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A PROCESS SYNTHESIS APPROACH TO LOW-PRESSURE METHANOL/DIMETHYL ETHER CO-PRODUCTION FROM SYNGAS OVER GOLD-BASED CATALYSTS

Arthur Nseka Mpela

A thesis submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Doctor of Philosophy.

Johannesburg, 2008

DECLARATION

I declare that this thesis is my own unaided work. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other university.

(Signature of candidate)

---------- day of ---------- year----------

ABSTRACT

Catalysts are involved in a very large number of processes leading to the production of industrial chemicals, fuels, pharmaceutical, and to the avoidance, as well as the clean-up of environmental pollutants. In respect to the latter aspect, efforts are being made by different stake-holders (governments, researchers, industrials, etc) in order to prevent or to minimize pollution of our cities. A notably way to reduce pollution for a friendly environment is to make use of clean fuels. After years of research work, it is only recently that dimethyl ether alone or when combined with methanol has been identified as a potential alternative clean fuel.

Nonetheless, the technology used for the methanol synthesis from syngas requires high pressure (>120 atm) to reach an acceptable CO conversion. The dimethyl ether production from methanol in a separate unit makes DME more expensive than methanol. However, the transformation of syngas directly into dimethyl ether can be used to relieve the thermodynamic constraints requiring operation at high pressure. If the synthesis of methanol and dimethyl ether takes place in the same reactor, the process should, in principle, be able to operate at a much lower pressure, making it a potentially cheaper process to produce methanol and dimethyl ether. The catalysts that need to be used for this co-production have to be catalytically stable, selective and able to catalyze the main reactions (methanol and dimethyl ether synthesis) involved in this process at the same temperature. Unfortunately, existing commercial methanol/DME catalysts are not able to function efficiently in the presence of large concentrations of water or at high temperature. Thus, it is relevant to have a catalyst satisfying the

above criteria. Recently, it has been reported that a supported gold catalyst could be used for methanol synthesis; accordingly this study has developed bifunctional gold-based catalysts for the methanol and DME synthesis.

This study utilized process synthesis approach to determine the optimal operating conditions for methanol/dimethyl ether production that yielded results used to drive an experimental programme to get the most useful information for designing a process route. In a comparative way and by using the feed compressor work load per unit of valuable material generated as objective function, this study showed that the system where methanol is co-produced with DME is more efficient than the one involving the production of methanol alone and this is applicable for the operating reactor temperatures of 500-700K and the loop pressure ranging from 10 to 100 atm. The catalysts systems chosen in this study were consisted in the physical mixture of gold-based catalysts incorporating respectively gamma-alumina and zeolite-Y. The gold-based catalysts were prepared by a co-precipitation method, then characterized by XRD, Raman Spectrometry and Transmission Electron Microscopy and, afterwards tested using a 1/4 inch tubular fixed bed reactor between 573 and 673K at 25 atm.

Amongst the catalysts tested at 673K, and 25 atm, 5%Au/ZnO/γ-Al_2O_3 produced both methanol and dimethyl ether with moderate yield, whereas 5%Au/ZnO/LZ Y-52 gave high dimethyl ether selectivity (75.7%) with a production rate of 252.3 $\mu mol.h^{-1}.g_{cat}^{-1}$. The presence of hydrocarbons detected by the GC-FID in the gas products requires that further investigations be done to determine the eventual source and optimize this new catalyst system based on gold for a large scale co-production of methanol and dimethyl ether from syngas.

DEDICATION

To

My genital parents Martin Sali and Leonie Bonkoto

My loving wife Abigail Mpela

My ever brave son Guerschom Mpela Mapamboli

My beautiful daughters Sarah and Elisabeth Mapamboli

and

My brothers and sisters from Sali’s family

PUBLICATIONS AND PRESENTATIONS ARISING FROM THIS WORK

Publications:

1. A. Mpela, Y. Zhao, D.I Enache, S.H Taylor, D. Hildebrandt, D. Glasser, G. J. Hutchings and M.S. Scurrell, Study of carbon monoxide hydrogenation over Au supported on zinc oxide catalysts, *Preprints - American Chemical Society, Division of Petroleum Chemistry*, 2005, **50**(2), 206-207.

2. A. Mpela, M.S. Scurrell, D. Hildebrandt, D. Glasser and G.J. Hutchings, A process synthesis approach to low-pressure methanol/dimethyl ether synthesis from syngas over gold-based catalysts, *Gold Bulletin 2007*, **40**-3, 219-224.

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LIST OF SYMBOLS AND ACRONYMS

Carbon Efficiency	CE
Compressed Natural Gas	CNG
Compressed work load	P_{ad}
Equilibrium constant	K_{eq}
Enthalpy of formation of compound at temperature T_o (K)	ΔH_f^o
Enthalpy of reaction at temperature T(K)	$\Delta H_{rxn}(T)$
Exhaust Gas Recirculation	EGR
Extended X-ray Absorption Fine Structure	EXAFS
Flame Ionization Detector	FID
Free energy of formation of compound at temperature T_o(K)	ΔG_f^o
Free energy of reaction at temperature T(K)	$\Delta G_{rxn}(T)$
Gasoline Direct Injection	GDI
Heat capacity at constant pressure	C_p
Heat capacity at constant volume	C_v
Homogeneous Charge Compression Ignition	HCCI
Hydrogen Efficiency	HE
Ideal gas constant	R
Isentropic constant	g
Liquid Petrol Gas	LPG
Methanol to gasoline	MTG
Micromole	µmol
Mole	mol
Nanometer	nm

Pressure	P
Platinum Group Metals	PGMs
Plug Flow Reactor	PFR
Proton Exchange Membrane	PEM
Revolution per minute	rpm
Small Angle X-ray Scattering	SAXS
Thermal Conductivity Detector	TCD
Transmission Electron Microscopy	TEM
Wide-Angle X-ray Scattering	WAXS
X-ray Photoelectron Spectroscopy	XPS

LIST OF CHEMICAL SYMBOLS

Aluminium oxide	Al_2O_3
Aluminophosphates	ALPOs
Butane	C_4H_{10}
Butene	C_4H_8
Carbon dioxide	CO_2
Carbon monoxide	CO
Copper	Cu
Dimethyl ether	CH_3OCH_3
Ethane	C_2H_6
Ethylene	C_2H_4
Ethanol	C_2H_5OH
Gold	Au
Hexane	C_6H_{14}
Hexene	C_6H_{12}
Heptane	C_7H_{16}
Heptene	C_7H_{14}
Hydrogen sulphide	H_2S
Hydrocarbons	HC
Iron carbonyl	$Fe(CO)_5$
Iron nitrate	$Fe(NO_3)_3$
Iron oxide	Fe_2O_3
Methane	CH_4
Methanol	CH_3OH
Nickel carbonyl	$Ni(CO)_4$

Nitrogen oxide	NO_x
Nitrous oxide	N_2O
Octane	C_8H_{18}
Octene	C_8H_{16}
Palladium	Pd
Platinum	Pt
Pentane	C_5H_{12}
Pentene	C_5H_{10}
Propane	C_3H_8
Propene	C_3H_6
Syngas	CO/H_2 mixture
Tetrachloro auric acid	$HAuCl_4.xH_2O$
Zinc sulphide	ZnS
Zeolite-Y	LZ-Y52

CHAPTER 1
GENERAL INTRODUCTION

1.1 Background

1.1.1 Climate change and global warming

It has been well documented that the by-products of gasoline or diesel combustion contain a variety of potentially harmful gases and particles that are released into the atmosphere. The pollutants that are of much concern are carbon monoxide (CO), sulphur dioxide (SO_2), volatile organic compounds (H_xC_y), nitrogen oxides (NO_x), tropospheric ozone (O_3) (which results from the emissions of hydrocarbons and nitrogen oxides), particulate matter, and some toxic hydrocarbons such as benzene[1-3]. Of the aforementioned, carbon monoxide is one that poses a serious threat to human health[4]. Exposure to high levels of CO can impair vision, working capability, manual dexterity, learning ability and performance of complex tasks. Nitrogen oxides also have adverse effects on health as well as the environment. NO_x reacts to form salts of particulate nitrate, acid aerosols, and NO_2, all of which can cause respiratory problems[5]. Moreover, components of particulate matter such as sulphuric or nitric acid also tend to lead to acid deposition. Greenhouse gases such as carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4) can also be identified in vehicle emissions[1-3]. These greenhouse gases accumulate in

Earth's atmosphere and cause surface air temperatures and sub-surface ocean temperatures to rise, creating overall global warming and subsequently climate change[6-8].

1.1.2 Approaches used for reducing vehicle emissions

In response to public requests to tackle the issues of emissions from vehicles, the automotive industry had identified energy conservation and environmental protection as two major tasks for research and development. In an attempt to lessen the dependence on fossil fuel and, in turn, decrease harmful emissions, researchers worldwide have investigated new technologies and alternative[9-20] fuels to be implemented in new vehicles.

1.1.2.1 Reduction of emissions from gasoline engines

In terms of gasoline engines, most technologies use two pronged approaches. Firstly, the exhaust gases are passed over a catalytic system that removes or converts some of the harmful species in the exhaust gases. The second approach is to try to reduce the formation of NO_x, CO, HC in the emissions by focusing on achieving the proper evenly blended air/fuel mixture to meet the full range of the combustion requirements.

Recently, some engine manufacturers have developed gasoline direct-injection (GDI) and stratified lean combustion processes to improve engine thermal and part-load efficiencies. However, the technology poses a challenge, as new

catalyst processes are then required by the engine systems to effectively remove nitrogen oxides from environment where free oxygen exists.

1.1.2.2 Reduction of emissions from diesel engines

With respect to diesel engines, new designs have incorporated a wide variety of technologies which enable better performance and fuel economy, and at the same time reduce emissions. Most of these new designs adopt the technology of high-injection pressure in combination with the common-rail unit injection system, advanced injection timing management, turbocharger, after-cooler and an integrated exhaust gas recirculation (EGR) manifold system. Additionally, a new propulsion theory called homogeneous charge compression ignition (HCCI) has been introduced for diesel engines. It states that if fuel/air ratio and starting temperature and pressure are all appropriately controlled, there is no chance for the combustion to take place at a temperature higher than 1850K. With such temperatures, no particulate matter or NO_2 will be generated. Unfortunately, up to now, the HCCI engines have been unable to deliver sufficient output due to the difficulties in maintaining correct fuel/air ratios.

1.1.2.3 Reduction of emissions by making lighter vehicles

Another approach to achieving better fuel economy lies in reducing vehicle weight. Lighter vehicles have more efficient power train and lower fuel consumption[1-3]. Although attractive, the lighter vehicles option with a systematic internal change of vehicle is more costly.

1.1.2.4 Development of fuel cells

Fossil fuel based vehicles have limits to which degree that emission can be reduced. Therefore, the automotive industry needs focus on goals such as comprehensive utilization of energy, zero emissions and lower noise levels. In pursuit of these goals, researchers have turned to the electric vehicles, where the high efficiency of energy utilization allows energy source reliability without threatening the environment. However, the pitfalls of electric vehicles are the high costs associated with the energy sources and the low operation mileage due to the insufficient energy density of the batteries [21]. Fuel cells are one promising option for an alternative fuel source.

