METHANOL SYNTHESIS USING CU/ZNO/AL$_2$O$_3$ CATALYST IN BLENDED SOLVENT

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CERTIFICATION OF APPROVAL

Methanol Synthesis using Cu/ZnO/Al_2O_3 Catalyst in Blended Solvent

by

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Chemical Engineering Programme
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Approved by,

(Dr. Chandra Mohan)

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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.

NUR AMIRA ZULKARNAIN

ABSTRACT

The objective of this project is to study the effect of product selectivity on the reaction of syngas and prepared $Cu/Zn/Al_2O_3$ catalyst at low-temperature for methanol synthesis via blended solvents in a 3 phase slurry reactor. The operating condition for this process will be as low as 150C and 30 to 50 bar of pressure. In order to have the catalytic surface reaction to occur, $Cu/ZnO/Al_2O_3$ catalyst need to be prepared first followed by chemical reaction to produce methanol via blended solvent in 3 phase slurry reactor. Two types of blended solvents have been chosen for this project. The first blended solvent consists of 50% of each butanol and n-hexane, while the second blended solvent consists of 25% of each butanol, n-hexane, toluene and iso-pentane. It can be concluded that methanol was successfully synthesized using $Cu/ZnO/Al_2O_3$ prepared catalyst without involving the deactivation process of catalyst.

ACKNOWLEDGEMENTS

I would like to express the deepest appreciation to my supervisor, Dr. Chandra Mohan, who has the attitude and the substance of a genius: he continually and convincingly conveyed a spirit of adventure in regard to research, and an excitement in regard to teaching. Without his guidance and persistent help this dissertation would not have been possible. I would like to thank my group members, Shaheen, Sazrin, Ariff and Lesmaulada, who's demonstrated commitment in teamwork in order to finish up this project fruitfully.

In addition, thank you to Associate Professor Dr. Anita Ramli, my co-supervisor for the first semester as well as both chemical and mechanical departments' technician who put their afford in giving their hand and time to guide and help in accomplishment of this project. I also want to thank the Universiti Teknologi PETRONAS for permission to include copyrighted photographs as part of my thesis/dissertation.

Last but not least, I would like to thank my family especially, mum and dad for helping me to always get inspired and for the strength that they give me in order to move on in highs and lows.

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ABBREVIATIONS AND NOMENCLATURES

Abbreviation	Meaning
AAS	Atomic Absorption Spectrometry
SEM	Scanning Electron Microscopy
TPR	Temperature Programmed Reduction
TGA	Thermo Gravimetric Analyzer
XRD	X-Ray Diffraction
BET	Brunauer, Emmett, and Teller Surface Area and Pore Size Analyzer
TPD	Temperature Programmed Desorption
TPO	Temperature Programmed Oxidation
RPM	Revolutions per minute
MeOH	Methanol
Mod.	Moderate

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Methanol was first produced on 1900 using destructive distillation of wood. In 1923 BASF produced the first synthetic methanol on a large scale. It is a high pressure synthesis on a $Zn/Cr2O_3$ catalyst at 300 to 400 °C and above 300 atm. The $Zn/Cr2O_3$ catalyst and the high pressure process were the most effective available technology until in 1966, ICI developed a substantially more active $Cu/ZnO/Al_2O_3$ catalyst which enable methanol to be synthesized at much lower temperature and pressure. The advantages of the latest technology were;

1. Reduced compression power
2. Longer catalyst life
3. Larger capacity, single-train converter designs
4. Improvement in productivity of methanol (from 770 tons to 1120 tons per million cubic meters of natural gas)

1.2 Problem Statement

Methanol has been produced in the industry for years using high operating pressure and temperature. The operating pressure range from 50 bar up to 150 bar while the operating temperature range from 200°C to 300°C. Conventionally, methanol is synthesis via two phase reactor which involves feed gases and solid catalyst only and the existing reactors currently in the industry are quench reactor, tubular isothermal reactor, annular gas reactor and adiabatic radial reactor. The problems involved in the conventional production process are

- getting the uniform temperature distribution,
- stabilizing the heat extraction and
- Improving the catalytic activity/selectivity (lowering the reaction temperature).

Producing methanol at high operating condition is not cost effective as it might lead to early deactivation of catalyst and requirement of high compression power

1.3 Objective and Scope of Study

1. Producing Cu/ZnO/Al$_2$O$_3$ catalyst which also involves characterizing and comparing it with the industrial property of it. Characterization on catalyst will also be done on spend and fresh catalyst. Suggested tests are;

   a) SEM : Scanning Electron Microscope

   b) TPR : Temperature Programmed Reduction
   c) TGA : Thermo Gravimetric Analyzer
   d) XRD : X-Ray Diffraction
   e) BET : BET Surface Area
   f) TPD : Temperature Programmed Desorption\

2. Studying the effect of product selectivity on the reaction of hydrogen and carbon monoxide using prepared Cu/ZnO/Al_2O_3 catalyst for synthesizing methanol via blended solvents in a 3 phase slurry reactor. The blended solvents consist of;

   a) n-hexane (paraffin)
   b) iso-pentane (iso-paraffin)
   c) toluene (aromatics)
   d) 1-butanol (alcohol)

CHAPTER 2:

LITERATURE REVIEW

2.1 Methanol

Methanol, with formula CH_3OH is also known with others name which are methyl alcohol, carbinol, wood alcohol, wood naphtha or wood spirits. This chemical is colorless and stable but very flammable and is "hygroscopic meaning it absorbs water" or miscible in water. It has a melting point of -98°C and boiling point of 64.7°C with specific gravity of 0.79. Methanol can be produced from any carbon-based source such as wood waste, natural gas, coal and seaweed.

In industry, methanol is primarily produced by steam reforming natural gas which creates a synthesis gas. Then syngas is then fed into a reactor vessel which contains a catalyst to produce methanol and water vapor. Distillation then removes the vapor from the methanol. Although other carbon-based sources can be used, natural gas is economically favored. (Source: http://library.thinkquest.org/04oct/00927/methanol.htm)

"By tradition, methanol is principally used to produce formaldehyde, methyl tertiary butyl ether (MTBE) and acetic acid as depicted in the diagram below. To a lesser extent, methanol is used as a general solvent and as fuel and for producing other chemicals. Global demand for methanol amounts to about 32 million tons per year, with growth rates at or near GDP. The demand corresponds to the capacity of about 35 million tons which is available worldwide." (Source: www.lurgi.com)

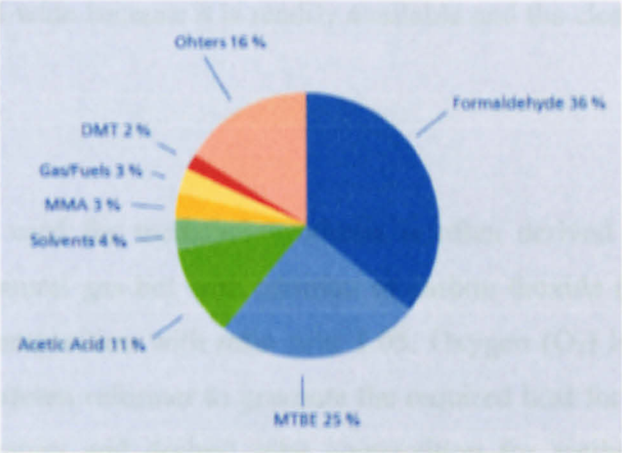

Figure 1: Demand for Methanol Worldwide

Methanol is a good fuel alternative source as it *produces lower emission, yields higher performance, has lower risk of flammability compare to gasoline* and *can be produced from any carbon-based source*. But the drawback of it, is, it is *more corrosive* compare to gasoline that will require parts that come into contact with it must be able to withstand the corrosive ability of methanol. Not only that, methanol is very dangerous to human being although a little amount of methanol still can be detected in human body. Methanol may lead to blindness, injury to nerves system or even death if it is fatally exposed.

2.2 Methanol Synthesis Process

In principle, any hydrocarbon containing fuel can be used in the production of synthesis gas for methanol plants. Natural gas is used in more than 80% of methanol plants world-wide because it is readily available and the cleanest, cheapest source of syngas.

Synthesis gas used for methanol synthesis is often derived directly from steam reforming of natural gas but with addition of carbon dioxide (CO_2) into the hydrogen (H_2) rich composition with ratio near 1.05. Oxygen (O_2) is added rather than air in secondary steam reformer to generate the required heat for achieving the desired outlet temperature and desired inlet composition for methanol synthesis while avoiding introduction of nitrogen gas (N_2) to the synthesis reactor. Reaction path for methanol synthesis was well known by;

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (2)$$

$$CO + 2H_2 \rightarrow CH_3OH \quad (3)$$

Figure 2: Reaction path for methanol synthesis process

The first reaction refers to water gas shift reaction of carbon monoxide with water to form carbon dioxide and hydrogen. This wills followed by hydrogenation of carbon dioxide with three mol of hydrogen to form methanol which is the main product and water as the byproduct. Carbon monoxide will reacted with hydrogen as well through hydrogenation to form the main product.

