AN EXPERIMENTAL STUDY ON EFFECT OF PARAFFIN AS LIQUID MEDIUM IN METHANOL SYNTHESIS

LEST MAULADA BUDIMAN

CHEMICAL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
JULY 2009

CERTIFICATION OF APPROVAL

An Experimental Study on Effect of Paraffin as Liquid Medium in Methanol Synthesis

by

Lest Maulada Budiman

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Dr. Chandra Mohan K V Sinnathambi)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2010

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.

LEST MAULADA BUDIMAN

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ABSTRACT

The objective of the project is to study the effect of product selectivity on the reaction of hydrogen and carbon oxides using CuO/ZnO/Al2O3 catalyst with paraffinic (n-hexane and n-octane) liquid medium in a three phase slurry reactor. The challenge in this project is to analyze the effect of using paraffinic liquid medium to the production of methanol performed in a temperature range of 150 – 200 C and total pressure of 30-50 bars. The catalyst used will be prepared manually in the lab using precipitation method apart from utilizing also the one available in the industry. Numerous catalyst characterization on the used span and catalyst will be done such as XRD, SEM, TPD, TPO, TPR, AAS, TGA, BET and GCMS/GC respectively. Nevertheless, this report is mostly the extension from the Progress Report submitted in April 2009. A much more detailed explanation in terms of the standards and procedures of the project is being documented, primarily on the catalyst characterization part. These will be the area where the author will be taking interest most in terms of the development of the **Effect of Paraffin as Liquid Medium in Methanol Synthesis.**

CHAPTER 1

INTRODUCTION

In this part, a brief description about methanol synthesis as well as the related problem statement with respect towards the project and followed by the objectives and scope of study.

1.1 BACKGROUND OF STUDY

Since the beginning of the century, methanol has been commercially synthesized from carbon monoxide and hydrogen. To obtain good conversion of the raw materials, the reaction is generally carried out at high pressures ranging from 750 to 10,000 psia and at temperatures from 200° to 400° C. Typical commercial practice involves introduction of vapors containing carbon monoxide and hydrogen (usually with carbon dioxide added) over a methanol-forming catalyst. This vapor phase reaction is highly exothermic.

Industrially, two methods are utilized to remove this high heat of reaction. In one of the method, heat is absorbed by cold feed gas introduced at multiple injection points along a multi-stage catalyst bed in an adiabatic reactor, thus reducing the temperature of the gas. Methanol formation is equilibrium limited and the theoretically realizable CO conversion is reduced by increasing temperature [1]. Even with the use of multiple feed injection points, the economic optimum methanol concentration in the exit gas is limited to 6 vol. %. This system also involve the heat of reaction is used to preheat feed rather than generate steam.

A newer process utilizes methanol-forming catalyst in packed beds in a shell and tube reactor in which the heat of reaction is used to generate steam on the shell side of the reactor. Although it is possible to react the gases so as to achieve high levels of CO conversion (and thus high methanol concentrations in the exit gases), the economic optimum for this reaction system is at 4.5-6.0 vol. % methanol in the exit gas [2].

1.2 PROBLEM STATEMENT

In both cases, the low exit methanol concentration has several disadvantages. The unreacted raw materials must be recycled to the reactor to achieve economic utilization of them. For example, 5.5 vol. % methanol in the exit gas requires that the recycle gas be almost 6 times the fresh feed gas. This requires compression equipment which is expensive to purchase and operate. Thus if the methanol concentration in the exit gas can be increased economically, the volume of recycle gas and the required compression equipment can be greatly reduced.

Even with the introduction of specialized catalysts, commercial practice prefers running the reaction with a low effluent concentration [3]. While these catalysts permit operation at lower temperatures and pressures than previously used (230°-275° C. and 750-1150 psia), thereby saving equipment and operating costs, the basic problem of low conversion per pass and the need to remove large amounts of heat have not been overcome. While there are a number of study done claiming that using different liquid medium as solvent for the reaction can contribute to a higher yield or methanol (such as alcohol and paraffin solvent) and heat removal are simplified, non of it truly describe the effect product selectivity on the reaction and would that bring of any effect to the catalyst used as well as the product being produced. On that note, this study is dedicated to study on that particular aspect of the reaction.