A fuel cell is an electrochemical device that produces electricity by transforming hydrogen molecules into electrons and protons via a catalyst[22]. Since the fuel is transformed directly into electricity, a fuel cell can operate at higher efficiencies than internal combustion engines by extracting more electricity from a certain volume of fuel without heat losses. Moreover, the fuel cell itself has no moving parts, making it quiet and reliable source of energy.

Currently, fuel cell technologies are being developed in a number of forms such as phosphoric acid fuel cell, molten carbonate fuel cell, solid oxide fuel cell, alkaline fuel cell, direct methanol fuel cell and regenerative fuel cell. In terms of transportation uses, the proton exchange membrane (PEM) fuel cell has demonstrated a few advantages. It has low operating temperature, high power density, and ability to rapidly adjust the output in response to the variation of the power demand. However, of all fuel cell types, only the direct hydrogen fuel cell can be characterized as having truly zero emissions. Hydrogen infrastructure

and onboard storage pose a huge challenge though. Overall, there are still fundamental problems associated with fuel cell technology, including fuel selection, fabrication, distribution and storage.

1.1.2.5 Other options for reducing vehicle emissions

1.1.2.5.1 Hybrid vehicles

Another alternative to gasoline engines are hybrid vehicles. There have been significant developments in order to improve the energy economy and reduction of harmful emissions using hybrid vehicles. The main technology of hybrid vehicles is the incorporation of an electronic motor with the combustion engine power system. The cars operate by both a heat power system and an electric power system alternatively. The hybrid system allows the gas engine to be shut off during vehicle stoppage, braking, deceleration and even low power operation, at which time a rechargeable battery system is used to supplement power[21, 23]. This type of hybrid offers major improvements on efficiency in urban operations. In addition, smaller combustion engines can be used in order to lower the emissions even further. When optimally designed and matched, the hybrid systems are expected to save approximately 50 percent of fuel and reduce emissions by 80 percent[21]. The disadvantages of hybrid rest in the extra materials and weight arising from housing dual power systems. Generally, the higher the battery capacity of the car, the greater the weight and higher the cost. Consequently, there is a trade off between energy efficiency and reduced emissions and vehicle weight and cost.

1.1.2.5.2 Alternative fuels: dimethyl ether and methanol

There has been international commitment to researching for alternative fuels, including synthetic fuels, since the first petroleum crisis in 1973. Compressed natural gas (CNG) and liquid petrol gas (LPG) are both acknowledged today as “clean fuel”. Next to CNG and LPG, methanol could be used either as an additive to gasoline forming M15 (85 % gasoline- 15% methanol) mixture or simply as a pure fuel[21, 24]. Likewise, dimethyl ether provides a good alternative to gasoline and diesel[21, 25]. However, the use of these two latter fuels is restricted by their availability on market. In order to be used as fuels, they would have to be produced in very large scale, and this would impact positively on their production costs.

Until today, methanol and dimethyl ether have been produced at a relatively small scale when compared to other hydrocarbons used as fuels. However, in view of the interest shown currently for both products to be used as alternative clean fuels, it is highly relevant to investigate an optimum route leading to large scale production of methanol and dimethyl ether. Although some recent research has been carried out on this issue with several patents, nonetheless one of the challenges faced lies in the behavior of the catalysts in the reactive environment. It is therefore intended in this study that the process synthesis approach be used to examine stages in developing a catalytic system route for methanol and dimethyl ether production.

1.2 Introduction

Recently, methanol and dimethyl ether have been identified as the preferred alternative clean fuel for diesel engines[26, 27]. This has led to an interest in their production on a large scale. The production of methanol from syngas requires high pressures (> 120 atm) to achieve acceptable carbon monoxide conversion, thereby making the process costly. The production of dimethyl ether from methanol in separate processes impacts negatively on the production costs of DME. Accordingly, this study intends in its first phase to analyze the possibility of making both products in a cheapest way, which could be the co-production of methanol and dimethyl ether in the same reactor. The second phase ascertains the feasibility of this study by preparing and testing a catalyst within operating conditions as set by the process synthesis approach.

The catalyst to be used in this process should be catalytically active, stable and selective in a reactive environment. However, different authors showed that the catalytic properties (activity, selectivity and catalysts life) of current based catalysts (copper and platinum group metals) used in methanol/DME synthesis are adversely affected by reaction conditions[28, 29].

In the case of copper, water which is a reaction product, acts as poison and deactivates the catalysts. In fact, Jaggin and Brookhaven [30, 31] observed that even though different methods have been attempted to modify Cu/ZnO methanol catalyst, the presence of water in the reactor deactivates the catalysts. This implies a high cost for the complete purification of syngas that contains water traces as well as the regeneration process of deactivated catalyst, making the commercialization of this method impossible as underlined by

Reubroycharoen[32]. In addition, when operating at relatively high temperature, the particles of copper catalyst suffer from sintering that lead to the decline of catalyst life. At such temperatures, the PGMs (platinum group metals) based-catalysts lead to the formation of higher alcohols, reducing the methanol and dimethyl ether selectivity. Moreover, PGMs are costly and less abundant in nature. Thus, it is of interest to identify a new generation of catalysts which are competitive, water tolerant and can allow a simultaneous synthesis of methanol and dimethyl ether.

While water seems to be a poison for many catalysts, it is in contrast a catalytic enhancer for gold based catalysts. These catalysts are used in different reactions such as CO oxidation [33-35] and the epoxidation of propene[36]. Recent works done by Haruta *et al.* on gold catalysts have shown that gold nanoparticles deposited on metal oxide support are catalytically active in the hydrogenation of carbon oxides and are not affected by water [37]. It is in this context that this study aimed at developing, in its second phase, hybrid gold-based catalysts for methanol and dimethyl ether synthesis at low pressure.

The first chapter of this work gives a background, a general introduction, the aim and objectives of the study. The second chapter deals with a process synthesis approach that analyzes a low cost route to make methanol and dimethyl ether. The third chapter analyzes optimum conditions for catalysts testing through a thermodynamic analysis route. The fourth chapter discusses on heterogeneous catalysis where emphasis is put on gold catalysts and support materials. A subsection in this chapter deals with the use of zeolites in petrochemistry. The fifth and sixth chapters report all experimental results of our published papers.

Finally, the seventh chapter gives the general conclusions of this study altogether with recommendations for related future work.

1.3 Aim of work

This study aims at developing a catalyst system for the production of methanol and dimethyl ether in the same reactor at low pressure.

1.4 Scope of this study

In respect to the simultaneous production of methanol and dimethyl ether, this research work addresses the following major issues:

- Using a process synthesis approach in order to show that making simultaneously methanol and dimethyl ether in the same reactor is more beneficial than producing separately both products.
- Utilizing a thermodynamic approach to setting up operating conditions for catalysts testing.
- Identifying the appropriate catalyst system through a theoretical assessment of catalysts behaviour by a concise literature survey.
- Running an experimental programme in which catalysts based on gold have to be prepared, characterized and tested for methanol/DME synthesis.

Theses issues represent the main objectives that should be achieved at the end of this study.

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CHAPTER 2
AN INTRODUCTION TO PROCESS SYNTHESIS

2. 1 Introduction

In view of developing a catalyst system that will enable to synthesize methanol and DME, an engineering approach is needed for analyzing and comparing alternatives from the early stages of development. In this study, process synthesis is the route adopted to achieve this goal.

The objective of this chapter is to ascertain parameters that will be used later to set optimum operating conditions within which the developed gold-based catalysts will be tested. The main concern of this chapter is of two-fold, firstly: to reduce the number of experiments when dealing with a new catalyst and secondly: to minimize production costs as much as possible since the viability of process depends on it.

2.2 Why combine methanol and dimethyl ether production?

The recent technology used for the methanol synthesis requires high pressure (>120 atm) to reach an acceptable CO conversion. The dimethyl ether

production from methanol in a separate unit makes DME more expensive than methanol.

However, the transformation of methanol directly into dimethyl ether can in theory be used to relieve the thermodynamic constraints requiring operation at high pressure. If the methanol and dimethyl ether synthesis take place in the same reactor, the process should, in principle, be able to operate at a much lower pressure, making a potentially cheaper process to produce methanol and dimethyl ether.

2.3 Using process synthesis to set catalyst testing conditions

When it is matter of testing a catalyst, different scenarios can take place. If the catalyst is already known or received freshly from the supplier, it is evident that the optimum testing conditions are set by the manufacturer in the way it should be used. However, if the catalyst is a new one and has to be tested for a particular process, there are competitive factors that have to be taken into account, these include: catalyst performance within certain operating conditions, reduction of production costs etc. For these reasons, the thermodynamic evaluation that will be exploited in this study are based on a process synthesis approach in view of setting operating conditions within which the prepared catalysts will be tested under an experimental programme. Moreover, the operating conditions must be such that the operating costs in terms of energy input are minimized. Before developing the latter aspect let us see what the process synthesis is and how it is used in this study.

2.3.1 Fundamentals of process synthesis

Process synthesis is a technique for developing a chemical process from concept to flowsheet. It encompasses the experimental programme, the modelling of the experimental results, the choice of the processing units, and the choice of process route for the optimal process and plant design [1, 4].

Since this study entails the examination of a new catalytic process for the production of methanol and dimethyl ether from syngas, it is essentially appropriate to use this engineering approach. In fact, the process synthesis approach attempts to develop a systematic route for design.

2.3.2 A systematic approach design

2.3.2.1 Introduction

This approach focuses on the application of strategies for preliminary design, the systematic development of representations for process synthesis, and the development of mathematical models for simulation and optimization for their use in computer-based solution techniques[2, 12, 13]. The objective here is to be able to synthesize and design the process flowsheet, understand the decisions involved in the reaction, separation, and heat integration subsystems, as well as their interactions and economic implications.

2.3.2.2 The preliminary design steps for Methanol-DME process

In order to perform a preliminary design a conceptual flowsheet for the process is essential. This task also requires generating and analyzing a number of suitable alternative process flowsheets[2]. Each flowsheet is described in terms of the types of equipment (e.g., compressors, reactor, and stripper) in it and how they are interconnected. A proposed flowsheet for methanol and DME synthesis is shown in Figure 2-1.

The conceptualization of the initial flowsheet is followed by the integration of chemistry and engineering where quick calculations are done at required accuracy. An experimental programme is developed leading to the modelling of process.