Thorough studies has been done on low-temperature methanol synthesis process utilizing alcohol as the solvent, and through the studies, a new reaction path for methanol synthesis using alcohol as solvent and CO_2 containing syngas has been proposed by P. Reubroycharoen, the author of "Development of A New Low-temperature Methanol Synthesis Process" paper which is as follow;

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (1)$$

$$CO_2 + \frac{1}{2}H_2 + Cu \rightarrow HCOOCu \qquad (2)$$

$$HCOOCu + ROH \rightarrow HCOOR + CuOH \qquad (3)$$

$$HCOOR + 2H_2 \rightarrow CH_3OH + ROH \qquad (4)$$

$$CuOH + \frac{1}{2}H_2 \rightarrow H_2O + Cu \qquad (5)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad (6)$$

Figure 3: New process path for methanol synthesis using alcohol as solvent for the reaction

The difference between the previous equation and the later one is the involvement of alcohol as the solvent which lead to a new process which called esterification (3). The later process consists of three main steps which are synthesis of formic acid from CO_2 and H_2, formation of ethyl formate from an esterification of formic acid and methanol, and formation of methanol from a hydrogenation of ethyl formate.

Table 1: Operating Characteristic of Low-Pressure Methanol Synthesis Fixed-Bed Reactor

Characteristics	**Quench**	**Tubular Isothermal**	**Annular gas/ Liquid HE**	**Adiabatic-radial**
Processes using reactor	ICI	Linde, Lurgi, TopsØe	Mitsubishi Heavy Industry	Kellogg, TopsØe
Operating Experience	Extensively/ Widely		Recent	Recent/Growing
Operating Conditions				
Pressure(bar)	50-100	40-100	50-80	50-150
Pressure drop (bar)	6-10	3.5-4	2.5	Lowest (thin bed)
Temperature Range (°C)	220-280	220	240-260	200-300
Exit MeOH conc. (%)	<7	3-8	14	3.5-5
Catalyst				
Yield, kg/L-h	Low (bypass)	Mod.-high		High(high effectiveness)
Activity	Moderate (mod.)	Mod.-high	High, >1kg/L-h	High(high effectiveness)
Selectivity to MeOH	<99	>99 (few byproducts)		
Catalyst life (yrs)	3	5		
Reactor				
No. of reactor(s)	1	1	1	3-4
Reactor type	Tray (3-6beds)	Tube-shell	Annular	Radial
Cooling method	**Cold quench**	**Boiler feed-water**	**Water & gas**	**Interstage cooling**
Size (m)	0.8(bed) x 6	5 x 6	20 x 0.085	Spheres, 3-5 diameter
Heat removal	Difficult/unstable	Simple/Very Stable	Mod. /Simple	Moderate/Simple
Thermal efficiency (%)	Low	High(high quality system)	High	Moderate-Low
Relative cost	Low	High	Moderate	Low
Major advantages	Proven reliability	1. High Thermal Efficiency 2. High Selectivity 3. Stable Temperature	1. Ideal T profile 2. Least catalyst 3. High MeOH conc.	1. High production rate 2. Low ΔP
Major disadvantages	1. Low thermal efficiency 2. Catalyst bypass		1. Complex 2. High cost reactor	1. High outlet T, P 2. Reduced Selectivity

The above table shows different methods in synthesizing methanol. Generally, the reactors are differentiating primarily by methods of removing heat generated during the reaction as the reaction that takes place is an exothermic reaction. The processes described above are using 2-phase reactor where both gas (reactant) and solid (catalyst) phase are present during the reaction. It can be observed that the operating conditions are high for both pressure and temperature and it is very hard to maintain and control the desire temperature especially when it involve exothermic reaction therefore I do think that it is the main reason on why the reactors are differentiate base on method of cooling or removing heat.

For my project, methanol will be synthesized in a process which involve 3-phase reactor. The reaction will be represented by gas phase (the feed gas -syngas), liquid (the solvent(s)) and solid (the catalyst). Therefore it is believe that the temperature can easily be maintained without the need of high technology and high cost heat removing system.

2.2.1 Comparison on Different Methanol Synthesis Papers

Researches through other papers are important before making up mind on condition suitable for the process. This is to make sure similar processes exist is not repeated and a modification to achieve better results can be made.

Table 2: Different Process on Synthesizing Methanol

	Title of Papers			
Characteristic	Development of a new low-temperature methanol synthesis process	A new method of low-temperature methanol synthesis on Cu/ZnO/Al$_2$O$_3$ catalyst from CO/CO$_2$/H$_2$	Catalytically active supercritical fluid to accelerate methanol synthesis	
Reactor Operating Condition	Flow type Semi batch	Continuous Reactor	Converted fixed-bed	Converted fixed-bed
Pressure (bar)	50	30	55	30.4
Temperature range (K)	273-443	443	538	507.6
Speed of stirrer (rpm)	1260	2000	-	-
Catalyst				
Catalyst Preparation	Co-Precipitation	Impregnation Method		
Catalyst Used	Cu/ZnO (3.0g)	Cu/ZnO/Al$_2$O$_3$	Cu/ZnO based of ICI Co. (0.50g)	Cu/ZnO based of ICI Co. (0.50g)
Solvents	Different type of alcohols	Ethanol	2-Butanol	n-hexane
Results	Solvents use and results for the reaction are:	Result gathered		

<table>
<tr><td></td><td>• Solvents;
o 1 – Ethanol
o 2 – 1-Propanol
o 3 - 2-Propanol
o 4 – 1-Butanol
o 5 – 2-Butanol
o 6 – *Iso*-Butanol
o 7 – 1-Pentanol
o 8 – 2-Pentanol
o 9 – 1-Hexanol</td><td>using uncalcined catalyst with Cu diameter 22nm and reduction Temperature at 493K. Molar ration of Zn/Cu is 1/1 shows the highest conversion and selectivity</td><td></td><td></td></tr>
<tr><td>**Total carbon conversion (%)**</td><td rowspan="2">• Results;<table><tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td></tr><tr><td>33.5</td><td>35.2</td><td>44.4</td><td>34.4</td><td>47.0</td><td>29.9</td><td>34.2</td><td>44.0</td><td>34.5</td></tr><tr><td>33.0</td><td>34.5</td><td>44.0</td><td>34.3</td><td>46.5</td><td>29.8</td><td>34.1</td><td>43.3</td><td>34.4</td></tr></table></td><td>14.4</td><td>48.1</td><td>21.4</td></tr>
<tr><td>**Selectivity (%)**</td><td>96.4</td><td>90.7</td><td>98.1</td></tr>
<tr><td>**Byproduct**</td><td>Methyl Formate & Ester (HCOOR)</td><td>Ester</td><td>Ester</td><td>CH_4</td></tr>
</table>

2.3 Catalyst

In order to produce a new low-temperature methanol synthesis process, varieties of catalysts have been used in a lot of studies and to be named, the catalyst are CuO based, Cu/ZnO based, and ZnO/CrO. For industry operation, the conventional processes are not yet fully satisfactory in respect of economy, yield of end product, simplicity of the operation, space time yield, activity and life of the catalyst. Activity or selectivity properties of supported $Cu/ZnO/Al_2O_3$ catalysts for high-temperature methanol synthesis reaction have been reported in papers by Robinson, however, activity or selectivity properties of supported $Cu/ZnO/Al_2O_3$ catalyst for a new low-temperature methanol synthesis in liquid medium from $CO/CO_2/H_2$ is not clear until now. Below table summarize some of the catalysts that had been used in studies and the disadvantages of them.

Table 3: Comparison on Methanol Synthesis' Catalysts

<u>**Inventor**</u>	<u>**Catalyst**</u>	<u>**Operating Condition**</u>	<u>**Results**</u>	<u>**Drawback**</u>
Wender et. Al	Alkolides and Copper based oxide	T=373-453 K (100 – 180C) P=5.0 – 6.5 MPa (50 – 65 bar)	• High methanol synthesis rate • High one-pass CO conversion	• Trace amount of CO_2 and H_2O in the feed gas or reaction system will deactivate the strongly basic catalyst which lead to ○ High cost for complete

				purification of syngas o High cost for reactivation process of the deactivated catalyst.
R. Yang et. Al	• Cu based oxide. • Using ethanol as promoter to synthesize mathanol	T=443K (170C) P=3.0 MPa (30 bar)	• Low temperature enabled a CO conversion to go as high as 50 -80% • High selectivity.	• Cu oxide based catalyst structurally too weak for use in slurry phase CH_3OH synthesis. • The catalyst undergo attrition at high stirring rate to fine particles.

2.3.1 Catalyst Characterization

Catalyst $Cu/ZnO/Al_2O_3$ will be used for producing methanol to enhance the performance as well as to make sure minimum operating condition can be applied for this project. Catalyst is produced through co-precipitation method instead of using commercialized ICI catalyst. Characterization test on the catalyst produce is important so that results gathered are comparable to the existing process. List of characterization test that had been identified important are as bellow;

Table 4: List of Characterization Test that will be carried out.

