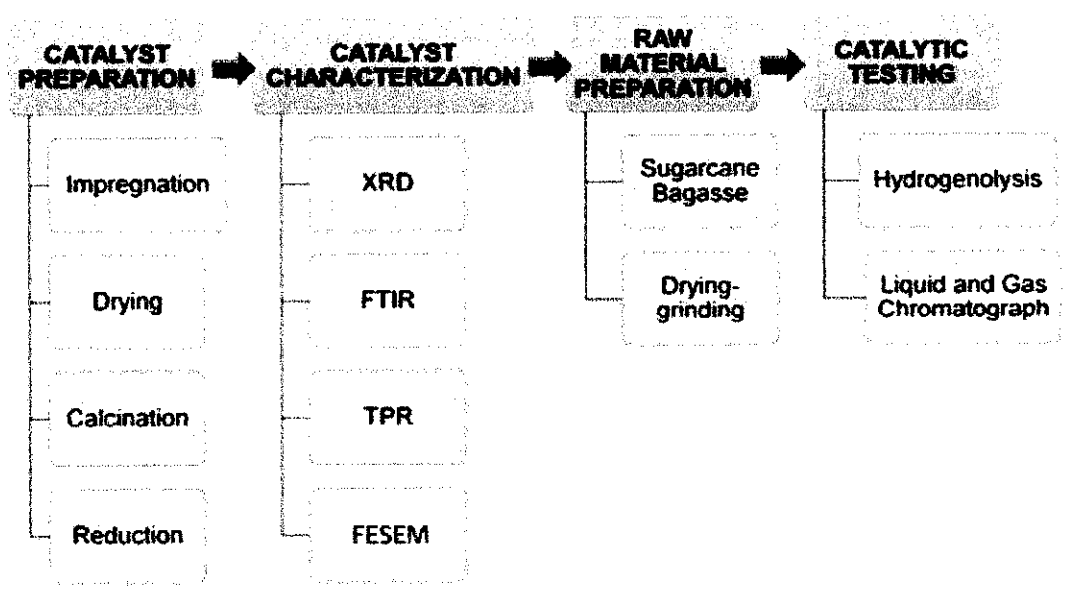
The market demand for 1,3-Propanediol recently increased as a result of the increased production of PTT. For instance, this new polyester based on 1,3-Propanediol that Shell Chemical recently announced for commercialization, has the elastic recovery of nylon and the chemical resistance of polyester (Stinson, 1995). Apart from its superior stretching and stretch recovery characteristics, it also famous for its biodegradable features that has upheld its potential in textile, carpets and upholstery manufacturing. Other than that, 1,3-Propanediol can also be used for the synthesis of polyurethanes, as a chain extender, lubricant, solvent and precursors for the chemical and pharmaceutical industries. It may also be used as biocides, e.g. PCT 3015 (Silvia Casali, 2011).

2.4. BIMETALLIC CATALYST

According to Merriam-Webster, catalyst can be defined as chemical substance that improves the rate or selectivity and also reduce the activation energy without being consumed in chemical reaction. For a better performance of the catalyst, it need support, which is a material usually solid with high surface area, to which a catalyst is affixed. The reactivity of heterogeneous catalysts occurs at the surface of atoms. Consequently great effort is made to maximize the surface area of a catalyst by distributing it over the support. The support may be inert or participate in the catalytic reactions. Typical supports include various kinds of zeolite, carbon, alumina as well as silica (Francisco Zaera, 2006).

“Supported Heterogeneous Catalysts” is far more superior if compared to mono-metallic. It can improve the desired product selectivity and yield by suppressing some of the side reactions (Jiang *et al.*, 2007). The formation of a surface bimetallic bond induces large changes in the band structure of the metals. Bimetallic bonds that display a large stability usually involve a significant redistribution of charge around the metal centres (JoséA *et al.*, 1996). Hence, for the purpose of this project, the catalyst that is going to be studied and developed through will be bimetallic catalysts with selected support.

CHAPTER 3 - METHODOLOGY



3.1. CATALYST PREPARATION

3.1.1. Tools and Chemicals Used

TOOLS	CHEMICALS
Parr Reactor	Copper (II) Nitrate Trihydrate
Rotary Furnace	Manganese (II) Sulphate.1-Hydrate
Hydrogen Gas Regulator	Cerium (III) Nitrate
Glassware/Plastic ware	Nickel (II) Chloride Hexahydrate
Grinder	Zinc Nitrate Hexahydrate
Oven	Cobalt (II) Nitrate Hexahydrate
	Silver Nitrate
	Titanium Oxide
	Processed solid biomass (sugarcane bagasse)

Table 1. List Tools and Chemicals

3.1.2. Calcination of Support (ZEOLITE)

Basically, the catalyst preparation process includes impregnation, drying, calcination and reduction as shown in figure 4. Incipient wetness impregnation (IWI) is applied for impregnation process. Also known as capillary impregnation or dry impregnation, this technique is used for the synthesis of heterogeneous catalysts. Firstly, the support, zeolite ZSM-5 will be calcined by putting it inside the rotary reactor furnace for 4 hours. The purpose of this process is to remove any impurities reside in the support. Overall process is simplified in figure 5 below.



Figure 4. Calcination of Support

3.1.3. Impregnation and Drying Process

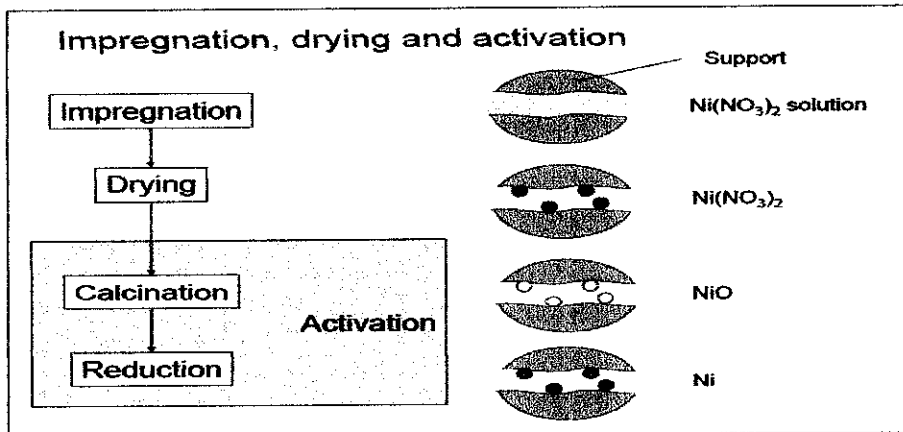


Figure 5. Overall Catalyst Preparation Process

After completing the process, then the catalyst can be prepared. During the process, the active metal precursor is dissolved in an aqueous or organic solution. Then the metal-containing solution is added to a catalyst support containing the same pore volume as the volume of solution that was added. Capillary action draws the solution into the pores. Solution added in excess

of the support pore volume causes the solution transport to change from a capillary action process to a diffusion process, which is much slower (Regalbuto, 2007).

It is decided that the catalyst prepared will be 50g. Since the metal loading is 5% for each metal, thus the support will be 45g and metals will be 5g overall of total catalyst prepared. So for the metal salt, since only 2.5g needed for each metal, the amount needed for Copper (Cu) is

$$\frac{\text{MW Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}}{\text{MW Cu}} = \frac{x \text{ g Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}}{2.5 \text{ g Cu}}$$

$$\frac{241.6 \text{ g}}{63.55 \text{ g}} \times 2.5 \text{ g Cu} = 9.5 \text{ g Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$$

The calculation method is repeated for all metals. Then, the weighed metal salt is mixed together with distilled water that act as solvent until it well dissolved. Then, after mixed thoroughly, the solution will be left on the magnetic stirrer for 4 hours so that the impregnation process can take place. The sequence below shows the whole impregnation process.

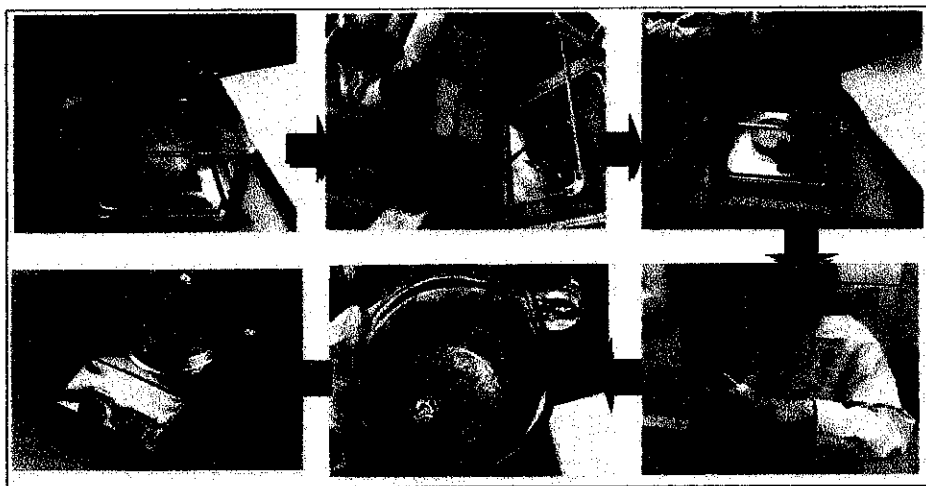


Figure 6. Impregnation Process

After 4 hours, the catalyst then is put inside the oven for overnight with temperature of 100°C for drying purpose.

3.1.4. Calcinations Of Catalyst

Then, the calcination process of catalyst is then takes place to drive off all volatile components within the solution and depositing the metal on the catalyst surface. Since the time is limited to vary the temperatures from 400°C to 600°C, the calcinations temperature is finally chosen to be 500°C. In the figure below shows the catalysts after calcinations process.

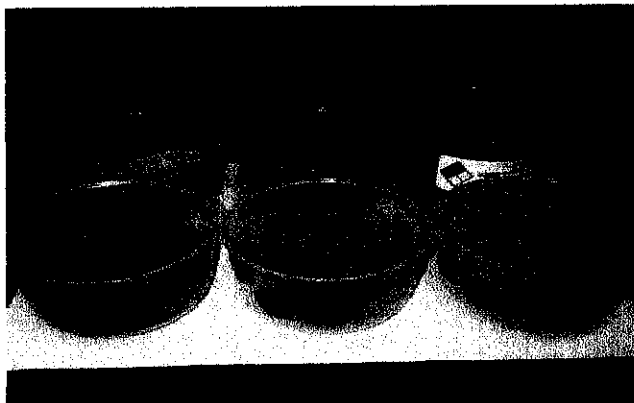


Figure 7. After Calcination

3.2. CATALYST CHARACTERIZATION

Characterization is essential to determine the catalysts type, performance as well as its physicochemical properties. Throughout this project, here are the equipments used for characterizing the catalysts:

3.2.1. X-Ray Diffraction (XRD)

XRD is useful for determination of the electron distribution within the atoms and throughout the unit cell. It can also measure strain and small grain size. Besides, it can determine elements inside the substance and measure the limits of solid solubility and also determine phase diagrams. Thus, it is very useful for characterizing the prepared catalyst and support.

3.2.2. Temperature Program Reduction (TPR)/ Desorption (TPD)

TPR measured the ease reduction of the metal oxide. The reducing gas mixture, flowing over the oxide will cause reduction at some point as the temperature is raise during a linear heating ramp. Changing the heating rate

can evaluate the activation energy for the process. Low loadings of metal oxides, especially surface oxides, generate little water and a successful analysis can also be done without trapping it. Whereas for TPD machine, it can evaluate relative acid site strength's for example zeolite. Basic sites can similarly be evaluated by TPD of carbon dioxide. Some materials may be characterized by decomposition, or dissociation, of the bulk solid, not merely by desorption from the surface (Automatic Chemisorption Analyzer).

3.2.3. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is capable in identifies chemical bond of functional groups by the absorption of infrared radiation that excites vibrational mode in the bond. It can detect the chemical bonds of organic materials and organic contaminants. Other than that, it identifies water, phosphates, sulfates, nitrates, nitrites, and ammonium ions (Analytical Laboratory for Rapid-Response Materials Characterization, 2006).