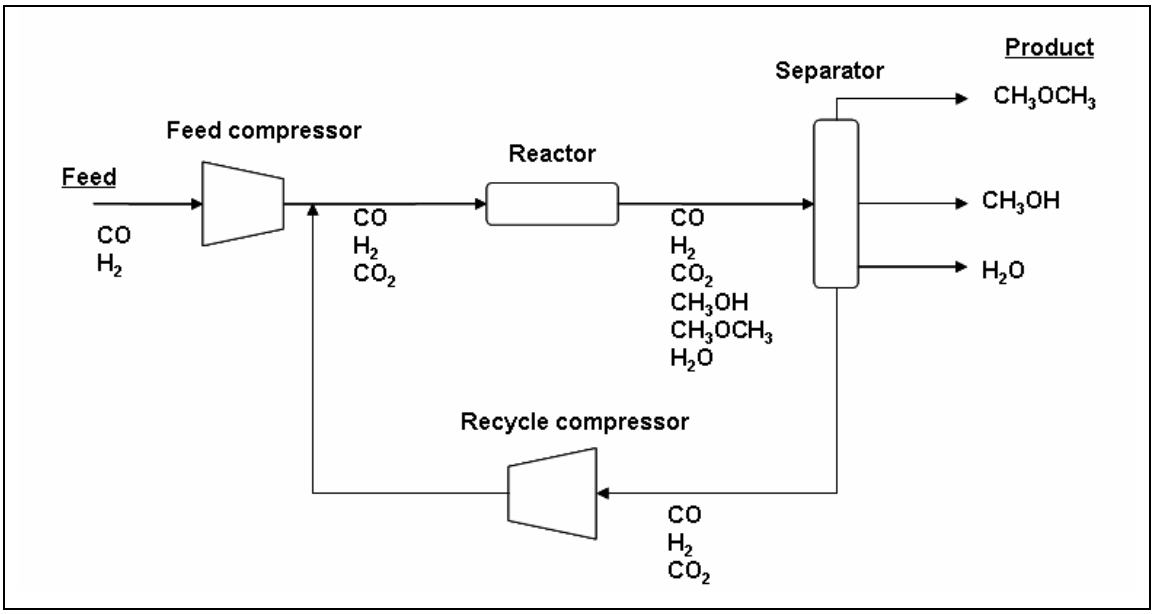

Figure 2-1: Preliminary flowsheet of methanol/DME production

At different stages, a check of decisions taken is made against criteria such as economics, feasibility and environment [1]. Bad options are eliminated in view of the process optimization and plant design. To make this procedure useful the goals of process have to be well established.

2.3.3 Establishment of goals

To make the design problem well-posed, one needs to establish a clear definition of its goals. Among them this might include: maximizing of profits, minimizing operating and investment costs, ensuring that design meets safety standards, creation of a design that can be controlled easily, maximizing flexibility of the process to feedstock fluctuations, creating a design that does not pollute [7], as people in society need to live in friendly environment.

Some of the goals might be constraints, whereas others will be objectives that have to be maximized or minimized. For example, the maximization of the profit in most cases is an objective function; however, the creation of a design which does not lead to environmental pollution is a constraint. The main goal assigned to the present study is to design a catalytic process for methanol/dimethyl ether production, in view of maximizing profit by minimizing operating and investment costs. However, it should be noted that each step of the process will be assigned specific goals.

2.3.4 Overview of flowsheet synthesis

2.3.4.1 Introduction

Preliminary design involves generating alternatives and, for each, carrying out analyses to determine how it performs, with a value placed on that performance. This activity occurs repeatedly as one progresses through a design. In this preliminary stage, one considers the creation of an entirely new process (termed grassroots design) or improves an existing process (a retrofit design). In the production of methanol and dimethyl ether, analyse of different alternatives will be carried out and in particular it will be investigated whether it is better to produce methanol alone or combine methanol and DME production.

2.3.4.2 Basic steps in flowsheet synthesis

This section presents an overview of the basic steps required to carry out the synthesis of chemical process. It should be noted that even for simple problems, the number of alternatives is generally enormous, and here the objective is to discover good alternatives without conducting an exhaustive search.

The first step in synthesizing and evaluating better flowsheet alternatives is to gather relevant information from the literature. The second step consists of representing alternatives in a concise way for decision making. The goal here is to provide a relevant, but concise depiction of the design space that allows an easier recognition and evaluation of available alternatives[4-10]. A third step

consists in assessing and evaluating the designs by deciding which measures to use, such as economics and safety. Thereafter, equations of physics are used to establish how a process performs, including mass and energy balances to establish streams flowrate, temperatures, and pressures.

The value of a design is assessed when asked if it will lead to a profitable process. Here, performance evaluation determines how economic, safe, flexible and so on, a process is. Moreover, different evaluations generally correspond to conflicting goals for a design and increasing the value for one usually requires decreasing the value for another.

2.3.5 Process flowsheet optimization

2.3.5.1 Introduction

The purpose of many simulation tasks in engineering is to develop a predictive model that can be used to improve a process, and the improvement depends mainly on optimization strategies used in a specific process.

2.3.5.2 Background on optimization

2.3.5.2.1 Definition of optimization

Optimization is a process of improving an existing situation, device, or system such as a chemical process. It consists in finding the best solution to the process within constraints. To quantify the *best solution*, an objective function that serves as a quantitative indicator of *goodness* for a particular solution is needed[2, 3, 11].

2.3.5.2.2 Types of optimization

There are essentially two types of optimization that a chemical engineer needs to consider. The first is termed topological optimization and deals with the topology or the arrangement of process equipment. The second type is parametric optimization and it is concerned with operating variables, such as temperature, pressure, and concentration of streams for a given piece of equipment or process.

2.3.5.2.3 Topological optimization

During the design of a new process unit or the upgrading of an existing unit, topological optimization should, in general, be considered first. The reasons for this are two-fold. First, topological changes usually have a large impact on the overall profitability of the plant. Second, parametric optimization is easy to

interpret when the topology of the flowsheet is fixed[2, 3,12]. It should be noted that combinations of both types of optimization strategies may have to be employed simultaneously but that the major topological changes are best handled early on in the optimization process. This study will deal first with this type of optimization before proceeding further.

2.3.5.2.4 Parametric optimization

In optimizing a chemical process, it is necessary that the key decision variables be identified early on in the optimization procedure. This is necessary in order to reduce the computational effort and time and make the problem tractable. The choice of key decision variables is crucial to the efficiency of the optimization process. An exhaustive list of potential decision variables is not presented; however, some important variables that should be considered[2,3] for most processes are:

- Operating conditions for the reactor, for example, temperature, pressure, concentration of reactants. The temperature range may be restricted by catalyst properties, such as the catalyst may sinter at high temperature or be inactive at low temperatures

- Single-pass conversion in the reactor

- Recovery of unused reactants

- Purge ratios for recycle streams containing inerts

- Purity of products (this is often set by the external market)

- Reflux ratio and component recovery in columns

- Operating pressure of separators

2.3.5.2.5 Objective functions

The optimization can only begin after the objective function is selected. It must be chosen such that the extreme maximum (or minimum) is the most desired condition. An objective function is a mathematical function that, for the best values of the decision variables, reaches a minimum or a maximum [2,3,12,13]. Thus, the objective function is a measure of value or goodness for the optimization problem. For a profit, it searches for the maximum while for a cost, it searches for the minimum. There is more than one objective function for a given optimization problem.

Most commonly objective functions are directly based on the economics of the system, however some others are not. In this study, the compressor work per unit of valuable material produced is considered as an objective function, which should be minimized in the design of methanol/DME production process. Furthermore, a rational basis for any objective function (monetary or non-monetary) should be developed.

2.3.5.2.6 Decision variables

The objective function is linked to independent variables called decision variables or design variables that should be identified and chosen efficiently before proceeding to optimization. The decision variables are independent parameters over which the engineer has some control. These can be continuous variables such as temperature or discrete (integer) variables such as the number of stages in a column.

A strategy to determine decision variables is to consider how the process is controlled. There are alternative control strategies for equipment and processes, but a well-designed control system reduces the degrees of freedom to zero without over constraining the process. The other types of decision variables are equipment characteristics. The reactor volume and the number of stages used are examples. In this study, temperature, pressure, and feed flow rate ratio, recycle products have been considered as decision variables. Once the decision variables have been identified and prioritized, the techniques of topological and parametric optimization can be applied.

2.3.5.2.7 Constraints

Values of the decision variables are limited by constraints. These may be linear or nonlinear, and may involve more than one decision variable. When a constraint is written as an equality involving two or more decision variables, it is called an equality constraint. When a constraint is written as an inequality involving one or more decision variables, it is called an inequality constraint. For

example, the catalyst may operate effectively only below 400ºC, or below 200 atm. An equality constraint effectively reduces the dimensionality (the number of truly independent decision variables) of the optimization problem. Inequality constraints reduce (and often bound) the search space of the decision variables.

2.3.5.2.8 Global optimum-local optimum

A global optimum is a point at which the objective function is the best for all allowable values of the decision variables. There is no better acceptable solution. In contrast, a local optimum is a point from which no small allowable change in decision variables in any direction will improve the objective function[2, 3, 13].

2.3.5.2.9 Linear programming-nonlinear programming and quadratic programming

Certain classes of optimization problems are given names. If the objective function is linear in all decision variables and all constraints are linear, the optimization method is called linear programming. Linear programming problems are inherently easier to solve than other problems and are generally solved with specialized algorithms. All other optimization problems are called nonlinear programming. If the objective function is second order in the decision variables and the constraints are linear, the nonlinear optimization method is called quadratic programming. For optimization problems involving both discrete and continuous decision variables, the terminology or objective mixed-integer is

used[2,3,13,14]. As it will be seen later in this study, the objective function: compressor work load per material generated is non-linear

2.3.5.2.10 Communication of optimization

It is necessary to explain the ranges of decision variables that were searched and show that the solution is (most likely) not merely a local minimum or local maximum, and show the degradation in the objective function from moving away from the solution. It is more efficient to change more than one decision variable at a time when searching for optimum; however, it is better to communicate the validity of the optimum with families of curves in which any single curve involves the variation of only one decision variable, for instance pressure. It is in this context at the end of thermodynamic calculations related to this work, optimization results will be communicated by making use of such diagrams.

2.4 Conclusion

The process synthesis approach enabled to identify parametric constraints (temperature, pressure, flowrate of reactive species, etc) and objective functions (maximizing the limiting reactant conversion, minimizing the feed compressor work load per unit of mass of oxygenate product) needed to optimize and decide on the involved process (methanol/DME). This will allow scrutinize alternatives in methanol and DME production and setting up catalysts testing conditions as will be seen in the next chapter.

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CHAPTER 3
A THERMODYNAMIC ANALYSIS OF THE PROCESS

3.1 Introduction

The decision on how to produce methanol and dimethyl ether is considered in this chapter, and in particular whether it is better to synthesize methanol alone, or to synthesize methanol followed by DME, or simultaneously produce both products in the same reactor. Thereafter, operating conditions such as temperatures and pressures within which synthesized catalysts should be tested will be determined. A thermodynamic analysis of the chemical reactions involved in the process will give insights into the above mentioned issues.

To achieve the assigned goals, our approach will be as follows:

- Formulate the problem as clearly as possible
- Define an objective function that should either be maximized or minimized
- Make some assumptions (for instance, that production costs are mainly due to the compressor work).
- Take into account the chemistry and thermodynamics considerations of the process (that will enable to identify decisions variables and set constraints)

- Relate the objective function and decision variables by a mathematical expression
- Set a range of feasible decision variables
- Do related calculations
- Communicate results through graphs
- Identify regions maximizing or minimizing the objective function from the graphs
- Hence, from the graphs the optimum operating conditions will be read-off

This study will consider the minimization of the compressor work load per unit of mass of material yielded as the main objective function. The assumption at an earlier stage of the process is that the production costs of methanol and DME are mainly due to the work of compressors relatively to the amount of valuable material. Thus, the alternatives that will be retained are the one minimizing this objective function as the production costs depend directly on. In the calculations, it will initially be assumed that reactor temperature, pressure and feed flow rate to reactor are decisions variables. Furthermore, from the calculations range of operating conditions for catalysts testing will be explored.