No.	**Characterization Test**	**Function/Objective**
1.	AAS (Atomic Absorption Spectroscopy)	• Provides accurate *quantitative analysis* (determining the concentration) for metals in water, sediments, soils or rocks. (Samples are analyzed in solution form, so solid samples must be leached or dissolved prior to analysis.) • Metal ions in a solution are converted to atomic state by means of a flame.
2	SEM (Scanning Electron Microscopy)	• Producing high-resolution images of a sample surface using electrons instead of light waves. • The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's *surface* topography, *composition* and other properties such as electrical conductivity. • Useful for *judging the surface structure* of the sample.
3.	TPR (Temperature Programmed Reduction)	• To *find the most efficient* reduction *conditions* • Analyze *reduction on catalyst surface*
4.	TGA (Thermo Gravimetric Analysis)	• Determine *changes in weight in relation to change in temperature*

		• It can be used to determine characteristics of materials such as *degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues.*
5.	XRD (X-Ray Diffraction)	• Non-destructive technique that reveals detailed information about the *chemical composition and crystallographic structure of materials.* • Useful for *determining the arrangement of the atoms.* • *Yields information about the structure of the crystal.*
6.	BET (Brunauer, Emmett, And Teller Surface Area And Pore Size Analyzer)	• Determining the *surface area* of powders as well as the *pore size distribution* of porous materials • It is an *extension of the Langmuir theory, which is a theory for monolayer molecular adsorption to multilayer adsorption.*
7.	TPD (Temperature Programmed Desorption)	• Method of *observing desorbed molecules from a surface when the surface temperature is increased* • Determining the quantity and strength of the acid sites on alumina, amorphous silica-alumina, and zeolite hence *help to understand and predict the performance of a catalyst.* • Can obtain the following information ~ *the amount and number of different kinds of surface species, the kinetics of the desorption*

		process, the enthalpy of desorption, and differentiation between simple desorption and chemical reaction-desorption
8	TPO (Temperature Programmed Oxidation)	- Characterizing the *nature of deposits (coke) of a deactivated catalyst.* - The *volume of oxygen consumed can tell directly total amount of coke present on the solid.*

2.4 Parr High Pressure Reactor

Below figure is the reactor that will be used in the project.

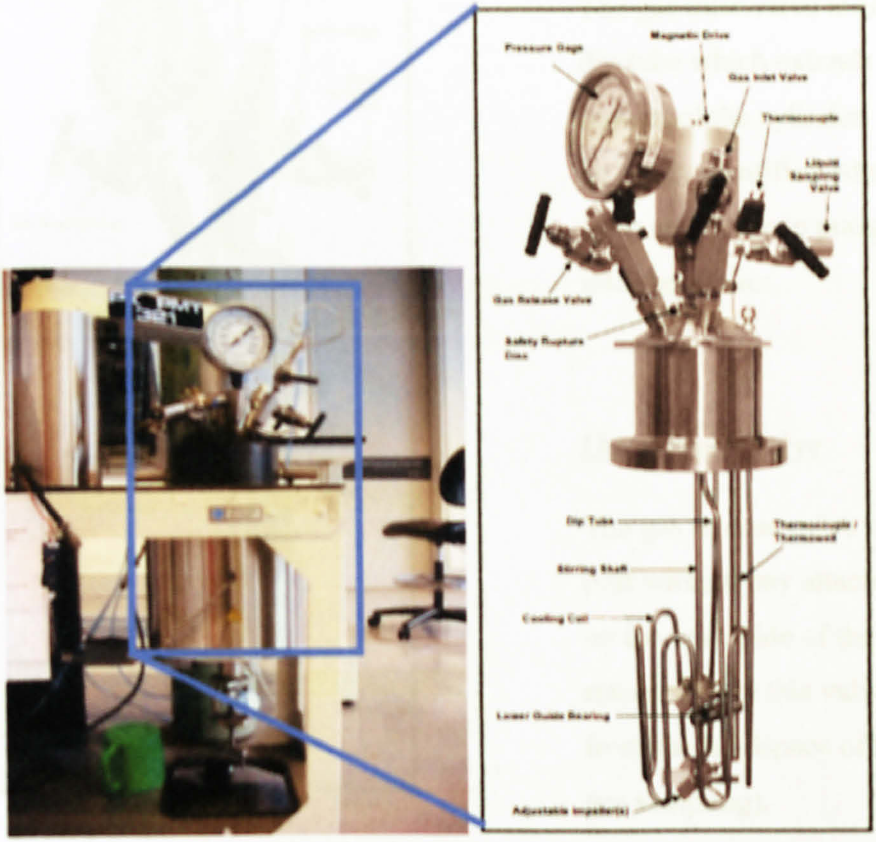

Figure 4: Parr High Pressure Reactor and its parts

2.4.1 Pressure and Temperature Limits

Table 5: Pressure and Temperature Limit for the Reactor

Pressure Limit	Temperature Limit
1450 psig 145 bar	500 °C

2.4.2 Valves and its functions

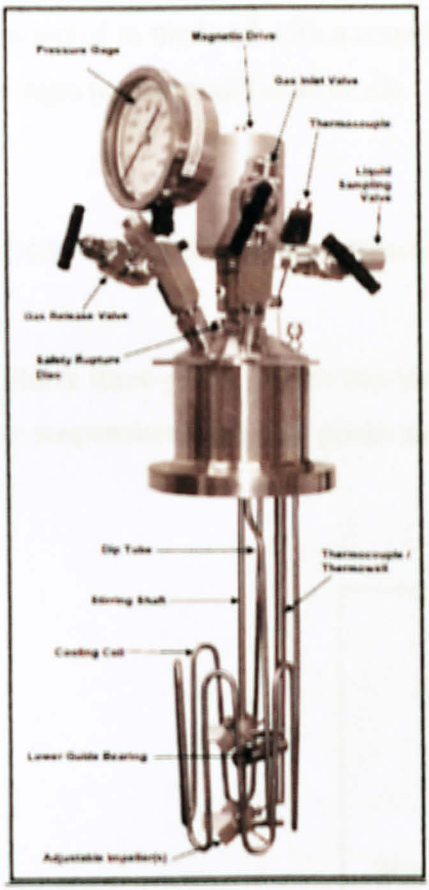

Figure 5: Parts of the reactor and its functions

Gas Inlet Valve

The gas inlet valve is connected to a dip tube which extends to a point near bottom of the cylinder. This valve can be easily identified when the bomb is open and is use to pump feed gaseous into the reactor.

Gas Release Valve

The gas release valve is installed in a port without any attachments installed on the underside of the head. Gas released from this valve will be drawn from the headspace of the vessel (for gas sampling).

Liquid Sampling Valve

The liquid sampling valve is attached to the same fitting as the gas inlet valve and connected to the same dip tube. With this arrangement, incoming gas is always introduced below the surface of the liquid and the operator is provided with a means for clearing the dip tube to be sure that any sample taken during a run will be representative of the charge. This can be done by opening the upper gas inlet valve momentarily to allow the inlet gas to force any liquid in the dip tube back into the reactor before withdrawing a sample from the sampling valve.

Pressure Gauge

A pressure gage, usually 0-5000 psi with a T316 stainless steel Bourdon tube [16], is mounted to the head with a coned adapter fitting. Gages are furnished in a variety of ranges to meet individual needs.

2.4.3 Slurry Three-Phase Reactor System

Slurry three-phase reactor has three phases in which solid catalyst particles are held in suspension in a liquid phase and contacting with gas phase reactant.

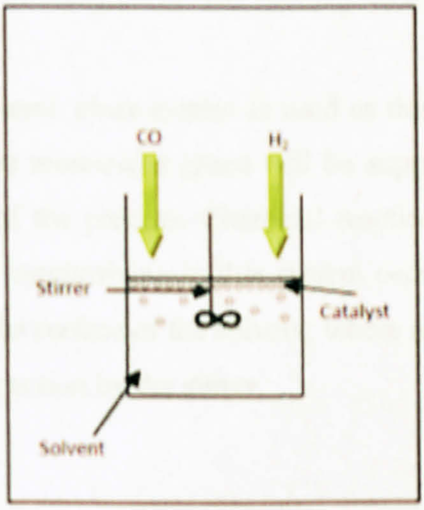

Figure 6: Illustrative picture inside the reactor

Conventional methanol reactors use fixed beds of catalyst pellets and operate in the phase. For my project, I am going to utilize the slurry three phase reactor using catalyst in powder form, and slurries in blended solvents. The solvents act as a temperature moderator and a heat removal medium, transferring the heat of reaction from the catalyst surface via the liquid slurry to the solvent. The stirrer function's is to stir the solvent and catalyst at the same while maintaining the catalyst particle on the surface of the solvent so that catalyst may have contact with the gas reactant and reacted.

2.5 Process involved in Methanol Synthesis Reaction

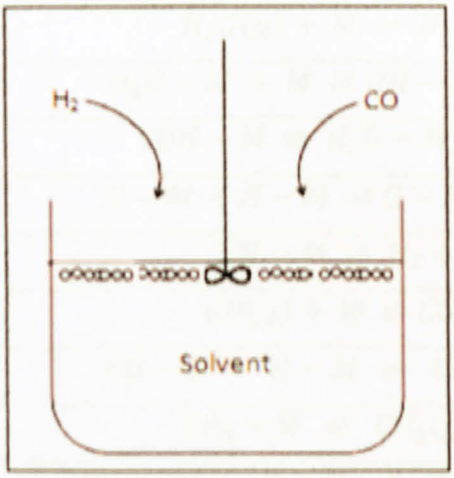

Figure 7: Interfacial Chemical Reaction in Methanol Synthesis Using $CuO/ZnO/Al_2O_3$ Catalyst

In producing methanol, close system is used as this reaction involves gases. Both hydrogen and carbon monoxides gases will be supplied up to 30 bars to the system at the beginning of the process. Chemical reaction between gases, solvent and catalyst for methanol synthesizing in this system occurs in a single layer. The single layer is located at the surface of the solvent, where majority of the catalyst are floating due to the stirring action by the stirrer.

Supplied hydrogen and carbon monoxides gases will sit on the catalyst, dispersed and react. Stirrer is used with certain amount of speed as to avoid vortex and formation of more than one layer surface of catalyst. It is best to avoid multilayer reaction as it might hinder catalyst surface reaction at the bottom layer. Therefore, in this system, we are more interested with the conversion, selectivity and kinetics at the solvent surface rather than inside the solvent itself. In addition, close monitoring on pressure drop is also important as it gives the indication on the gases absorbed to the catalyst pores that produces the methanol.

