Catalytic Activity of Cu/ZrO2 Catalyst Prepared by Coprecipitation Method for Methanol Synthesis

by

Ahmed Ismail Mohamed Ramily

Dissertation submitted in partial fulfillment of

The requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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Approved by,

(Dr. Maizatul Shima bt Shaharun)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2012

CERTIFICATION OF ORIGINALITY

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

Ahmed Ramily

AHMED ISMAIL MOHAMED RAMILY

ABSTRACT

The purpose of this project is to study the catalytic activity of Cu/ZnO-based catalysts and compare them with some other modified catalyst with Zirconia ZrO_2. This study is based on the physical properties of each catalyst plus the reaction kinetics. A practical methanol synthesis process greatly requires a high performance catalyst, which must be highly active and selective for methanol synthesis and also stable for a long period in a continuous operation. For the preparation of Cu/ZnO-based catalyst, which had high activity for methanol synthesis, was proposed and verified in experiments. Co-precipitation reaction was found to be an effective route for the preparation of a highly active and selective catalyst. Beside that it was found preparation conditions have a significant influence on the structure and surface properties of the precursors and the catalysts, as well as on the catalytic activities for methanol synthesis from CO_2 hydrogenation. The role of metal oxides contained in Cu/ZnO-based ternary catalysts is considered as a main concern for researchers to develop Cu/ZnO-based multicomponent catalysts containing two or three metal oxides. Furthermore, they have examined the change in the activity of the multicomponent catalysts during a long term methanol synthesis test, and investigated the methanol synthesis over the multicomponent catalysts by using a reactor with recycling equipment for unreacted gases.

ACKNOWLEDGEMENT

Praise to Allah for His guidance and blessings He has given me throughout this Final Year Project. It's the strength from Him that is what keeps us going in everything we do in our lives. My greatest appreciation goes to my supervisor, Dr. Maizatul Shima bt Shaharun for giving me such tremendous helps, advices, opinions and courage all the way through the completion of this project. I appreciate the time she allocates for me, to sit and discuss the problems I've faced along the way. A million thanks to her for having such confidence in me.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

Methanol is very commonly used as a feedstock in the chemical industries. It is also used as fuel and as a solvent. Commercially it is produced from synthesis gas (CO/CO2/H2) under high pressure and temperature. The used catalyst is mainly the copper/zinc based oxide catalyst. Methanol is used when producing for example formaldehyde, acetic acid and methyl tertiary butyl ether (MBTE). As a fuel, methanol is used for example in indy cars and in fuel cells.

The commercial methanol synthesis was implemented in 1923 by BASF in Germany. This process was known as the "high-pressure" process. The operation point in this process was 250 - 350 bar and 320 - 450°C. The catalyst used in this process was based on chromate. In the 1960s, the so called "low-pressure" process replaced the old one. The ability to produce sulfur free synthesis gas made it possible to use the more active Cu-based catalysts. The process was operated in the lower pressure and temperature, 60 - 80 bar and 250 - 280°C. Two low-pressure processes dominate the markets nowadays: ICI- and Lurgi-processes.

The commercial catalysts for the methanol synthesis consist of Cu particles with ZnO and Al2O3 as chemical and structural promoters.

Numerous investigations have been performed on the Cu/ZnO system, but the nature of the active sites and the reaction mechanisms still generate substantial controversy. The central point of argument is whether catalyzed methanol synthesis is a structure sensitive reaction or not.

Efficient conversion of carbon dioxide has received increased attention from the viewpoint of environmental protection and effective utilization of carbon resources, and the catalytic hydrogenation of carbon dioxide is a hot point. Most of the research was focused on CO_2 hydrogenation to methanol. Cu/ZrO_2 catalyst series are prepared and investigated the influence of the preparation variables on the catalytic behavior, and high activity and selectivity for methanol synthesis from CO_2 hydrogenation have been obtained. However, the zirconia bears the disadvantages of low surface area and poor thermal stability compared to the alumina counterparts. One simple and effective way to solve this question is to spread zirconia in supports with relative higher surface area, such as γ-alumina. In this project, we report CO_2 hydrogenation of Cu based catalysts supported on zirconia modified γ-Al_2O_3.

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

In current processes, selectivity and yield are too low. Higher selectivities and yields have to be achieved mainly by development of more selective catalysts, but optimization of reaction conditions and kinetics and operation also offers possibilities to improve catalytic performance. The production of methanol is strongly influenced by thermodynamics. The thermodynamic equilibrium limits the process to a low conversion and thus modifying the reaction kinetics is required if a high conversion is desired.

In order to optimize the conditions of the methanol synthesis using the Cu/Zno based catalyst containing some of metal oxides such as Al_2O_3 and ZrO_2 for finding the ideal operating conditions of the process, we have to study the other catalyst performance affecting the reaction with same operating conditions to observe the kinetics study of the process of production of methanol using synthesis of Co2 and H2 to get higher desired conversion with low cost operating conditions.

1.2.2 Significance of the Project

This project is significant to the industry as the analysis and deep understanding study of the methanol synthesis process, the behavior of each different catalysts regarding to its physical properties and the reaction kinetics behavior can help to further improve the process economically and operationally.

It will also aid in further understand the mechanism involved in the process in order to reach optimization of the process.

1.3 PROJECT'S OBJECTIVES

Towards completing the project, a few objectives needed to be achieved:

a) To study the catalytic activity of various composition of $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Al_2O_3/ZrO_2$ catalyst by determining the conversion of CO_2 and selectivity to methanol.

b) To correlate the physical properties such as surface area, pore size and pore volume with catalyst activity.

c) To compare the activity of various copper loading on $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Al_2O_3/ZrO_2$ catalyst.

1.4 SCOPE OF STUDY

The study of this project will be focused on breaking the thermodynamics limitations of getting high conversion and good selectivity and determine the optimum reaction conditions and parameters that influence on kinetics of the reaction by studying the catalytic activity of each catalyst and its physical properties.

CHAPTER 2

LITERATURE REVIEW/ THEORY

2.1 Process Description

The process chain for producing methanol is rather simple including the following phases:

- Production of synthesis gas
- Conversion of synthesis gas to methanol and
- Distillation of the reactor effluent to obtain the required product specifications.

Synthesis gas is a mixture of CO, CO_2 and H_2 produced from various sources through steam reforming, partial oxidation, CO2 reforming or autothermal reforming. In methanol synthesis, either CO or CO2 or both hydrogenates to methanol. The reactions are:

$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$ (ΔH298K, 50Bar = -40.9 kJ/mol)

$CO + 2H_2 \longrightarrow CH_3OH$ (ΔH298K, 50Bar = -90.7 kJ/mol)

$CO_2 + H_2 \longrightarrow CO + H_2O$ (ΔH298K, 50Bar = -49.8 kJ/mol)

Also the water gas shift reaction may occur. The water gas shift reaction is

$$CO + H2O \longrightarrow H2 + CO2$$

The production of methanol is strongly influenced by thermodynamics. The thermodynamic equilibrium limits the process to a low conversion and thus the recycling of the outlet is required if a high conversion is desired. The overall reaction is also strongly exothermic and thus a significant cooling is enquired. The recycling and the cooling are the main causes of the investment costs. The methanol synthesis reactors have been designed based on three principles: the high cooling demand, the low pressure drop and the favorable economy of scale.

The production of methanol from synthesis gas may take place under the low or high pressure. The high pressure process operates typically at 200 atm and 350°C while the low pressure process operates at 50 - 100 atm and 220 - 250°C. The low pressure process has such economical and operational benefits that almost all the methanol plants built after year 1967 operate at the low pressure.

The methanol synthesis may be performed in two-phase or three-phase reactors. Two phase reactors can be categorized in two classes based on the mechanism of the cooling.

In multiple catalyst bed reactors, the catalyst is divided into several sections and the cooling is performed between the sections. The sizes of the catalyst beds are designed so that the reactions reach the equilibrium. The cooling may be arranged with heat exchangers or by the injection of cold synthesis gas. In single bed designs, heat is continuously removed through a media such as water. In three-phase processes, methanol is removed from the reactor with the liquid phase through which the heat is also regulated.

2.2 Catalysts in methanol synthesis

Catalysts increase the reaction rates of the chemical reactions but are not consumed in the reactions. They lower the energy required for the initiation of the reactions and thus make the reactions easier to occur. Catalysts do not have influence on the position of the equilibrium and do not enable the reactions that are forbidden by the thermodynamics. Typically more than one chemical reaction occurs in chemical reactors. Catalysts may influence only the desired reaction and thus increase the selectivity of the process. This improves the utilization of the feedstock materials.

Heterogeneous catalyzed reactions occur on the gas/solid or liquid/solid interface. Thus the actual chemical reactions are preceded by the diffusion and adsorption of the reacting substances to the surface and into the pores of the catalysts and followed by the desorption and diffusion of the products to the bulk phase. The diffusion of the substances can be divided into the external and internal diffusion. In the external diffusion, the reacting substances are transported to the surface of the catalyst. In the internal diffusion, the reacting substances are transported into the pores of the catalyst where the adsorption takes place as the substances attach to the active sites of the catalyst. The chemical reaction takes place in the active sites. After the reaction, the products detach through the desorption and then diffuse to the bulk phase through the internal and external diffusion.

The structure of the catalyst is important concerning its usability. The shape and size influence the fluid flow through the catalyst bed and the mechanical strength ensures the long enough lifetime. High activity and selectivity are ensured if the catalyst has the correct chemical components and a high enough surface area. The stable operation of the catalyst may be achieved by the addition of components. The catalysts have typically three components: the support, active components and promoters. The active sites are responsible for the chemical reactions. The support is the basis of the catalyst over which the active components are placed. It must provide a high enough surface area for the active components to be evenly distributed to avoid undesired sintering. It is desired that the support does not have the catalytic activity. Promoters are substances that either enhance or inhibit the catalytic activity. Only a small amount of promoters is typically added to catalysts to obtain the desired activity, selectivity and stability properties.

The preparation of the catalysts is essential because the operation of the catalytic processes depends on the properties of the catalyst. Catalyst preparation procedure is typically obtained through time-consuming empirical studies. May be the most widely used methods for preparing heterogeneous catalysts are the impregnation and precipitation. In the impregnation method, the support of the catalyst is fabricated to small cylindrical shapes, such as pellets, rings or spheres. The support material is then exposed to a solution with an appropriate compound, which provides the active phase or a compound that is easily converted into the active phase. Precipitated catalysts are prepared by the rapid mixing of the concentrated solutions of metal salts leading to precipitates in a high surface area form. The precipitation step is followed by filtering and washing, where unwanted soluble salts are removed. Then the precipitate is dried and heated to convert the suitable oxides for the active phase.

The decrease in the activity of catalysts is called the deactivation. The deactivation is associated with the reduction in the number of active sites on the catalyst surface. The reasons for the deactivation are mechanical, thermal or chemical. The poisoning of catalysts is due to the adsorption of impurities on the catalyst surface, which blocks the access to the active sites. Fouling of catalysts is caused by an unfavorable interaction of catalyst with the reactants or products . Fouling is very common cause of deactivation. The third mechanism of the deactivation is sintering, which is associated with supported metal catalysts. The loss of the active sites is due to the sintering process, where the active metal particles agglomerate to form bigger particles in expense of the number of the active sites.

2.3 Used catalysts for methanol synthesis

The hydrogenation of carbon monoxide and carbon dioxide favors higher alcohols over methanol as products and dimethylether may also form in methanol synthesis. Thus an efficient and elective catalyst is required to produce methanol. Nowadays, there are catalysts allowing the production of almost pure methanol from synthesis gas under the low pressure (< 100 atm). These catalysts contain copper and a mixture of oxides such as ZnO - Al_2O_3 or ZnO – Cr_2O_3. Other oxides have also been used.

The effect of the catalyst preparation is essential concerning the usability of the catalyst as has been mentioned earlier. The preparation of the catalyst for the methanol synthesis has been studied and it has been found out that among the number of substances also the preparation methods and the conditions (pressure and temperature) have a great influence to the catalyst performance.

2.3.1 $Cu/ZnO-Al_2O_3$ catalysts

The first catalyst used for the methanol production from the synthesis gas was ZnOCr2O3. It was commercialized by BASF and used in the high pressure and high temperature synthesis. The improvements in the purification of the methanol synthesis feed (especially removal of sulphur) led to a major improvement in catalysts as the use of Cu-ZnO catalyst was enabled. The Cu/ZnO catalyst has a high activity and the synthesis can be operated at the lower pressure and temperature. Nowadays, the $Cu/ZnO-Al_2O_3$ catalyst is almost exclusively used in industry.

The $Cu/ZnO-Al_2O_3$ catalyst is widely studied in the literature. Also, studies with Cr_2O_3-based catalysts can be found . The $Cu/ZnO-Al_2O_3$ catalyst is very active for CO-rich feed but loses some activity with CO_2-rich feed .However, the utilization of CO_2 is very topical due to the environmental regulations and thus many studies have been carried out in order to find a catalyst that is active with CO_2-rich feed.

Saito et al (1996) presented that Cu/ZnO-based catalysts perform well with CO-rich feed but lose their activity with the increased amount of CO_2 in the feed. They noticed that the activity loss is due to water, which is produced along with methanol in CO_2 hydrogenation. Also, Novak et al. (1991) obtained results proving that water is responsible for the activity loss of the CuO/ZnO-Al2O3 catalyst. Wu et al. (2001) used different feed compositions to prove the detrimental effect of water to the Cu/ZnO catalysts. They found that the methanol yield decreases and water yield increases with the increasing amount of CO_2 in the feed. They concluded that the presence of water accelerates the deactivation of the Cu/ZnO-based catalysts. However, Wu et al. (2001) supposed that silica added to a Cu/ZnO-based catalyst could inhibit the detrimental effect of water thus allowing the methanol synthesis from the CO_2-rich feed with the Cu/ZnO based catalysts. Thermal sintering, sulphur and chloride poisoning, carbon deposition and physical damage may decrease the activity of the Cu-based catalysts in processes with methanol according to Twigg and Spencer (2003). Quinn et al. (2004) present that in three-phase methanol synthesis there may be arsine in the feed. They found that arsine is a strong deactivator of the Cu/ZnO-Al_2O_3 catalyst.

A new method for the low-pressure methanol synthesis has been proposed [Yang et al. 2006, Yang et al. 2008, Zhang et al. 2008]. It utilizes Cu/ZnO catalysts with alcohol promoters. Reubroycharoen et al. (2004) and Yang et al. (2008) used a Cu/ZnO-Al_2O_3 catalyst and Zhang et al. (2008) used a Cu/ZnO catalyst. In these studies, ethanol, propanol and buthanol have been studied as possible alcohol promoters. This new method was operated at the temperature of 443 K and at the pressure of 3.0 MPa. The low reaction temperature led to the high CO conversion (50 - 80 %).