3.2 Factors in methanol and DME synthesis

The synthesis of methanol and dimethyl ether from synthesis gas involves the following main chemical reactions:

		ΔG^{o}_{298K} (kJ/mol)	ΔH^{o}_{298K} (kJ/mol)
$CO_{(g)} + 2\ H_{2(g)} = CH_3OH_{(g)}$	**(1)**	-25.2	-90.6
$2\ CH_3OH_{(g)} = CH_3OCH_{3(g)} + H_2O_{(g)}$	**(2)**	-16.5	-23.5

In addition the Water Gas Shift reaction can also occur according:

		ΔG^{o}_{298K} (kJ/mol)	ΔH^{o}_{298K} (kJ/mol)
$CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)}$	**(3)**	-28.5	-41.2

It should be noted from thermodynamics point of view that reaction (1) alone represents a conventional methanol synthesis that requires high synthesis pressure (100-300 atm) in order to reach acceptable CO conversions as the reaction is equilibrium limited. Dimethyl ether is produced from methanol (reaction (2)) and the reaction equilibrium is not pressure sensitive as there is no change in number of moles. Thus, the introduction of the dimethyl ether reaction (2) could theoretically serve to relieve the thermodynamic constraints inherent to the methanol synthesis by transforming the methanol into DME. In principle, this might be used to lower operating pressures in methanol production. In this chapter, an investigation is being conducted to see whether there are indeed advantages to simultaneously making methanol and DME.

The systems that are considered in the course of this study include:

- System I, which is defined as the process involving the chemical reaction (1) in which only methanol is the desired product.

- System II is the process involving the chemical reactions (1), (2) and (3), and leading to the production of methanol and dimethyl ether as desired products.

3.3 Equilibrium constant (K_{eq})

The CO conversion depends on the equilibrium constant K_{eq}, which in its turn depends on operating temperature in the reactor. Before describing how the CO conversion changes with temperature, the relationship between the equilibrium constants for the reactions involved in methanol/dimethyl ether synthesis and temperatures need to be analyzed.

The Gibbs free energy and enthalpy of a chemical reaction can be evaluated from the standard energy of formation of each of the components using the following thermodynamic equations:

$$\Delta G_{rxn} = \Sigma \Delta G^{o}_{products} - \Sigma \Delta G^{o}_{reac\,tan\,ts} \qquad [3.3\text{-}1]$$

$$\Delta H_{rxn} = \Sigma \Delta H^{o}_{products} - \Sigma \Delta H^{o}_{reac\,tan\,ts} \qquad [3.3\text{-}2]$$

The temperature dependence of the equilibrium constant K_{eq} for the above thermodynamic properties is determined from the van't Hoff expressions given by:

$$K_{eq}(T) = exp[-\frac{\Delta G_{rxn}}{RT}] \qquad [3.3\text{-}3]$$

$$\frac{d \ln K_{eq}(T)}{dT} = \frac{\Delta H_{rxn}(T)}{RT^2} \qquad [3.3\text{-}4]$$

The equilibrium constants as a function of temperature were considered within the temperature range of 400K-800K. For the temperature range under consideration, calculations were done by combining equations [3.3-1], [3.3-2], [3.3-3], and [3.3-4], whose results are displayed in Table A-2 of Appendix A and represented by curves of Figure 3-1 , which show how the equilibrium constants (ΔH_{rxn} is assumed constant) depend on temperature.

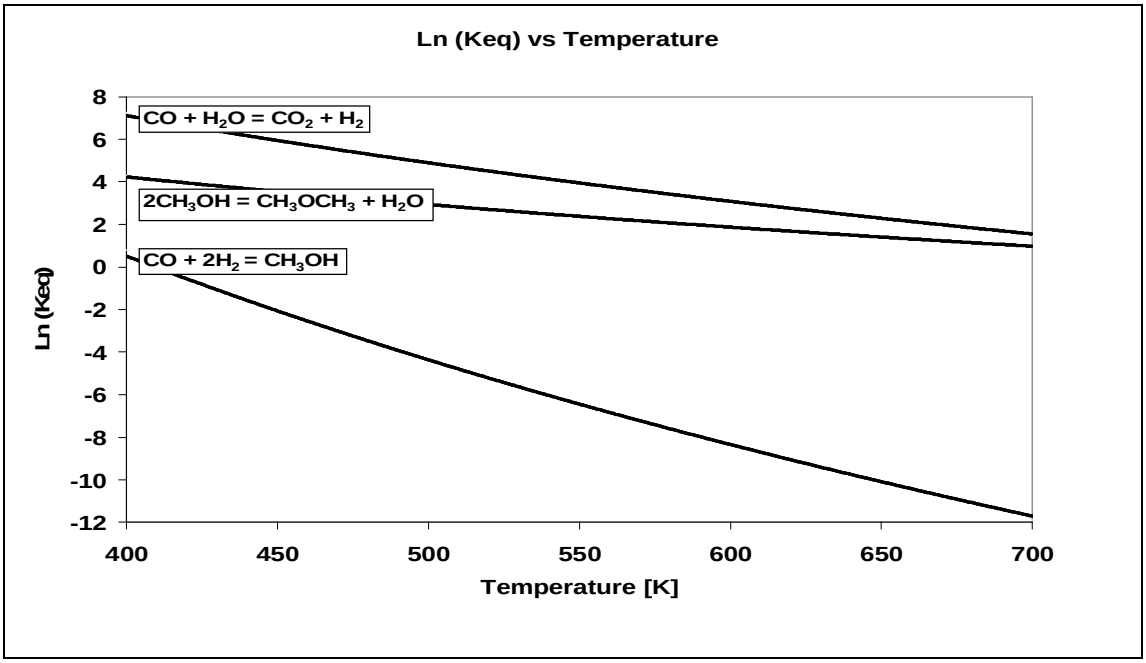

Figure 3-1: Effects of temperature on equilibrium constant of reactions involved in methanol/DME synthesis

From Figure 3-1 it can be seen that the equilibrium constant of reactions involved in methanol and dimethyl ether synthesis decreases with temperature. In a comparative way, the water gas shift reaction (reaction (3)) has the largest equilibrium constant over the temperatures range considered in this work. This is followed by the equilibrium constant of reaction (2), which is the transformation of methanol into dimethyl ether and then reaction (1) with the lowest equilibrium constant. When the three reactions are in competition in the same reactive environment, the water gas shift reaction is likely to take place more easily than reactions (1) and (2). Knowing the equilibrium constant values for each reaction at a particular temperature, it is possible to evaluate the theoretical equilibrium conversion of reactants with respect to temperature.

3.4 Equilibrium conversion of CO

The equation used for the evaluation of the degree of conversion of a particular reactant in a considered reaction is given by:

$$K_{eq} = \frac{\prod_i n_i A_{pi}^{a\,i}}{\prod_j n_j A_{rj}^{b\,j}} \qquad [3.4\text{-}1]$$

where,

K_{eq} is the equilibrium constant.

A_{pi}^{ai} is the activity of the ith product to the power α_i

A_{rj}^{bj} is the activity of the jth reactant to the power β_j

v_i is the stoichiometry coefficient of the ith product

v_j is the stoichiometry coefficient of the jth reactant

For ideal gaseous systems, the activities of reactants and products correspond to their respective partial pressures. For pressures which are not too high, the assumption of ideality is probably not a bad one. In any event, in the initial stage of study, ideality will be assumed. The economic viability of a process is influenced by operating temperatures and pressures, and it will be shown in the next section how these two factors influence the process.

3.4.1 Temperature and pressure effects on the equilibrium conversion of CO

The flowsheet in Figure 3-2, which is the modification of the flow-sheet of Figure 2-1, this time without recycle (the apparatus set-up used in our laboratory facility does not separate, neither recycle the unreacted products exiting the reactor) is a flow diagram of the process used to evaluate the single pass CO equilibrium conversion for Systems I, and II respectively.

Assume that the target is to produce a ton of methanol a day (for System I) in ideal conditions using the synthesis gas as raw material. From the mass balance point of view, 97500 kmol/day of syngas needs to enter the system by the feed compressor (Figure 3-2). Prior fixing the appropriate molar flow rate ratio between CO and H_2 to feed into the reactor, preliminary calculations were done for the CO:H_2 ratio equals to r = 1:1, 1:2, and 1:3 respectively. Results (appendices B and C) obtained have shown that the stoichiometric ratio CO:H_2 = 1:2 is the one that gives relatively high carbon efficiency (CE) and hydrogen efficiency (HE) for both Systems I (MeOH) and II (MeOH+DME+WGSR). For the

moment the conversion of CO in the reactor is taken as the important variable. In further calculations the same molar feed flow rate and ratio for System II will be used for consistency.

The synthesis gas (stream F_1) is sent to the feed compressor at pressure P_1 as Figure 3-2 shows, which is pressurized to loop pressure P_2, the pressure at which the reactor operates. Assume materials leaving the reactor are at equilibrium at temperature T and pressure P (stream F_3) are separated by a separator system into water, methanol, and dimethyl ether, these two later being the desired products. The unreacted (CO and H_2) and undesired (CO_2) compounds are subject to recycling.

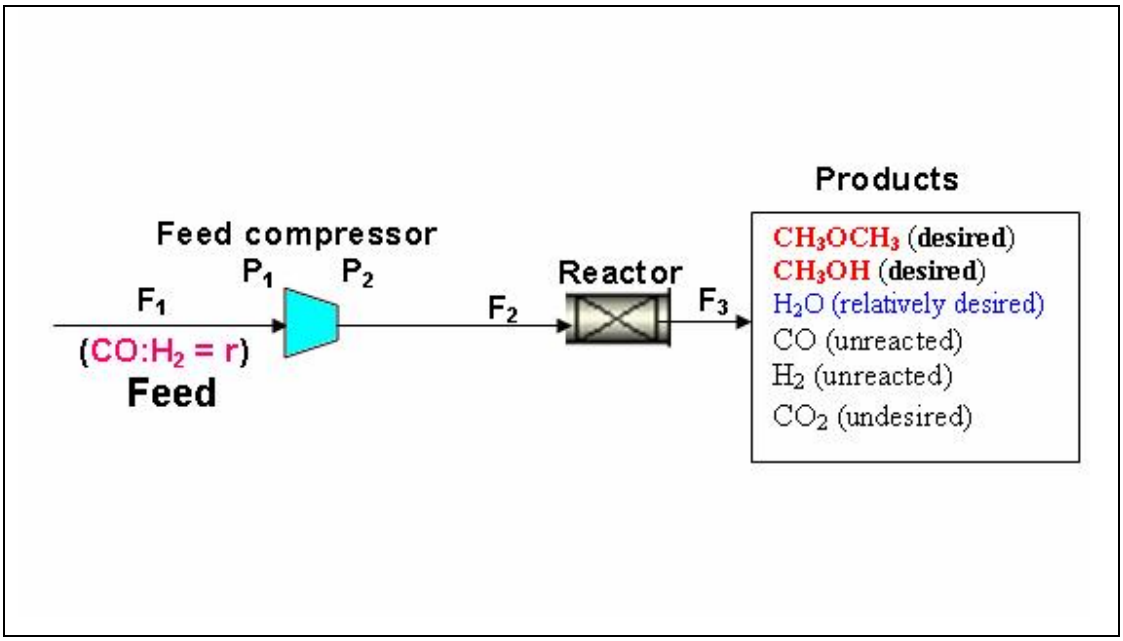

Figure 3-2: Modified flow diagram for methanol/DME production

Calculations were made in considering the flow diagram of Figure 3-2, the mass balance of materials and chemical reactions involved in the process. The numbers of moles at equilibrium are displayed in Tables Bs and Cs of Appendices B and C. The results obtained in terms of the CO conversion for the Systems I, and II in the temperature range of 400-800K, and pressure range of 1-100 atm are illustrated in Figure 3-3.