Elementary step involve in the above process for synthesizing methanol using alcohol are;

Table 6: Elementary Steps in the Kinetic Model of Methanol Synthesis

Step	Surface Reaction
1	$H_2O(g) + M \rightleftharpoons H_2O - M$
2	$H_2O - M + M \rightleftharpoons OH - M + O - M$
3	$2OH - M \rightleftharpoons H_2O - M + O - M$
4	$O - M + H - M \rightleftharpoons O - M + H - M$
5	$2H - M \rightleftharpoons H_2 + 2M$
6	$CO(g) + M \rightleftharpoons CO - M$
7	$CO - M + O - M \rightleftharpoons CO_2 - M + M$
8	$CO_2 - M \rightleftharpoons CO_2(g) + M$
9	$CO_2 - M + H - M \rightleftharpoons HCOO - M + M$
10	$HCOO - M + H - M \rightleftharpoons H_2COO - M + M$
11^C	$H_2COO - M + H - M \rightleftharpoons H_3CO - M + O - M$
12	$H_3CO - M + H - M \rightleftharpoons H_3COH - M + M$
13	$CH_3OH - M \rightleftharpoons CH_3OH(g) + M$
14	$H_2COO - M + M \rightleftharpoons HCH - M + O - M$
15	$HCH - M \rightleftharpoons HCHO(g)$ +M
16	$H_2COO - M + H - M \rightleftharpoons HCHO - M + OH - M$

(Source: Bartholomew, Farrauto, 2005, p.387)

Step 13 in the above table shows that methanol is produced in gaseous form. It is believed that the gaseous methanol will condense and mixed together with the solvent at the end. Therefore, we expect to have the main product in liquid form instead of in gaseous form. In order to prove that methanol was produced in the gaseous form before condensed to liquid form and to know how much methanol been produces, both gas and liquid samples will be taken at the predetermined hours and will be analyze using gas and liquid chromatography . Material balance will be done at the end of the process to get more understanding of the process.

The specialty of the system introduce in this project is that three-phase reactor system help much on the temperature control as the reaction involved is an exothermic reaction. For the two-phase reactor system, the temperature control is not easy to deal with, which causes temperature raises rapidly in the system. In addition, the separation of methanol from the methanol synthesis is not an easy task as water and methanol can form immiscible liquid which in turn required azeotropic distillation. In azeotropic distillation, another component is introduced in order to break the water-methanol immiscible liquid phase. With the new system introduced (three-phase), the necessary of introducing the third component is eliminated and the separation can take place.

The reaction involves in the process is surface reaction where both hydrogen and carbon monoxides gases will sit on the $Cu/ZnO/Al_2O_3$ catalyst and interact to produce methanol. Solvents that present in the reactor act as promoters that enhance the reaction of the catalyst and the feed gases. Not only that, it also act as cooling medium to maintain the temperature as well as to help the system to capture the methanol produces during the reaction. The process of separating solvents and the methanol will not be an issue as we are not going to separate both promoter and product. The quantity of methanol inside the solvents is the main issue as if the process is going to be industrialized, gasification will took place and reaction will involve solid-gas catalysis reaction.

CHAPTER 3

METHODOLOGY

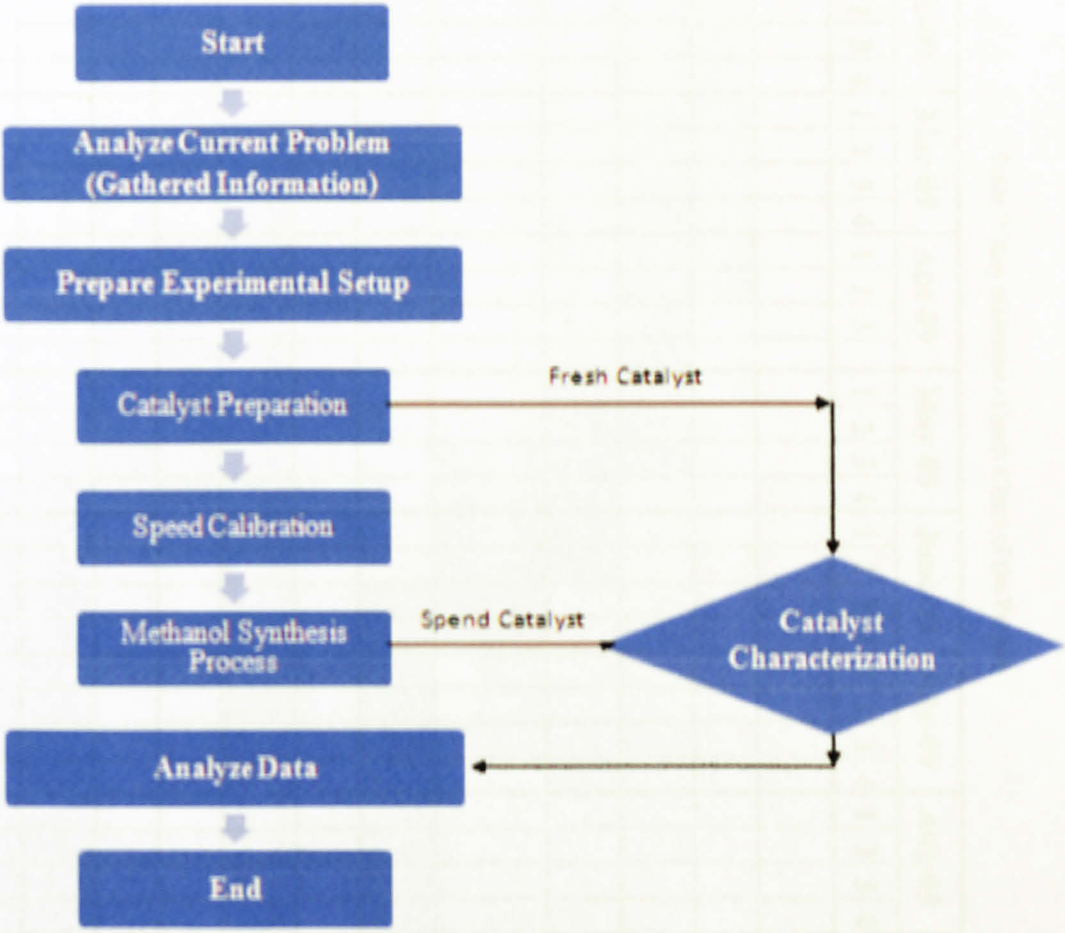

Figure 8: Process Flow for the Project

Table 7: Key milestone / Gantt Chart of the Project

No	Task Name	Feb-09				Mar-09				Apr-09				May-09				June-09				July-09				Aug-09				Sep-09				Oct-09				Nov-09			
		1	2	3	4	1	2	3	4	1	2	3		1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
1.0	**Analyze Problem & Literature Review**																																								
	1.1 Methanol and its demand	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨																														
	1.2 Characteristics of current methanol synthesis process	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨																									
	1.3 Comparison on methanol synthesis literature									-	-	-	-	▨ -	▨ -	▨ -	▨ -	▨ -	▨ -																						
	1.4 Catalyst involved in methanol synthesis and characterization needed															▨	▨	▨	▨	▨	▨																				
	1.5 Process involved in methanol synthesis reaction																			▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
2.0	**Prepare Experimental Setup**																																								
	2.1 Finding suitable chemicals for lab experiment								▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨												
	2.2 Catalyst preparation									▨	▨	▨	▨	▨	▨	▨	▨																								
	2.3 Speed calibration															▨																									
	2.4 Methonal synthesis process																▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				
	2.4.1 Specific Solvent (butanol, ethanol, iso-octane, iso-pentane, toluene, xylene)																▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨												
	2.4.2 Blended Solvent 1 (50% each of butanol and n-hexane)																													▨	▨	▨	▨								

	2.4.3 Blended Solvent 2 (50% each of butanol, n-hexane, toluene and iso-pentane)																																	▨	▨	▨	▨				
	2.5 Characterization of Catalyst															▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
	2.5.1 XRD, TGA, SEM, TPR, TPO, TPA, BET, AAS															▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
3.0	**Analyzing Result**																																								
	3.1 Fresh catalyst																	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	3.2 Methanol production on blended solvent 1 and blended solvent 2																													▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	3.3 Methanol production and effects on the spend catalyst																																	▨	▨	▨	▨	▨	▨	▨	▨
4.0	**Final Report Preparation**																▨	▨	▨	▨				▨				▨				▨				▨	▨	▨	▨	▨

3.1 Catalyst Preparation

3.1.1 Catalyst Preparation Procedure

1. Solution 1 is prepared by using
    a. 139.075g of copper oxide, 89.67g of zinc acetate and 18.75g of aluminum nitrate which are dissolved in 1.011 liters of water.
2. Solution 2 is then prepared with
    a. 158.04g of sodium bicarbonate and dissolved in 1.011 liters of water.
3. Both solutions are separately heated to 90°C. Solution 1 is then added rapidly, in the course of from 1 to 2 minutes to solution 2, whilst stirring using a magnetic stirrer to enhance mixing process.
4. The mixture is stirred for a further of 15 minutes for aging process by maintaining pH of 7.0
5. The precipitation is then filtered off (forming cake) and washed nitrate-free with water.
6. The filter cake is then dried at 110°C overnight for moisture removal and crushed or comminuted the next day to enhance the effectiveness of calcinations process.
7. Calcine the dried filter cake for 4 hours at 270°C under nitrogen atmosphere to remove volatile fraction.