Other than Zn oxides have been tested with Cu-based catalysts. For example, Huang et al. (2004) studied the influence of Zn, Cr and CO oxide additives to Cu-based catalysts. They noticed significant improvements in the catalyst activities for the water gas shift reaction and methanol synthesis when Cr_2O_3 was added to a Cu catalyst. No significant activity changes were observed with CO addition. Also, SiO_2 and its influence to the activity of the Cu-based catalysts have been studied (Fisher et al. 1997, Choi et al. 2001). Choi et al. (2001) noticed that the addition of SiO_2 increased the catalytic activity for the methanol synthesis from CO_2.

2.3.2 Catalysts with Zirconium

Zirconium has been recognized as an interesting support material to Cu-based catalysts, since it has been shown to improve the activity of catalysts for methanol synthesis from both CO and CO_2 . Jung et al. (2002) studied the use of the Cu/ZrO_2 catalyst for methanol synthesis. They found that the activity of the catalyst is strongly dependent on the phase of the ZrO_2. This has been reported also by Liu et al. (2005), who studied the Cu-based catalysts with the nanocrystalline Zr addition. Yang et al. (2006) compared a Cu/ZnO catalyst supported by Zr to the pure Cu/ZnO catalyst. They presented that the Cu/ZnO with the Zr support showed the high activity and selectivity towards CO and

CO_2, especially CO_2. A ZrO2 doped Cu/ZnO catalyst showed also the high stability in a long period test. Yang et al. (2006) noticed that the conversion and selectivity were higher with the Zr supported catalyst.

Słoczyński et al. (2004) compared the use Cu, Ag and Au in the catalysts for methanol synthesis. The studied catalysts were of $M/(3ZnO{\cdot}ZrO_2)$ from, where M is Cu, Ag or Au. They found out that the catalyst with Cu showed the highest activity in methanol synthesis. They concluded that the synergy between Cu and the support is apparent and advantageous for methanol synthesis.

Fisher et al. (1997) studied Cu/SiO_2 catalyst with Zr addition. They experimented with the catalyst with different Zr loadings and noticed that the increase in the Zr loading increased the rate of methanol synthesis. The effect was found out to be more significant for CO hydrogenation than for CO_2 hydrogenation. They also noticed that the maximum selectivity to methanol is obtained with intermediate Zr loadings.

2.4 Performance of CO_2 hydrogenation on Cu based catalyst

The products of CO_2 hydrogenation over Cu based catalyst are CO, CH_4, CH_3OH and H_2O. The catalytic activity and selectivity of products, besides H_2O, of the Cu based catalyst with various Zr loading are listed in Table 1.1. From this table, it can be seen that the $Cu–Zr/\gamma\text{-}Al_2O_3$ catalyst has a higher activity and CH_3OH selectivity in CO_2 hydrogenation compared to the $Cu/\gamma\text{-}Al_2O_3$ catalyst. It indicates that the modification of $\gamma\text{-}Al_2O_3$ with zirconia can improve the catalytic performance of Cu based catalysts. The largest CH_3OH yield is obtained on the $12Cu10Zr/\gamma\text{-}Al_2O_3$ catalyst under the reaction conditions.

Catalyst	Reaction temperature (°C)	Space velocity (h^{-1})	CO_2 conv. (%)	Selectivity (%)		
				CO	CH_4	CH_3OH
$12Cu/\gamma\text{-}Al_2O_3$	240	3600	5.50	78.0	5.1	16.9
$12Cu5Zr/\gamma\text{-}Al_2O_3$			5.73	78.5	4.8	16.7
$12Cu10Zr/\gamma\text{-}Al_2O_3$			5.75	75.9	3.8	20.3
$12Cu15Zr/\gamma\text{-}Al_2O_3$			7.38	77.4	3.7	18.9
$12Cu/\gamma\text{-}Al_2O_3$	260	3600	9.21	81.7	7.6	10.7
$12Cu5Zr/\gamma\text{-}Al_2O_3$			10.20	80.9	7.0	12.1
$12Cu10Zr/\gamma\text{-}Al_2O_3$			10.46	79.4	6.0	14.6
$12Cu15Zr/\gamma\text{-}Al_2O_3$			11.36	80.2	6.8	13.0
$12Cu/\gamma\text{-}Al_2O_3$	240	1800	11.06	80.2	6.2	13.6
$12Cu5Zr/\gamma\text{-}Al_2O_3$			13.91	79.0	5.9	15.1
$12Cu10Zr/\gamma\text{-}Al_2O_3$			14.30	77.4	5.5	17.1
$12Cu15Zr/\gamma\text{-}Al_2O_3$			14.14	78.2	5.8	16.0

Table 2.1. Performance of CO_2 hydrogenation on various catalysts

Note: Reaction conditions: $P = 3.0$ MPa, $H_2/CO_2 = 3:1$ (molar ratio).

2.4.1 Effect of reaction temperature on CO_2 hydrogenation over 12Cu/γ-Al_2O_3 and 12Cu10Zr/γ-Al_2O_3 catalyst

The effect of temperature on the catalytic performance of 12Cu/γ-Al_2O_3 and 12Cu10Zr/γ-Al_2O_3 is shown in Figure 2.1. It can be seen that the conversion of CO_2 and the CH_3OH selectivity over 12Cu10Zr/γ-Al_2O_3 at any temperature are higher than those over 12Cu/γ-Al_2O_3. This proves further that the modification of γ-$Al_2O_3$with zirconia can improve the catalytic performance of Cu based catalysts as mentioned above. From Figure 2.1, it can also be seen that with the increase of reaction temperature, the conversion of CO_2 is enhanced while the CH_3OH selectivity decreases on both catalysts. The ΔH_{298} of CH_3OH synthesis from CO_2 and H_2 is -49.43 kJ mol^{-1}, it is an exothermal reaction and, therefore, it is disadvantageous to CH_3OH synthesis when the reaction temperature increases.

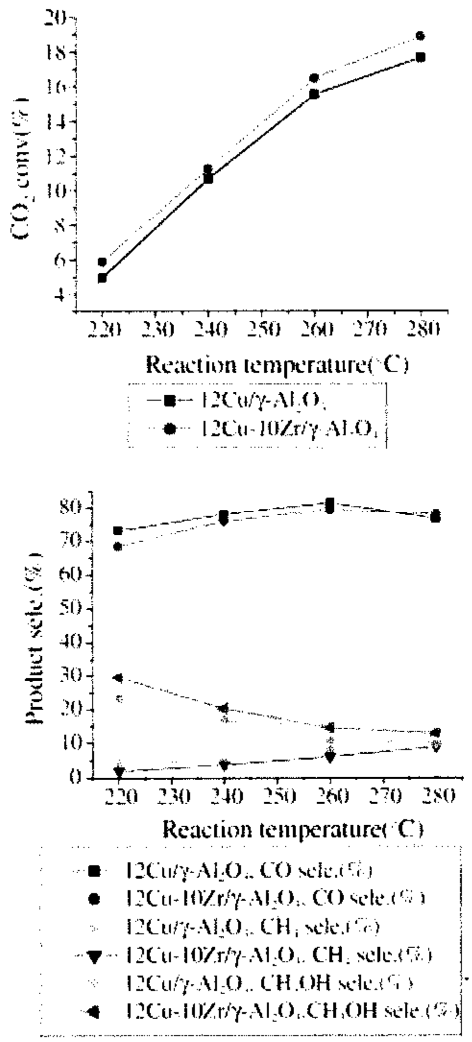


Figure 2.1. Effect of reaction temperature on CO2 Hydrogenation over 12Cu/γ-Al2O3 and 12Cu10Zr/γ-Al2O3 catalyst. Reaction conditions: $P = 3.0$ MPa, GHSV = 3600 h−1, H2/CO2 = 3:1 (molar ratio).

2.4.2 Effect of molar ratio of H_2/CO_2 on reaction behaviors over 12Cu/γ-Al_2O_3 and 12Cu10Zr/γ-Al_2O_3 catalyst

Figure 2.2 shows the effect of the molar ratio of H_2/CO_2 on the catalytic activity and selectivity over 12Cu/γ-Al_2O_3 and 12Cu10Zr/γ-Al_2O_3 catalysts. It can be seen that the CO_2 conversion increases along with the molar ratio as H_2/CO_2 of the reactant gas increases from 1 to 10. The selectivity of CH_3OH is the highest, by a small amount, when $H_2/CO_2 = 3$, and then decreases slightly. As the molar ratio of H_2/CO_2 increases, the selectivity of CH_4 increases while the selectivity of CO decreases. The equation of CO_2 hydrogenation to CH_3OH is as follows:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (1)$$

There are also two main by-reactions, the products being CO and CH_4:

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (2)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (3)$$

Reaction (1) generates CH_3OH. The coefficient ratio of H_2/CO_2 is 3:1, so the highest value of CH_3OH selectivity is obtained when $H_2/CO_2 = 3$. Reaction (2) generates CO with the coefficient ratio of H_2/CO_2 of 1:1, and reaction (3) generates CH_4 with the coefficient ratio of H_2/CO_2 of 4:1. Hence, the CH_4 selectivity increases while the CO selectivity decreases as the molar ratio of H_2/CO_2 increases.

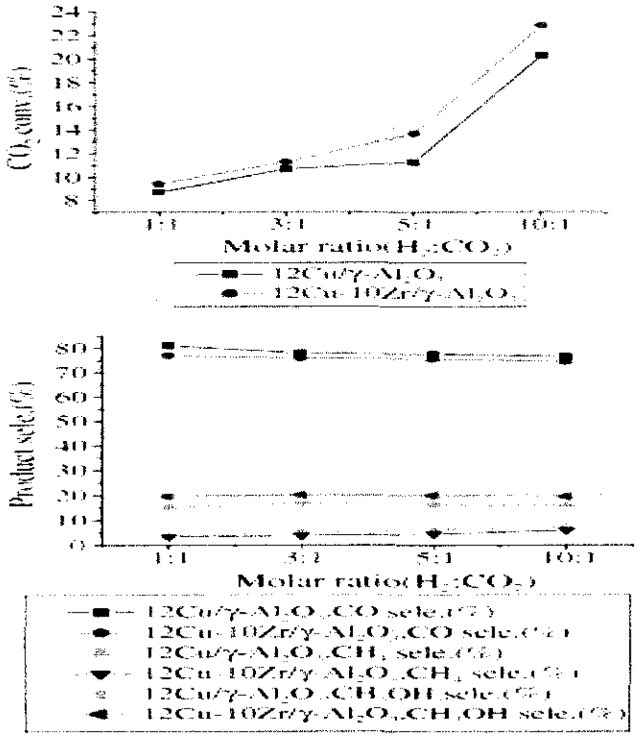


Figure 2.2. The effect of molar ratio of CO_2 and H_2 reaction behaviors over 12Cu/γ-Al_2O_3 and 12Cu10Zr/γ-Al_2O_3 $_{catalyst}$. Reaction conditions:

T = 240 °C, P = 3.0 MPa, GHSV = 3600 h^{-1}.

2.4.3 X-ray diffraction (XRD) analyses of various catalysts

The activity of catalysts is associated with the interaction between the metal and the support to a large extent. The Cu based catalysts supported on zirconia modified γ-Al_2O_3 were examined by XRD to determine the present phase. The XRD pattern of Cu–Zr/γ-Al_2O_3 catalysts is shown in Figure 2.3. When the support was not modified by zirconia, apparent diffraction peaks of CuO are observed in pattern (a) of 12Cu/γ-Al_2O_3. Along with the addition of zirconia and the increase of zirconia loading, the intensity of the diffraction peaks of CuO weakened gradually, while the line width broadened slightly. It indicates that the modification of the support with zirconia promoted the dispersion of the CuO species. Furthermore, no other diffraction peaks, such as a zirconium phase, were detected by XRD on Cu–Zr/γ-Al_2O_3 besides the diffraction peaks of CuO. The compositional analysis of the catalysts by means of energy dispersive spectroscopy (EDS) in scanning electron microscopy proves there is only a small standard deviation between the experimental EDS data and the nominal composition. This suggests that ZrO_2 was highly dispersed on the support in the presence of CuO. As a conclusion, there are strong interactions between the CuO species and the ZrO_2 species. It is no other than this interaction that promotes the dispersion of the two species.

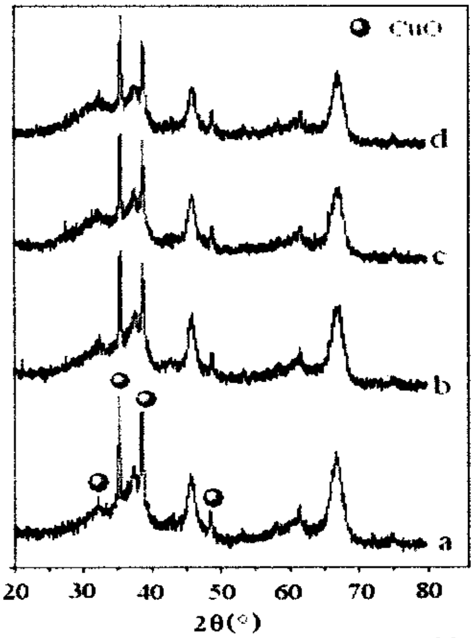


Figure 2.3. XRD patterns of Cu–Zr/γ-Al_2O_3 catalysts with various Zr loading (a) 12Cu/γ-Al_2O_3; (b) 12Cu5Zr/γ-Al_2O_3; (c) 12Cu10Zr/γ-Al_2O_3; (d) 12Cu15Zr/γ-Al_2O_3.

2.5 Designs of methanol synthesis reactors

Different designs of methanol synthesis reactors have been used:

- Quench reactor
- Adiabatic reactors in series
- Boiling water reactors (BWR)

A **quench** reactor consists of a number of adiabatic catalyst beds installed in series in one pressure shell. In practice, up to five catalyst beds have been used. The reactor feed is split into several fractions and distributed to the synthesis reactor between the individual catalyst beds. The quench reactor design is today considered obsolete and not suitable for large capacity plants.

A synthesis loop with **adiabatic** reactors normally comprises a number (2-4) of fixed bed reactors placed in series with cooling between the reactors. The cooling may be by preheat of high pressure boiler feed water, generation of medium pressure steam, and/or by preheat of feed to the first reactor. The adiabatic reactor system features good economy of scale. Mechanical simplicity contributes to low investment cost. The design can be scaled up to single-line capacities of 10,000 MTPD or more.

The **BWR** is in principle a shell and tube heat exchanger with catalyst on the tube side. Cooling of the reactor is provided by circulating boiling water on the shell side. By controlling the pressure of the circulating boiling water the reaction temperature is controlled and optimized. The steam produced may be used as process steam, either direct or via a falling film saturator.