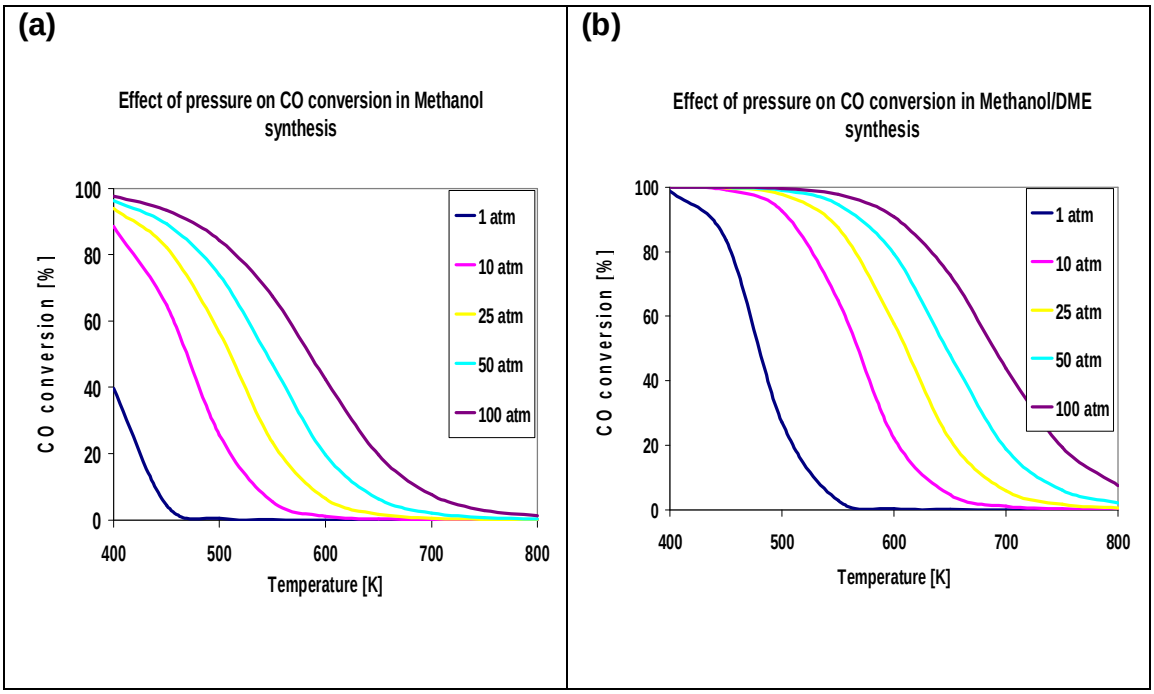

Figure 3-3: Effects of temperature and pressure on CO conversion for (a) System I and (b) System II

It is evident that the equilibrium conversion of CO in both systems (I and II) increases with pressure, but decreases with temperature. This is as expected, since all the reactions involved are reversible and exothermic. A temperature increase shifts the equilibrium of reaction (1) to the left and thereby decreases the carbon monoxide conversion. Because of the change in the number of moles in reaction (1), the increase in pressure shifts the reaction equilibrium to the right. This is in agreement with Le Chatelier's principle which states that when a stress is applied to a system at equilibrium the system will adjust to relieve the stress.

Looking at equilibrium curves of Figures 3-3, it can be attempted to operate at high pressure and low temperature to maximize the CO conversion. That is not always the case in industrial practice, since the optimization of a process takes into account more than one constraint and other decision variables as it will be seen later. To complete the analysis there is a need to optimize the operating conditions. Additionally, as both Systems (I and II) do not behave in the same way; therefore, to see which one takes advantage on the other in respect to the CO conversion, it is essential to compare the results from calculations based on thermodynamics considerations, and then draw a conclusion. Figure 3-4 shows the dependence of the equilibrium conversion of CO on pressure and temperature of Systems I and II. In a comparative way, Figures 3-4 (a), (b), (c) and (d) show that the conversion of carbon monoxide when methanol is co-produced with dimethyl ether is higher for all range of pressures and temperatures, in particular at relatively low and moderate temperatures. This tendency is not more pronounced at high temperatures because the thermodynamics of reactions leading to methanol and dimethyl ether is such as the conversion of carbon monoxide is limited. Moreover, further investigation is

needed to quantify the amount of carbon in valuable products (methanol and dimethyl ether) with respect to carbon in the feed stream. This is called carbon efficiency, one of the comparative parameters, which does not account for CO_2 produced.

3.4.2 Outcome of temperature and pressure effects on equilibrium conversion of CO

It can be deducted from the one pass CO conversion point of view that System II where methanol is simultaneously produced with dimethyl ether is more efficient than System I, which consists in methanol production alone, and this is related to the nature of chemical reactions involved in these two systems. This conclusion does not take into account the carbon efficiency neither the work needed to run the feed compressor, which is the matter of discussion in the next two sections.

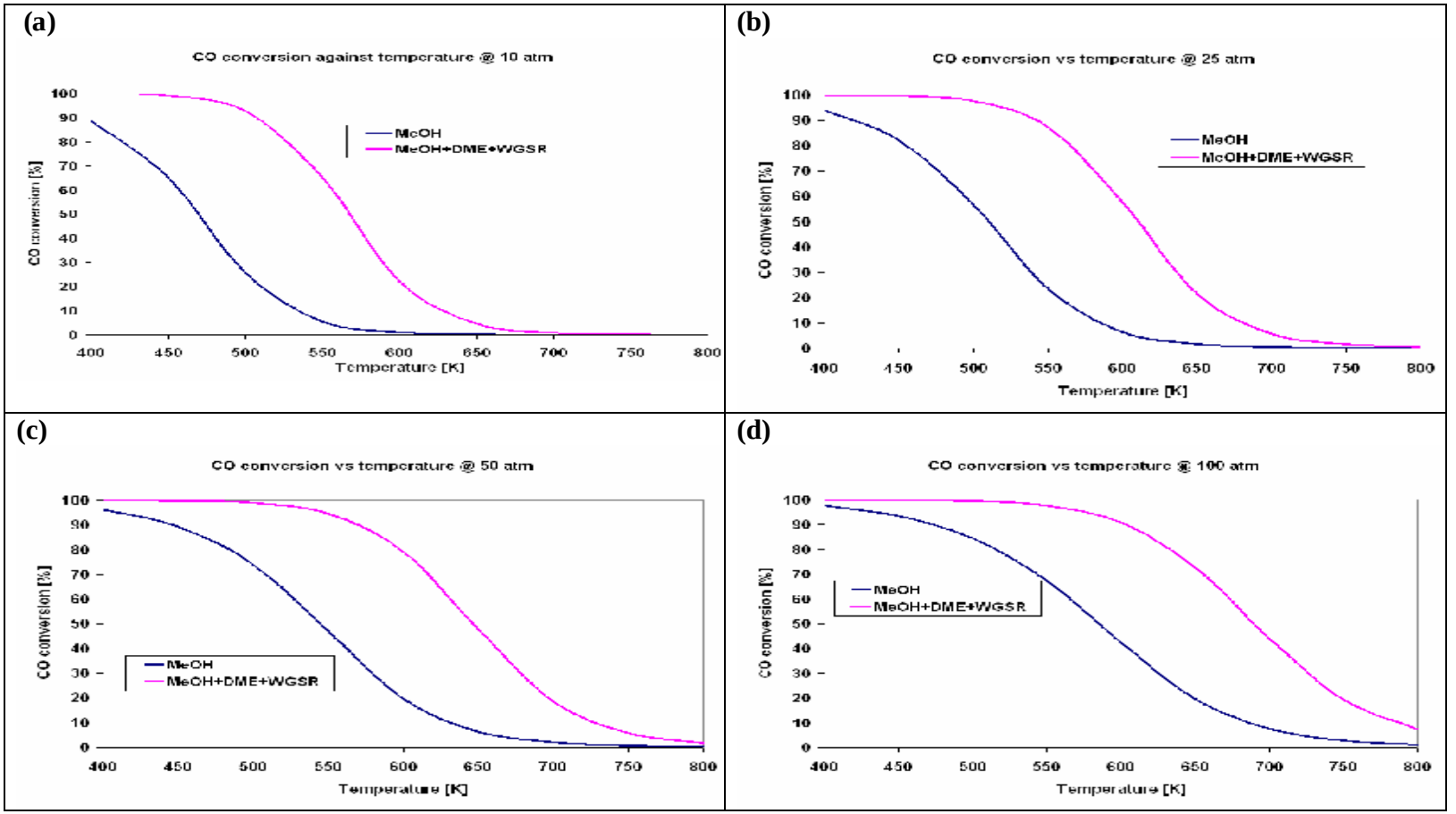

Figure 3-4: Effect of temperature on CO conversion in System I (MeOH) and System II (MeOH+DME+WGSR)

3.5 Effect of temperature on carbon efficiency and compressor work load per unit material yielded

In order to ascertain the system with a better performance in terms of carbon efficiency and compressor work load per unit of mass of oxygenate (methanol and dimethyl ether) produced, we present in the following sections results of calculations carried out for the two Systems (I and II), as displayed in Tables (Bs and Cs) of Appendices B and C. 10 atm, 25 atm, 50 atm and 100 atm are considered as very low, low, moderate and high pressure respectively and temperatures around 400K as low, between 450 and 550K as moderate, and around 600K and above as high.

3.5.1 Effect of temperature on Carbon Efficiency (CE)

Carbon efficiency (CE) represents the ratio of amount of carbon in valuable products (methanol and dimethyl ether) exiting the reactor by the amount of carbon in the feed products (carbon monoxide) entering the same reactor. Based on carbon efficiency, the system that has high carbon efficiency is the one presenting a good performance.