3.1.2 Sequence in Catalyst Preparation Process

Figure 9: Preparation on acidic solution (Solution 1) and alkylate solution (Solution 2)

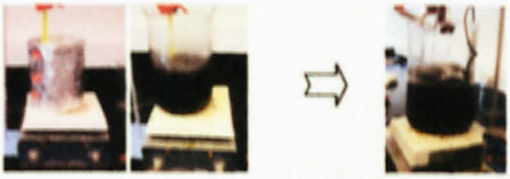

Figure 10: Solutions is heated separately to 90°C before being mix and stirred rapidly with magnetic stirrer. pH meter is used to monitor pH of the solution.

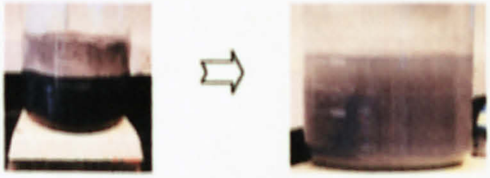

Figure 11: Aging process happened and at the end of the process, precipitate or catalyst settle down at the bottom of the beaker

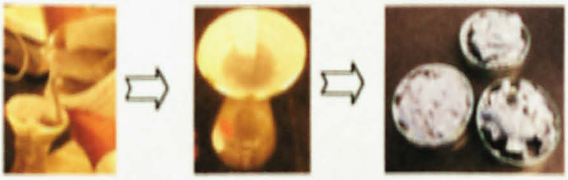

Figure 12: Precipitate/Catalyst is filtered and undergo drying process in the oven at 110°C

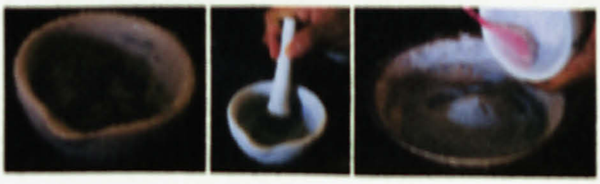

Figure 13: Dried catalyst is then crushed or comminuted to increase surface area

Figure 14: Calcination process took part in the furnace at 270°C

3.2 Speed Calibration

Speed calibration is important to determine the suitable speed for the stirrer so that surface reaction can take place during methanol synthesis characterization.

1. Prepare 500ml of solvent and 2g of catalyst.
2. Both solvent and catalyst are mixed in the reactor flask.
3. Carefully insert reactor stirrer into the reactor flask.
4. Switch On the main power supply.
5. Press the "High Limit Button" at the back of the main controller panel to reset alarm system.
6. Switch ON Display.
7. Switch ON the stirrer and slowly increase the RPM of the stirrer until the catalyst is floating on the surface of the solvent. The optimum RPM gives no turbulence on the solvent's surface while maintaining the catalyst on the surface of the solvent.
8. Lower the revolution per minute (rpm) of the stirrer after the suitable speed is identified and turn of the stirrer.
9. Switch OFF the display.

Figure 15: Stirrer is inserted into the container used in the reactor; Speed of the stirrer is increased until suitable speed is achieved and turbulence at the surface of the solvent happened when the speed is too high

3.3 Standard Operating Procedure Parr High Pressure Reactor

Starting Up the Reactor

1. Switch On the main power supply
2. Press the "High Limit Button". The High Limit will not switch of if;
    a. Pressure transducer not connected, or
    b. The controller not working.
3. Switch ON Display
4. Wait for a few minutes until the reading on the display stabilized.
5. Insert carbon monoxide (CO) gas into the reactor followed by CO/H_2 gas while referring to the display until required pressure is achieved (30bar).
    a. Open (a little) the inlet gas valve of Carbon monoxide (CO) (on top of the gas tank) while ensure the outlet valve gas (on gas regulator) is fully closed.
    b. Crack open the main gas valve that connect the reactor to the gas supply.
    c. Open a little the outlet gas valve just to ensure enough flow to the reactor.
    d. Slowly increase the outlet gas valve pressure while referring to the display until required pressure is achieved.
    e. Close main gas valve when desired pressure is achieved.
    f. Close outlet gas valve follow by the inlet gas valve.
    g. Repeat the above steps for CO_2/H_2 gas until total pressure required is achieved.
6. Set temperature required for the system (150°C) and on Heater II.
7. Change from Heater II to Heater I to maintain the temperature after required temperature is achieved.
8. On the stirrer and set the speed to 300 to 315 RPM range to make sure turbulence will not occur in the system. (speed is based on speed calibration process)
9. Every time the temperature increase or go down beyond the required temperature, heater will be shut down or change to Heater II.

10. Both gas and liquid samples will be taken for the first, second, third, fifth, seventh, and ninth hour of the operation.

Shutting Down the Reactor

1. OFF the heater.
2. Decreased the temperature set point by 50°C and after nearly reach 50°C, change set point to 35°C.
3. Zero the stirrer speed and switch OFF the stirrer.
4. Pressurized the system with inert gases such as N_2 to ensure all reaction gases are dissolved in the solvent.
5. Depressurize the reactor and take out the solvent and products.

3.3.1 Methanol Synthesis via Parr High Pressure Reactor

Figure 16: 500g of solvents and 2g of catalyst is prepared for the reaction

Figure 17: (1) Flask containing solvent and catalyst is inserted into the reactor, (2)Reactor is setting up, and (3)Reactor is locked with tools required

Figure 18: Pressure and temperature are set at 30bar and 150C

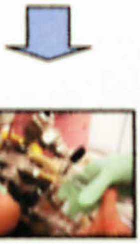

Figure 19: Both liquid and gas samples are taken after 1st, 2nd, 3rd, 5th and 7th hour of reaction

CHAPTER 4

RESULT AND DISCUSSION

4.1 Catalyst Preparation and Characterization

Figure 20: Catalyst that has successfully been produced

As showed in figure 20, $Cu/ZnO/Al_2O_3$ catalyst has successfully been produced using four different chemicals which were copper oxide, zinc acetate, aluminum nitrate and sodium bicarbonate via co-precipitation method as cited in US Patent 4436833. In this method, two solutions were prepared; the first solution consist of water, copper oxide, zinc acetate and aluminum nitrate while another solution consist of sodium bicarbonate and water. The first solution was added rapidly into the second solution and stirred before filtering it off; followed by washed nitrate free with water. Then, drying process took part at 110°C to remove moisture in the precipitate and finally the filter cake will be calcined at 270°C under nitrogen atmosphere to remove volatile fraction that exist.

As it is appear in the figure above, the $Cu/ZnO/Al_2O_3$ catalyst was prepared in powder form and will not be granulated as the reaction that took part at the later stage of the project will require surface reaction to occur therefore, it is important to let the catalyst in its original form so that catalyst surface area will be maximized for the surface reaction to take place. In Methanol synthesis process, every component of the catalyst played a major role. It has been proven that $Cu/ZnO/Al_2O_3$ is the best catalyst for Methanol production as copper based oxide catalyst is structurally to weak (R.Yang et al/ Fuel 87(2008) pg:444). Copper that existed in the catalyst help to drive water gas shift reaction to occur while the element of zinc help to trap sulfide and drive dehydration effects. Aluminum which has the acid sites, help to increase the strength of the catalyst (structural promoter) and decrease the effects of sintering; where catalyst particles tend to adhere to each other.

As mention previously, copper oxide has been used to make the catalyst. For the betterment of this project in the future, copper oxide should not be used during catalyst preparation and copper nitrate should be replaced with as copper oxide did not dissolved in the solvent. Due to limited knowledge and limited chemical sources, this mistake has took placed and only been realized at the final stage of the project.

4.1.1 Scanning Electron Microscopy Test, SEM

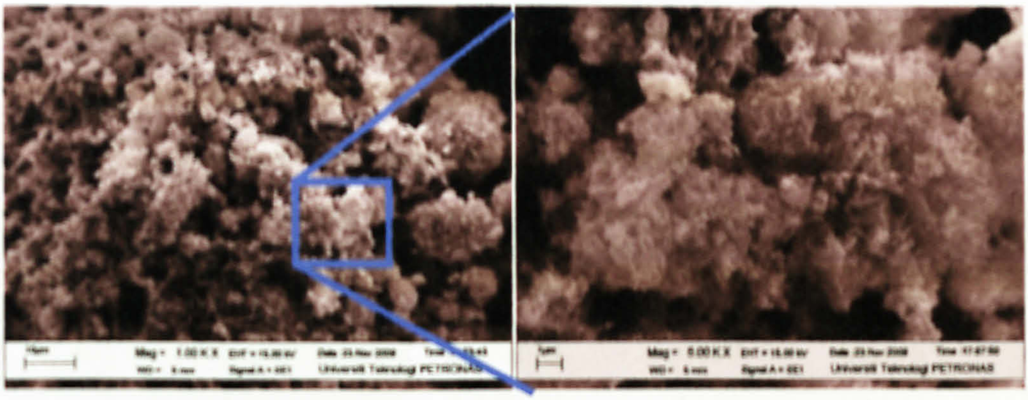

Figure 21: SEM Result for Fresh Prepared Cu/ZnO/Al2O3 Catalyst

The above figure shows the topography of $Cu/ZnO/Al_2O_3$ catalyst under 1000 and 5000 magnification. It can be observed that the prepared catalyst is not well dispersed and it accumulated at specific spot which decrease the surface area of it. Modification need to be done on the catalyst in order to have a wider dispersion of its components therefore maximum surface area for reaction to take place can be offered. Adding in citric acid during catalyst preparation is believed can lead to the betterment of catalyst dispersion, specifically the copper element, hence increase the rate of surface reaction during hydrogenation process.