3.2.4. Field Emission Scanning Electron Microscopy (FESEM)

FESEM produces clearer, less electrostatic distorted images with spatial resolution down to 1 1/2 nm. That's 3 to 6 times better than conventional SEM. It also reduced penetration of low kinetic energy electrons probes closer to the immediate material surface (Principle of FESEM, 2011). Thus, by applying FESEM, high-resolution images of samples at high and low voltages can be analyzed.

3.3. RAW MATERIAL PREPARATION

Raw material used for this project is sugarcane bagasse. The preparation procedure for this material is rather simple. First the bagasse is washed thoroughly and dried inside the oven with the temperature of 100°C for overnight. Then, the dried bagasse will be grinded with the conventional blender until it turned into very fine solid particle. The purpose for this procedure is to ensure that the raw materials will be perfectly mixed with the catalysts.

3.4. CATALYTIC TEST

Literally, catalytic test means analyzing the effectiveness and usefulness of catalyst in particular reaction. For this project, hydrogenolysis process has been the chosen method for testing the efficacy of bimetallic catalysts. The combination and interaction of two metal catalysts is considered compatible based on high percentage in conversion, selectivity and yield of desired product, by which in this case is 1,3-Propanediol.

There are many factors contributed to the result of this reaction process. Operating temperature, pressure and weight of catalyst plays important role in getting the desired result. At 200 psi and 200°C, the selectivity to propylene glycol decreased due to excessive hydrogenolysis of the propylene glycol (Mohanprasad A. Dasari, 2005). Based on the reference, this condition is not optimum for getting high selectivity of propylene glycol. Thus, at the stated temperature and pressure, the amount of propylene glycol produced is lower compared to the other product. Hence, we can use this reference to decide on the suitable operating temperature and pressure for our reaction. This article stated that pressure between 200 psi to 300 psi has the highest selectivity of 1,3 propanediol as compared to the others. Whereby for temperature, 200°C to 230°C is found to be most suitable. Based on these findings, the suitable operating pressure for high selectivity and yield of 1,3-propanediol is chosen to be in between 260 to 290 psi, while for temperature it is set to constant 200°C. Based on the research, weight of catalyst is vital in determining the high selectivity and yield of certain product. 5% of weight catalyst shows the highest possibility of producing the favoured product.

3.4.1. Procedure of Hydrogenolysis

Figure 8 below shows the sequence of steps for hydrogenolysis process. The reactor used for this process is Parr Reactor. Operating pressure is kept in between 260 to 290 psi while temperature will be kept constant at 200°C. The sample preparation is rather simple. The raw material is weighed at 5g. For the catalyst, since the catalyst weight is 5% from the total sample, thus the catalyst used will be 0.25g. Then both raw material and catalyst will be mixed together and put inside the cylinder glass of the reactor. Lastly, it will be filled up with distilled water until it reached 250 mL. Last but not least,

the cylinder will be put inside the reactor and hydrogen gas will be purged once in every 30 minutes inside the reactor for 8 hours continuously.

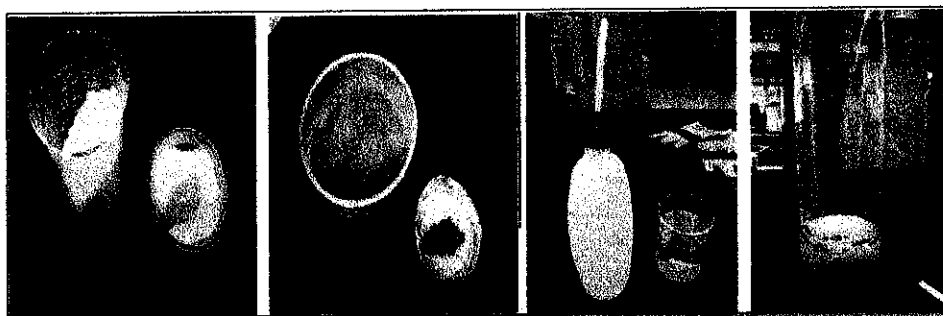


Figure 8. Sample Preparation for Hydrogenolysis

3.4.2. Sample Testing

After running all the samples, the sample testing will be conducted. The method chosen for this test is Gas Chromatography (GC). The reason why GC is used is that this machine is able to separate and analyze compounds that can be vaporized without decomposition. This method helps identifying a compound. GC can also identify liquid and gas samples which by this case are particularly vital for getting the final product. This is the most crucial stage in the project as this will indicate whether 1,3-propanediol is exist in the sample or not, and whether the experiment is a success or a failure. Figure 9 shows the sequence of preparing the sample for GC.

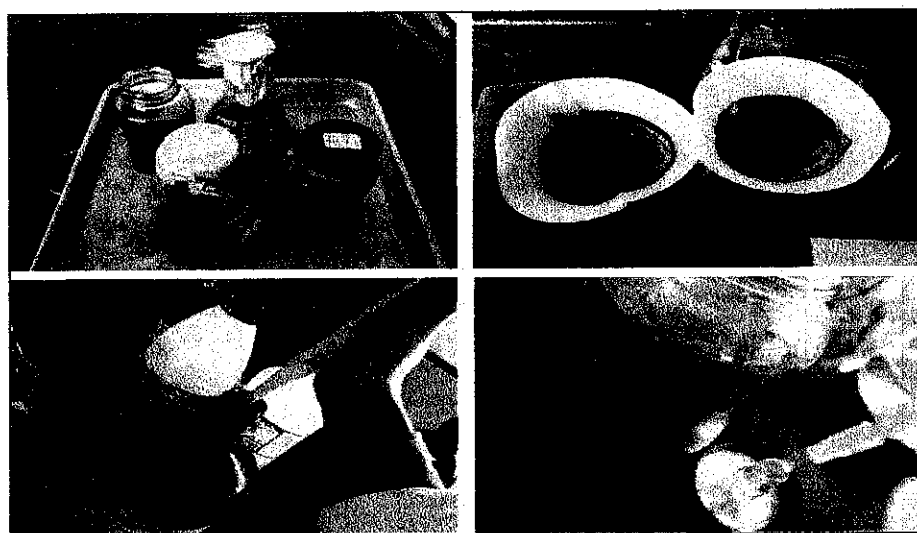


Figure 9. Sample Preparation of GC

CHAPTER 4 - RESULT AND DISCUSSION

4.1. CATALYST CHARACTERIZATION ANALYSIS

4.1.1. FTIR

This analysis is conducted for the purpose of finding whether the calcinations process is conducted successfully or not. The success to the test will be based on the before and after graphs. The peaks in the graph determine the particular functional groups for particular metal. If the peak is not exists in the “after calcined” graph, the calcinations can be considered as a success.

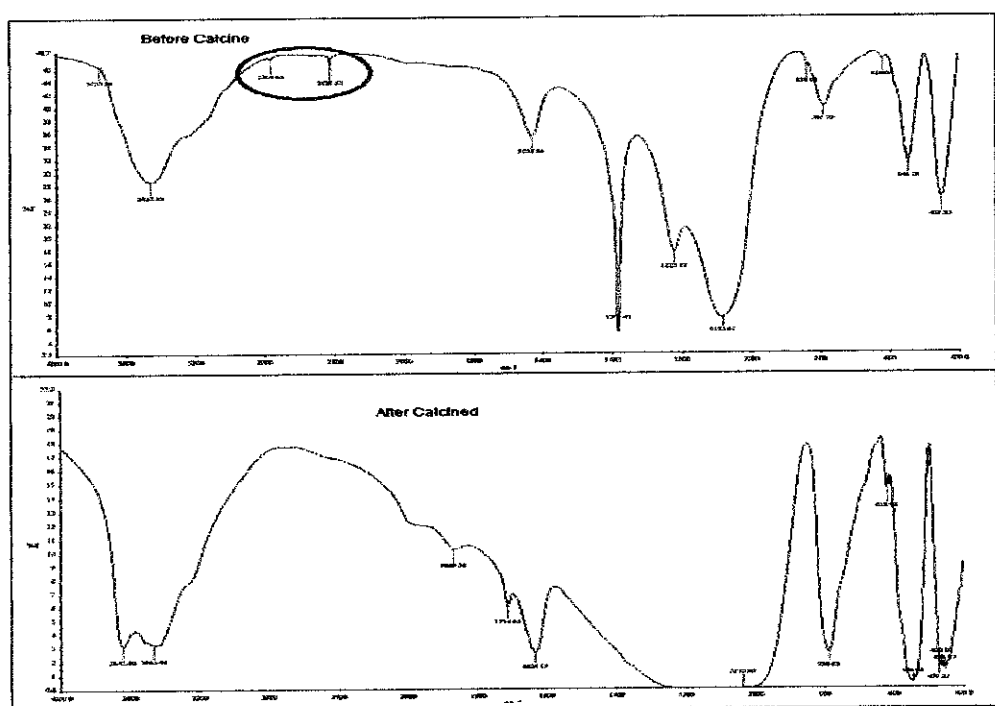


Figure 10(a). Graph Comparison of Cu-Ag (FTIR)

In figure 10(a) above shows the result for Copper-Silver. There have been few peaks absence in the “after calcined” graph. Red circle indicates that C-H in aldehydes bond exists before the calcinations process for all metals are gone.

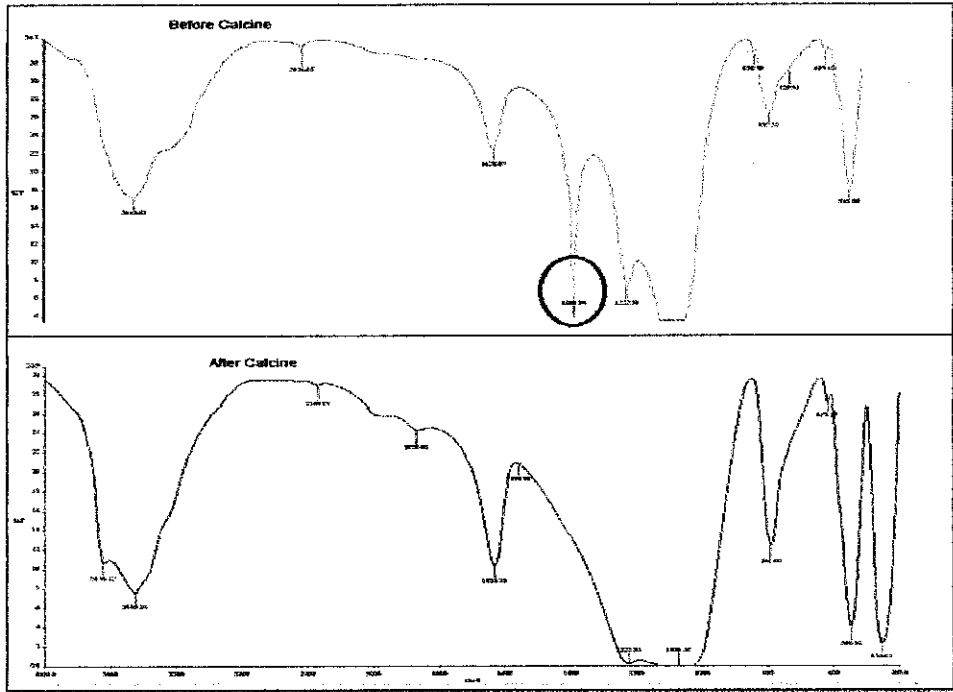


Figure 10(b) Graph Comparison of Cu-Ba (FTIR)

In figure 10(b) above shows the result for Copper-Barium. There have been one peak absent in the “after calcined” graph. Red circle indicates that -C=C- stretch in alkenes exists before the calcinations process for all metals are gone.