When looking at the CE coefficient in both systems, it can be seen from graphs of Figure 3-5 that there are temperature regions where producing methanol alone is more convenient than combining its production with DME. In fact, low

temperatures give high carbon efficiency for System I (MeOH), however, moderate and high temperatures show high carbon efficiency for System II (MeOH+DME+WGSR), which are represented by the shadowed yellow regions. The hypersensitivity of reaction involved in the methanol synthesis to temperature could be the reason behind the fast decay in the carbon efficiency against temperature for System I; in fact for a particular pressure, the methanol yield declines faster with temperature (Figure 3-6 a) for System I (MeOH) than does methanol+DME yield (Figure 3-6b) for System II (MeOH+DME+WGSR). Furthermore some amounts of carbon are being taken away in System II by the carbon dioxide, which is highly produced at low temperatures than it does at high temperatures as shown in Figure 3-7.

Another parameter that can also be considered for the evaluation of the process is the hydrogen efficiency (HE), which ascertains the amount of hydrogen in the valuable products (methanol or dimethyl ether). This parameter enables to make a comparison amongst Systems (I or II) dealt with according to molar feed ratio. Values of hydrogen efficiency (HE) for each system exploited in this study are presented in tables Bs and Cs of appendices B and C.

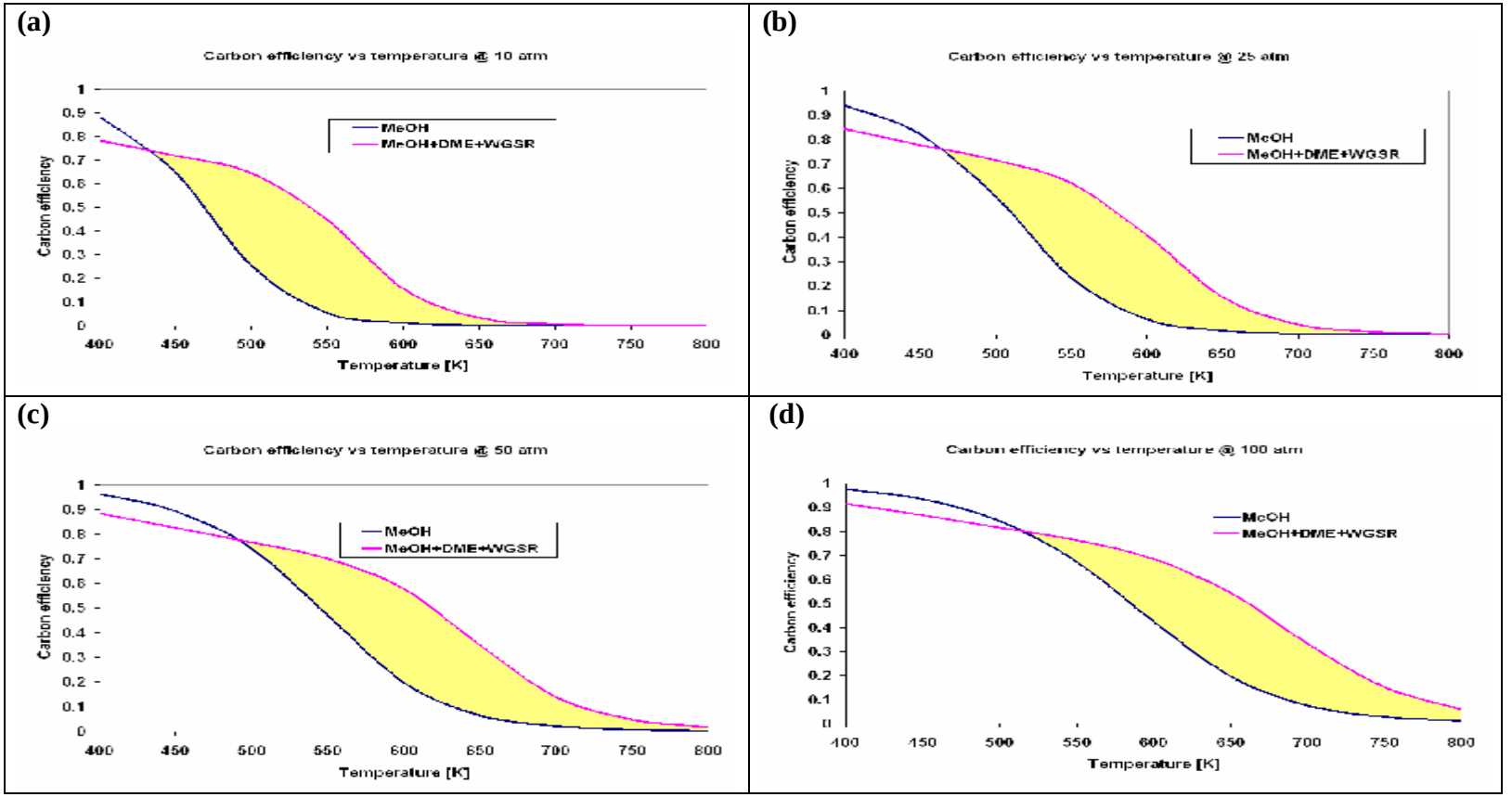

Figure 3-5: Temperature region (yellow colour) for relative high carbon efficiency for System II (MeOH+DME+WGSR) in comparison with System I (MeOH)

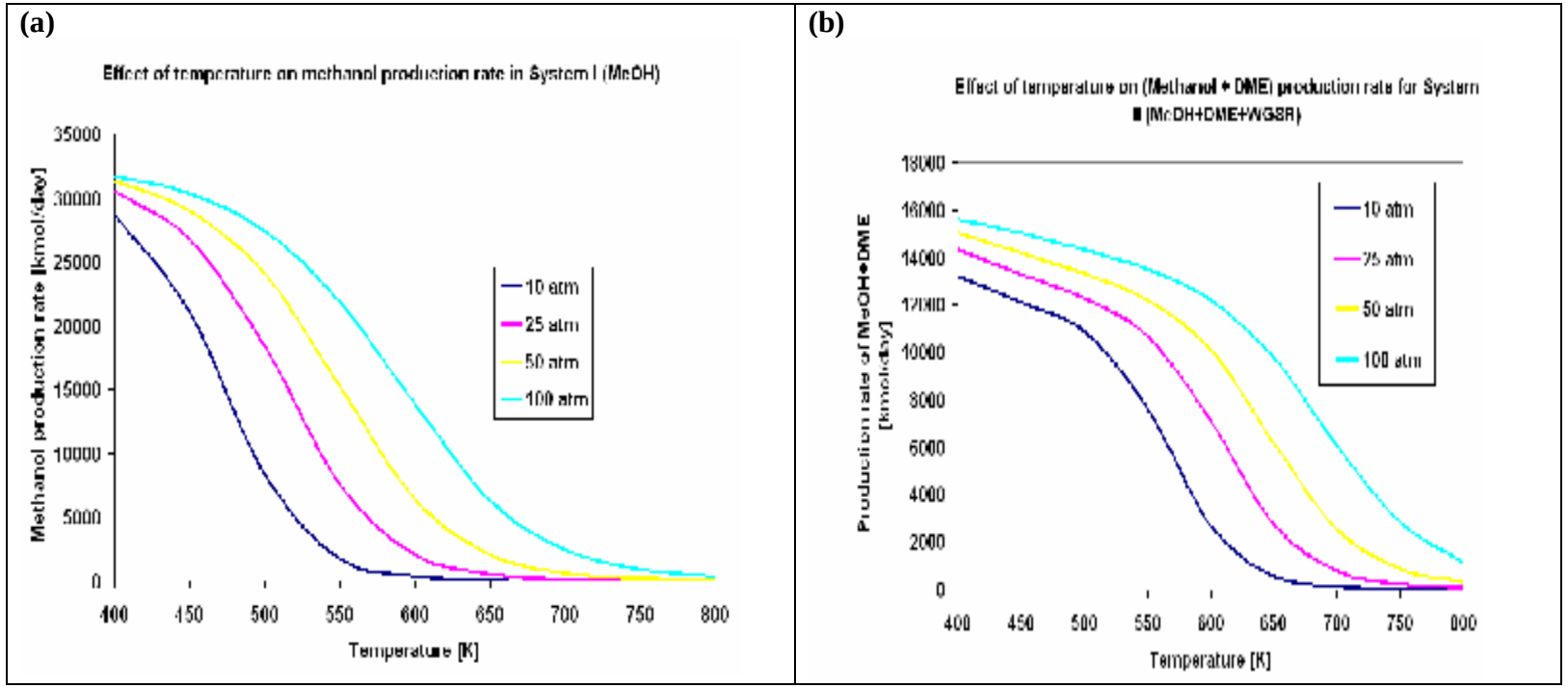

Figure 3-6: Temperature effect on oxygenate (MeOH/DME) production rate-Hypersensitivity of System I to temperature

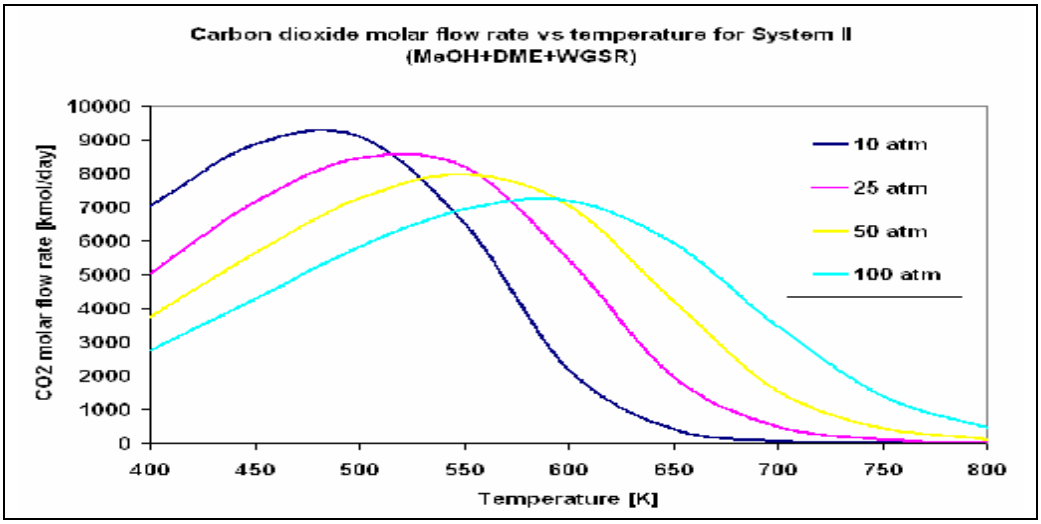

Figure 3-7: Effect of temperature on production rate of CO_2 in System II

3.5.2 Temperature effect on feed compressor work load per unit of material produced

Compressors are units inserted in the process to pressurize reactants along the system loop (feed compressor) or recycle products into the loop (recycle compressor). To run these units requires energy which is related to the operating conditions and types of systems (I or II) involved in the process. From these reasons this section considers the power consumption of the feed compressor per unit of oxygenate product as the objective function in order to find the optimal operating conditions for the two systems. Process operating temperatures and pressures that minimize the compressor work load per unit of generated material are therefore investigated. Thus, at the end of this chapter one should be able to

define the range of temperatures that the catalysts should be tested as well as the pressure.