4.2 Methanol Synthesis via $Cu/ZnO/Al_2O_3$ Catalyst in Blended Solvent

4.2.1 Methanol Synthesis via $Cu/ZnO/Al_2O_3$ Catalyst in 1:1 butanol and n-hexane

Table 8 : Results gathered from gas chromatograph done on gas sample

Chemical	MeoH	CO2	CO	H2
1:1 butanol and n-hexane (50% each)	5.69E-01	-	23.34	48.16
	3.28E-01	3.069	60.716	-
	1.22E-01	7.118	59.643	-
	5.70E-02	8.41E-01	7.392	-
	5.48E-02	-	-	-

The above table shows result gathered from gas chromatography done on 1:1 blended butanol and n-hexane sample. Traces amount of methanol can be observed in gas sampling which indicate that methanol did successfully been synthesized using prepared $Cu/ZnO/Al_2O_3$ catalyst via the blended solvents which act as a promoter. The hypothesis that we have made upon having this result is, methanol that has been successfully synthesis in gas form; diffuses into the solvents, and that's make the percentage volume (% vol) of methanol in the gas phase drop off.

Based on literature review, it is expected that both butanol and n-hexane solvents will promote higher production of methanol as study on the usage of both the solvents have been done thoroughly but yet in a small scale study. Therefore, based on the study, I draw a hypothesis that the combination of both solvents may successfully produce methanol and experimental work is done to prove that. The above table shows that methanol did successfully been produced based on traces amount of methanol in the gas samples but the amount is much smaller compare when butanol and n-hexane is used individually as the promoter. I believed that the time between when experiment took place and the time to process the data play a major role as the gas samples has been kept for quit some times before being process using gas chromatograph therefore some component of the gases might have been escape somehow as I am using a typical plastic sampling bag.

Table 9 : Results gathered from liquid chromatography done on 1:1 blended butanol and n-hexane liquid samples

Sample	Sampling No	Area	Methanol % Conc.
1:1 butanol and n-hexane (50% each)	1	0	0
	2	7157913	7.42
	3	1569453	1.63
	4	689782	0.71
	After Cooling	1132	0.001

Based on gas chromatography results, it shows that methanol did successfully be synthesis as traces amount of it appear s in gas chromatography results. But when it comes to liquid chromatography, very low methanol is detected and it only appears in certain samples using certain solvent only to be named, ethanol, n-octane and 50% butanol and 50% n-hexane. Methanol being produced or synthesis in gas phase and we believed that the gas will condensed into the solvent. Reason behind this problem may have been contributed when liquid sample is taken out. Some of the component may evaporate as the samples were taken at 150°C. The sample did expose to the environment before being kept inside a small bottle. Leaking maybe another factor that contributed for this problem as when we run the experiment, the gas detector keep on detecting feed gas which is gas monoxide and several steps have been taken in order to counter it but it still happen almost every run.

4.2.1.1 Effects of Reaction on Catalyst

4.2.1.1.1 Scanning Electron Microscopy

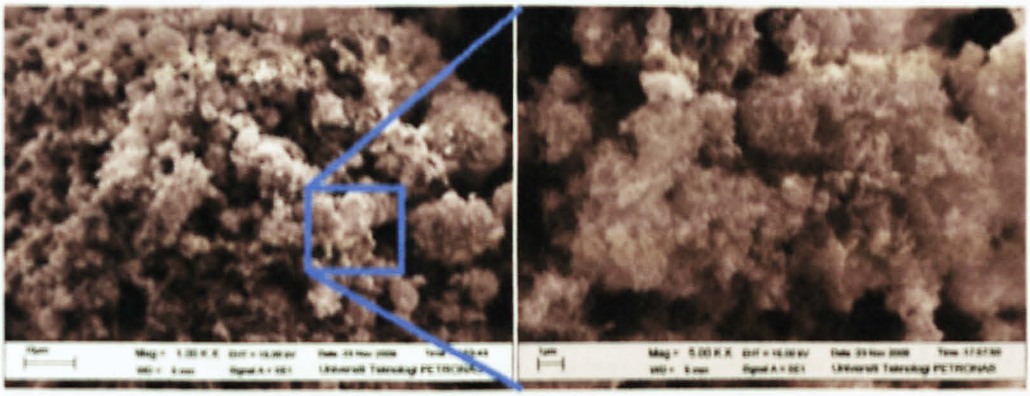

Figure 22: SEM Result for Fresh Prepared Cu/Zn/Al2O3 Catalyst

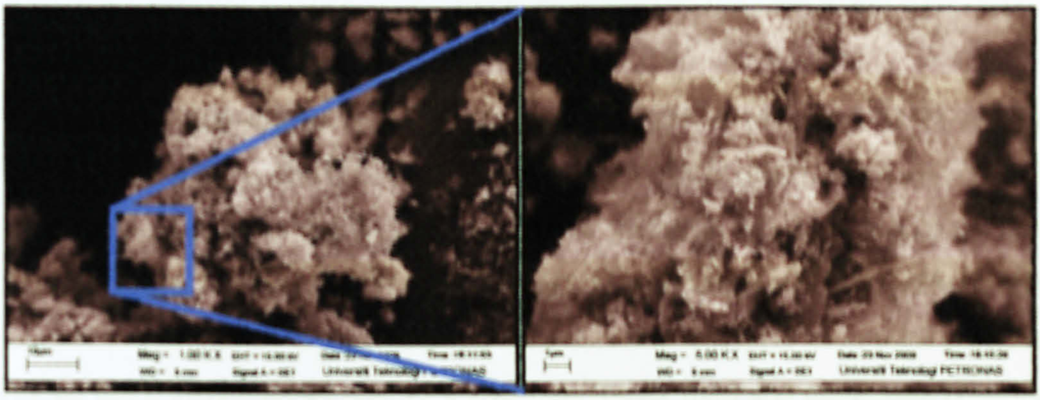

Figure 23: SEM Result for Spend Cu/ZnO/Al2O3 Catalyst on 50% Butanol-50%n-hexane

Both figures show Cu/ZnO/Al_2O_3 catalysts before and after reaction with 1:1 butanol and n-hexane blended solvent. Based on the SEM results, there are not significant changes on the structure of the catalyst. This is a good indication that the catalyst do not deactivated after undergoing surface reaction promoted by the blended solvent.

4.2.1.1.2 X-Ray Diffraction, XRD

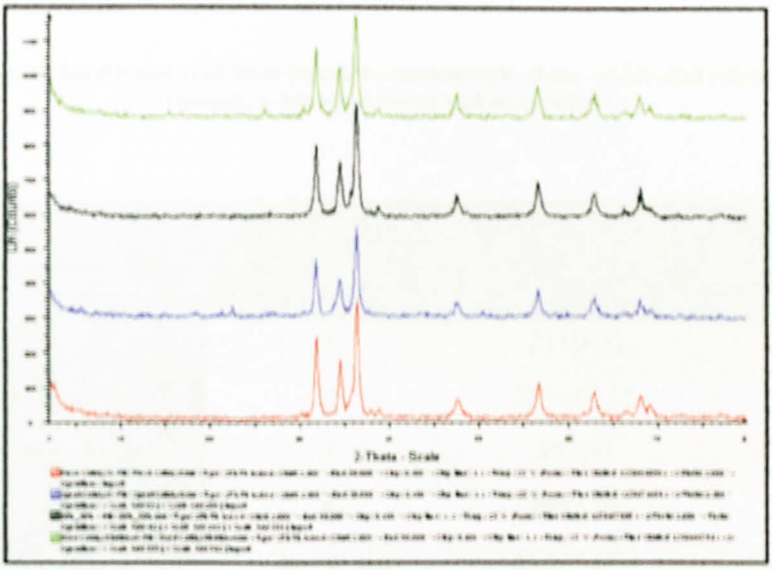

Figure 24: Result for XRD on fresh and spend catalyst

Peaks that appear in XRD result shows that the catalyst is in crystal form. The red line refer to fresh $Cu/ZnO/Al_2O_3$ catalyst while green, black and blue lines refer to spent catalyst that have been used in methanol synthesis reaction via Parr High Pressure Reactor in different solvents to promote methanol synthesis which has been catalyzed by $Cy/ZnO/Al_2O_3$. The solvents that have been used are butanol (green line), 50% butanol and 50% n-hexane (black line) and iso-octane (blue line). The same pattern of peaks can be observed from the figure before and after methanol synthesis reaction took place and this indicates that the catalyst has not be deactivated after the reaction has took place.

4.2.2 Methanol Synthesis via $Cu/ZnO/Al_2O_3$ Catalyst in 1:1:1:1 Blended Solvents (butanol, n-hexane, toluene and iso-pentane)

Table 10 :Liquid Results gathered from liquid chromatography done on blended solvent consists of butanol , n-hexane, toluene and iso-pentane

Sample	Sampling No	Area	Methanol % Conc.
1:1:1:1 Blended Solvent (25% each from butanol, n-hexane, toluene, and iso-pentane)	1	211010	0.39
	2	23969111	24.84
	3	48269	0.05
	4	294135	0.3
	Overnight	41433153	42.94

The above table resembled liquid chromatograph results on blende solvent consist of 25 percent of each butanol, n-hexane, toluene and iso-pentane. It can be observed that at low temperature, methanol has successfully been synthesis using $Cu/ZnO/Al_2O_3$ catalyst.