1.3 OBJECTIVE AND SCOPE OF STUDY

To study the effect product selectivity on the reaction of hydrogen and carbon oxides using $CuO/ZnO/Al_2O_3$ (MeOH synthesis) catalyst with paraffin (n-hexane and n-octane) medium in a three (3) phase slurry reactor. Catalyst characterization on the used span and catalyst were conducted to check the effect of the paraffin solvent on the product selectivity. The analyses done are listed below:

1. ***Atomic absorption spectroscopy (AAS)***
2. ***Scanning electron microscopy (SEM)***
3. ***Temperature programmed reduction (TPR)***
4. ***Temperature programmed oxidation (TPO)***
5. ***Temperature programmed desorption (TPD)***
6. ***Thermo gravimetric analysis (TGA)***
7. ***X-ray diffraction (XRD)***
8. **Gas chromatography (GC)**

CHAPTER 2

LITERATURE REVIEW / THEORY

Related theories with respect to the work in the study of Effect of Paraffin as Liquid Medium in Methanol Synthesis are documented in this section.

2.1 INTRODUCTION

Carbon dioxide is the most important "greenhouse gas" which may cause global warming. Various measures have been proposed to stabilize the atmospheric CO2 concentration. Conversion of CO2 to methanol by catalytic hydrogenation (Reaction 1) has been recognized as a promising route for the purpose because of a potentially large demand for methanol as fuel and basic chemical.

$$CO2+3H2 \longrightarrow CH3OH+H2O \text{ ---------- } (1)$$

The process is closely related to established methanol synthesis technology from CO/H2 (Reaction 2) because current industrial feeds contain 5 vol% of CO2 in addition to CO/H2

$$CO+2H2 \longrightarrow CH3OH \text{ ----------- } (2)$$

The processes are operating at 50-100 bar and 220-240°C with catalyst composed of Cu/ZnO/Al2O3.

2.2 PREPARATION OF SUPPORTED CATALYSTS BY PRECIPITATION

According to Calvin H. Bartholomew (2006)

The objective of this method is to precipitate the catalyst precursor in the form of a hydroxide or carbonate in the pores and on the surface of the carrier by adjusting the pH of the metal salt solution support slurry through addition of a base such as NaOH, NH4OH, NA2CO. Alternatively, support and catalyst precursor are coprecipitated together, such as coprecipitation of Ni hydroxide on silica by pouring together aqueous solutions of sodium silicate and nickel nitrate. Base and metal salt are carefully chosen to avoid the presence of species in the final catalyst that might later act as poisons, such as Na+ and SO42- for hydrogenation processes.

Although deposition on the support interior and in the pores is desirable, precipitation in the bulk solution should be avoided. Since this is likely to occur in the vicinity of the alkali drops entering the solution, rapid mixing and sometimes cooling, which lowers nucleation/precipitation rates, are generally effective in minimizing this problem.

In using precipitation for preparation of catalysts, it is highly desirable to obtain uniform, finely divided deposits, since this will ultimately translate to a highly dispersed, high surface area catalyst of high activity. Control of the precipitation rate inside the catalyst is a key to obtain uniform, well dispersed precipitate.

After precipitation, the precursor support is generally wash to remove undesirable, soluble ions, dried, and finally calcined to decomposed the catalyst precursor. The temperature required for calcinations may vary considerably with different precursor support combinations.

2.3 REACTOR

Below in **Figure 1** is the exact reactor that will be used in the project.