The isothermal nature of the BWR gives a high conversion compared to the amount of catalyst installed. However, to ensure a proper reaction rate the reactor will operate at intermediate temperatures - say between 240°C and 260°C - and consequently the recycle ratio may still be significant.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 PROJECT FLOW

The Project flow has been determined and has been commenced for two semesters. The flow of this particular study can be defined as below:

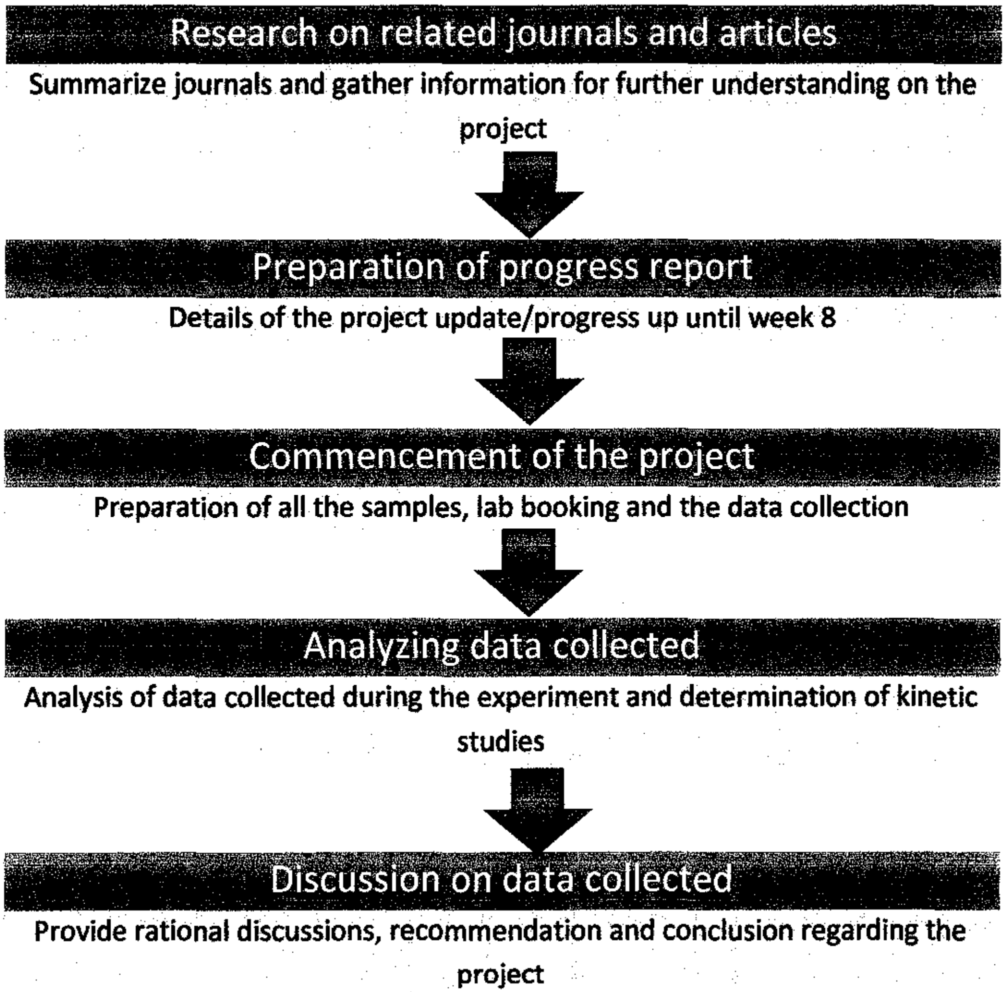
a) Goal settings
The objectives are set up according to the study needs and should be completed within the specified time frame.

b) Development of appropriate course of action
Each process should be parallel to the objectives stated at the beginning of the project. Process that is developed should be logical and can be done without interfering with the purpose of the study.

c) Data collection
Data is gathered from any established journals and articles that is related to the project title to further understand the basic of the project and provide the flow of experiment that will be conducted.

d) Data analysis
Data is interpreted from the results of the experiment that has been conducted. The catalytic activity of each catalyst is analyzed and the kinetics of the reaction is being studied.

3.2 PROJECT PLANNING



Research on related journals and articles

Summarize journals and gather information for further understanding on the project

Preparation of progress report

Details of the project update/progress up until week 8

Commencement of the project

Preparation of all the samples, lab booking and the data collection

Analyzing data collected

Analysis of data collected during the experiment and determination of kinetic studies

Discussion on data collected

Provide rational discussions, recommendation and conclusion regarding the project

Figure 3.1 Project planning

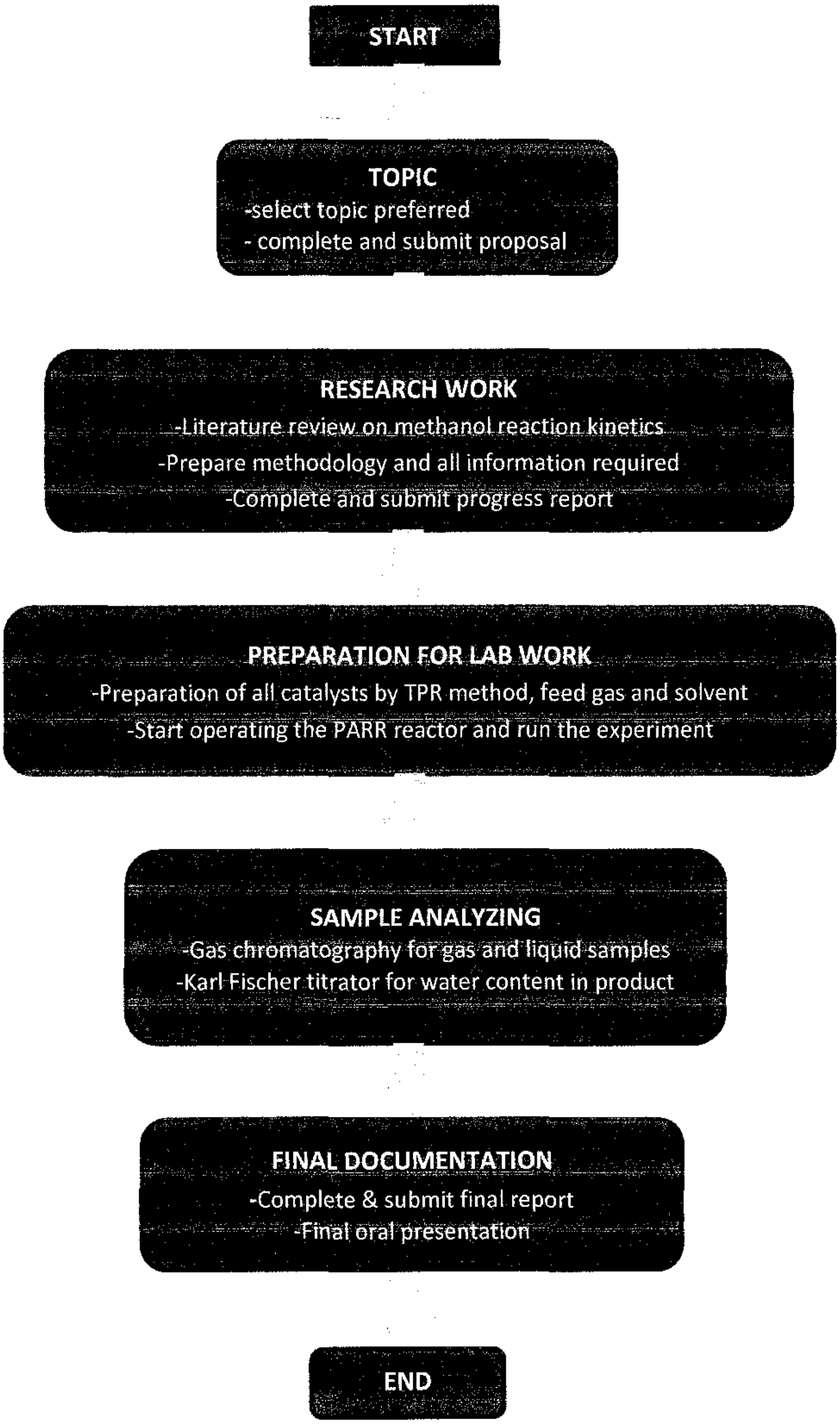
3.3 PROJECT MILESTONE (GANTT CHART)

Timelines for FYP 2

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■	Mid-Semester Break								
2	Submission of Progress Report									●							
3	Project Work Continues									■	■	■	■	■			
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

Figure 3.2 Project milestone/Gantt chart

3.4 REASEARCH METHODOLOGY



3.5 SAMPLES PREPARATION

3.5.1 Chemicals/ samples

Here are the samples to be used for each run of the experiment for different catalyst:

1) 25 ml Ethanol 95% as solvent.
2) 0.5 g of the desired catalyst for each run.
3) Feed gas of H_2 , CO_2 with mol ratio of 3:1 respectively.

3.5.2 Tools/ Machines

This project involved four different kind of machines, each has specifications and contribution in data gathering process :

a) Temperature programmed reduction tool (TPR).
b) High pressure stirred reactor (PARR).
c) Gas chromatography (GC) for gas and liquid samples.
d) Karl Fischer titrator.

a) Temperature-Programmed Reduction Method for catalyst activation :

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

A simple container (U-tube) is filled with the catalyst. This sample vessel is positioned in a furnace with temperature control equipment. A thermocouple is placed in the solid for temperature measurement. To remove the present air the container is filled with an inert gas (nitrogen, argon). Flow controllers are used to add hydrogen (for example, 10 Vol -% hydrogen in nitrogen). The composition of the gaseous mixture is measured at the exit of the sample container with appropriate detectors (thermal conductivity detector, mass spectrometer). Now, the sample in the oven is heated up on predefined values. Heating values are usually between 1 K/min and 20K/min. If a reduction takes place at a certain temperature, hydrogen is consumed which is recorded by the detector. In practice the production of water is a more accurate way of measuring the reduction. This is due to the potential for varying hydrogen concentrations at the inlet, so the decrease in this number may not be precise, however as the starting concentration of water will be zero, any increase can be measured more accurately.

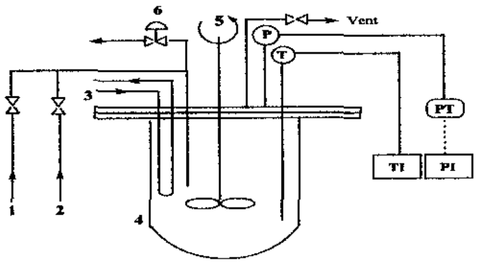
(TCD) is used to measure changes in the thermal conductivity of the gas stream. The TCD signal is then converted to concentration of active gas using a level calibration. Integrating the area under the concentration vs. time (or temperature) yields total gas consumed

TPR Operating Conditions:

- Temperature : 350 °C
- Gas used : H_2
- Gas flowrate : 20 ml/min

b) High Pressure Stirred reactor (PARR 4590)

The hydrogenation of CO_2 with existence of each catalyst reaction was carried out by using a batch type tube reactor. PARR reactor which can sustain high pressure and temperature needed in the process.



(1) CO_2; (2) H_2; (3) cooling water in; (4) high pressure reactor; (5) stirrer; (6) sampling valve; (T) thermocouple; (P) pressure gauge

Figure 3.3: PARR Reactor 4590

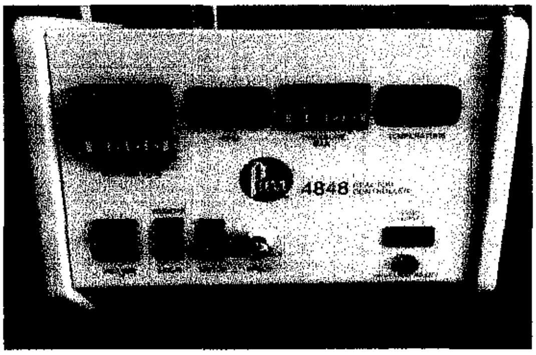


Figure 3.4: PARR Reactor Controller 4848

c) Gas chromatography:

- Gas sample analysis using Gas Chromatography:

Chromatography is a very important analytical tool because it allows the chemist to separate components in a mixture for subsequent use or quantification. Most samples that chemists want to analyze are mixtures as our sample consists of H_2 and CO_2. If the method of quantification is selective for a given component in the mixture, separation is not required. However, it is often the case that the detector is not specific enough, and a separation must first be performed. There are several types of chromatography depending on the type of sample involved. In this experiment, we'll use gas chromatography.

The gas chromatograph makes it possible to separate the volatile components of a very small sample and to determine the amount of each component present. The essentials required for the method are an injection port through which samples are loaded, a "column" on which the components are separated, a regulated flow of a carrier gas which carries the sample through the instrument, a detector, and a data processor. In gas chromatography, the temperature of the injection port, column, and detector are controlled by thermostatted heaters. Figures 1 and 2 are pictures of the instrument from the front and rear respectively, with important components labeled.

➢ Detector Used :

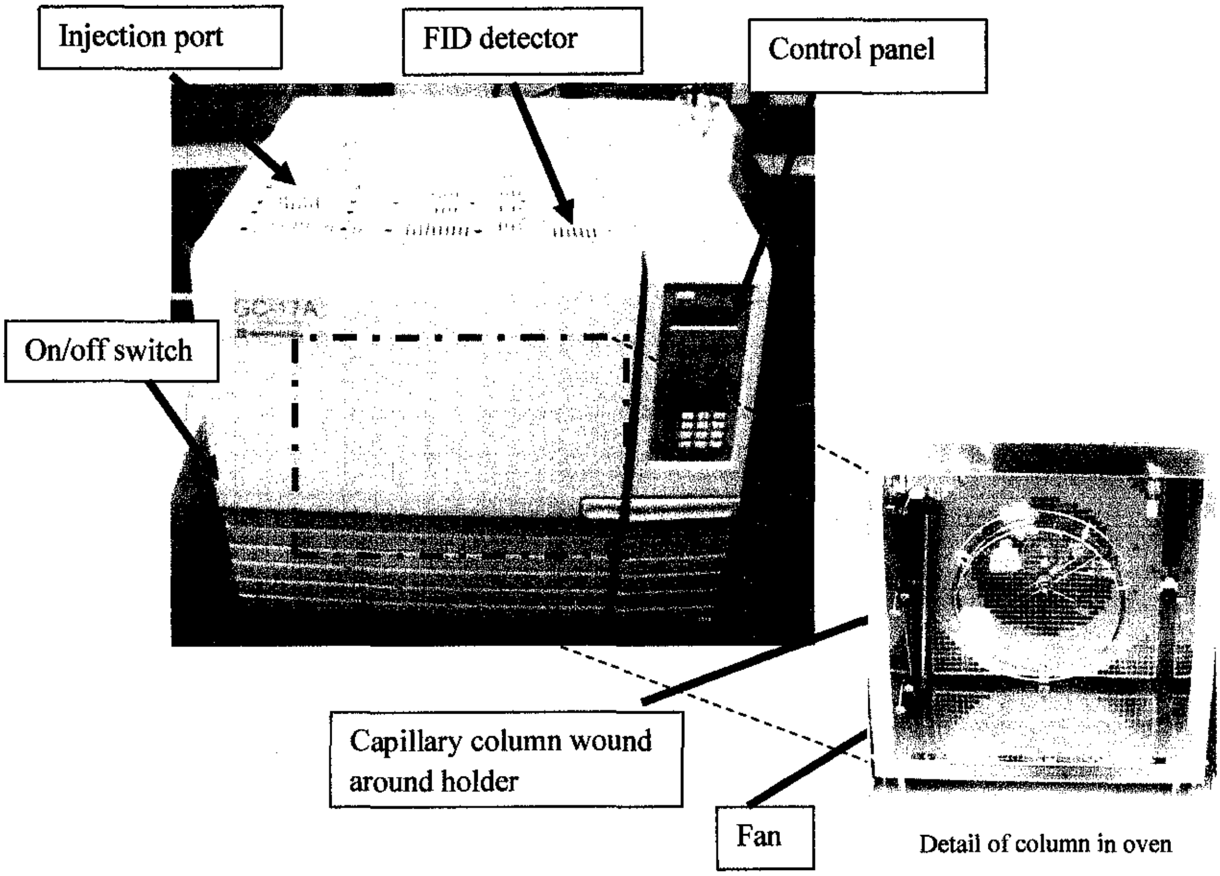
<u>Thermal Conductivity Detector (TCD).</u> It is based on the comparison of two gas streams, one containing only the carrier gas, the other one the carrier gas and the compound. Naturally, a carrier gas with a high thermal conductivity which is Nitrogen used in order to maximize the temperature difference (and therefore the difference in resistance) between two thin tungsten wires. The large surface-to-mass ratio permits a fast equilibration to a steady state. The temperature difference between the reference cell and the sample cell filaments is monitored by a Wheatstone bridge circuit.