The concentration of methanol was not consistent throughout the experiment most probably because at temperature 150C, the product was permit to appear in gas phase as boiling point for methanol is 64.7C.

After overnight indicated that the product already achieved room temperature, therefore, the methanol appeared to be in liquid phase as methanol in gaseous form diffuse into the solvent due to its heavy property.

4.2.2.1 Effects of React

4.2.2.2 ion on Catalyst

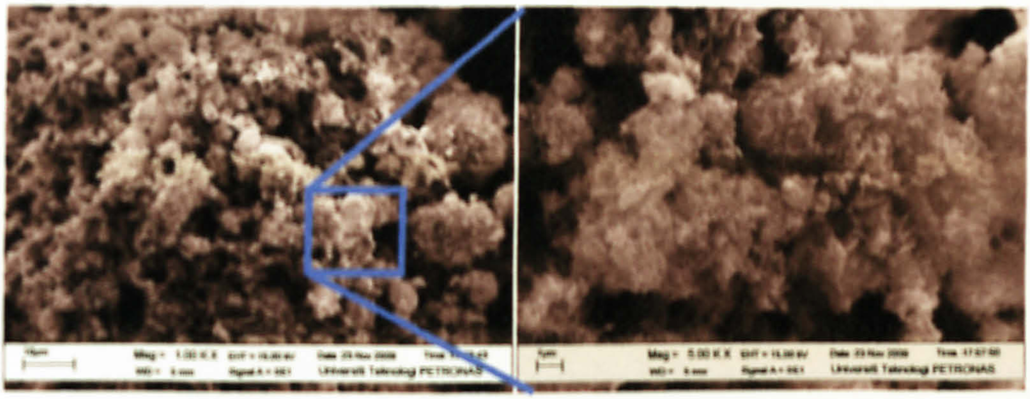

Figure 25: SEM Result for Fresh Prepared Cu/ZnO/Al2O3 Catalyst

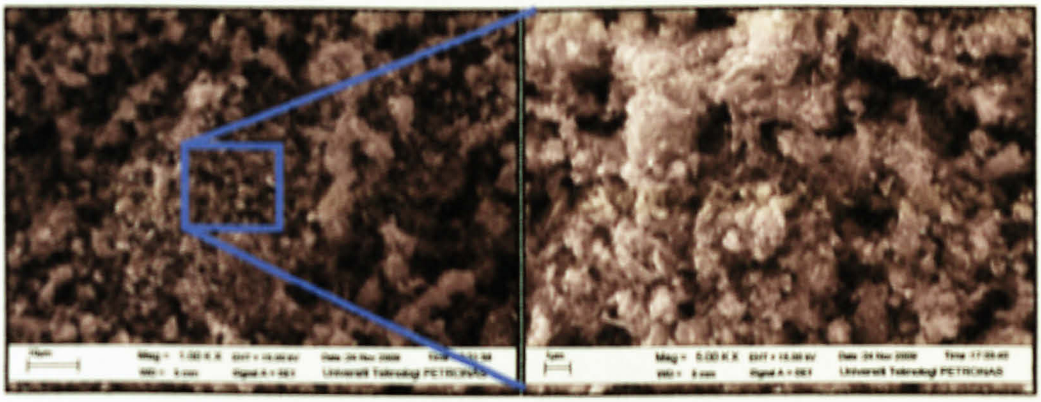

Figure 26: SEM Result on Spend Cu/ZnO/Al2O3 Catalyst on Blended Solvent (25% of each butanol, n-hexane, toluene and iso-pentane)

From both SEM results' figures, changes in the structure of the catalyst can be detected based on the size of the catalyst particle. The spend catalyst appeared to have a finer catalyst size compared to the fresh catalyst. Attrition may have occurred and contributed to this problem. Attrition is a phenomena where a reduction or decrease in numbers, size, or strength happened.

One of the factors that may lead to attrition problem is the usage of toluene as one of the solvent component. When toluene was used as the only solvent for the reaction, there were significant changes on the color of the catalyst and the size of the catalyst particle (become finer). Toluene is an aromatic solvent which is commonly been used to thin oil-based paint and maybe the ability of the toluene to erode has contributed to attrition problem.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1. Conclusion

$Cu/ZnO/Al_2O_3$ catalyst has been successfully produced although with a little mistake took place during the preparation process of it. Result from XRD and SEM characterization tests showed that the catalyst produced is in crystal form and it does not deactivated even after reaction to synthesis methanol has took place.

Not only that, it can also be concluded that $Cu/ZnO/Al_2O_3$ catalyst that has been produced successfully catalyzed methanol synthesis reaction as small traced of methanol can be detected via gas chromatography data for the first blended solvent and quit a big amount of methanol has been detected by liquid chromatography for second blended solvent. Although methanol as the main product for this process fruitfully been synthesis, the selectivity of both methanol production using different blended solvent can't be calculated due to limitation access to some of the equipments and therefore, material balance and calculation on selectivity of the main product of the process cannot be done.

5.2. Recommendation

To produce a catalyst with high dispersion, acetic acid can be introduced during catalyst preparation process. Wide dispersion of the catalyst is important to increase the surface area of reaction and hence increase the conversion of the reaction. Not only that, copper oxide should not be used during catalyst preparation as the source of copper but instead use copper nitrate as the later dissolved in solvent. In determining the right amount of metal salt that need to be mix together to form metal salt solution, only the amount (weight) of salt element should be taken into consideration by ignoring the functional group of it.

During the experiment, both reactor and product should be left overnight instead of cooling it down and depressurized it as during depressurized process, methanol in gas phase might have been released to the environment and contributed to low methanol level in liquid product.

For future work, in order to study the effect of using solvent as promoter, aromatic solvents should be eliminated as it cause attrition on the spend catalyst. This may contribute to high cost for regenerating new catalyst as the catalyst life is shorter due to the attrition.

In order to calculate the selectivity of the process, both quantities of the main product and byproducts are required therefore, material balance should be carried out first by gaining data from both gas and liquid sample through gas and liquid chromatography equipments. Leaking is the main problem that should be chattered before conducting the reactor as it may lead to inconsistence and inaccurate result at the final stage.

REFERENCES

1 'Chemical Process Technology' by Jacob A. Moulijin, Michiel Makkee, Annelies Van Diepen; John Wiley & Sons, Ltd. Pg: 187

2 'Fundamental of Industrial Catalytic Processes' by C.H. Bartholomew and R.J. Farrauto; 2nd Edition; John Wiley & Sons, Inc, Publication.

3 P.Reubroycharoen et. al. 2004. Development of A New Low-temperature Methanol Synthesis Process. Catalysis Today 89. Pg:447 - 454

4 'Preparation of Methanol Synthesis Catalyst Comprising Zinc, Copper and Alumina' by Franz J. Broecker, Ludwigshafen; Karl-Heinz Gruendler, Limburgerhof; Matthias Schwarzmann, Limburgerhof; Bruno Triebskorn; Guenter Zirker, both of Ludwigshafen, all of Fed. Rep of Germany. US Patent 4436833, Mar 13, 1984.

5 'Making a Methanol Product in a Slurry Bubble Reactor' by James R. Lattner, LaPorte US Patent 2007/0027221 A1

6 'A New Method of Low Temperature Methanol Synthesis on Cu/ZnO/Al2O3 catalysts from CO/CO_2/H_2'by Ruiqin Yang; Xiaocai Yu; Yi Zhang; Wenze Li; Noritatsu Tsubaki. Fuel 87 (2008) 443-450

7 Development of Highly Efficient Methanol Synthesis Process with New Catalysts. Archived from http://www.nsc.co.jp/en/tech/report/pdf/n9219.pdf

8 Chin J Catal. 2008. Use of Citric Acid in Synthesizing a Highly Dispersed Copper Catalyst for Selectivite Hydrogenolysis. Chinese Journal of Catalysis. Volume 29, Issue 6. Pg: 566-570

9 http://en.wikipedia.org/wiki/Water_gas_shift_reaction

10 http://en.wikipedia.org/wiki/Fugacity

11 http://www.weatherquestions.com/What_is_dewpoint_temperature.htm

12 Material Safety Data Sheet for chemicals based on (refer appendix);

  12.1 http://cartwright.chem.ox.ac.uk/hsci/chemicals/hexane.html

  12.2 http://msds.chem.ox.ac.uk/TR/2,2,4-trimethylpentane.html

  12.3 http://www.americhemsales.com/MSDS%20HTMLS/0196onnv.htm

  12.4 http://cartwright.chem.ox.ac.uk/hsci/chemicals/1-butanol.html

  12.5 http://cartwright.chem.ox.ac.uk/hsci/chemicals/methanol.html

12.6 http://cartwright.chem.ox.ac.uk/hsci/chemicals/copper_II_nitrate.html

12.7 http://www.sciencestuff.com/msds/C2995.html

12.8 http://www.sciencestuff.com/msds/C1180.html

12.9 http://msds.chem.ox.ac.uk/SO/sodium_bicarbonate.html

APPENDIXES

Material Safety Data Sheet (MSDS)

Material Safety Data Sheet (MSDS) for Hexane

Chemical	**Hexane** , C_6H_{14} (aka n-hexane, normal hexane)
Physical Properties	▪ Form: colorless liquid with a petrol-like smell ▪ Stability: Stable, but highly flammable ▪ Melting point: -95 C ▪ Boiling point: 69 C ▪ Flash point: -23 C ▪ Water solubility: negligible ▪ Specific gravity: 0.659 ▪ Vapor density: 3 (air = 1) ▪ Vapor pressure: 132 mm Hg at 20 C ▪ Explosion limits: 1.2 - 7.7%
Principal Hazard	▪ Very flammable. ▪ It is highly volatile, dangerous concentrations can develop in ambient air, creating a possible explosion risk.
Emergency	▪ **Eye contact:** Immediately flush the eye with plenty of water. If irritation persists, call for medical help. ▪ **Skin contact:** Wash off with plenty of water. Remove any contaminated clothing immediately. Note that clothes

	soaked in hexane will present an extreme fire risk, so rapid action is essential. Place clothes in a safe location, such as outside the building (and do not forget to deal with them subsequently!). If the skin reddens or appears damaged, call for medical aid. ▪ **If swallowed:** Call for immediate medical help.
Protective Equipment / Safe Handling	▪ Always wear safety glasses. Do not work in an area in which sources of ignition, such as a Bunsen burner or hot air gun, are used. Ensure good ventilation at all times - use a fume cupboard for your work if possible. ▪ If gloves are needed, nitrile or PVA are suitable.