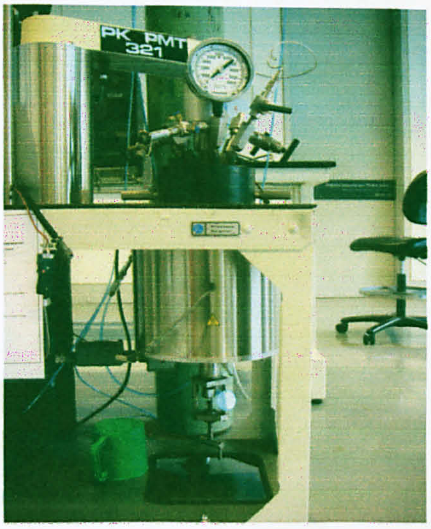

Figure 1: Slurry Three Phase Reactor

2.3.1 Pressure and Temperature Limits

Pressure Limit	Temperature Limit
1450 psig 145 bar	500 °C

2.3.2 Valves

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.

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.

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.

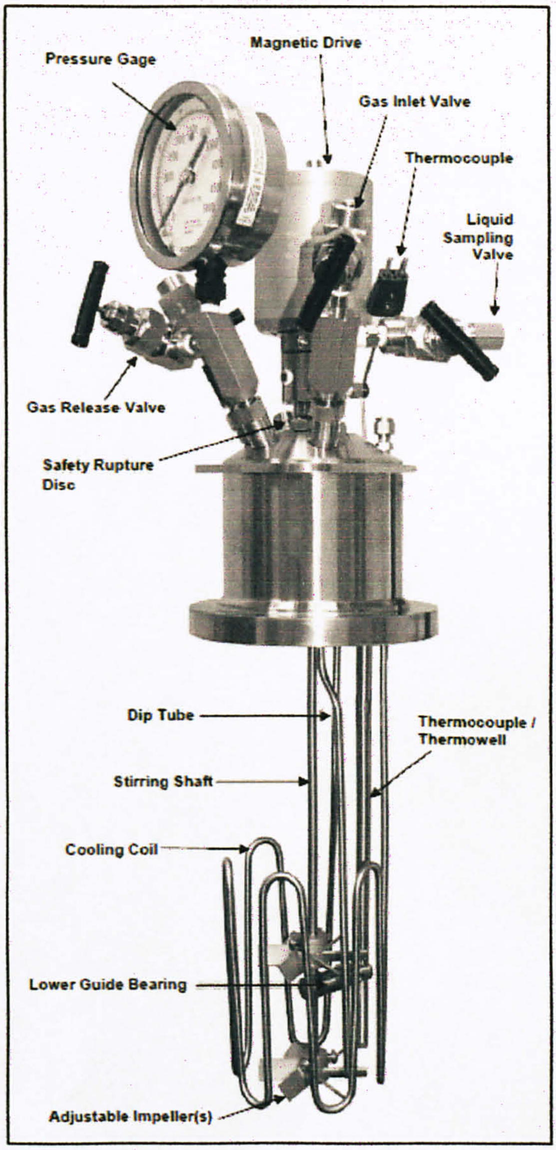

Figure 2: The Valves

Pressure Gauge

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

2.3.3 Slurry Three-Phase Reactor

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.

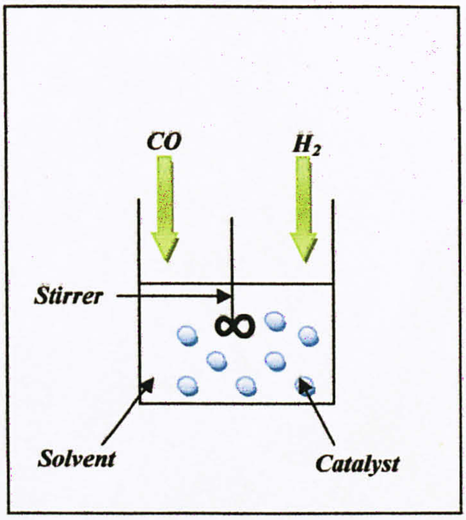

Figure 3: Illustrative picture inside the reactor

Conventional methanol reactors use fixed beds of catalyst pellets and operate in the phase. The slurry three phase reactor uses catalyst in powder form, and slurried in paraffin solvents which are n-hexane and n-octane. 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 water. The stirrer functions are to stir the solvent with catalyst to contact with the gas reactant and to uniformly divide heat in the solvent.