Since, a comparative study has to be made based on this objective function, it is necessary to look at first factors that influence it and then evaluate this work load for both systems.

Previous calculations enabled to compute molar flow rates of all streams in the flow sheet of Figure 3-2, which are recorded in Appendix B and C. Assuming that the compressors are operating adiabatically, the equation for adiabatic work of a compressor is given by:

$$P_{ad} = \frac{g}{g-1} MRT\left[\left(\frac{P_2}{P_1}\right)^{\frac{(g-1)}{g}} - 1\right] \qquad [3.6\text{-}1]$$

with:

P_{ad}	:	compressor work load [kW]
M	:	molar flow rate [kmol/s]
R	:	ideal gas constant (R = 8.314 kJ/kmolK)
T	:	feed temperature to compressor [K] (taken as 298K for feed compressor)
γ	:	$\equiv \frac{C_P}{C_v}$ = 1.4 (for most gases)
C_p	:	heat capacity at constant pressure
C_v	:	heat capacity at constant volume
P_1	:	feed pressure to compressor [atm]
P_2	:	exit pressure from compressor [atm]

The flowsheet of Figure 3-2 shows that the feed compressor pressurizes the feed to the desired loop pressure. Initially, it is assumed that the reactor output is at equilibrium. It is proposed that an “optimal process” be designed so as to minimize the operating costs and it is assumed that the major operating costs are the compressor work loads per unit of mass of oxygenate product.

Equation [3.6-1] shows that the work of compressor depends mainly on the molar flow rate across the compressors. The molar flow rates are on their turn related to the operating pressure of reactor and the temperature. For that reason, the next section will examine the effects of these decision variables on the compressor work load per unit of material produced.

When the feed compressor runs at 10 atm, Figure 3-8 a (shadowed yellow region) shows that for temperatures greater than 475K System II where methanol is co-produced with dimethyl ether presents more advantages than System I in which methanol is made alone.

At 25 atm, Figure 3-8 b shows that for temperatures higher than 500K, it is convenient to consider the process where methanol is simultaneously made with dimethyl ether as at such temperatures this system requires less work to run the feed compressor per unit of oxygenate to be made than does the system where methanol is produced alone. At 50 and 100 atm, Figure 3-8 c and Figure 3-8 d show that from respectively 550 K and 575K onward, System II (MeOH+DME+WGSR) presents more advantages than does System I (MeOH).

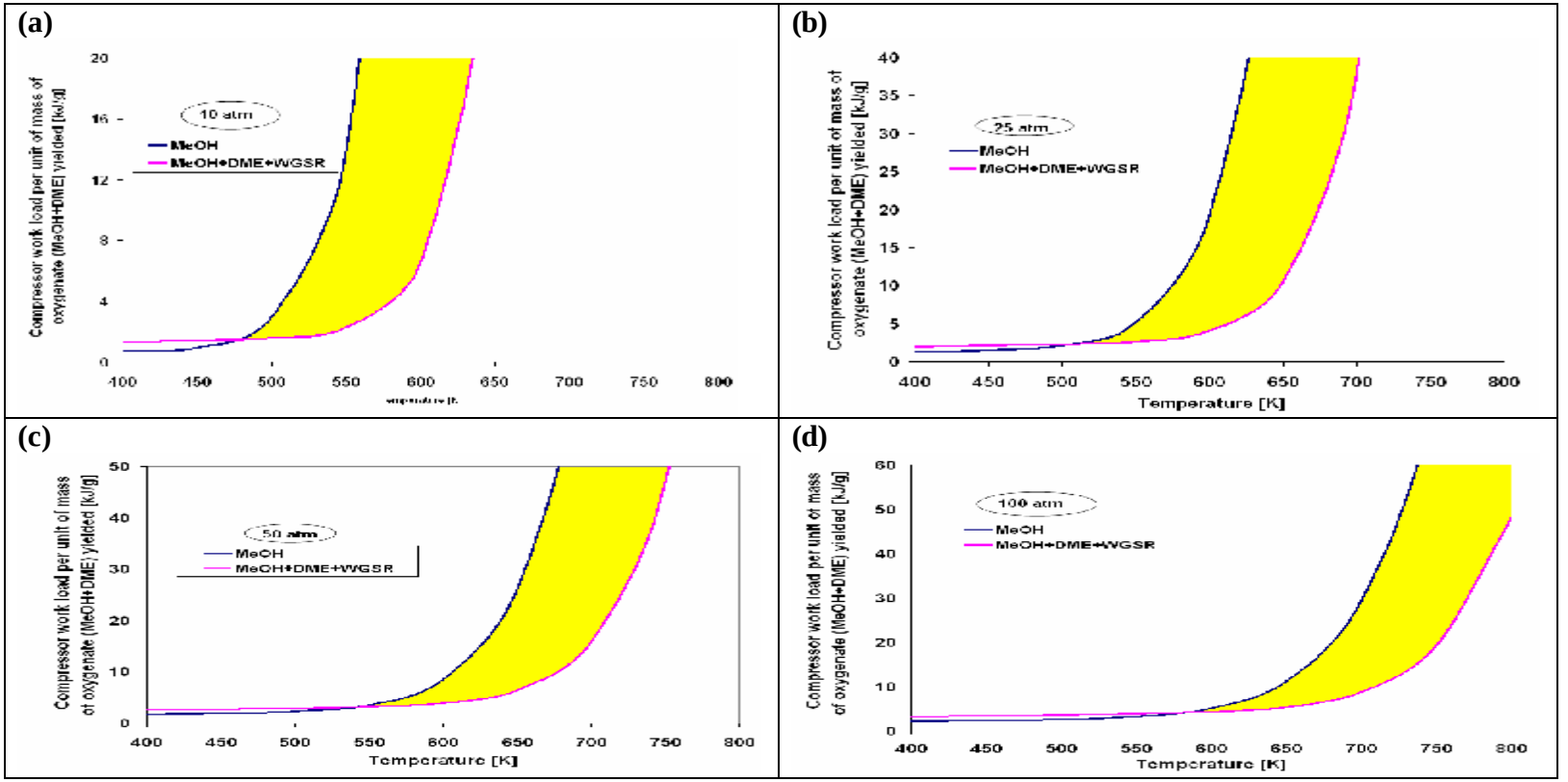

Figure 3-8: Temperature region (yellow colour) for minimum work load per unit of oxygenate product for System I (MeOH) and System II (MeOH+DME+WGSR)

This tendency is related to the hypersensitivity of System I to temperature compared to System II, as illustrated in Figure 3-6.

All curves of Figure 3-8 show that the compressor load per unit of material yielded increases with temperature, and this tendency is more significant for moderate and high temperatures.

Given that during the experimental programme, our laboratory facilities could only use pressure not higher than 25 atm, the maximum pressure was set at 25 atm, and from Figure 3-8 b, it can be seen than the temperature region favourable for producing simultaneously both methanol and DME is from 500K up to around 675K where the pink curve bends asymptotically. These are in fact conditions that were exploited to test catalysts used in the experimental part of the thesis.

3.6 Conclusions

From all observations made, it may be deduced that loop pressure and reactor operating temperature do really have influence on the total compressor work load for System I (MeOH) and System II (MeOH/DME/WGSR). Based on the energy rate to spend for running the feed compressor per unit of valuable material to be made, it was noticed that System II where methanol is co-produced with dimethyl ether presents more advantages than the system where methanol has to be made alone since System II uses less energy for running the feed compressor for the same amount of material to be yielded. This is applicable at moderate and high temperatures for all range of pressure. The

generated graphs enabled to determine favourable temperature regions for a particular pressure for catalysts testing conditions, which are in fact the regions for relatively low compressor work load per unit mass of oxygenate material for System II (MeOH+DME+WGSR) in comparison with System I (MeOH).

Based on the objective function (compressor work load per unit of oxygenate product) used in this work, it was shown that coproducing methanol and dimethyl ether in the same reactor is more efficient than making methanol alone within specific operating conditions. Since the target of this work is to simultaneously synthesizing methanol and DME at 25 atm, thermodynamic calculations enabled to set temperature region for catalysts testing ($500K \leq T \leq 700K$) for the experimental programme as dealt with in chapter six of this thesis.

CHAPTER 4
GOLD HETEROGENEOUS CATALYSIS

4.1 Theoretical concepts of heterogeneous catalysis

Before examining the catalytic properties of gold, which is the metal of interest in this study, it is essential to have an overview of some theoretical concepts of heterogeneous catalysis that will provide insights for gold catalysis.

4.1.1 Heterogeneous catalysis and catalyst characteristics[1, 2]

A catalyst is a substance that increases the rate of reaction toward equilibrium without being appreciably consumed in the process. When the catalyst is solid and reactants are liquids or gases, one speaks about *heterogeneous catalysis*. Each catalyst is characterized by its "catalytic activity" that refers to the rate at which it causes the reaction to proceed to chemical equilibrium. A good catalyst must possess both high activity and long-term stability. The "*catalytic selectivity*" is a measure to which the catalyst accelerates the reaction to form one or more of the desired products, and usually varies with pressure, temperature, reactant composition, and extent of conversion, as well as with the nature of the catalyst.

The *catalytic life* which is one of catalyst characteristics is the period for which a catalyst is actively utilizable. In industrial applications, if a variety of products are possible, selectivity is usually the more important.

Moreover the yield is an engineering or industrially used term that refers to the quantity of product formed per quantity of reactant consumed in the overall reactor operation. The sites of a catalyst are specific locations on the catalyst where reaction takes place. A catalyst may lose its activity or selectivity (catalyst deactivation) for different reasons: poisoning, fouling, reduction of active area by sintering or migration, loss of active species or sites. Poisoning can be caused by chemical environment surrounding the catalyst, which for some catalysts might be due to presence of sulphur, whereas for other catalysts water or other substances can act as poisons.

4.1.2 Development of new catalysts

Developing a new catalyst consists either in using and improving an existing catalyst for a particular chemical reaction or wisely choosing/combining catalysts amongst those that already exist and could catalyze a typical reaction. In some instance, developing new catalysts might consist in preparing in particular way a catalyst that never existed before. However, the difficulty of choosing or developing a catalyst may vary greatly as indicated by a scheme of the order of increasing complexity as suggested by Satterfield[1]:

- Selection among known catalysts
  - For known reactions
  - For reactions analogous to known catalytic reactions
  - For new reactions

- Search for new catalysts
  - For well-known catalytic reactions
  - For reactions analogous to those well known
  - For reactions of new types, having no analogues among well-known reactions.

In this study, the reactions involved in the Methanol/DME process are known and we used a combinatory approach to develop the catalysts needed to achieve the set goals.