Material Safety Data Sheet (MSDS) for 1-butanol

Chemical	**1-butanol, C_4H_9OH** (aka n-butanol, butanol, butyl alcohol, 1-butyl acohol, n-butyl alcohol, butan-1-ol)
Physical Properties	▪ Form: colourless liquid ▪ Stability: Stable ▪ Melting point: -89 C ▪ Boiling point: 118 C ▪ Water solubility: high ▪ Specific gravity: 0.81
Principal Hazard	▪ Butanol is harmful if you swallow or inhale it. ▪ This material is very flammable.
Emergency	▪ **Eye contact:** Immediately flush the eye with plenty of water. If irritation persists call for medical help. ▪ **Skin contact:** Wash off with water. Remove any contaminated clothing. If the skin reddens or appears damaged, call for medical aid. Be aware that clothes soaked in butanol present a serious fire risk, so ensure that clothes (and anybody in them!) are kept well away from sources of ignition. ▪ **If swallowed:** Wash out the mouth with water if the person is conscious. If a significant quantity has been swallowed call for immediate medical help.
Protective Equipment/ Safe Handling	▪ Wear safety glasses. ▪ Ensure adequate ventilation. ▪ Do not work near a source of ignition. Very flammable chemicals may be ignited by contact with a hot plate or even a hot water pipe - a naked flame is not required. ▪ If gloves are needed, neoprene or butyl rubber is suitable.

Material Safety Data Sheet (MSDS) for Methanol

Chemical	**Methanol, CH_3OH** (aka Methyl alcohol, wood alcohol, meths)
Physical Properties	▪ Form: colourless liquid with a characteristic smell ▪ Stability: Stable, but very flammable ▪ Melting point: -98 C ▪ Boiling point: 64.7 C ▪ Flash point: 11 C ▪ Explosion limits 6% - 36% ▪ Water solubility: miscible in all ▪ Specific gravity: 0.79
Principal Hazard	▪ Methanol is toxic. If ingested or inhaled it can cause a wide range of harmful effects, from sickness, heart and liver damage to reproductive harm, blindess or death. ▪ Methanol is often a component in "bootleg" liquor (illegally brewed and distilled alcohol) and there have been numerous cases in the past in which the consumption of such a drink has been fatal. ▪ Methanol is very flammable. The pure liquid catches fire easily and aqueous solutions containing a significant amount of methanol can also catch fire. ▪ The flame above burning methanol is virtually invisible, so it is not always easy to tell whether a methanol flame is still alight. ▪ The explosion limits for methanol (the lower and upper percentage limits of methanol in an air-methanol mixture giving a vapour that can explode) are unusually wide.

Emergency	▪ **Eye contact:** Immediately flush the eye with plenty of water. Continue for several minutes and call for medical help. ▪ **Skin contact:** A person whose clothes are soaked in methanol will be at serious risk from fire, so immediately remove any contaminated clothing and store well away from a source of ignition (preferably outside). Wash exposed skin with soap and water. If the skin reddens or appears damaged, or if methanol may have been swallowed, call for medical aid. ▪ **If swallowed:** Call for immediate medical help; if the quantity swallowed is significant urgent medical action is vital.
Protective Equipment/ Safe Handling	▪ Safety glasses. ▪ If gloves are needed, butyl rubber is a suitable material. ▪ Remove any source of ignition from the working area. Don't forget that a hot air gun, a hot plate or even a radiator may be sufficiently hot to ignite the vapour. ▪ Do not breathe in the vapor. Use a fume cupboard if available. If this is not possible, ensure that the area in which you work is very well ventilated.

Material Safety Data Sheet (MSDS) for Copper Nitrate

Chemical	**Copper Nitrate, $Cu(NO_3)_2$ $3H_2O$** (aka Cupric nitrate, copper (II) nitrate trihydrate, cupric nitrate trihydrate)
Physical Properties	▪ Form: blue crystalline powder ▪ Stability: Stable, but a strong oxidant ▪ Melting point: 114 C ▪ Water solubility: substantial ▪ Specific gravity: 2.32
Principal Hazard	▪ Contact with the eyes can cause serious irritation. ▪ This material is harmful if swallowed and may cause burns in contact with the skin. ▪ Solid copper nitrate is a strong oxidizing agent; contact with combustible materials could lead to fire. ▪ Disposal - Small amounts of copper nitrate can be flushed down a sink with a large quantity of water, unless local rules prohibit this. Do not dispose of the solid with normal laboratory waste because of the possibility of fire.
Emergency	▪ **Eye contact:** Immediately flush the eye with plenty of water. If irritation persists call for medical help. ▪ **Skin contact:** Wash off with water. ▪ **If swallowed:** If the person is conscious wash the mouth out with water. Call for medical help.
Protective Equipment/ Safe Handling	▪ Safety glasses. If gloves are required, rubber is a suitable material.

Material Safety Data Sheet (MSDS) for Zinc Nitrate

Chemical	**Zinc Nitrate, Zn(NO")'½6H'O**
Physical Properties	▪ Evaporation Standard: Solubility in Water: ▪ Melting Point:36.4° C ▪ Appearance and Odor: Moist white crystal Lower ▪ Boiling Point:105° C ▪ Specific Gravity2.065
Principal Hazard	▪ Heat, shock, friction, or contact with other materials may cause fire or explosion. Harmful if swallowed. Avoid breathing vapor or dust. Use adequate ventilation. Avoid contact with eyes, skin or clothes. Wash thoroughly after handling. Keep closed.
Emergency	▪ **Skin Contact:** Remove contaminated clothing. Wash exposed area with soap and water. If symptoms persist, seek medical attention ▪ **Eye Contact:** Wash eyes with plenty of water for at least 15 minutes, lifting lids occasionally. Seek Medical Aid. ▪ **Inhalation:** Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen ▪ **Ingestion:** If swallowed, induce vomiting immediately after giving two glasses of water. Never give anything by mouth to an unconscious person.
Protective Equipment/ Safe Handling	▪ Store in a cool, dry, well-ventilated place away from incompatible materials. Wash thoroughly after handling. ▪ NIOSH approved gloved ▪ Splash goggles ▪ Wear appropriate clothing to prevent skin exposure

Material Safety Data Sheet (MSDS) for Aluminum Nitrate

Chemical	**Aluminum Nitrate, Al_2O_3**
Physical Properties	▪ Melting Point:73° C ▪ Boiling Point:135° C (decomposes) ▪ Solubility in Water: Soluble ▪ Appearance and Odor: White crystals / no odor
Principal Hazard	▪ Heat, shock, friction, or contact with other materials may cause fire or explosion. Harmful if swallowed. Avoid breathing vapor or dust. Use adequate ventilation. Avoid contact with eyes, skin or clothes. Wash thoroughly after handling. Keep closed.
Emergency	▪ **Skin Contact:** Remove contaminated clothing. Wash exposed area with soap and water. If symptoms persist, seek medical attention ▪ **Eye Contact:** Wash eyes with plenty of water for at least 15 minutes, lifting lids occasionally. Seek Medical Aid. ▪ **Inhalation:** Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen ▪ **Ingestion:** If swallowed, induce vomiting immediately after giving two glasses of water. Never give anything by mouth to an unconscious person.
Protective Equipment/ Safe Handling	▪ Safety Glasses, ▪ Use safe laboratory handling procedures. ▪ NIOSH Approved Gloves

Material Safety Data Sheet (MSDS) for Sodium Bicarbonate

Chemical	**Sodium Bicarbonate, $NaHCO_3$** (aka Sodium hydrogen carbonate, baking soda, bicarb, bicarbonate of soda)
Physical Properties	▪ Form: white crystalline powder ▪ Stability: Stable ▪ Specific gravity: 2.16
Principal Hazard	▪ Sodium bicarbonate is not believed to be harmful.
Emergency	▪ **Eye contact:** Immediately flush the eye with water. If irritation persists, call for medical help. ▪ **Skin contact:** Wash off with soap and water. ▪ **If swallowed:** Call for medical help if the amount swallowed is large.
Protective Equipment/ Safe Handling	▪ Safety glasses. ▪ Small amounts of sodium bicarbonate can be flushed down the sink.