2.4 CHARACTERIZATION ON PREPARED CATALYST

Table 1: Characterization Test

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 zeolites 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.*

CHAPTER 3

METHODOLOGY / PROJECT WORK

For this section, the author describes the methodology of the project work process. Related applications from the start of the project towards the end are to be described. Certain changes might occur along the way, but will not change or disrupt the whole objective of the study of the Effect of Paraffin as Liquid Medium in Methanol Synthesis.

3.1 CATALYST PREPARATION

Step 1: 139.075g of copper oxide, 89.67g of zinc acetate and 18.75g of aluminum nitrate are dissolved in 1.011 liters of water (Solution 1)

Figure 4: Solution 1

Step 2: 158.04g of sodium bicarbonate is dissolved in 1.011 liters of water (Solution 2)

Figure 5: Solution 2

Step 3: Both solutions are heated to 90°C separately. Solution 2 is added rapidly to solution 1. A magnetic stirrer is utilized to enhance the mixing process.

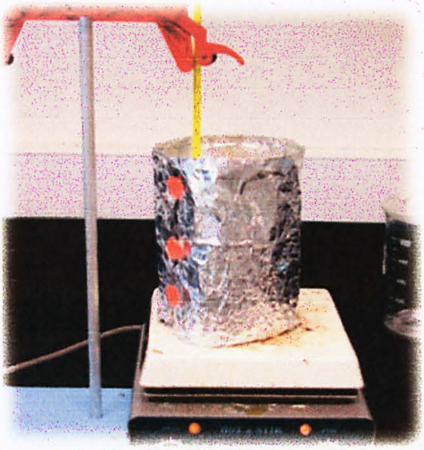

Figure 6: Both solutions are heated to 90 C

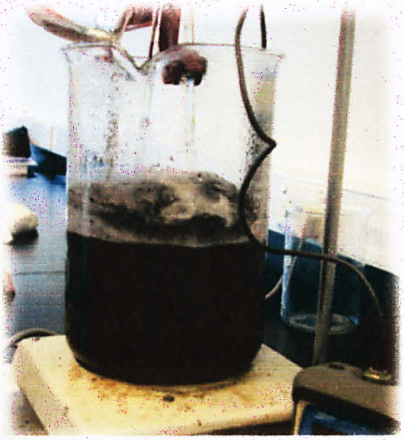

Figure 7: pH is closely monitored using pH meter

Step 4: The mixture is stirred for a further 15 minutes for aging process after pH is around 7.0.

Figure 8: After the aging process, the catalyst starts to settle at the bottom of the beaker

Step 5: The precipitate is then filtered off and washed nitrate-free with water

Figure 9: Catalyst precipitate

Figure 10: After filtration

Step 6: The filtered catalyst is then dried in oven for overnight at temperature of 110°C in order to remove the moisture from the catalyst. Then the catalyst is calcination (a thermal treatment process applied for removal of a volatile fraction, in this example the leftover nitrate or acetate)

Figure 11: The dried catalyst is comminuted in order to enhance the effectiveness of the calcination process

Figure 12: Calcination is done in furnace at temperature of 350°C for one night

3.2 SPEED CALIBRATION

1. 500ml of solvent and 2g of catalyst are prepared.
2. Both solvent and catalyst are mixed into the reactor flask.
3. Carefully insert the 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 to reset the alarm.
6. Switch ON Display button.
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 solvent's surface.
8. Lower the RPM of the stirrer after the suitable speed is identified and turn off the stirrer.
9. Switch OFF the display.