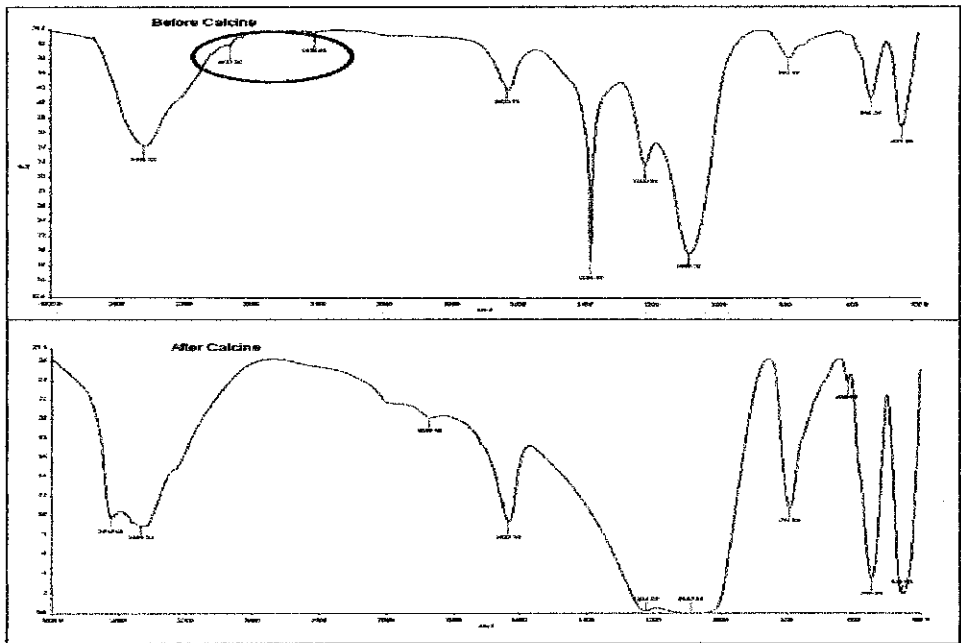


Figure 10(c) Graph Comparison of Cu-Ce (FTIR)

In figure 10(c) above shows the result for Copper-Cerium. There have been two peaks absent in the “after calcined” graph. Red circles in the data shows that C-H in aldehydes bond exists before the calcinations process for all metals are gone.

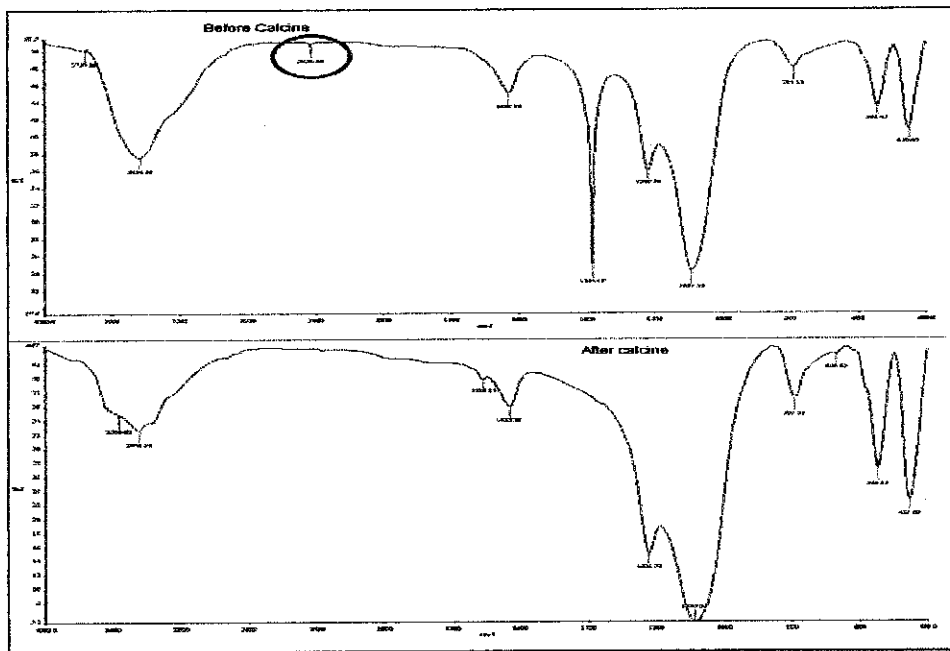


Figure 10(d) Graph Comparison of Cu-Co (FTIR)

In figure 10(d) above shows the result for Copper-Cobalt. There have been one peak absent in the “after calcined” graph. Red circle in the data shows that $-C=C-$ stretch in alkenes exists before the calcinations process for all metals are gone.

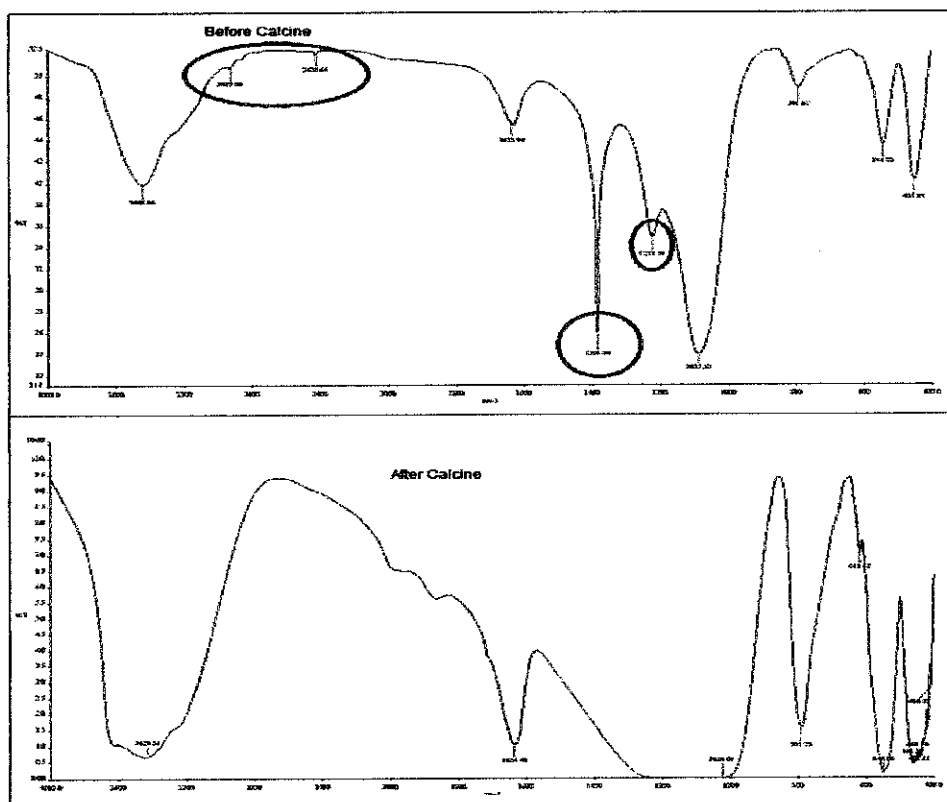


Figure 10(e) Graph Comparison of Cu-Mn (FTIR)

In figure 10(e) above shows the result for Copper-Mangan. There have been three peaks absent in the “after calcined” graph. Red circles indicate that -C=C- stretch in alkenes and C-H in aldehydes exist before the calcinations process for all metals are definitely gone.

4.1.2. TPR

The purpose of conducting this analysis is mainly to determine the reduction temperature of catalyst. The reduction temperature will determine the most optimum condition for the catalyst. The catalyst is not active if the temperature is too low and too high. Thus, this analysis is vital in determining the reaction condition for hydrogenolysis process later on. Looking at the results below, the graphs show the reduction temperature for all 6 catalysts. It varies at the similar range, in between 400 to 600 degrees celcius. Thus, while conducting the catalytic testing later on this result must be taken into consideration for having the best result.

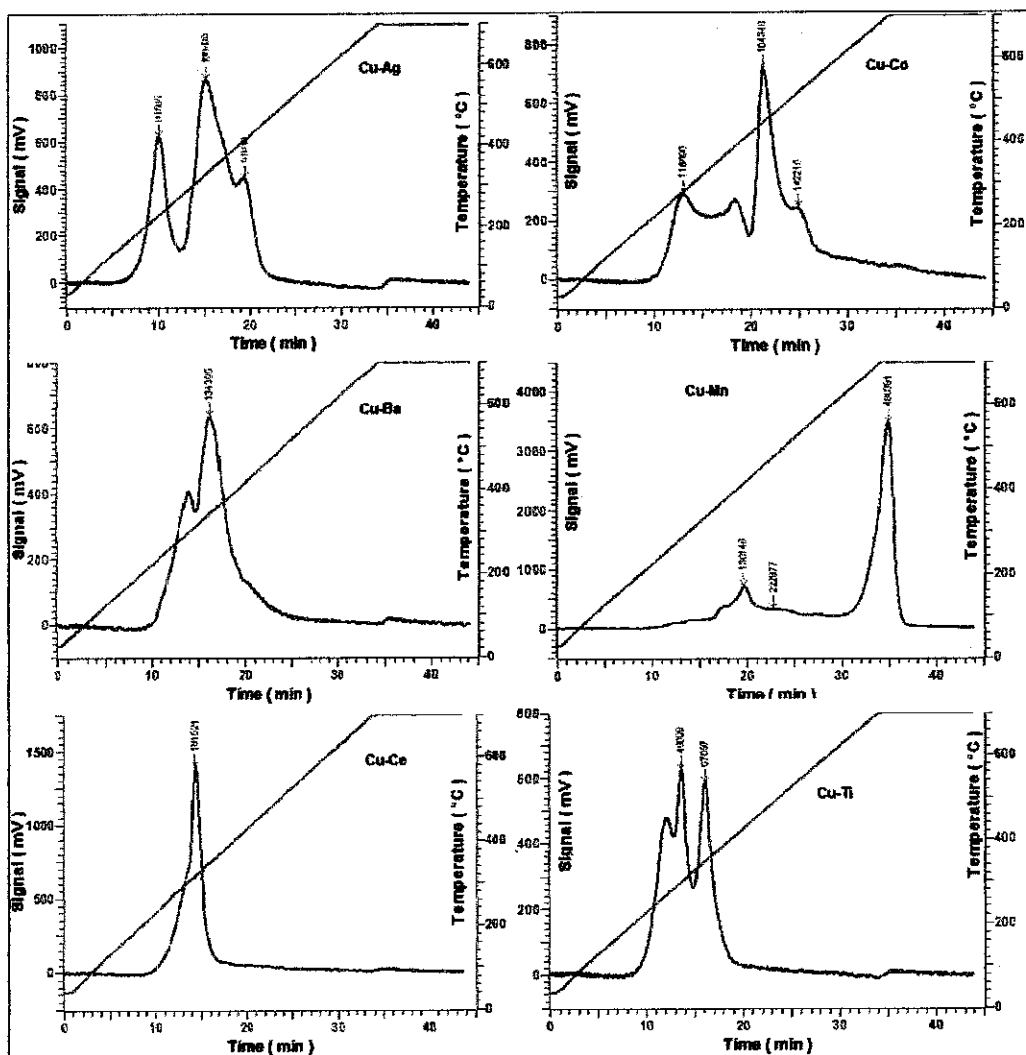


Figure 11. TPR Results for Catalysts

4.1.3. XRD

The result of XRD can determine a lot of things, from the size and the compositions of metal substance to its degree of crystallinity. The graphs below indicate the crystallinity of all the metals in the catalyst. Looking at the graph we can find 2 coloured peaks in every catalyst. The black coloured peak is the standard calibration of sample, while the red colour indicates the sample of bimetallic catalyst. Looking at the graph closely, Silicone oxide is being mentioned. According to the manufacturer, *Zeolyst*, silicone oxide is the main element used for producing the zeolite, which is the support for the bimetallic catalyst. While preparing for bimetallic catalyst, the combination of 90 wt% support is added into 10 wt% metals

explained the results of XRD. Thus, the peak obtained in XRD graph mostly indicating the degree of crystalline of support, especially silicon oxide.