➢ Column Selection:

The choice of column depends on the sample and the active measured. The main chemical attribute regarded when choosing a column is the polarity of the mixture, but functional groups can play a large part in column selection. The polarity of the sample must closely match the polarity of the column stationary phase to increase resolution and separation while reducing run time. The separation and run time also depends on the film thickness (of the stationary phase), the column diameter and the column length.

Here are the operating conditions for the gas chromatography instrument:

- Temperature : 60 °C
- Pressure : 30 kpa
- Carrier Gas : Nitrogen
- Column type : GC-Q 113-3422
- Column length : 25 m
- Column ID : 0.32 mm
- Column flow : 0.99 ml/min
- Linear Velocity : 19.8 cm/sec



Detail of column in oven

Figure 3.5. Front view of gas chromatograph

- **Liquid Sampling analysis using Gas Chromatography :**

  - **Detector Used**

Flame Ionization Detector (FID). The detector is very sensitive towards organic molecules (10^{-12} g/s, linear range: $10^{6}-10^{7}$), but relative insensitive to a few small molecules e.g. N_2, H_2, H_2S, CO, CO_2, H_2O. If proper amounts of hydrogen/air are mixed, the combustion does not afford any ions. If other components are introduced that contain carbon atoms cations are produced in the effluent stream. The more carbon atoms are in the molecule, the more fragments are formed and the more sensitive the detector is for this compound (-- > response factor). However, due to the fact that the sample is burnt (pyrolysis), this technique is not suitable for preparative GC. In addition, several gases are usually required to operate a FID: hydrogen, oxygen (compressed air), and carrier gas. Besides, it concerns more about analysis of methanol composition as main product as well as ethanol as solvent.

Here are the operating conditions for the gas chromatography instrument:

- Injection Temperature : 250 °C
- Detector Temperature : 260 °C
- Pressure : 77 kpa
- Carrier Gas : Helium
- Column type : BP-20 SGE
- Column length : 30 m
- Column ID : 0.25 mm
- Column flow : 1.00 ml/min
- Linear Velocity : 26.1 cm/sec

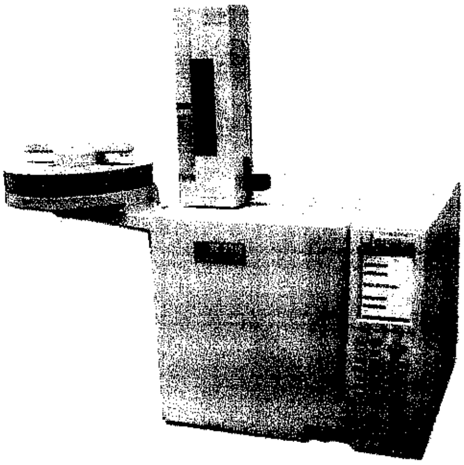


Figure 3.6 Gas Chromatography for liquid samples

d) Karl Fischer titrator for analyzing water content.

The Water Determination Test (Karl Fischer Method) is designed to determine water content in substances, utilizing the quantitative reaction of water with iodine and sulfur dioxide in the presence of a lower alcohol such as methanol and an organic base such as pyridine.

There are two determination methods different in iodine-providing principle: the volumetric titration method and the coulometric titration method.

In the volumetric titration method, iodine required for reaction with water is previously dissolved in water determination TS, and water content is determined by measuring the amount of iodine consumed as a result of reaction with water in a sample.

In the coulometric titration method, first, iodine is produced by electrolysis of the reagent containing iodide ion, and then, the water content in a sample is determined by measuring the quantity of electricity which is required for the electrolysis (i.e., for the production of iodine), based on the quantitative reaction of the generated iodine with water.

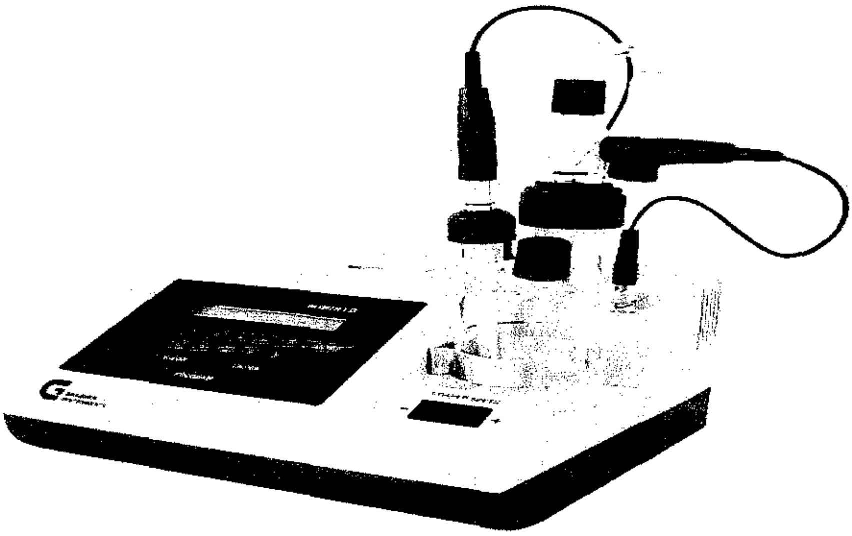
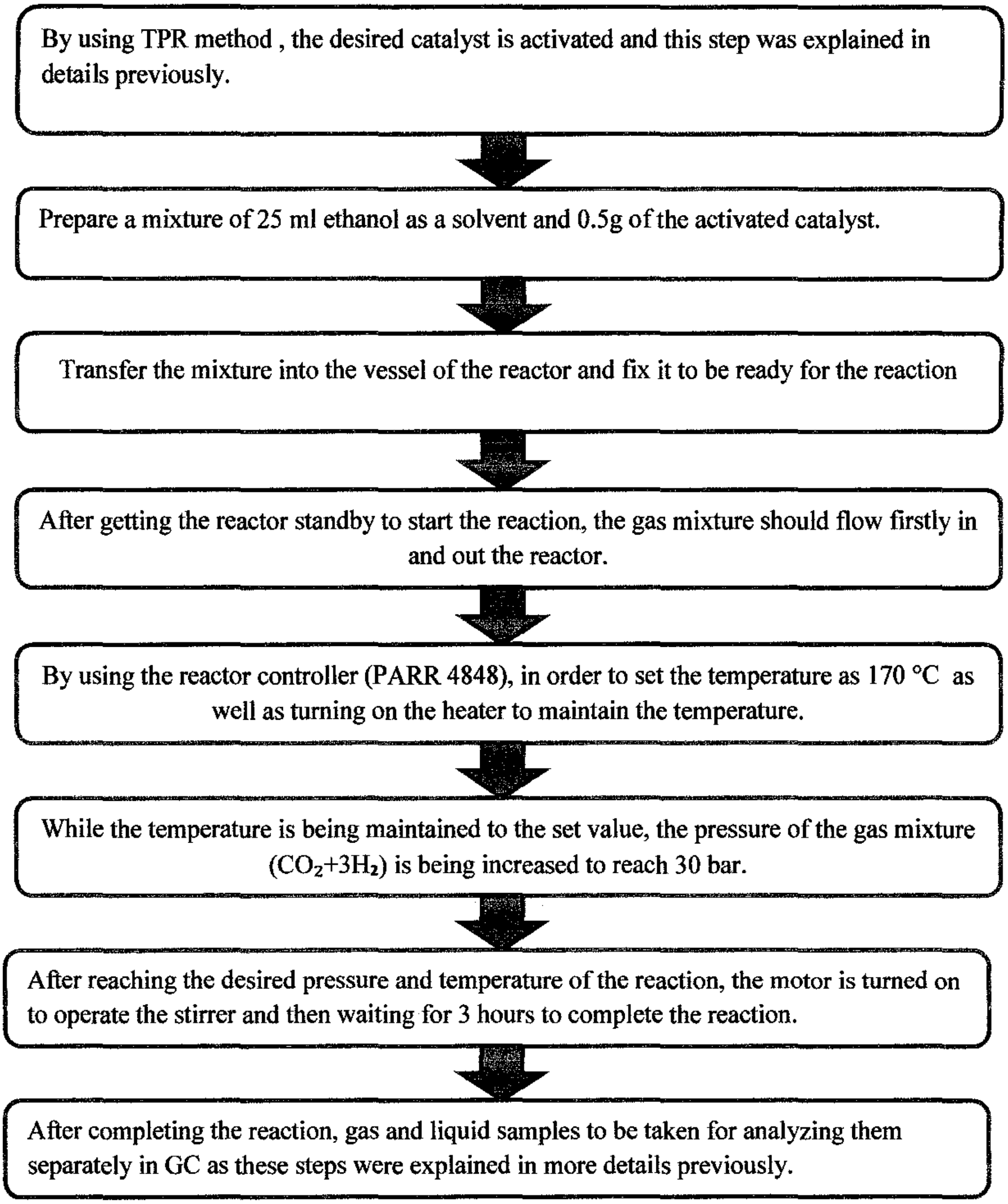


Figure 3.7 Karl Fischer titrator

3.6 EXPERIMENTAL METHODOLOGY:



By using TPR method , the desired catalyst is activated and this step was explained in details previously.

Prepare a mixture of 25 ml ethanol as a solvent and 0.5g of the activated catalyst.

Transfer the mixture into the vessel of the reactor and fix it to be ready for the reaction

After getting the reactor standby to start the reaction, the gas mixture should flow firstly in and out the reactor.

By using the reactor controller (PARR 4848), in order to set the temperature as 170 °C as well as turning on the heater to maintain the temperature.

While the temperature is being maintained to the set value, the pressure of the gas mixture (CO_2+$3H_2$) is being increased to reach 30 bar.

After reaching the desired pressure and temperature of the reaction, the motor is turned on to operate the stirrer and then waiting for 3 hours to complete the reaction.

After completing the reaction, gas and liquid samples to be taken for analyzing them separately in GC as these steps were explained in more details previously.

Figure 3.8 Experimental Methodology

3.7 PHYSICAL PROPERTIES OF USED CATALYSTS:

Catalyst	Cu Loading %	BET Surface (m^2/g)	Pore Size (nm)	Pore Volume (cm^3/g)
Cu-ZnO/Al_2O_3				
CZA02-45	45	59.87	27.3	0.449
CZA02-60	60	26.67	42.4	0.221
Cu-ZnO/Al_2O_3/ZrO_2				
CZAZ-30	30	21.22	45.6	0.238
CZAZ-45	45	42.62	29.8	0.275
CZAZ-60	60	35.71	43.1	0.305
CZAZ-75	75	48.69	22.3	0.291

Table 3.1: Physical properties of used catalysts

- Compositions of the used Catalysts:

Catalyst	Cu (%)	ZnO (%)	Al_2O_3 (%)	ZrO_2 (%)
Cu-ZnO/Al_2O_3				
CZA02-45	45	45	10	-
CZA02-60	60	30	10	-
Cu-ZnO/Al_2O_3/ZrO_2				
CZAZ-30	30	60	5	5
CZAZ-45	45	45	5	5
CZAZ-60	60	30	5	5
CZAZ-75	75	15	5	5

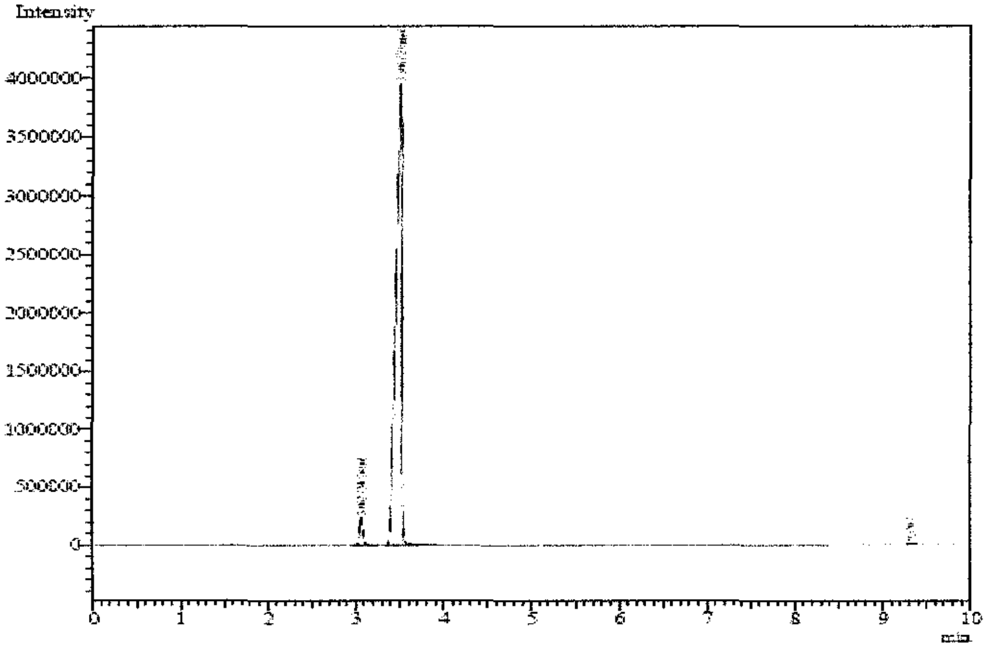
Table 3.2: Compositions of the used Catalysts