Figure 13: Stirrer is inserted into the reactor flask; RPM of the stirrer is increased until catalyst is floating on surface and no turbulence at the surface occurs

3.3 STANDARD OPERATING PROCEDURE FOR PARR HIGH PRESSURE REACTOR

Prepare 500ml solvent and 2g of catalyst and mixed both of them in a container before inserting the container into the reactor.

Starting Up the Reactor

1. Switch ON the main power supply
2. Press the "High Limit Button". The High Limit will not switch off if;
    a. Pressure transducer not connected, or
    b. The controller not working.
3. Switch ON Display button
4. Wait for a few minutes until the reading on the display stabilized.
5. Insert reaction gases into the system as follow:
    i Open a little Carbon monoxide (CO) inlet gas valve (on top of the gas tank) while ensure the outlet valve gas (on gas regulator) is fully closed.
    ii Crack open the main gas valve that connect the reactor to the gas supply.
    iii Open a little the outlet gas valve just to ensure enough flow to the reactor.
    iv Slowly increase the outlet gas valve pressure while referring to the display until required pressure is achieved.
    v Close main gas valve when desired pressure is achieved.

   - vi Close outlet gas valve follow by the inlet gas valve.
   - vii 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.
8. On the stirrer after desired temperature is achieved. Set the speed of the stirrer to be 300 to 315 RPM (optimum calibrated RPM)
9. Take both gas and liquid samples at 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 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.
6. Flush the reactor with acetone for cleaning up process.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results

4.1.1 Gas Chromatography (GC)

In a GC analysis, a known volume of gaseous or liquid analyte is injected into the head of the column. As the carrier gas sweeps the analyte molecules through the column, this motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto packing materials in the column. The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components of the analyte mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column. Thus, the time at which each component reaches the outlet and the amount of that component can be determined. Generally, substances are identified qualitatively by the order in which they emerge from the column and by the retention time of the analyte in the column.

Below are the results obtained from both liquid and gas samples taken from the experiment. A comparison between the benchmark sample, which uses ethanol as liquid solvent during the experiment as apart from n-hexane and n-octane:

Table 2: GC result for gas sampling

Chemical	Methanol (MeoH)	Carbon dioxide (CO2)	Carbon monoxide (CO)	Hydrogen (H2)
N-hexane	3.48e00	-	-	-
	1.52e00	128.6314	-	-
	1.98e00	-	-	-
	-	1.4971	-	-
	2.18e-01	3.59e-01	-	-
N-octane	8.97e-02	1.6170	5.6970	-
	1.42e-01	8.2900	55.2430	28.3200
	4.75e-02	4.3100	45.3650	-
	1.11e-01	7.253	54.1460	26.9900

Table 3: GC result for liquid sampling

Chemical	Area	Methanol % concentration	Ethanol % concentration
Ethanol (benchmark)	15481	0.014635853	0
N-hexane	0	0	0
	0	0	0
N-octane	9263	0.008757309	0
	1476	0.001395421	0

Discussion

Based on the result obtained, it can be concluded that by using paraffin namely n-hexane and n-octane, methanol is successfully synthesized. The paraffin also plays the role to "capture" the methanol existing in the gas form during the experiment into the liquid phase (liquid methanol). That can be seen by comparing the amount of methanol in both liquid and gas phase. Liquid phase methanol presence is higher as compared to the gas phase methanol.

It is also noted that the amount of methanol produce in ethanol (alcohol) is higher as compared to n-hexane and n-octane (paraffin). Although in theory paraffin is said to be having a greater specific heat capacity (Cp) than alcohol so that paraffin can absorb more reaction heat produced, but there maybe other intermediate reaction occurs during the process of producing methanol which deviates from the usual reaction scheme proposed by Chinchen and Spencer (1991):

$\mathrm{H2\ (g)} \rightleftharpoons \mathrm{2H\ (a)}$ .... (1)

$\mathrm{CO2\ (g)} \rightleftharpoons \mathrm{CO2\ (a)}$ .... (2)