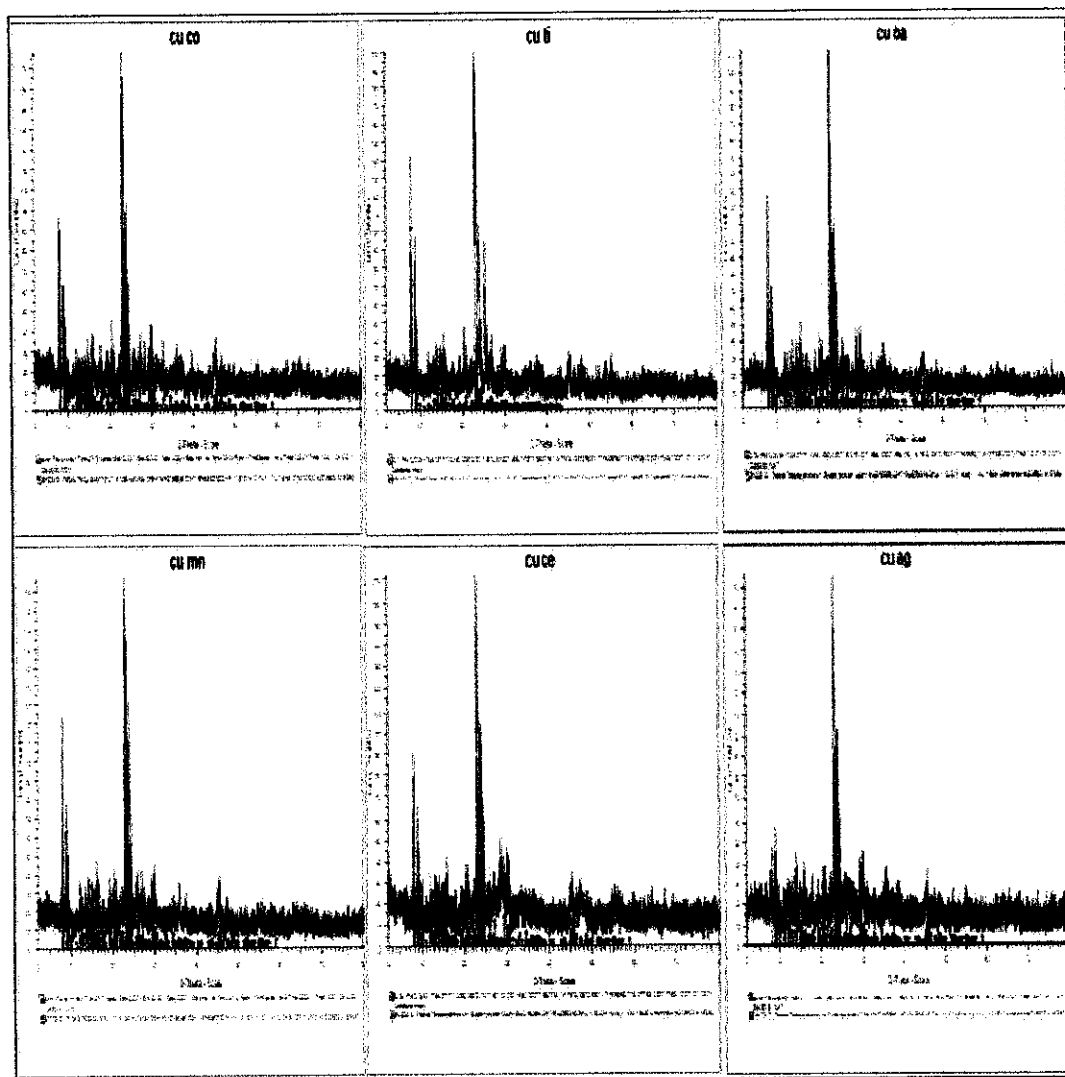


Figure 12. XRD Results

4.1.4. FESEM

The analysis of FESEM is a quantitative analysis to determine the element (weight) wt.% and (atomic) at. % of each coating layer. This was done by spot analyses on each layer, where spot always located at the centre of the layer. This was to avoid as much as possible contribution from other layers.

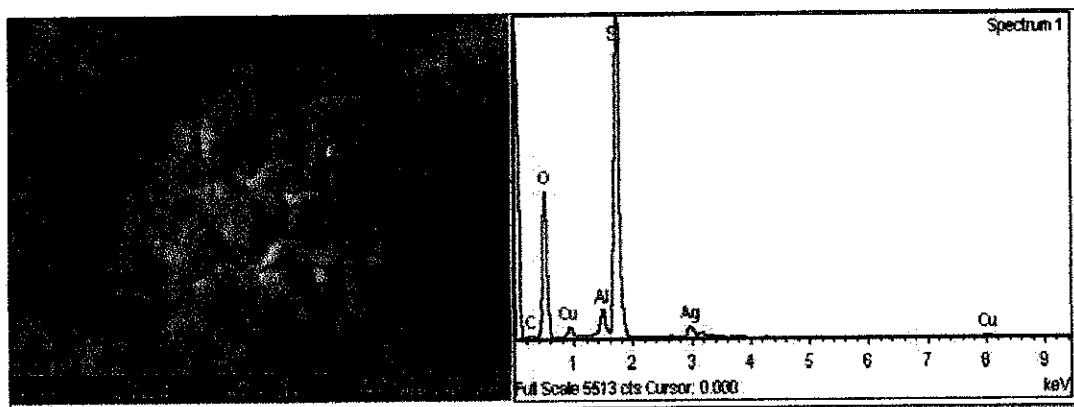


Figure 13. FESEM Result (Cu-Ag)

Thus, in figure 13 it shows the magnification of Cu-Ag catalyst on the left side while on the right side shows the wt.% and at.% of all elements exist inside the bimetallic catalyst, as well as the support since the peak for silicon also exist. Table 2 below shows the distributions of all elements exists in the sample.

Element	Weight%	Atomic%
C	8.02	12.60
O	55.07	64.93
Al	1.99	1.39
Si	29.68	19.94
Cu	1.86	0.55
Ag	3.39	0.59
Totals	100.00	

Table 2. wt % and at.% of elements in Cu-Ag

4. 2. CATALYTIC TESTING ANALYSIS (Gas Chromatography)

4.2.1. Mass Balance and Conversion

After 8 hours of reaction, the sample is taken and filtered for GC sampling purposes as in the figure 9. Then, the solid sample that has been filtered will be dried and weighed for conversion calculation. Table 2 below shows the result after drying of the sample.

Sample Catalyst	Sample Weight After Reaction (g)
Cu-Mn	3.58
Cu-Co	3.57
Cu-Ag	3.85
Cu-Ba	3.75

Table 3. Weight of Samples after Reaction

Based on the concentration of iso-propanol indicated in the peak of GC (Cu-Mn) graph, the % of conversion can be calculated. The sample weighed after the reaction can indicate how much product that has been converted successfully. A simple material and mass balance calculation is used. Below is the example of calculation:

$$0.0229 \text{ mol} \times 60.1 \frac{\text{g}}{\text{mol}} \text{ iso - propanol}$$

$$= 1.3763 \text{ g iso - propanol}$$

$$\frac{1.3763 \text{ g isopropanol}}{3.58 \text{ g sample}} \times 100\%$$

$$= 38.44\% \text{ isopropanol has been converted}$$

The calculation will be repeated for all samples. Table 3 below shows the final product and % of product that has been converted successfully.

CATALYST	CONVERSION	% CONVERTED	% CONVERTED
Cu-Ag	Iso-propanol	37.9	17.7
	Ethylene glycol	9.02	Na
Cu-Ba	Iso-propanol	35.5	-
	Ethylene glycol	7.58	-
Cu-Co	Iso-propanol	34.7	19.5
	Ethylene glycol	7.95	Na
Cu-Mn	Iso-propanol	36.6	19.4
	Ethylene glycol	7.28	Na

Table 4. Conversion Liquid Product

CATALYST	CONVERSION	% MOL CONCENTRATION
Cu-Ag	Hydrogen	73.7
	CO2	1.39
Cu-Ba	Hydrogen	72.9
	CO2	0.59
Cu-Co	Hydrogen	83.0
	CO2	-
Cu-Mn	Hydrogen	69.4
	CO2	2.69

Table 5. Conversion of Gas Sample

4.3. DISCUSSION

Based on the result obtained in table 3, it is obvious that the product favoured for this project which is 1,3-propanediol is not exist in the final product. The liquid GC graph indicated that only iso-propanol exist after 8 hours of reaction. In contrary, by looking at the result of gas sample for GC, the peak for hydrogen gives highest concentration. Supposedly, hydrogen gas peak should not be visible in the graph, since the reaction is only considered successful when the hydrogen is fully reacted with the sample. Here are the lists of all circumstances and possible reasons that contribute to the result.

PROBLEMS	LIMITATION/MODIFICATION
<p>Limited sources of information. The actual operating pressure and temperature for hydrogenolysis process of sugarcane is unknown.</p>	<p>Follows glycerol operating condition. May not be compatible.</p>
<p>Optimum working temperature for catalysts between 400°C-600°C. High operating P/T, high conversion of products.</p>	<p>Equipment limitation. For safety purposes, experiment cannot be conducted in the actual condition.</p>
<p>The amount of sugarcane bagasse and catalyst is for the reaction is limited. Only 5g of sugarcane can be reacted in one run for safety purposes</p>	<p>The volume of glass cylinder in parr reactor is for the laboratory purpose.</p>
<p>Hydrogen gas is produced actively by reformation of biomass over low temperature (200°C) and supported metal catalyst.</p>	<p>In GC result, high concentration of Hydrogen gas obtained. Maximum operating T for parr reactor is 300°C.</p>

Table 6. Modification/Limitation for Repeating Experiment

CHAPTER 5 - CONCLUSION

5. 1. CONCLUSION

After going through all the results, here we can conclude that the study of catalyst that can obtain high selectivity and conversion of 1,3-propanediol as the product from solid biomass is still needed a modification and further development in the future.

5. 2. RECOMMENDATIONS

Based on table 6 in the discussion column earlier, the limitations and modifications can actually be improved for getting better results in the future. First regarding on the analytical equipment that been used. For example BET. This equipment is vital for determining the characteristic of catalyst surface. However, due to limited quantity of this equipment in the lab and long queue, this analysis can't be conducted. The same case goes to the reactor used for the project, which is parr reactor. Besides, this reactor was designed for the laboratory scale. Thus, the experiment can't be simply conducted following the references and sources that we obtained from the journals and articles. Some modifications must be made before running the experiment. Because of this, it can be one of the reasons why the experimental results obtained is not like what is expected. Below are the lists recommended for improvements for the future project:

- Equipments used for characterization is limited in laboratory. Long queue, equipment defect and time constrain.
- Reactor used is designed for lab purposes. Limited to certain T/P, experiment can't be conducted in actual condition.
- Limited sources(journals, articles etc.)
- Limited time given to conduct experiments