CHAPTER 4

RESULTS AND DISCUSSION

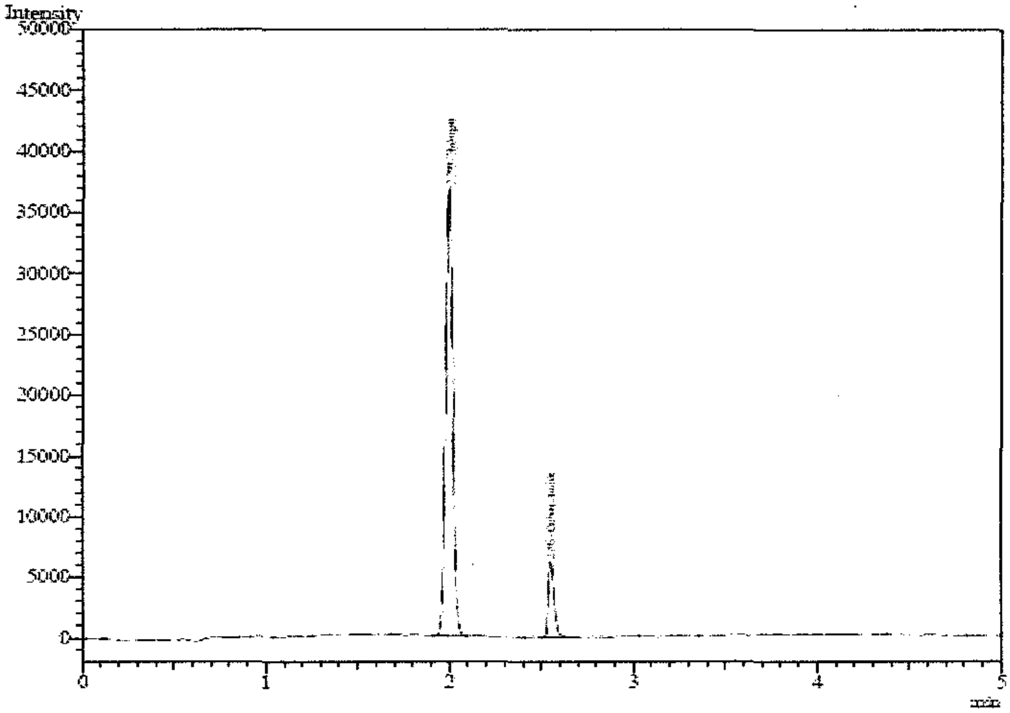
4.1 Sample Analysis by Gas Chromatography (GC)

All the six samples-which have been run in the presence of six different catalysts-were analyzed successfully by the gas chromatography tool. After each other one gas sample and another liquid sample to be test by the GC, one test for gas sample to analyze the output composition of the syn gas for calculating the gas conversion, while the other test was conducting for the liquid sample to analyze the CH_3OH yield. Here is a sample of the GC analysis while all the analysis results obtained for all the different catalysts are attached in the APPENDIX.



Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	3.062	640443.51	242837.46	6.3653	%	Methanol
2	3.506	17572940.08	3948642.88	119.9957	%	Ethanol
3	9.320	17391.68	9299.78	0.0000		
4	19.721	241778.42	39495.83	0.0000		
Total		18472553.69		126.3610		

Figure 4.1 Gas Chromatography analysis result for liquid sample



Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.299	89440.39	36885.00	63.1810	%	Hydrogen
2	2.795	12574.44	6166.84	14.4578	%	Carbon Dioxide
Total		102014.83		77.6388		

Figure 4.2 Gas Chromatography analysis result for Gas sample

4.2 Data and Results obtained from the GC analysis

4.2.1 Yield of CH_3OH for all samples of all different catalysts

Catalyst	**Yield %**
Cu-ZnO/Al_2O_3	
CZA02-45	2.2893
CZA02-60	5.8383
Cu-ZnO/Al_2O_3/ZrO_2	
CZAZ-30	5.9312
CZAZ-45	4.4218
CZAZ-60	5.8747
CZAZ-75	6.3653

Table 4.1 Yield of methanol for all catalysts

Note: Reaction conditions: *P*=30 bar T=170 °C, $H_2/CO_2 = 3{:}1$ (molar ratio).

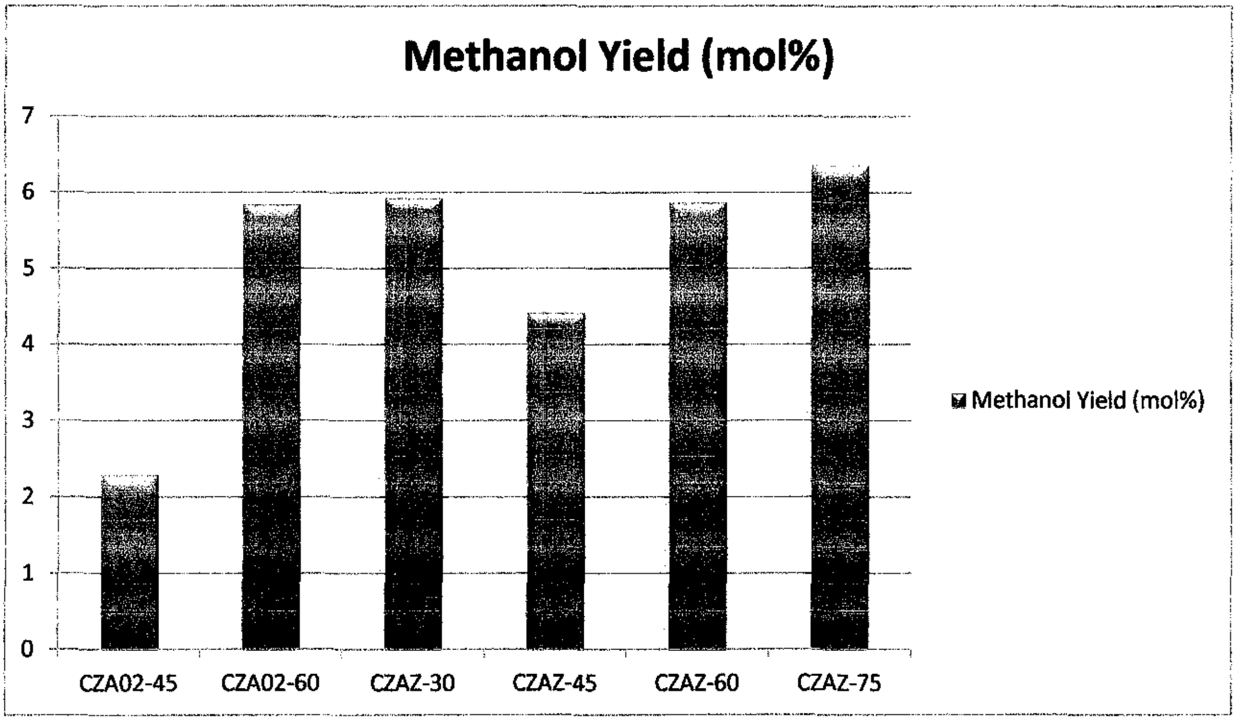


Figure 4.3 Yield of methanol for all catalysts

4.2.2 Conversion of CO_2 for all samples of all different catalysts

In order to calculate the amount of CO_2 consumed in the reaction by this formula:

$$X_{CO_2} = \frac{(Nco_{2})_0 - (Nco_{2})_t}{(Nco_{2})_0} * 100\%$$

While: $(Nco_{2})_0$ is the mole fraction of CO_2 in the feed gas sample.

$(Nco_{2})_t$ is the mole fraction of CO_2 in the product sample.

- By applying this formula for all catalysts, we can obtain this data :

Catalyst	**CO_2 Conversion %**
Cu-ZnO/Al_2O_3	
CZA02-45	5.7964
CZA02-60	6.8021
Cu-ZnO/Al_2O_3/ZrO_2	
CZAZ-30	6.3145
CZAZ-45	7.9342
CZAZ-60	10.2270
CZAZ-75	15.8066

Table 4.2 CO_2 Conversion (%)

Note: Reaction conditions: *P*=30 bar T=170 °C, H_2/CO_2 = 3:1 (molar ratio).

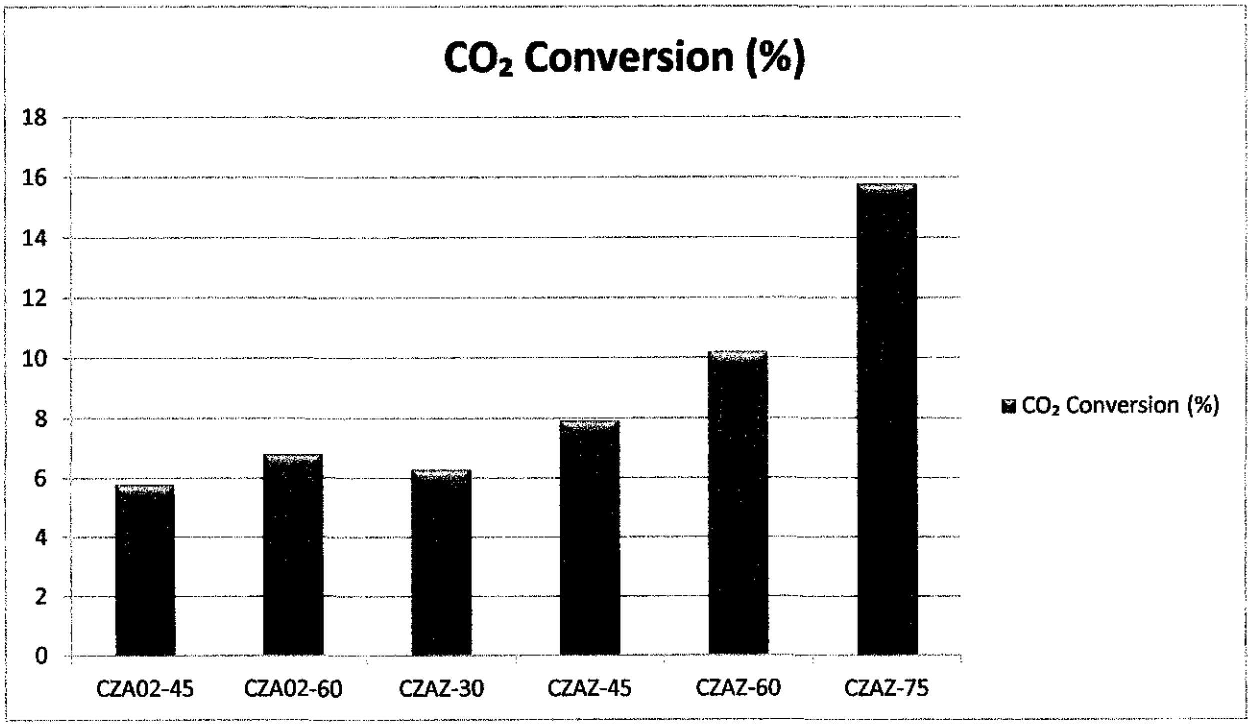


Figure 4.4 CO_2 Conversion (%)

4.2.3 Calculating Selectivity

It can be calculated by this formula:

$$\% \text{ Selectivity} = \frac{X_{CH_3OH}}{X_{CO_2}}$$

In other words, Yield = Conversion * Selectivity

- By applying this formula for all catalysts, we can obtain this data :
-

Catalyst	**Selectivity %**
Cu-ZnO/Al_2O_3	
CZA02-45	39.4958
CZA02-60	85.8308
Cu-ZnO/Al_2O_3/ZrO_2	
CZAZ-30	93.9298
CZAZ-45	55.7308
CZAZ-60	57.4430
CZAZ-75	40.2698

Table 4.3 Selectivity (%)

Note: Reaction conditions: P=30 bar T=170 °C, H_2/CO_2 = 3:1 (molar ratio).

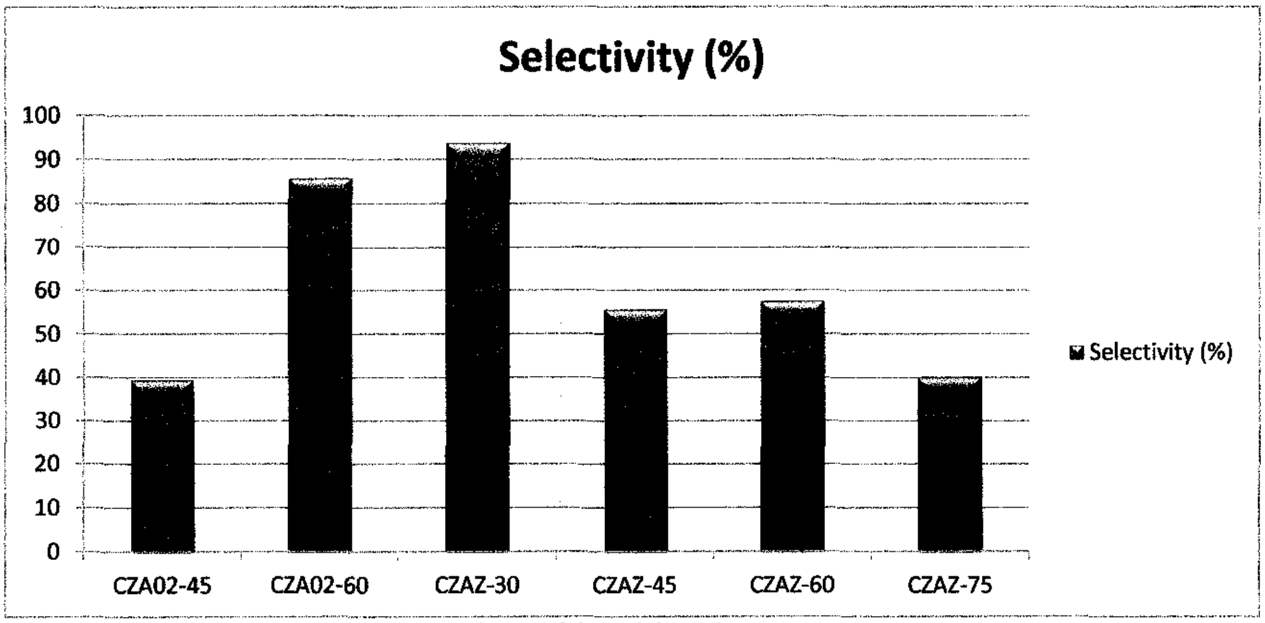


Figure 4.5 Selectivity (%)

4.3 Water content analysis by Karl Fischer titration method

Also the water gas shift reaction may occur. The water gas shift reaction is

CO + H2O ——> H2 + CO2

- By using the titrator to analyze the water content in the liquid sample, this data obtained :

Catalyst	**Water Content %**
Cu-ZnO/Al_2O_3	
CZA02-45	1.304
CZA02-60	1.239
Cu-ZnO/Al_2O_3/ZrO_2	
CZAZ-30	1.218
CZAZ-45	0.937
CZAZ-60	1.042
CZAZ-75	0.908

Table 4.4 Water Content (%)

Note: Reaction conditions: P=30 bar T=170 °C, H_2/CO_2 = 3:1 (molar ratio).