$\mathrm{CO2\ (a) + H\ (a)} \rightleftharpoons \mathrm{HCO2\ (a)}$ .... (3)

$\mathrm{HCO2\ (a) + H\ (a)} \rightleftharpoons \mathrm{CH3O\ (a) + O\ (a)}$ .... (4)

$\mathrm{CH3O\ (a) + H\ (a)} \rightleftharpoons \mathrm{CH3OH\ (g)}$ .... (5)

$\mathrm{CO\ (g) + O\ (a)} \rightleftharpoons \mathrm{CO2\ (g)}$ .... (6)

$\mathrm{H2\ (g) + O\ (a)} \rightleftharpoons \mathrm{H2O\ (g)}$ .... (7)

As a result, the amount of methanol production using paraffin is lower than when alcohol is used as liquid solvent in the experiment.

4.1.2 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. 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.

Below are the result obtained from SEM. A fresh Cu/ZnO/Al2O3 catalyst was used as the first sample. The results are as shown below:

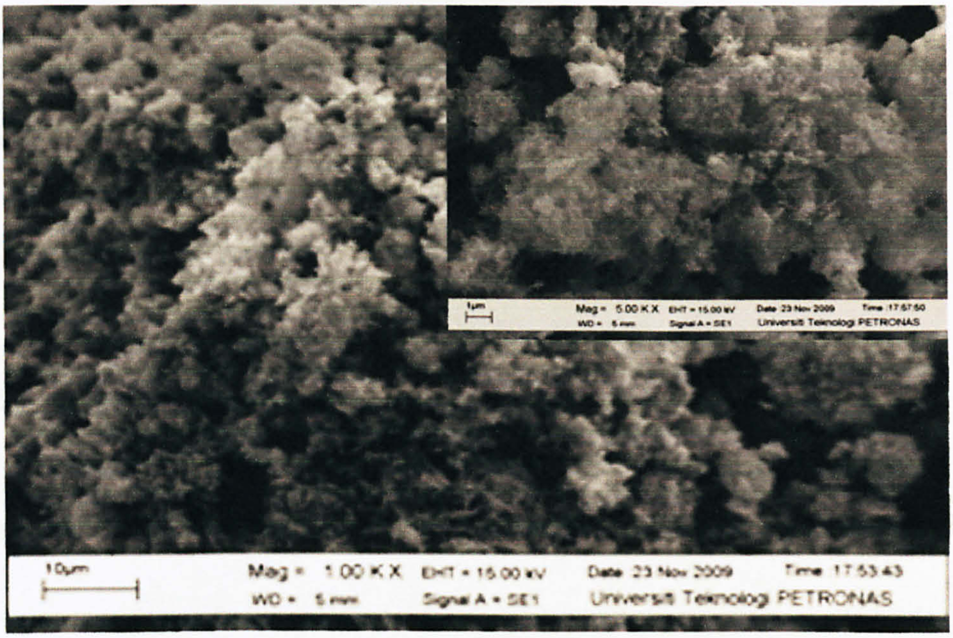

Figure 14: SEM on Cu/ZnO/Al2O3 fresh catalyst

Discussion

From the figure obtained from SEM, it can be seen that the topography of the Cu/ZnO/Al2O3 is not well distributed (dispersed) through out the entire area equally. A comparison between the result with the one used in the industry is made. Below is the SEM sample image of what the catalyst topography should actually look like:

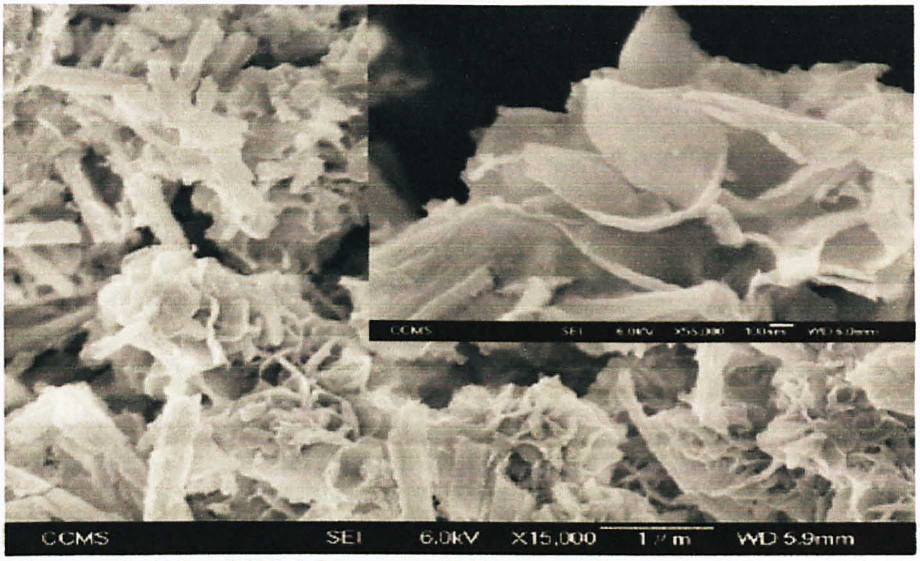

Figure 15: SEM image of flower-like homogeneous precipitation Cu/ZnO/Al2O3 catalyst

This behavior should be strongly depending on the catalyst parameters such as catalyst composition, nature of catalyst support, promoters or poisons (impurities) and method of catalyst preparation. One way to cater this problem is by introducing an acid solvent (citric acid) while preparing the catalyst. The acid functions as a medium to help disperse the Cu/ZnO on the Al2O3 support base surface. In addition to that, constant stirring also plays a crucial role in ensuring the Cu/ZnO will be well dispersed.

4.2 Findings

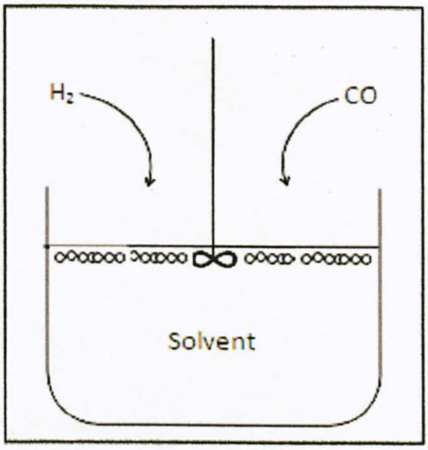

Figure 16: Interfacial Chemical Reaction in Methanol Synthesis Using $Cu/ZnO/Al_2O_3$ Catalyst

In producing methanol, close system is used as this reaction involves gases. Both hydrogen and carbon oxides gases will be supplied up to 30 bars to the system at the beginning of the process. A single layer chemical reaction producing methanol is expected to happen in this system consisting the gases, solvent and catalyst. The single layer reaction is occurred at the surface of the solvent, where most of the catalyst particles are floating due to the stirring effect.

Supplied hydrogen and carbon oxides gases will be absorbed to the catalyst pores, dispersed and react. A right RPM for the stirrer is required as to avoid vortex or turbulent and formation of multi layer catalysis surface reaction. It is best to avoid multilayer reaction as it might hinder catalysis 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. In the early work of the experiment, a benchmark solvent is used (ethanol) to determine the number of operating hour should the experiment be ran. This result will be applied to the other solvent afterwards. To get the number of operating hour, the pressure drop of the process is closely monitored. When the pressure drop became stable, this indicates how long the experiment should be run. A graphical explanation of the situation is as shown below:

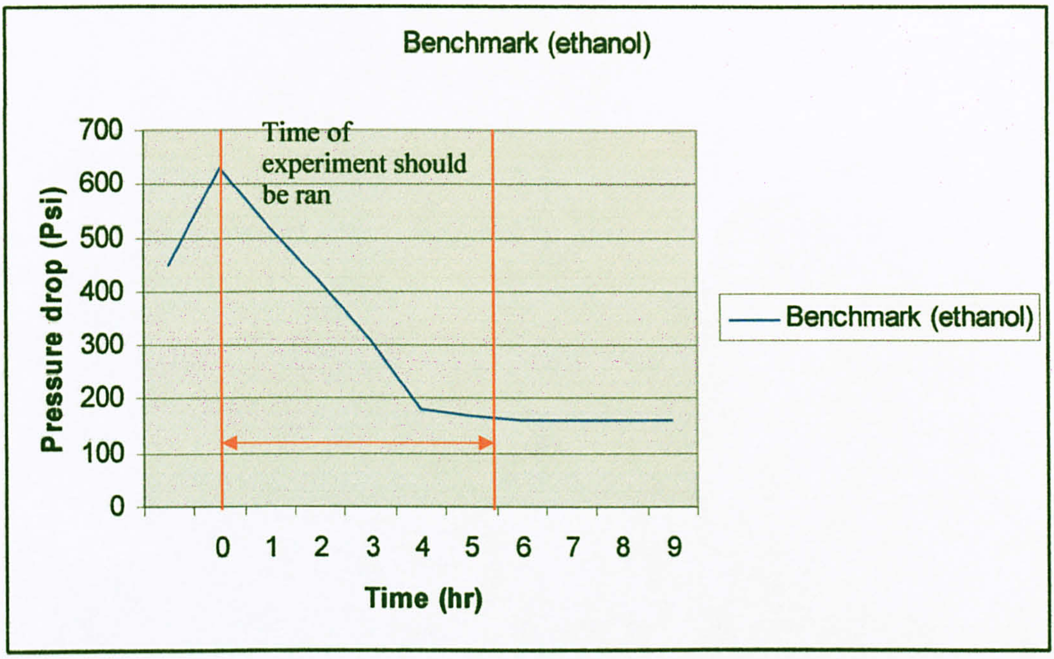

Figure 17: Calibration of Time of Experiment should be run

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

After running the experimental study on the effect of paraffin as liquid medium in methanol synthesis, there are a few conclusion can be drawn as listed below:

- Methanol is produce when using paraffin as liquid solvent in the experiment. But the amount of methanol produce is lower as compared to alcohol (ethanol) which being used as a benchmark for the experiment. This behavior maybe indicates that the methanol synthesis process for paraffin does not follow the usual proposed reaction scheme by Chinchen and Spencer (1991). There maybe different intermediate formed during the reaction in which needed a dedicated study on that particular area of interest.
- From the GC result, it is found that for n-hexane, methanol does not exist in the liquid form. Whereas there some amount of methanol exist in the gas form. This maybe concluded that n-hexane is not a good gas "capture" medium to turn the gas phase methanol into liquid form.
- From the SEM result, it is found that the topography of the catalyst used for the experiment is different as compared to the industrial catalyst (flower-like shape). This indicates that the synthesis of methanol from carbon dioxide over Cu/ZnO/Al2O3 is a sensitive reaction (Burch et al. 1990), meaning that the specific activity (turnover frequency) under standard conditions depends a lot on the catalysts parameters such as catalyst composition, metal crystallite size, nature of support, method of catalyst preparation, promoters or poisons (impurities).

5.2 Recommendation

A few recommendations are suggested with regard to the experimental study on the effect of paraffin as liquid medium in methanol synthesis. The recommendations are as below:

- To do a more thorough study on the kinetics and thermodynamics of the methanol synthesis using paraffin as liquid solvent. This is to get better understanding on what might be happening to the raw feed (CO + CO2 + H2) during the reaction.
- Use another paraffinic material as to replacing n-hexane with new paraffin having the ability to "capture" the methanol in liquid form.
- Find a new set of specific activity (turnover frequency) that will play around with the catalyst parameters. An immediate action for the above problem is to add in citric acid onto the surface of the catalyst to allow the Cu/ZnO be well dispersed on the catalyst surface.

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