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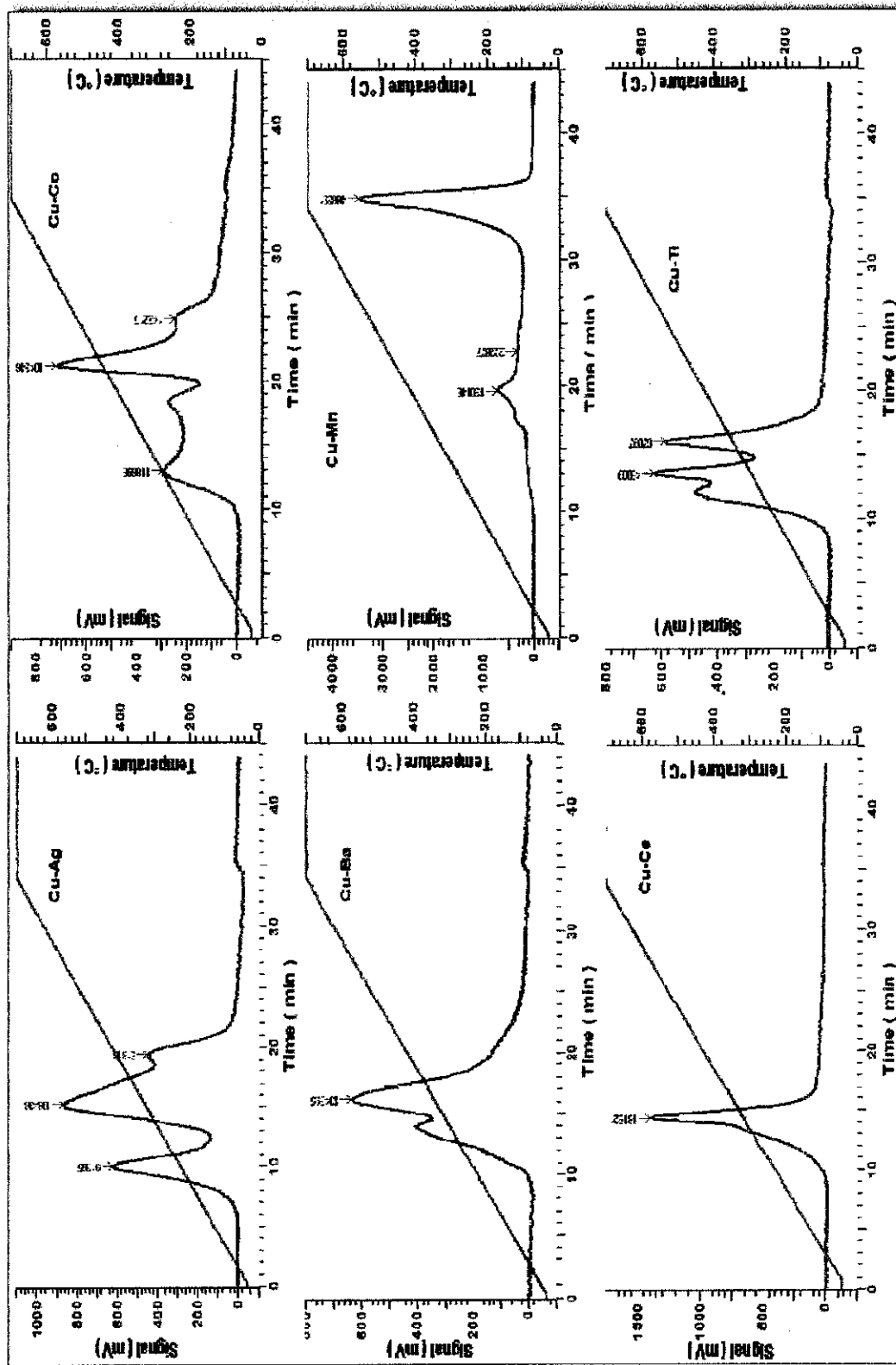
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APPENDIXES

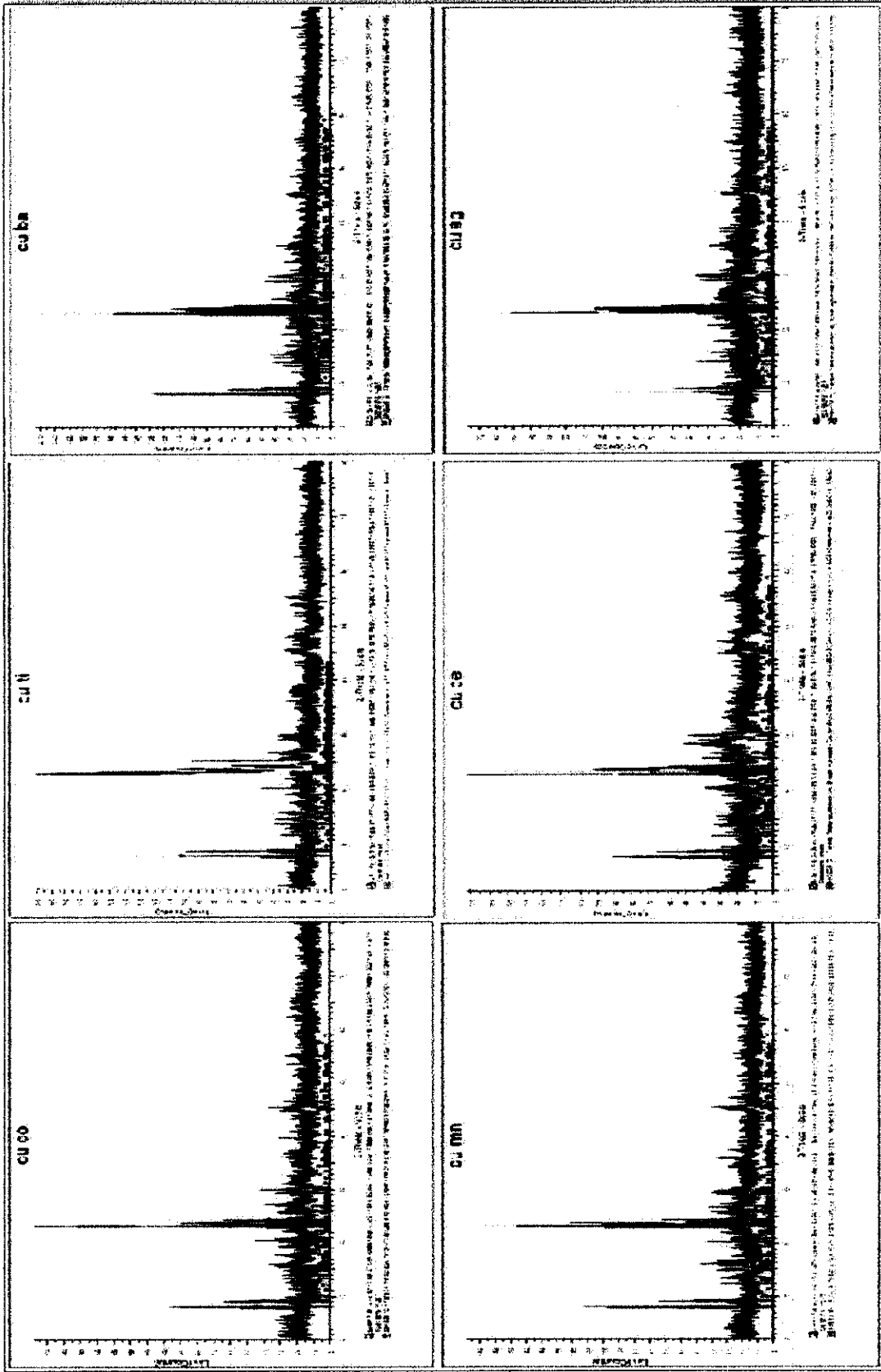
1. GANTT CHART AND KEY MILESTONE FYP II

No	Details/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Meeting with Supervisor	X	X	X	X	X	X	X	X	X	X	X	X	X	X
2	Calcination of Support	X	X	X	X	X	X	X	X	X					
3	Catalyst Preparation <ul style="list-style-type: none"> • Impregnation • Drying • Activation 	X	X	X	X	X	X	X	X	X	X	X	X		
4	Catalyst Characterization <ul style="list-style-type: none"> • XRD • BET • TPD • TPR 	X			X				X				X		
5	Raw Material Preparation		X	X	X	X	X	X							
6	Catalytic Testing <ul style="list-style-type: none"> • Hydrogenolysis Process 				X	X	X	X	X	X	X	X	X	X	
7	Submission of Progress Report													X	
8	Submission of Dissertation														X