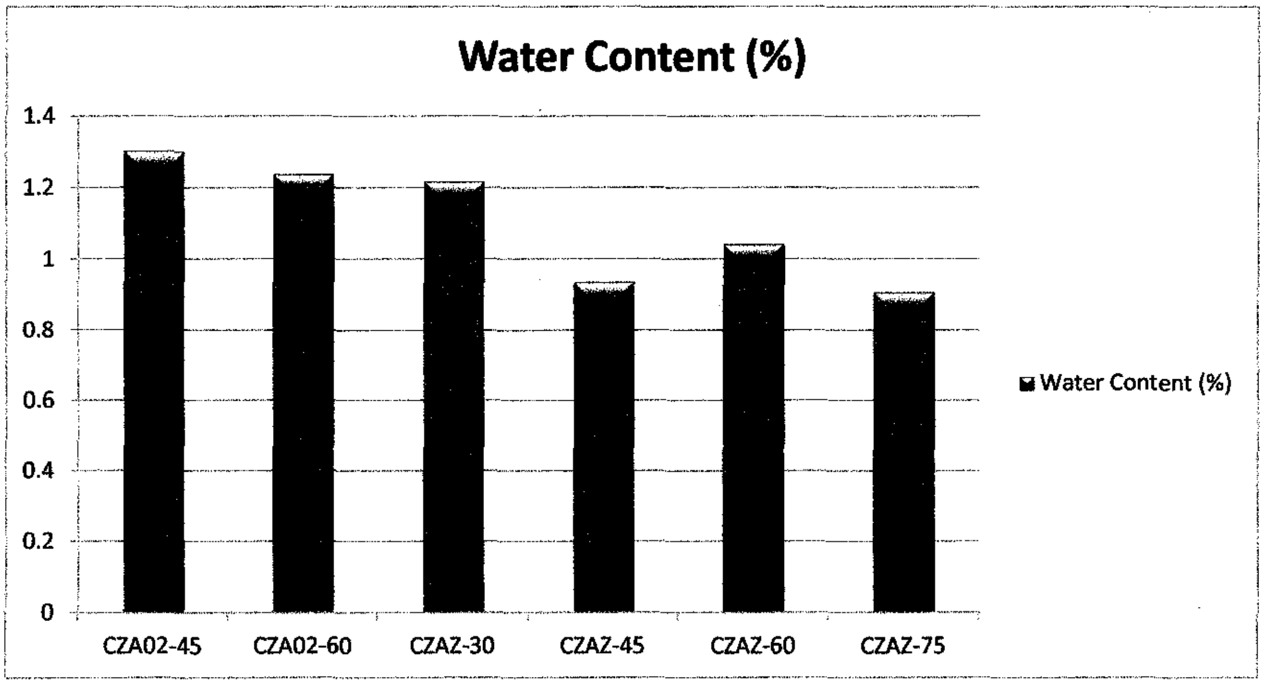


Figure 4.6 Water content (%)

4.4 Discussion

Based on the results obtained by analyzing the gas and liquid samples of the reaction output, it's noticed that the results of calculating the CO_2 conversion and getting CH_3OH yield are significantly satisfying the requirements of processing methanol synthesis under low pressure and low temperature to meet the need of the optimization to a successful process economically and operationally.

The experiment was run under conditions of 30 bar of pressure, 170 °C of temperature and mole ratio of 3H: $1CO_2$ in the presence of ethanol as a solvent as it helps to increase CO_2 conversion and get higher methanol yield.

Analyzing the performance of each catalyst based on its physical properties, It was found that The role of metal oxides such as ZrO_2 and Al_2O_3 contained in Cu/ZnO-based ternary catalysts for methanol synthesis from CO_2 and H_2 was classified into two categories: to improve the Cu dispersion and to increase the specific activity.

Besides, The best physical properties of the used catalyst which gives highest methanol yield and CO_2 conversion are lowest pore size, highest BET surface and highest Cu loading amount.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

For methanol synthesis, higher CO_2 and higher CH_3OH yield to be achieved under economical and operational reaction conditions with a higher performance of the used catalyst, as modifying the current catalysts by adding ZrO_2 with specific physical properties of lower pore size, higher BET surface and higher Cu loading amount.

The Cu/ZnO-based multicomponent catalysts developed on the basis of the role of metal oxides were highly active and stable for a long period in a continuous methanol synthesis operation.

In conclusion, The modification of $Cu/ZnO/Al_2O_3$ with zirconia can improve the catalytic performance of Cu based catalysts used for methanol synthesis from CO_2 and H_2. The low temperature, the high space velocity and the proper molar ratio of H_2/CO_2 are advantageous to the methanol synthesis. The results of previous researches show that the addition of zirconia is beneficial in enhancing the dispersion of the supported Cu species, indicating there is strong interaction between the Cu and ZrO_2 species, which is responsible for the enhanced catalytic performance of Cu based catalyst supported on zirconia modified $Cu/ZnO/Al_2O_3$ catalyst.

This project meets the objectives at the beginning of the process work where the catalytic activity in methanol synthesis to studies. This project proves that each different type of catalyst produce different range of results. The project and experiments which have been done give basic knowledge and ideas of the process to help in order to reach a better optimization of the process.

Its recommended more for the future studies on that field to concentrate more about the catalyst with ZrO_2 and to be applied in large production scale of the industry.

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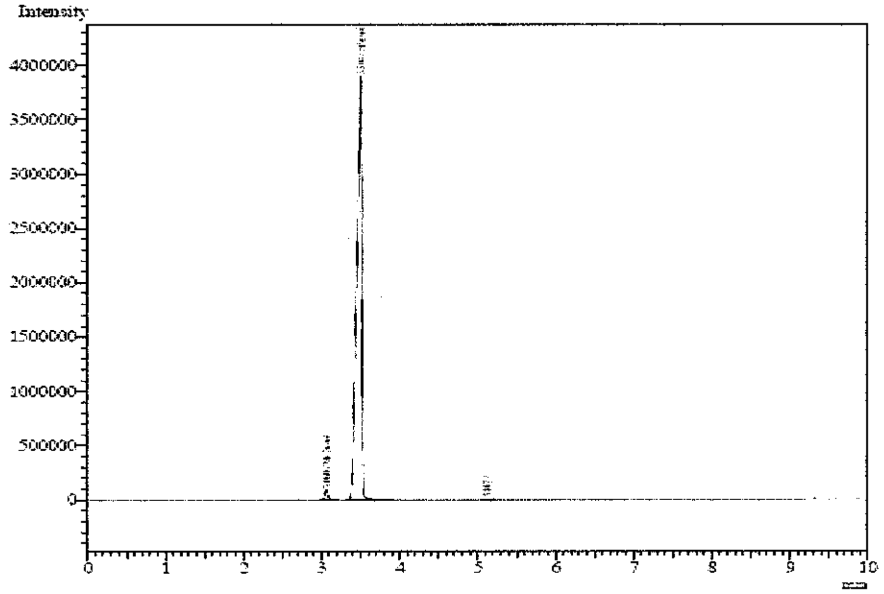
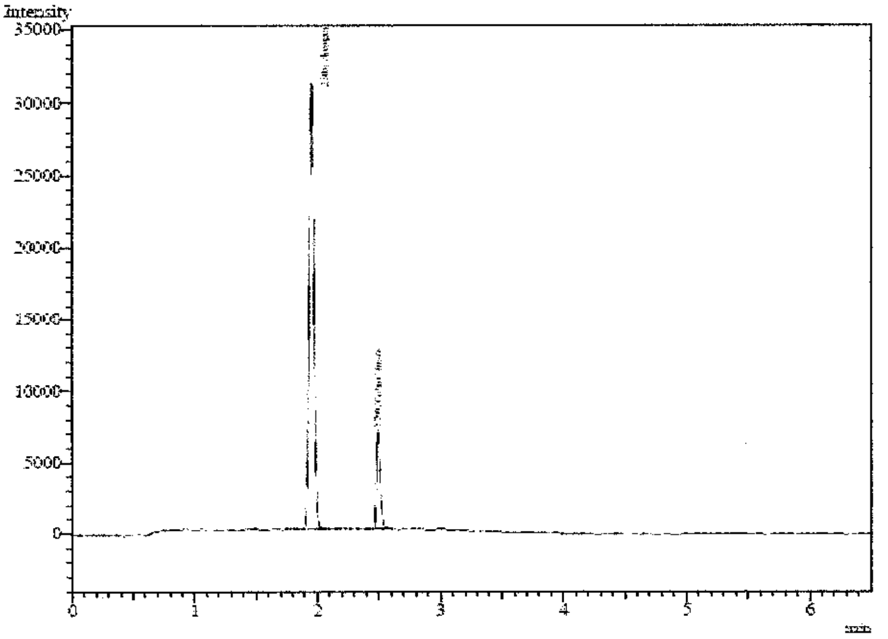
APPENDIX

- **GAS CHORMATOGRAPHY ANAYSIS REULTS FOR LIQUID AND GAS SAMPLES RESPECTIVELY**

1. **Catalyst :** Cu-ZnO/Al_2O_3 (CZA02-45)

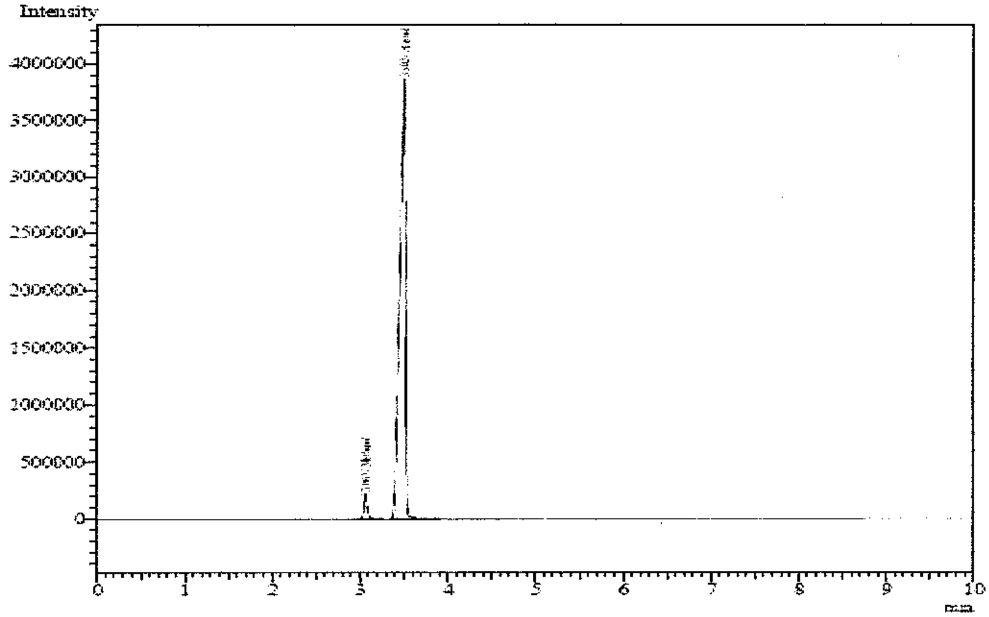


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	3.060	230333.73	88684.74	2.2893	%	Methanol
2	3.504	17225643.12	3872387.92	117.6242	%	Ethanol
3	5.117	10953.34	3231.69	0.0000		
Total		17466930.18		119.9135		

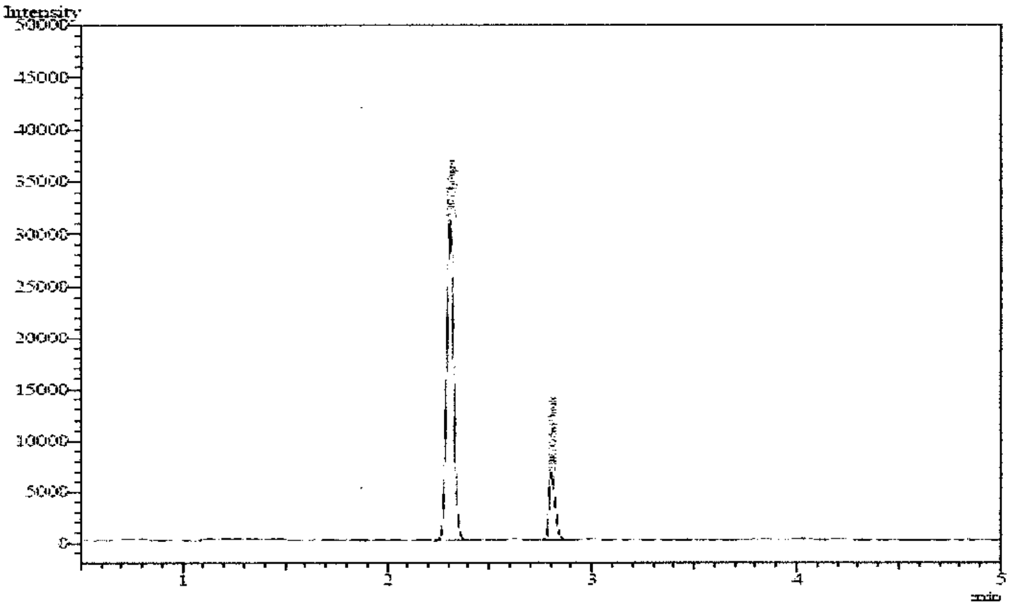


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.303	75049.52	30879.22	70.1286	mole %	Hydrogen
2	2.799	14262.12	6934.11	18.4577	mole %	Carbon Dioxide
Total		89311.64		88.5863		

2. Catalyst : Cu-ZnO/Al_2O_3 (CZA02-60)

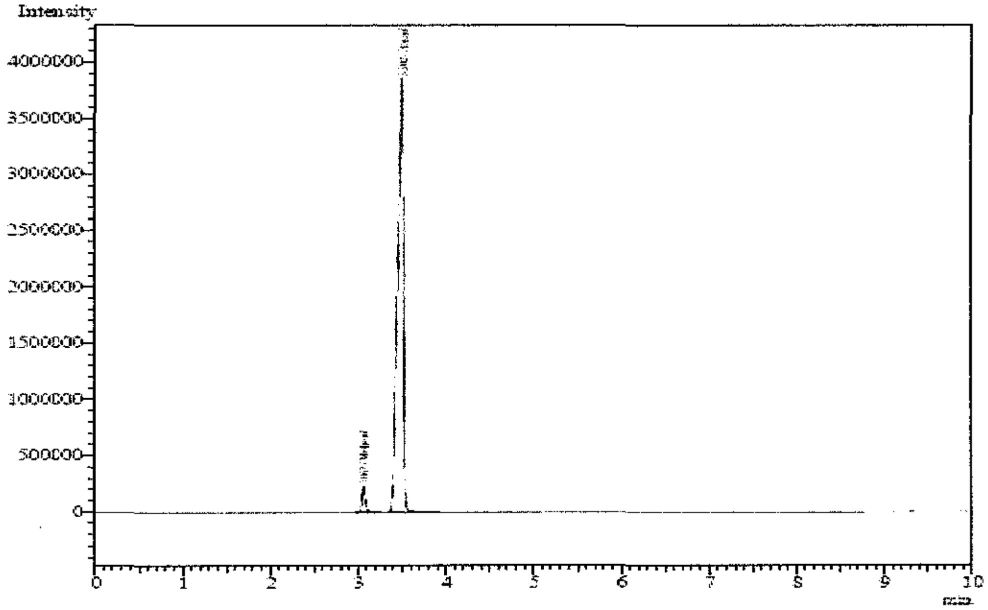


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	3.062	587422.02	223113.38	5.8383	%	Methanol
2	3.502	16874478.21	3855959.25	115.2263	%	Ethanol
Total		17461900.23		121.0646		

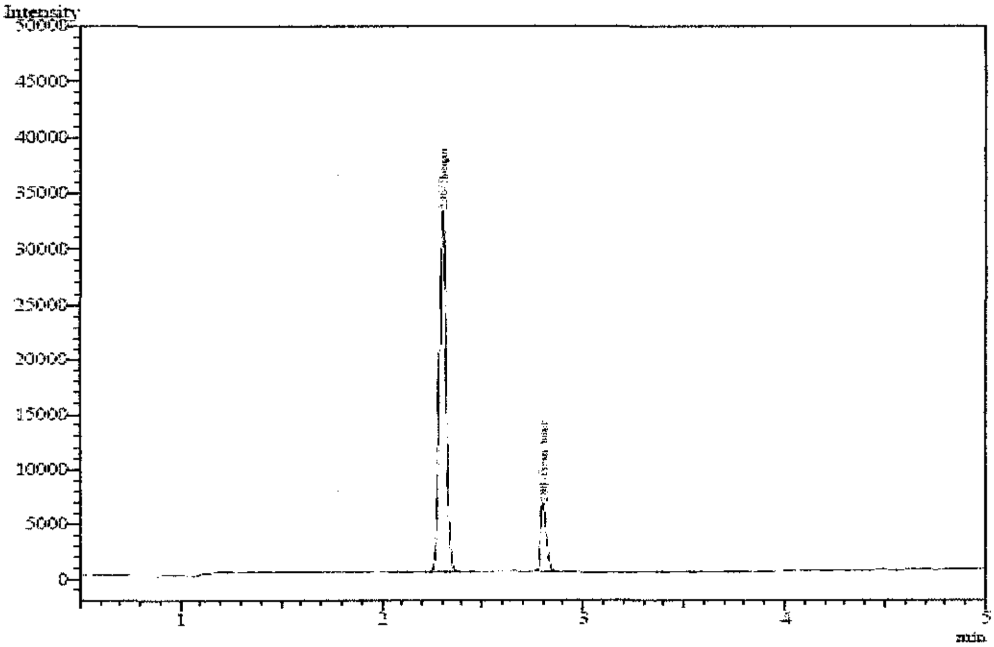


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.307	75623.68	30995.54	**69.7635**	mole %	Hydrogen
2	2.804	13206.51	6527.56	**18.1146**	mole %	Carbon Dioxide
Total		88830.19		87.8781		

3. Catalyst : Cu-ZnO/Al_2O_3/ZrO_2 (CZAZ-30)

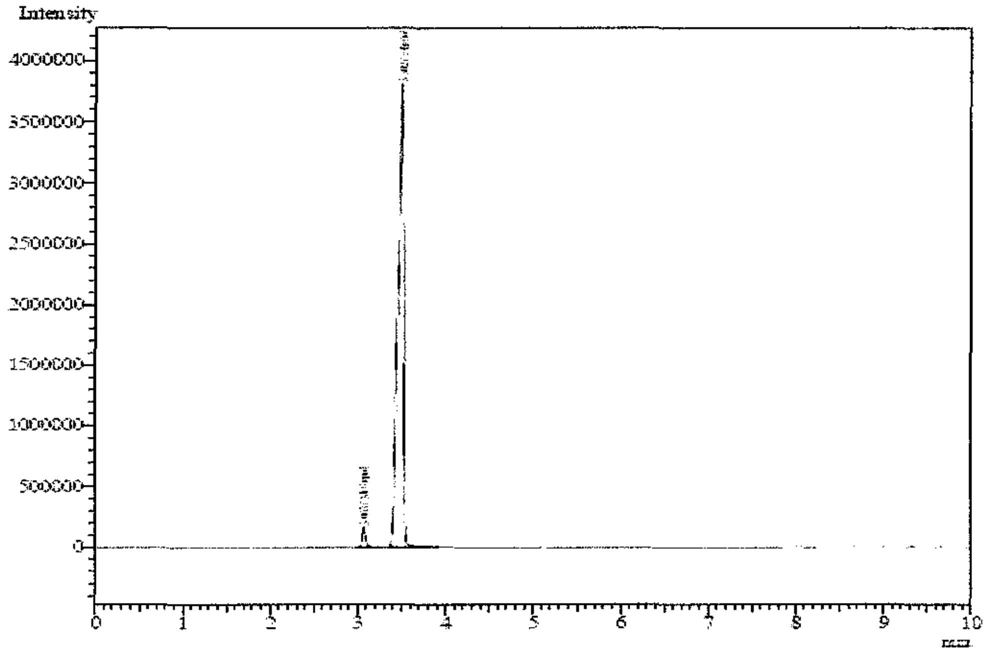


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	3.062	596769.82	229756.82	5.9312	%	Methanol
2	3.502	16853569.00	5847472.81	115.0835	%	Ethanol
Total		17450338.82		121.0148		

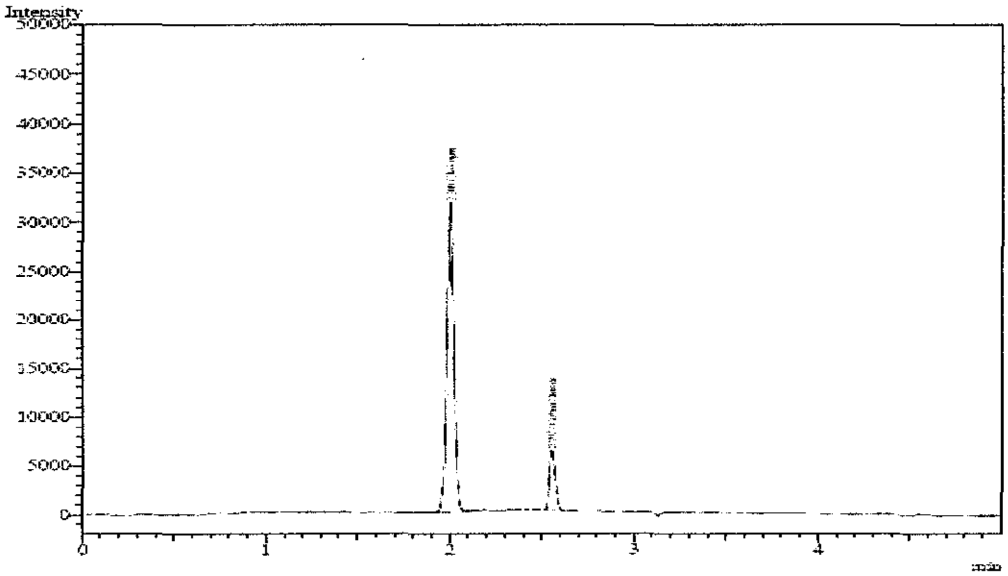


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.303	79143.71	32467.66	**72.1630**	mole %	Hydrogen
2	2.801	12214.35	6137.72	**18.8614**	mole %	Carbon Dioxide
Total		91358.06		91.0244		

4. Catalyst : Cu-ZnO/Al_2O_3/ZrO_2 (CZAZ-45)

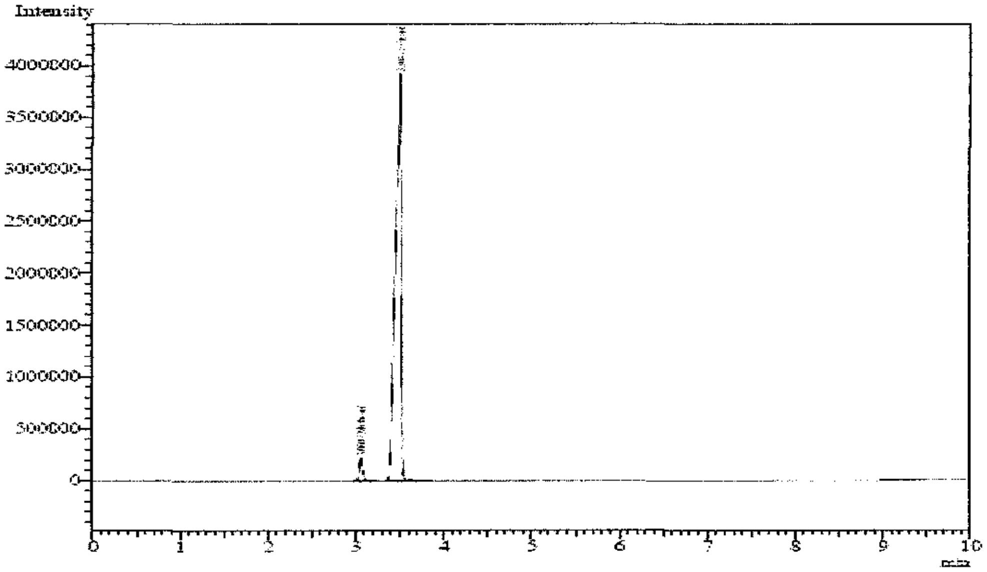


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	3.063	444898.20	164664.50	4.4218	%	Methanol
2	3.502	16533829.61	3799070.38	112.9002	%	Ethanol
3	19.714	84997.08	13757.83	0.0000		
Total		17063724.89		117.3220		

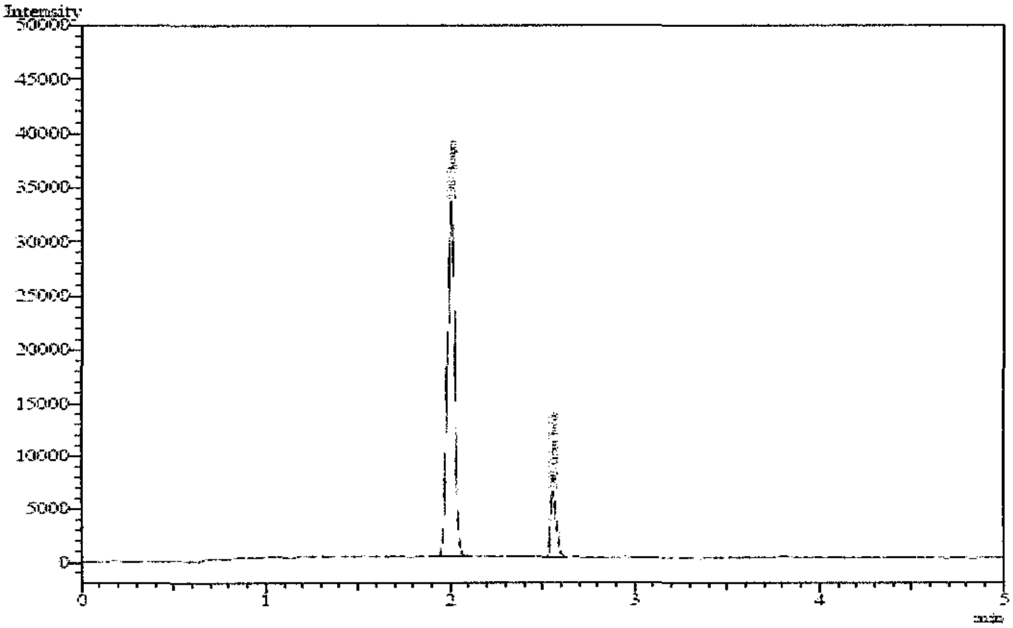


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.300	76878.10	31498.56	54.3070	%	Hydrogen
2	2.797	12077.34	6313.40	13.8862	%	Carbon Dioxide
Total		88955.44		68.1932		

5. Catalyst : Cu-ZnO/Al$_2$O$_3$/ZrO$_2$ (CZAZ-60)

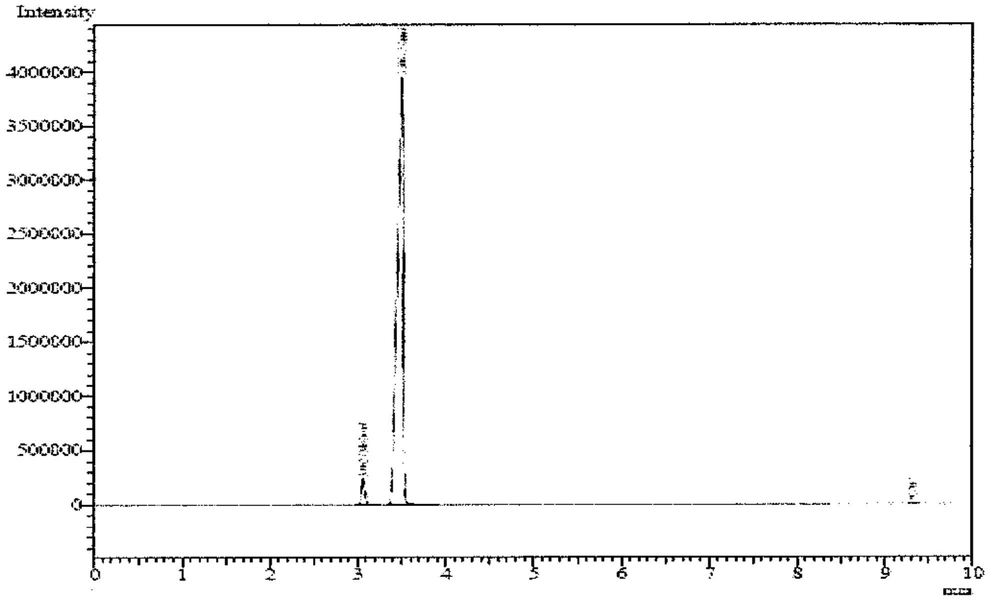


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	3.060	591079.43	222177.16	5.8747	%	Methanol
2	3.504	17450785.02	3894416.84	119.1616	%	Ethanol
3	19.700	16255.58	2667.12	0.0000		
Total		18058120.03		125.0363		

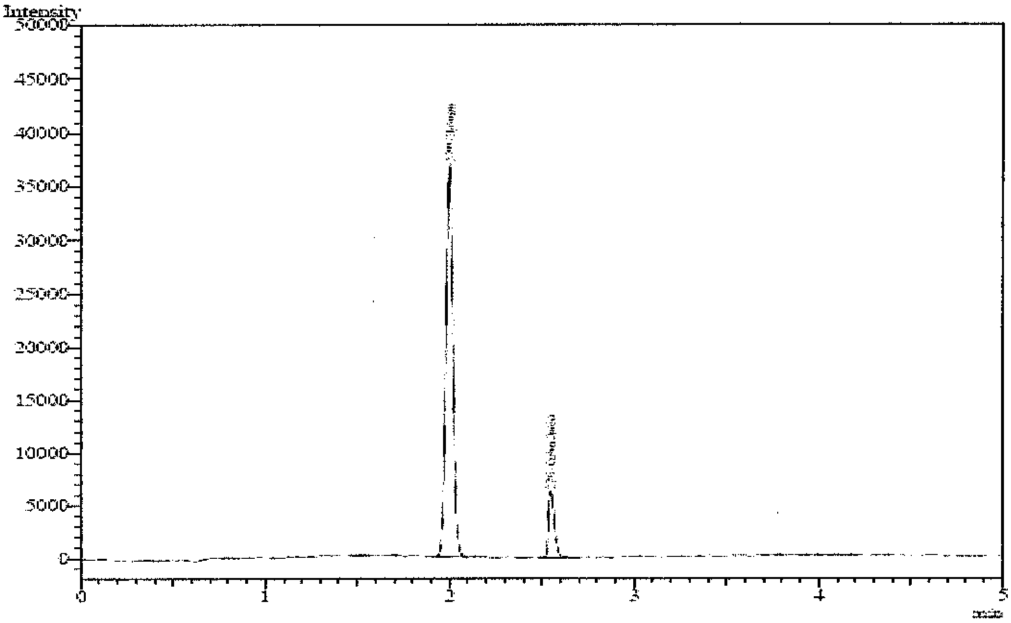


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.303	80496.66	33059.18	56.8631	%	Hydrogen
2	2.802	12252.86	6126.54	14.0880	%	Carbon Dioxide
Total		92749.52		70.9511		