2. TPR RESULTS

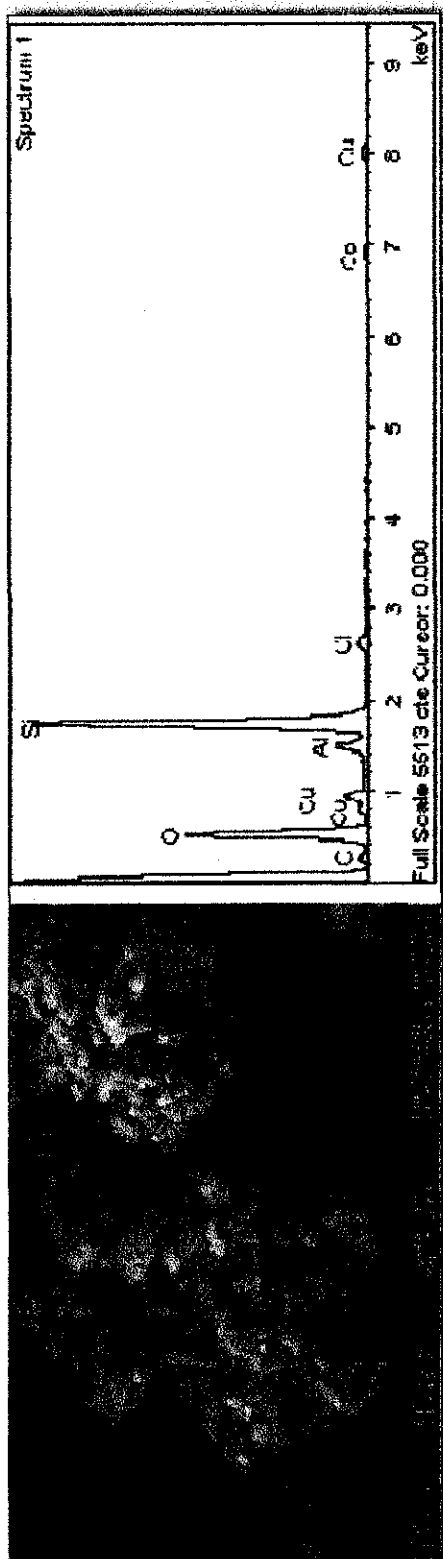


3. XRD RESULTS



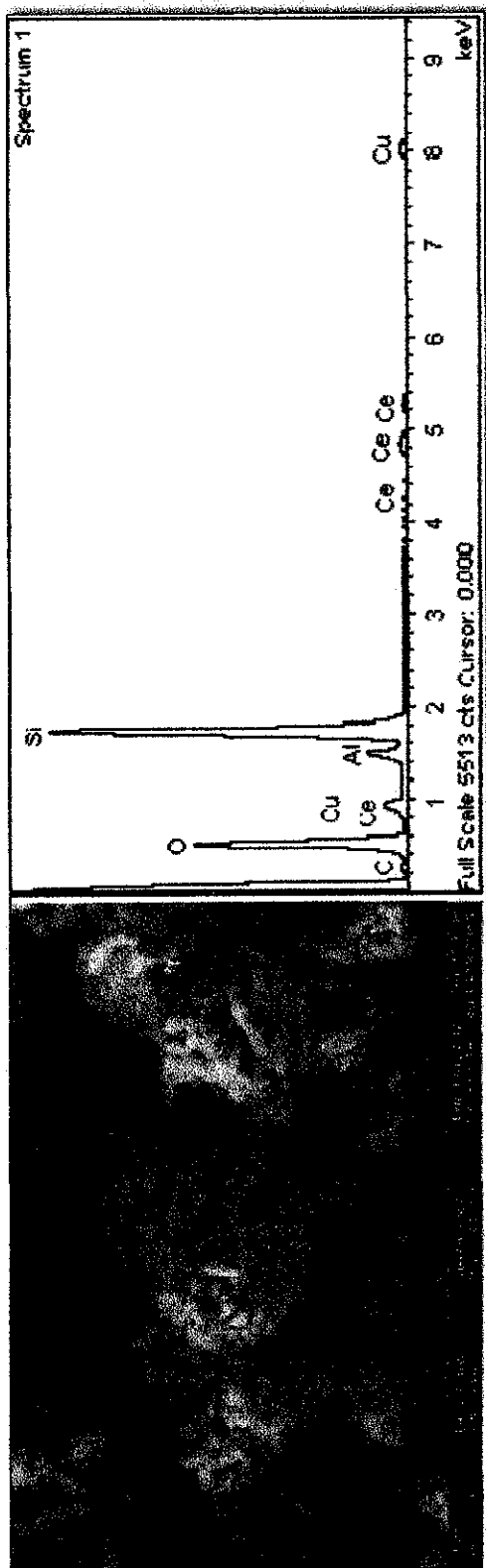
4. FESEM RESULTS

5.1. Cu-Co



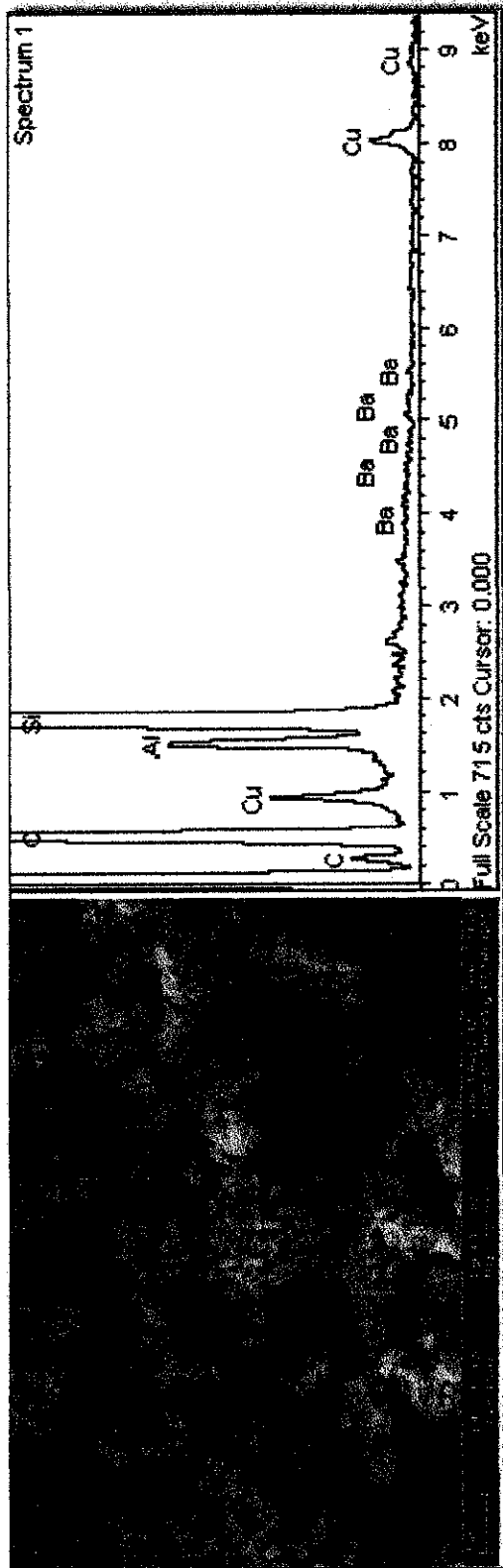
Element	Weight%	Atomic%
C	3.89	6.21
O	58.18	69.64
Al	2.38	1.69
Si	30.12	20.54
Cl	1.05	0.57
Co	1.34	0.44
Cu	3.04	0.92

5.2. Cu-Ce



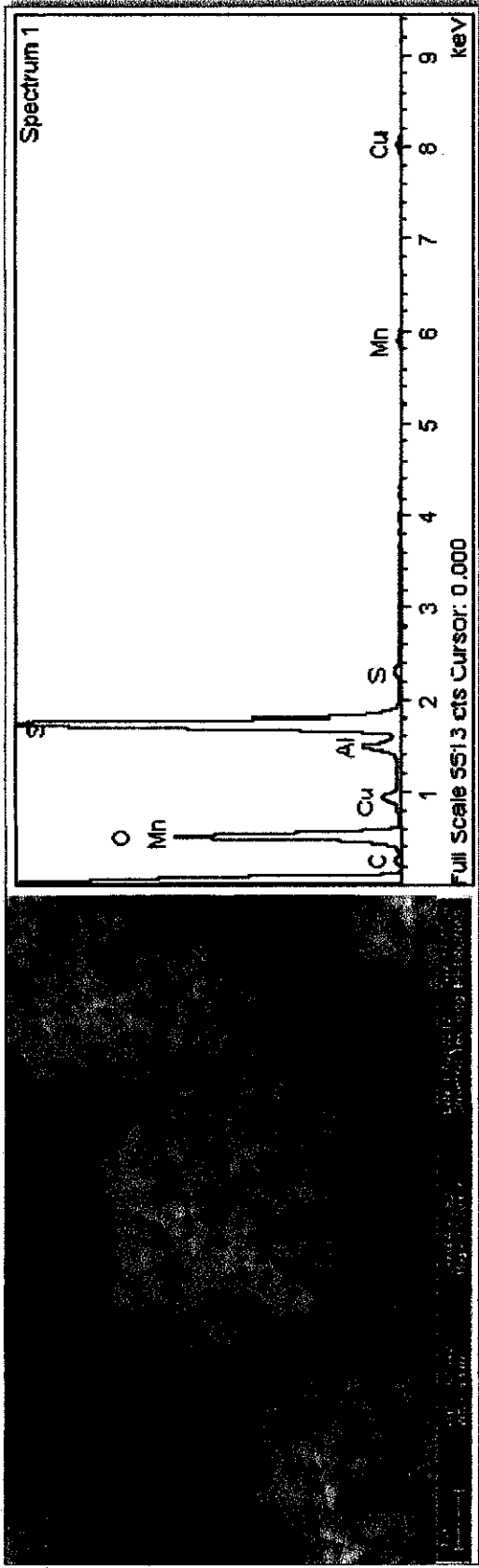
Element	Weight%	Atomic%
C	7.66	12.03
O	56.64	66.79
Al	2.34	1.64
Si	27.00	18.13
Cu	3.41	1.01
Ce	2.96	0.40

5.3. Cu-Ba



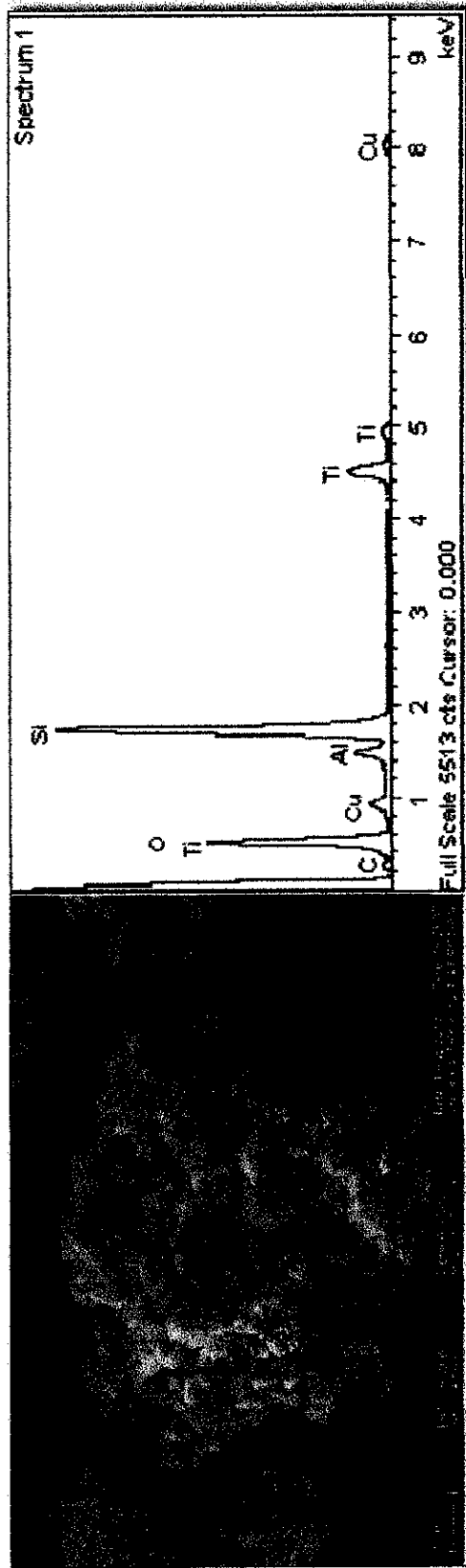
Element	Weight%	Atomic%
C	12.84	19.13
O	54.98	61.50
Al	2.12	1.40
Si	26.74	17.04
Cu	3.26	0.92
Ba	0.07	0.01

5.4. Cu-Mn



Element	Weight%	Atomic%
C	9.25	14.01
O	57.79	65.68
Al	2.17	1.46
Si	27.36	17.71
S	0.39	0.22
Mn	0.82	0.27
Cu	2.21	0.63

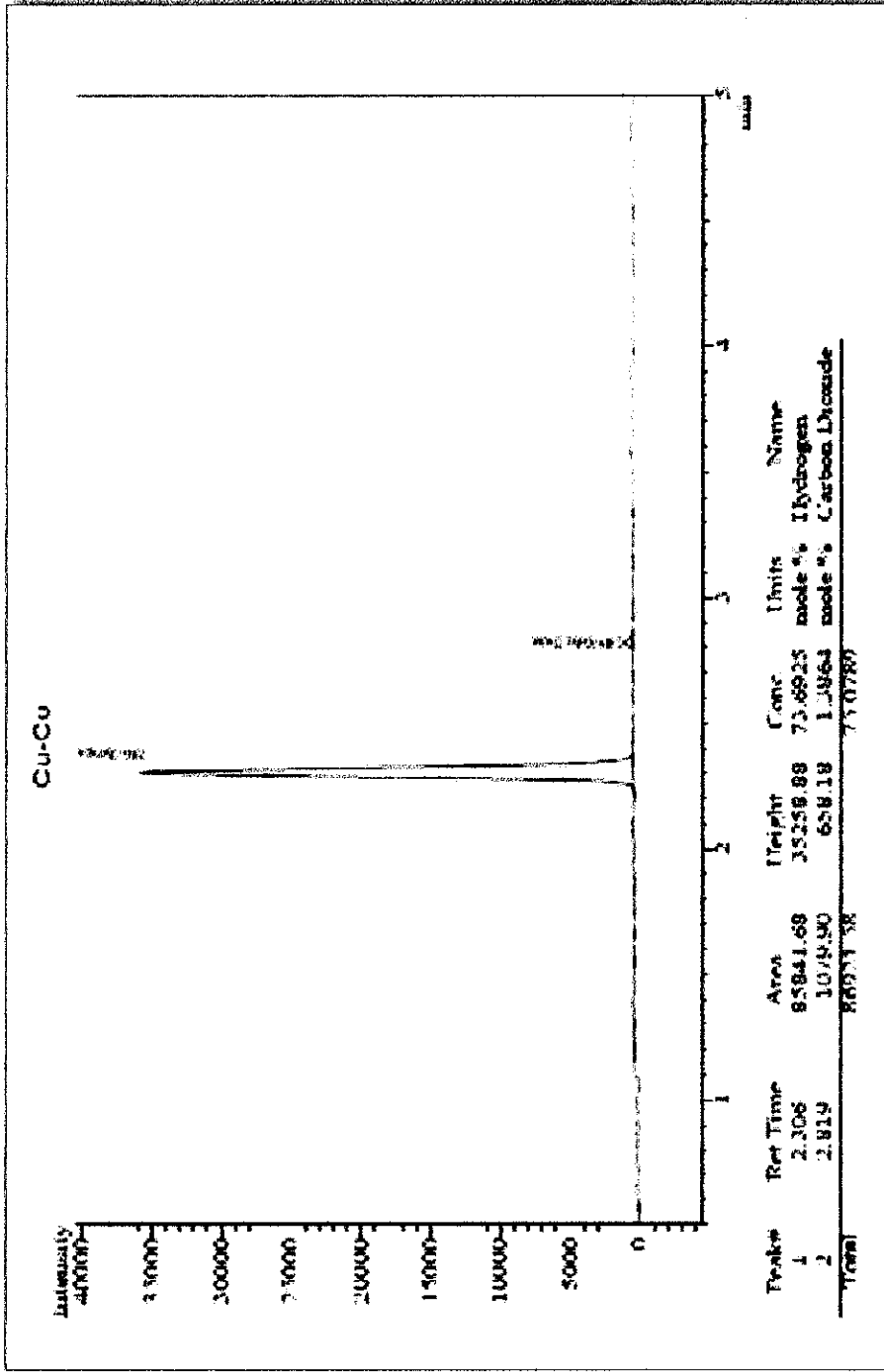
5.5. Cu-Ti



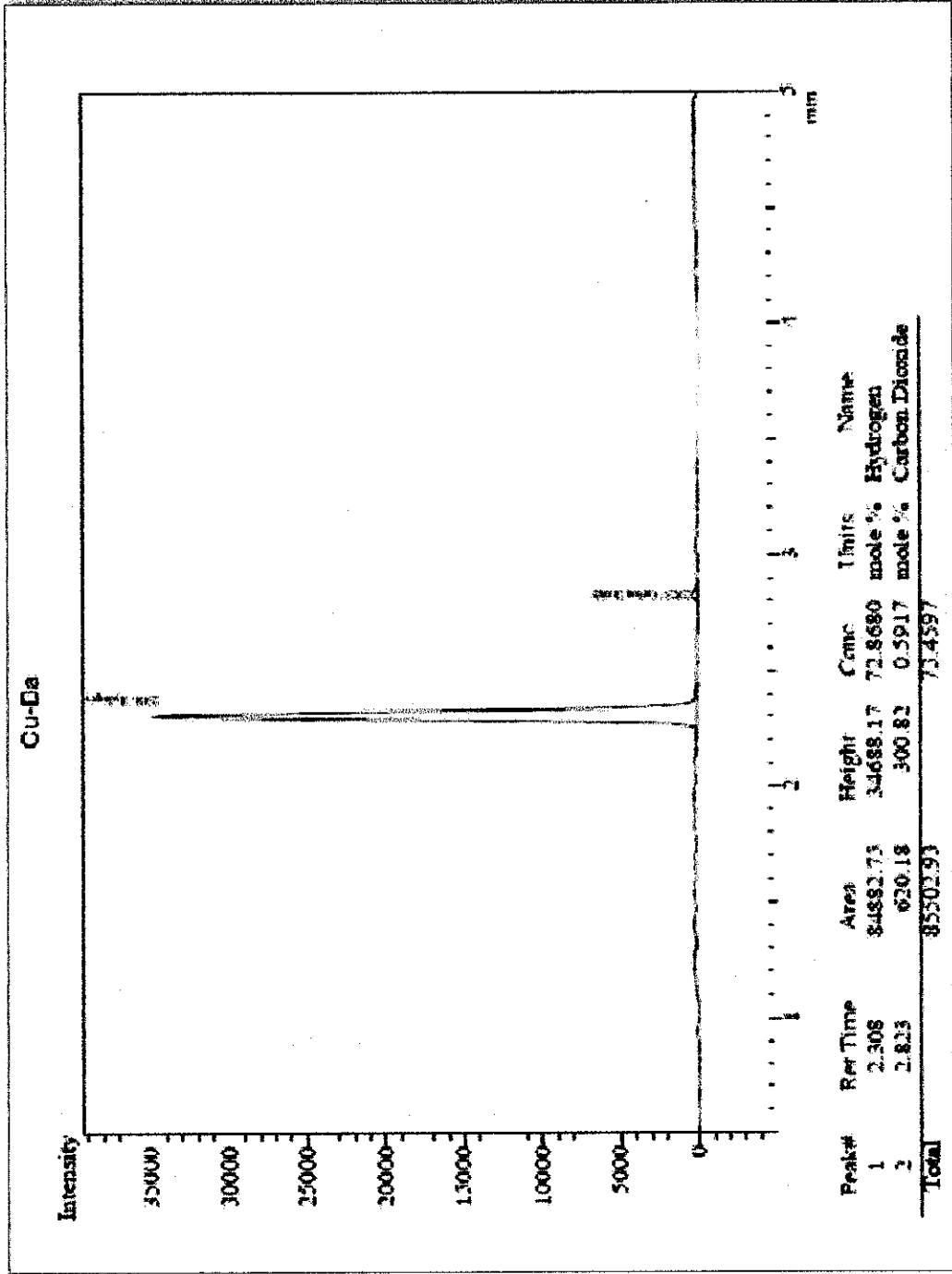
Element	Weight%	Atomic%
C	8.79	13.66
O	56.93	66.39
Al	1.90	1.31
Si	22.89	15.21
Ti	6.72	2.62
Cu	2.77	0.81