6. Catalyst : Cu-ZnO/Al_2O_3/ZrO_2 (CZAZ-75)

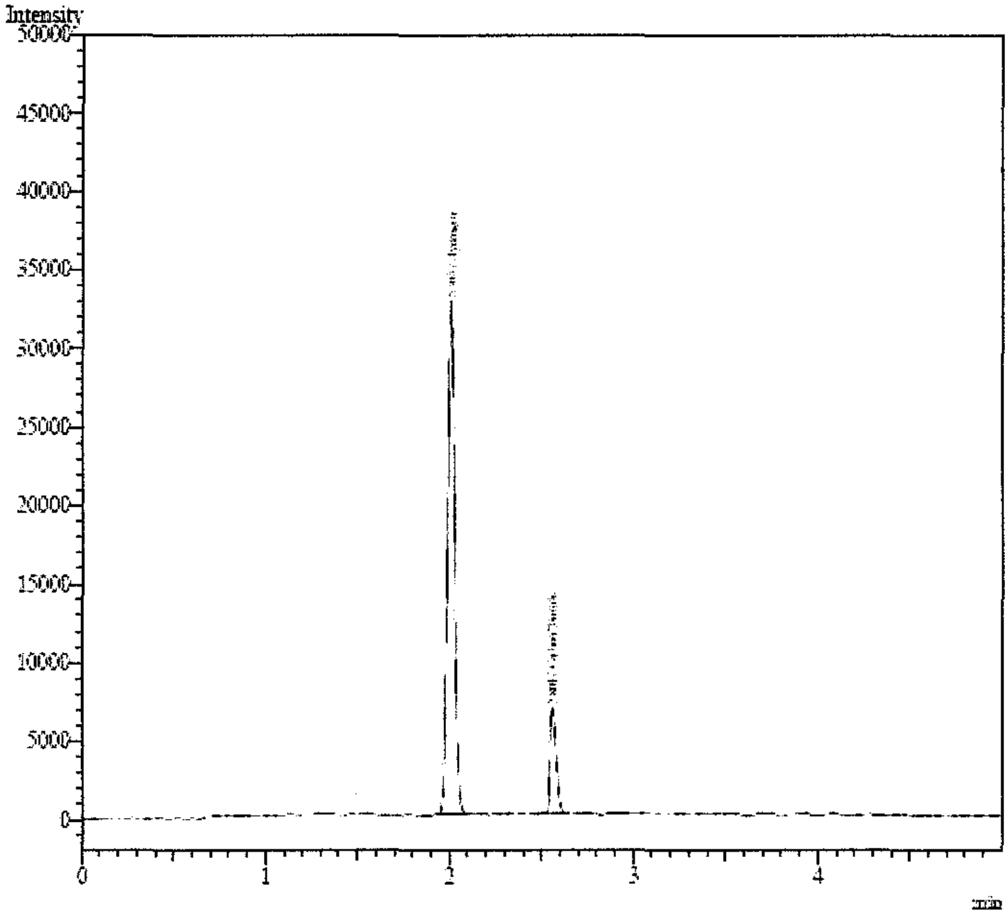


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	3.062	640443.51	242837.46	6.3653	%	Methanol
2	3.506	17572940.08	3948642.88	119.9957	%	Ethanol
3	9.320	17391.68	9299.78	0.0000		
4	19.721	241778.42	39495.83	0.0000		
Total		18472553.69		126.3610		



Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.299	89440.39	36885.00	63.1810	%	Hydrogen
2	2.795	12574.44	6166.84	14.4578	%	Carbon Dioxide
Total		102014.83		77.6388		

7. Feed gas



Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.303	79075.34	32468.06	55.9106	%	Hydrogen
2	2.801	13590.35	6640.85	15.8782	%	Carbon Dioxide
Total		92665.69		71.7888		

➢ Calculating CO_2 Conversion

In order to calculate the amount of CO_2 consumed in the reaction by this formula :

$$X_{CO_2} = \frac{(Nco_2)_0 - (Nco_2)_t}{(Nco_2)_0} * 100\%$$

While: $(Nco_2)_0$ is the mole fraction of CO_2 in the feed gas sample.

$(Nco_2)_t$ is the mole fraction of CO_2 in the product sample.

1. **Catalyst : Cu-ZnO/Al_2O_3 (CZA02-45)**

$$X_{CO_2} = \frac{22.1179-20.8358}{22.1179} * 100\% = 5.7964\ \%$$

2. **Catalyst : Cu-ZnO/Al_2O_3 (CZA02-60)**

$$X_{CO_2} = \frac{22.1179-20.6133}{22.1179} * 100\% = 6.8021\ \%$$

3. **Catalyst : Cu-ZnO/Al_2O_3/ZrO_2 (CZAZ-30)**

$$X_{CO_2} = \frac{22.1179-20.7212}{22.1179} * 100\% = 6.3145\ \%$$

4. **Catalyst : Cu-ZnO/Al_2O_3/ZrO_2 (CZAZ-45)**

$$X_{CO_2} = \frac{22.1179-20.3630}{22.1179} * 100\% = 7.9342\ \%$$

5. **Catalyst : Cu-ZnO/Al_2O_3/ZrO_2 (CZAZ-60)**

$$X_{CO_2} = \frac{22.1179-19.8559}{22.1179} * 100\% = 10.2270\ \%$$

6. **Catalyst : Cu-ZnO/Al_2O_3/ZrO_2 (CZAZ-75)**

$$X_{CO_2} = \frac{22.1179-18.6218}{22.1179} * 100\% = 15.8066\ \%$$

➢ Calculating Selectivity

It can be calculated by this formula:

$$\% \text{ Selectivity} = \frac{X_{CH_3OH}}{X_{CO_2}}$$

In other words, Yield = Conversion * Selectivity

1. **Catalyst : Cu-ZnO/Al$_2$O$_3$ (CZA02-45)**

$$\% \text{ Selectivity} = \frac{2.2893}{5.7963} * 100\% = 39.4958\%$$

2. **Catalyst : Cu-ZnO/Al$_2$O$_3$ (CZA02-60)**

$$\% \text{ Selectivity} = \frac{5.8383}{6.8021} * 100\% = 85.8308\ \%$$

3. **Catalyst : Cu-ZnO/Al$_2$O$_3$/ZrO$_2$ (CZAZ-30)**

$$\% \text{ Selectivity} = \frac{5.9312}{6.3145} * 100\% = 93.9298\ \%$$

4. **Catalyst : Cu-ZnO/Al$_2$O$_3$/ZrO$_2$ (CZAZ-45)**

$$\% \text{ Selectivity} = \frac{4.4218}{7.9342} * 100\% = 55.7308\ \%$$

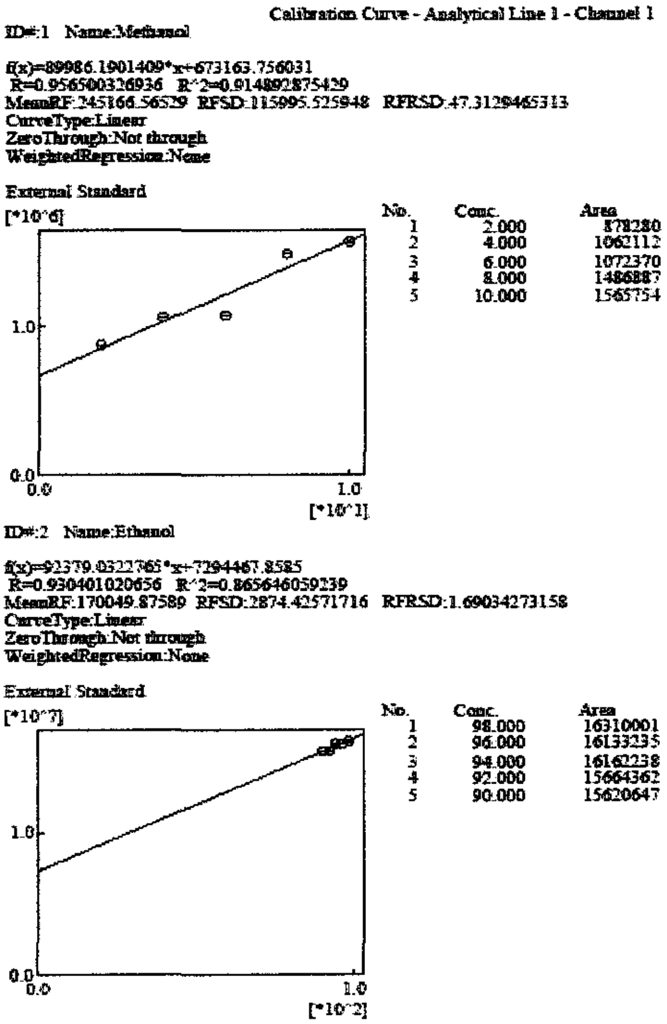
5. **Catalyst : Cu-ZnO/Al$_2$O$_3$/ZrO$_2$ (CZAZ-60)**

$$\% \text{ Selectivity} = \frac{5.8747}{10.2270} * 100\% = 57.4430\ \%$$

6. **Catalyst : Cu-ZnO/Al$_2$O$_3$/ZrO$_2$ (CZAZ-75)**

$$\% \text{ Selectivity} = \frac{6.3653}{15.8066} * 100\% = 40.2698\ \%$$

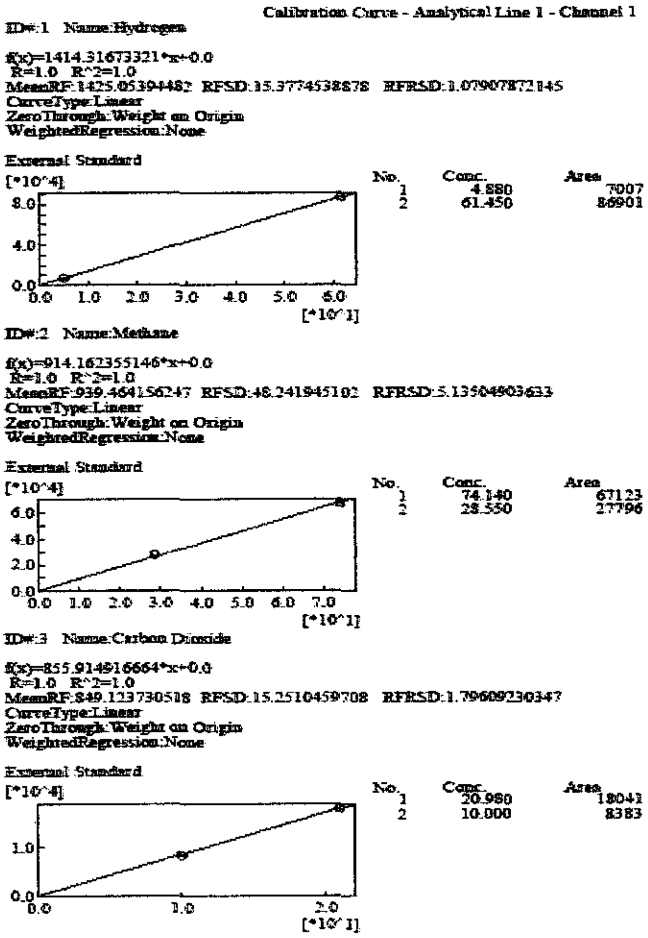
- **Gas Chromatography calibration curve used for liquid analysis.**



```
                         Calibration Curve - Analytical Line 1 - Channel 1
ID#:1   Name:Methanol

f(x)=89986.1901409*x+673163.756031
 R=0.956500326936   R^2=0.914892875429
MeanRF:245166.56529  RFSD:115995.525948   RFRSD:47.3129465313
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard
                                   No.      Conc.          Area
                                    1        2.000         878280
                                    2        4.000        1062112
                                    3        6.000        1072370
                                    4        8.000        1486887
                                    5       10.000        1565754
```

```
ID#:2   Name:Ethanol

f(x)=92379.0322765*x+7294467.8585
 R=0.930401020656   R^2=0.865646059239
MeanRF:170049.87589  RFSD:2874.42571716   RFRSD:1.69034273158
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard
                                   No.      Conc.          Area
                                    1       98.000       16310001
                                    2       96.000       16133235
                                    3       94.000       16162238
                                    4       92.000       15664362
                                    5       90.000       15620647
```

➢ Gas Chromatography calibration curve used for gas analysis.



```
                                    Calibration Curve - Analytical Line 1 - Channel 1
ID#:1   Name:Hydrogen

f(x)=1414.31673321*x+0.0
 R=1.0  R^2=1.0
MeanRF:1425.05394482  RFSD:15.3774538878   RFRSD:1.07907872145
CurveType:Linear
ZeroThrough:Weight on Origin
WeightedRegression:None

External Standard
                                  No.      Conc.          Area
                                    1        4.880          7007
                                    2       61.450         86901

ID#:2   Name:Methane

f(x)=914.162355146*x+0.0
 R=1.0  R^2=1.0
MeanRF:939.464156247  RFSD:48.241945102   RFRSD:5.13504903633
CurveType:Linear
ZeroThrough:Weight on Origin
WeighredRegression:None

External Standard
                                  No.      Conc.          Area
                                    1       74.140         67123
                                    2       28.550         27796

ID#:3   Name:Carbon Dioxide

f(x)=855.914916664*x+0.0
 R=1.0  R^2=1.0
MeanRF:849.123730518  RFSD:15.2510459708   RFRSD:1.79609230347
CurveType:Linear
ZeroThrough:Weight on Origin
WeightedRegression:None

External Standard
                                  No.      Conc.          Area
                                    1       20.980         18041
                                    2       10.000          8383
```

- **Gantt chart for final year project first semester (FYP I)**

No	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
									Mid-Semester Break							
1	Selection of Project Topic															
2	Preliminary Research Work															
3	Submission of Extended Proposal						●									
4	Oral Proposal Defence						●				●					
5	Project Work Continues															
6	Submission of Interim Draft Report														●	
7	Submission of Finalized Interim Report															●

➢ Gantt chart for final year project first semester (FYP 2)

No	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
									Mid-Semester Break								
1	Project Work Continues																
2	Submission of Progress Report									●							
3	Project Work Continues																
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)													●			
7	Submission of Technical Paper														●		
																●	
8	Oral Presentation																
9	Submission of Project Dissertation (hard bound)																●