5. GAS CHROMATOGRAPHY (GAS SAMPLE)

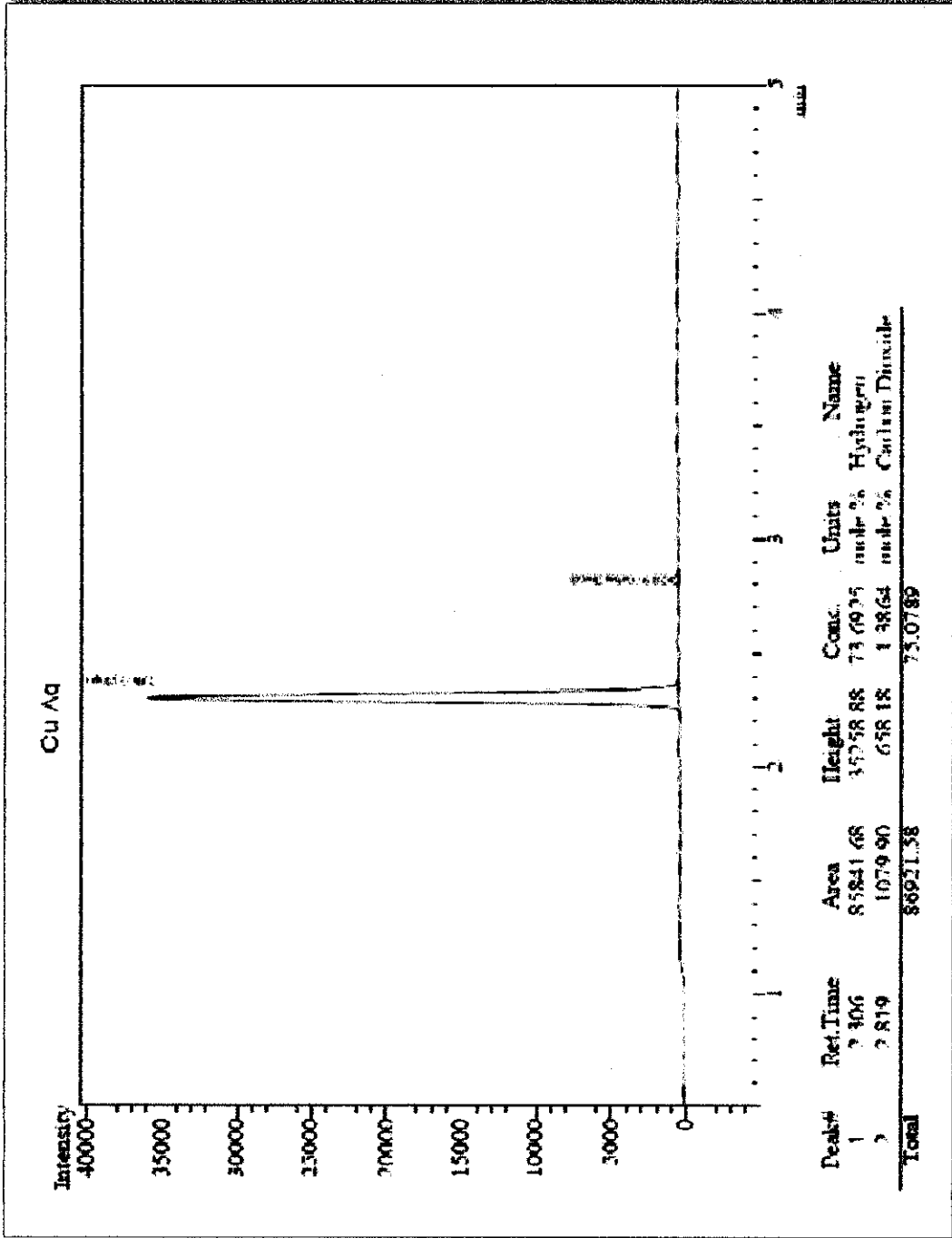
6.1. Cu-Co



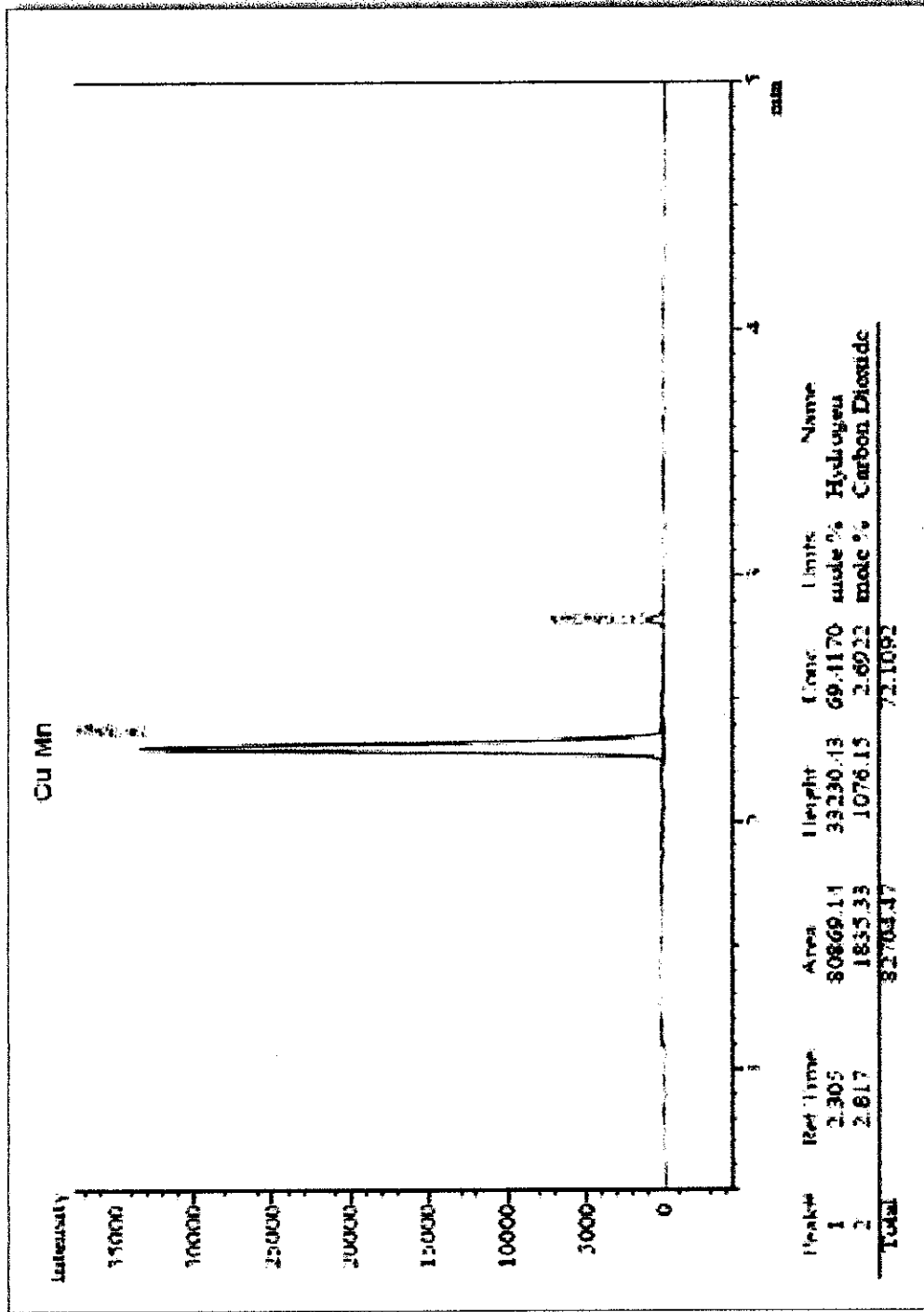
6. 2. Cu-Ba



6.3. Cu-Ag

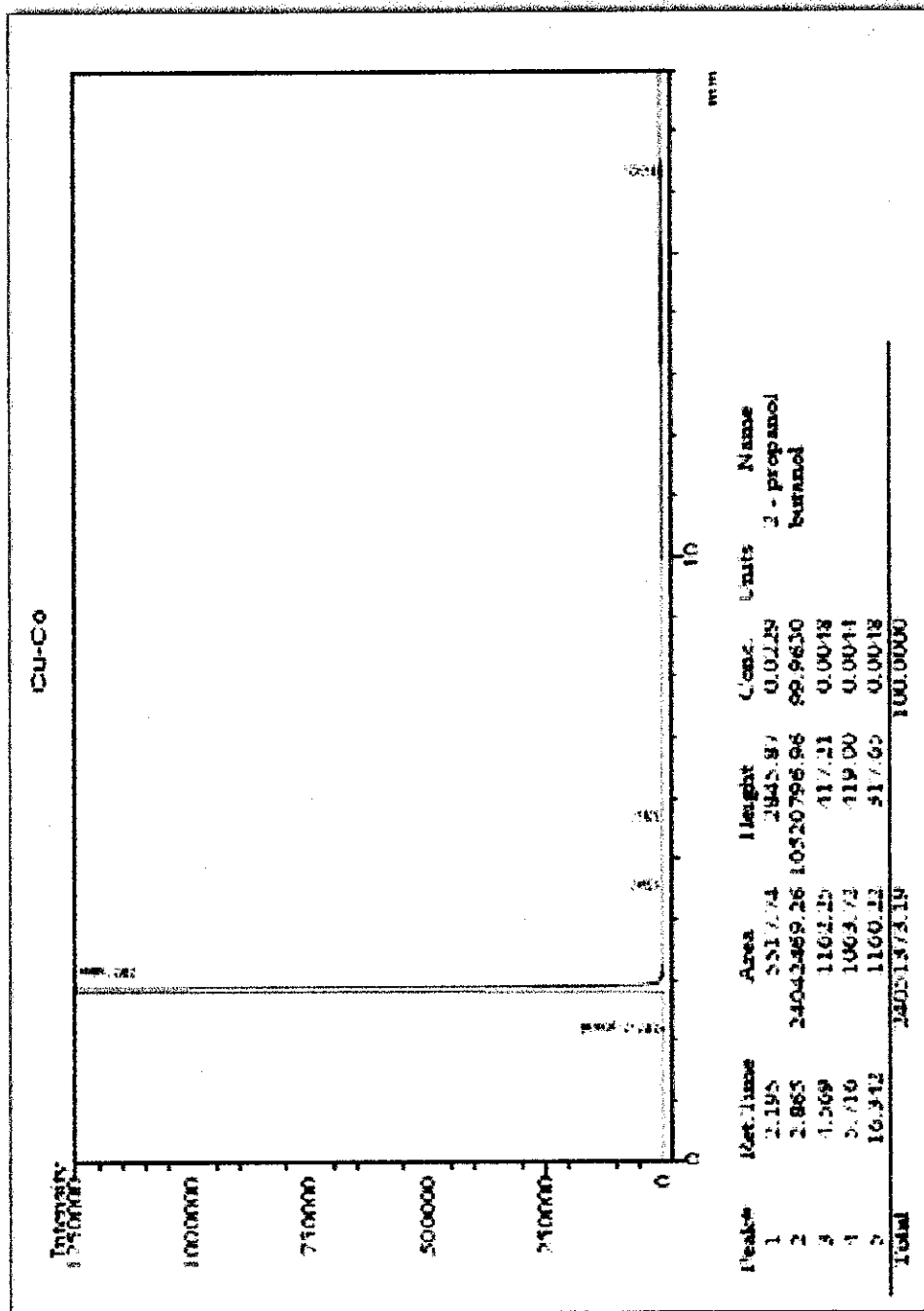


6.4. Cu-Mn

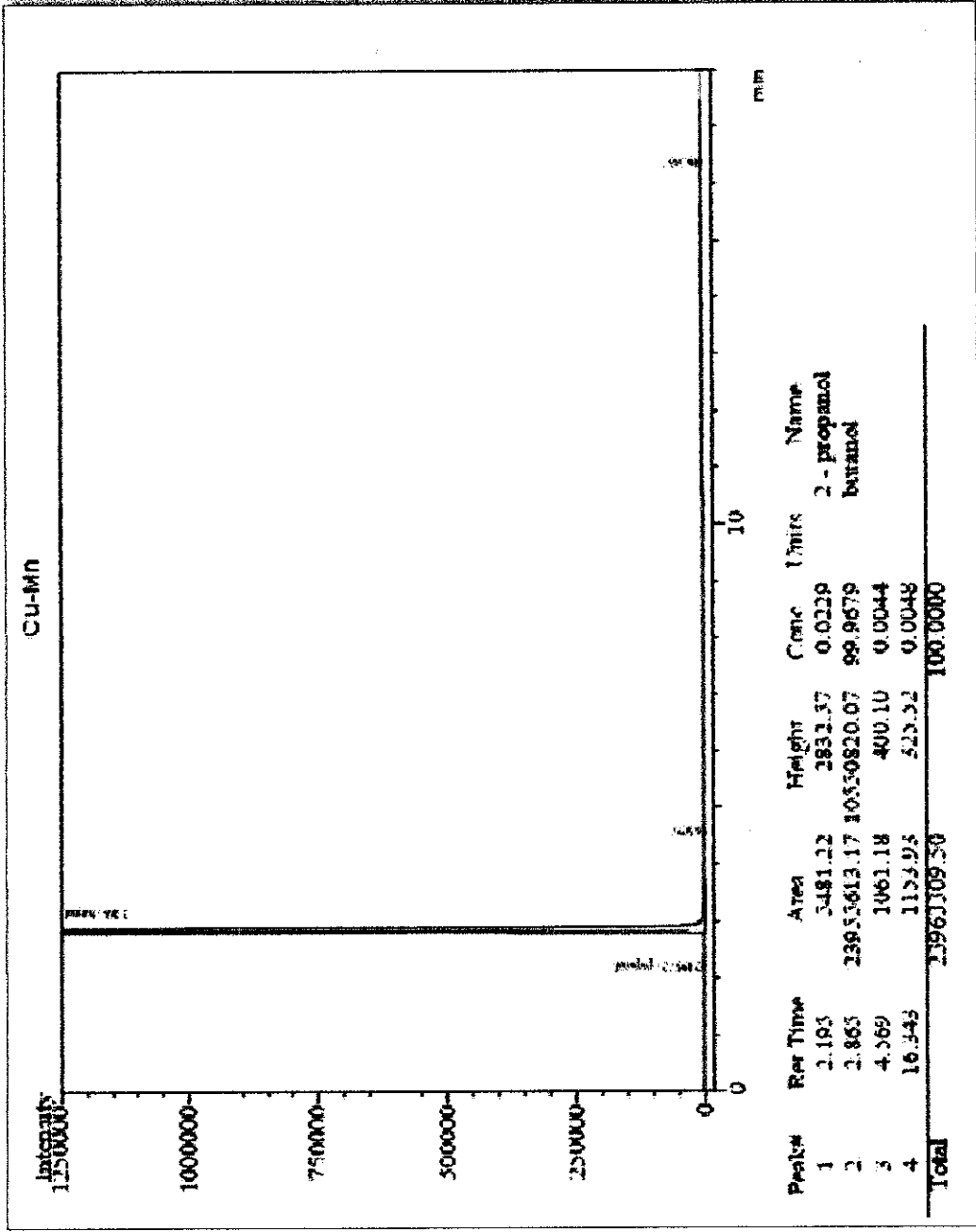


6. GAS CHROMATOGRAPHY (LIQUID SAMPLE)

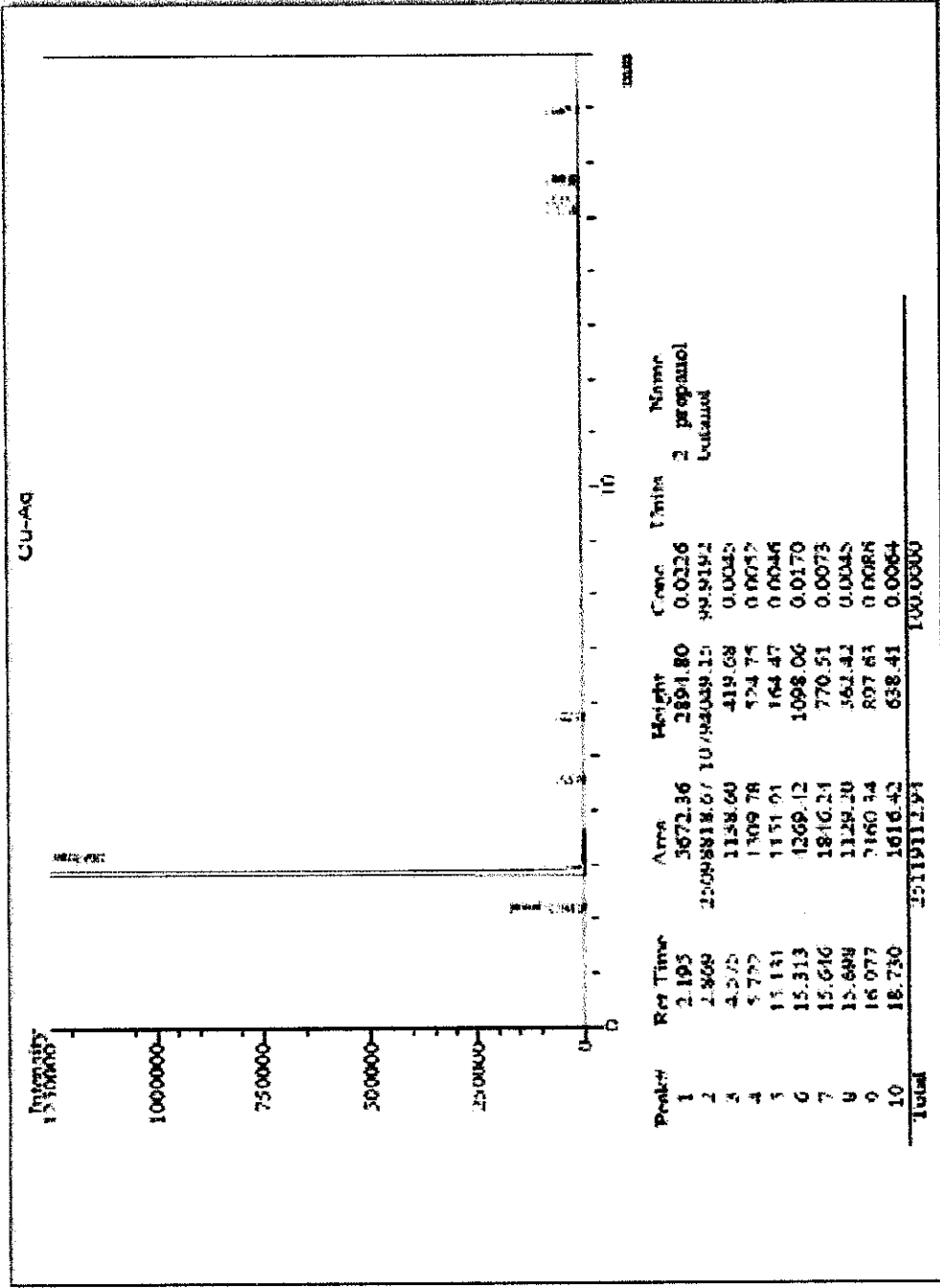
6.1. Cu-Co



6.2. Cu-Mn



6.3. Cu-Ag



6. 4. Cu-Ba