4.1.3 Preliminary literature survey on DME/methanol synthesis catalysts

This section is designed to examine the various catalyst-types, and determine the catalysts, which are the most efficient and active for methanol/DME synthesis. Based on the search done, three groups of catalysts are suitable for this application, these include:

- PGM (Platinum Group Metals) supported catalysts [3]
- Gold supported catalysts [4-10]
- Copper supported catalysts [11-15]

Many studies conducted on the synthesis of methanol alone, or methanol combined with DME showed the efficiency in the use of PGM and Copper as metal based catalysts. However, although good for their catalytic activity, PGM (particularly platinum) are more expensive than gold, and their market prices are unstable. Furthermore, the high working temperatures of PGM catalysts makes them unsuitable for certain range of temperature since they lead to the formation of higher alcohols, thus, affecting the methanol selectivity. Copper on the other hand, is catalytically less stable vis-à-vis to environment than gold. In fact, the low-pressure methanol synthesis, technique introduced by ICI in 1966 and Lurgi in 1971 uses a combination of Cu/Zn as catalysts which are readily poisoned by sulphur from natural gas. The reaction takes place at lower pressure, in the range of about 50 to 100 atm, and a temperature of about 240 to 260ºC. Above 270ºC deactivation by sintering becomes appreciable[1,2]. Copper as catalyst is more sensitive to deactivation by thermal sintering since it has a relatively low melting point. A maximum operating temperature of about 250ºC is typical. Moreover, the catalytic activity of Cu based catalyst decreases with the presence of water in the reactor.

Some years ago, catalytic studies done on metallic gold have shown that supported gold nano-particles can be used as a catalyst in low-temperature oxidation of carbon monoxide (CO) as well as in the hydrogenation of carbon oxides and manifested some tolerance for water[16]. Stephen Roberts (2001) [17] showed that nano-gold particles supported on zinc oxide is able to catalyze the WGSR at low-temperature (188 and 192ºC). Zubrin[18] reported that at 10 atm, the yield of methanol is severely limited by thermodynamics. However, if methanol synthesis and dehydration of methanol are combined, the CO conversion at equilibrium can go up to nearly 40%, compared with 8% in the

case of methanol synthesis alone. In their project, they used Cu/ZnO as catalyst combined with $H_3PW_{12}O_{40}$.

Sofianos and Scurrell[19] have also reported their results from syngas conversion into DME over bifunctional catalysts. According to the study, the combination of methanol synthesis and dehydration of methanol gave high syngas conversion to form a mixture of methanol/DME. The best result was obtained when they used co-precipitated Cu-Zn-Al catalyst for methanol formation and gamma alumina for dehydration. The two catalysts were mixed and placed in one reactor. Sakurai and Masatake[5] reported that basic catalyst support manifest high selectivity for methanol and in the study, ZnO support was the one used since amongst all the systems studied, Au/ZnO gave good result for the methanol production from CO_2 at 250ºC and 8 atm.

Although not much research has been done on the use of gold as catalyst for the combined synthesis of DME and methanol, Au based-catalysts have recently attracted great interest due to their potential applicability to many reactions of both industrial and environmental importance as mentioned above. Gold has long been regarded as a poor catalyst; however, when Au is deposited as nanoparticles on metal oxides by means of co-precipitation or deposition-precipitation, it exhibits surprisingly high catalytic activity for different reactions. This finding has motivated many scientists and engineers to investigate the catalysis of Au in the 1990s and the recent reversal of the market prices of Au (US $ 9/g) with respect to Pd (US $ 14/g) and Pt (US $ 14/g)[20] can drive Au catalysts to commercialization with an economical advantage.

Taking into account the above considerations, gold supported on zinc oxide mixed physically with the gamma alumina or zeolite is proposed as a potentially suitable catalyst for the DME/methanol synthesis for this study. However, before investigating the gold catalyst characteristics, it is worthwhile to give some details about the catalytic synthesis of methanol and dimethyl ether and the catalysts deactivation.

4.1.4 Catalytic synthesis of methanol[21]

The basis of almost all present-day commercial units for the production of methanol is the ICI process, which converts a high-pressure gas mixture of CO, CO_2 and H_2 into alcohol, using a catalyst containing copper, zinc oxide (ZnO) and alumina (Al_2O_3) at temperatures between 250 and 300˚C. This synthesis is of enormous industrial importance, since it is an effective method for converting "syngas" into a product which is pivotal as a precursor for other useful chemicals (e.g. formaldehyde and acetic acid), for high-octane fuels (e.g. petrol), and for blending agents (e.g. by addition to olefins or dimethyl ether).

4.1.5 Catalytic synthesis of dimethyl ether

Dimethyl ether (DME), is the simplest ether. It is a colorless gas at ambient temperature and pressure, with a slight odor. It is used today as an aerosol propellant in hair sprays and other personal care products and was formerly used as a medical anesthetic. It burns without soot formation, is non-carcinogenic, non-mutagenic and virtually non-toxic. With a colorific value of 6

Mcal/kg and a cetane number of 60, DME represents a potential alternative for diesel compression-ignited engines, with the major advantage of quite lower pollutants and dusts emission than gas oil.[22, 23]

Because of its potential use as a fuel, DME may need to be produced in very large scale. Previously, dimethyl ether was made from the dehydration of methanol and this was made in a small scale, while in recent times technologies have attempted to produce DME directly from coal or syngas via methanol [24-27], in large scale, using different types of catalysts available in literature and others not yet divulgated since they are still under patent. Also till present day gold-based catalysts have not yet been used to produce dimethyl ether directly from syngas via methanol; hence the originality of this study.

4.1.6 Methanol catalyst deactivation

Given that dimethyl ether can be made from or via methanol, this section will discuss mainly the deactivation of methanol catalysts. The literature reveals that the deactivation of methanol synthesis catalysts may be caused by temperature or chemical poisons (sulphur, water, etc).

4.1.6.1 Sintering of methanol catalyst particles

Methanol synthesis catalysts undergo a relatively fast deactivation even in the absence of poisons. More than one-third of the activity is lost during the first thousand hours of operation[28, 29]. Despite this fact, which often determines the

economic lifetime of an industrial catalyst charge, very little has been published on this topic.

Thermal sintering of dispersed crystallites should, according to the rule of Tammann ($T_{mobility} > 0.5T_{bulk\ melting\ point}$) not occur for copper with a melting point 1358K at industrially used operating temperatures of 480-580K. The XRD analysis of spent methanol synthesis catalysts do, however, reveal a growth in the copper crystallite sizes, from 7 to more than 20 nm[30]. Irreversible deactivation is observed, when Cu/ZnO is operated in CO/H_2 gases without CO_2 [31, 32], which has been interpreted to be reduction of Cu^{+1} from the ZnO matrix.

4.1.6.2 Sulphur poisoning of methanol catalyst

Though rare in the syngas, the presence of sulfur, more likely hydrogen sulfide that comes from lubrication oil from the make-up gas compressor and the recirculator, may have negative effect on the catalysts**[33]**. H_2S will be absorbed according to the equilibrium:

$$ZnO + H_2S = ZnS + H_2O$$

The formation of residual zinc sulfide, depending on temperature is able to block the active sites of catalyst[34-36].

4.1.6.3 Water effect on methanol catalysts

Water has a negative effect on the catalytic activity of methanol synthesis catalysts. In fact, different authors [37-38] have shown that water is a catalysts-killer since it deactivates those catalysts and some times the deactivation might be irreversible.

4.1.6.4 Other methanol/DME catalyst poisons

Chlorine is not often present in the feed gas to methanol reactors, but it is a severe poison because it induces an accelerated sintering of both Cu and ZnO leading to the formation of copper and zinc chloride[39-41]. The carbonyls $Fe(CO)_5$ or $Ni(CO)_4$ have also been studied as catalyst poisons. These carbonyls can be present in the make-up gases from gasification plants or be generated within the synthesis loop, from the steel in heat-exchangers or in the reactor. The carbonyls are catalytically decomposed to free metal over the methanol synthesis catalysts. Iron is a strong poison, even below 1000 wt ppm [42-44]. Part of the poisoning by Fe can be explained by Fischer-Tropsch activity of Fe, which will ultimately cover the catalyst by high-boiling waxes (aliphatic alkanes C_{20} to C_{50}). Most of spent catalysts used in industry containing significant amounts (0.4 wt%) of Ni have shown only a very modest deactivating effect [45].

4.2. Catalysis by Gold

4.2.1 Properties of metal gold[20]

Gold is a highly sought-after precious metal that has been used as money, a store of value and in jewelry for centuries. The metal occurs as nuggets or grains in rocks and in alluvial deposits and is one of the coinage metals. It is soft, shiny, yellow, dense, and malleable. It is an element in the periodic table with the symbol Au and atomic number 79. Table 4-1 shows the summary of characteristics of gold. Gold does not react with most chemicals but is attacked by chlorine, fluorine, aqua regia and cyanide. It is known to dissolve in mercury.

Gold is a good conductor of heat and electricity, and is not affected by air and most reagents. Heat, moisture, oxygen, and most corrosive agents have little chemical effect on gold, making it well-suited for use in coins. Common oxidation states of gold include +1 (gold(I) or aurous compounds) and +3 (gold(III) or auric compounds). Gold ions solution are readily reduced and precipitated out as gold metal by addition of virtually any other metal as the reducing agent. The added metal is oxidized and dissolved allowing the gold to be replaced from solution and be recovered as a solid precipitate.

Table 4-1

Chemical and physical properties of gold

Properties of gold	
Atomic mass	196.967 g/mol
Electron configuration	[Xe] $4f^{14}5d^{10}6s^{1}$
Electrons per shell	2, 8, 18, 32, 18, 1
Name, Symbol, Number	Gold, Au, 79
Chemical series	Transition metals
Group, Period, Block	11, 6, d
Lattice constant (nm)	0.408
Phase	Solid
Melting point	1337.33K
Boiling point	3129K
Heat of fusion	12.55 kJ/mol
Heat of vaporization	324 kJ/mol
Heat capacity	25.418 J/mol/K
Crystal structure	Cubic face centered
Oxidation states	3, 1 (amphoteric oxide)
Electronegativity	2.54 (Pauling scale)
Ionization energies	1st : 890.1 kJ/mol 2nd: 1980 kJ/mol
Atomic radius	135 pm
Covalent radius	144 pm
Van der Waals radius	166 pm

4.2.2 Applications of highly dispersed gold nanoparticles and its commercial aspects

Gold nanoparticles find several applications in different areas of our daily life. These applications are motivated by the fact that nano-gold particles supported on oxide supports or when alloyed see their physical or chemical properties enhanced. Despite various applications of nano-gold, we can actually summarize them in five broad market sectors in which they are also commercialized:

- Pollution and emission control technologies, including fuel cells
- New uses for gold in advanced electronics, electrical systems and devices
- Chemical processing of a range of bulk and chemicals, using gold based catalysts
- Advanced coatings exploiting the novel properties of gold, particularly in nanoparticulate form
- New biomedical uses for gold including medical treatments, drugs, implants, sensors and devices.

4.2.3 Economic advantages of gold over platinum group metals

There is an improved recognition that gold is neither expensive compared to the platinum group metals (PGMs), nor has its price varied as widely as the PGMs costs have in recent years. Industrialists prefer stable prices, and Figure 4-1 illustrates the stability in gold price versus its main platinum group metal

competitors. It is also relevant to note that gold supply is much more plentiful, by an order of magnitude than that of the PGMs as shown in Figure 4-1. Thus any significant new demand is unlikely to impact on gold price to any extent, unlike the PGMs. This is a powerful economic factor in the choice of technology.[20]

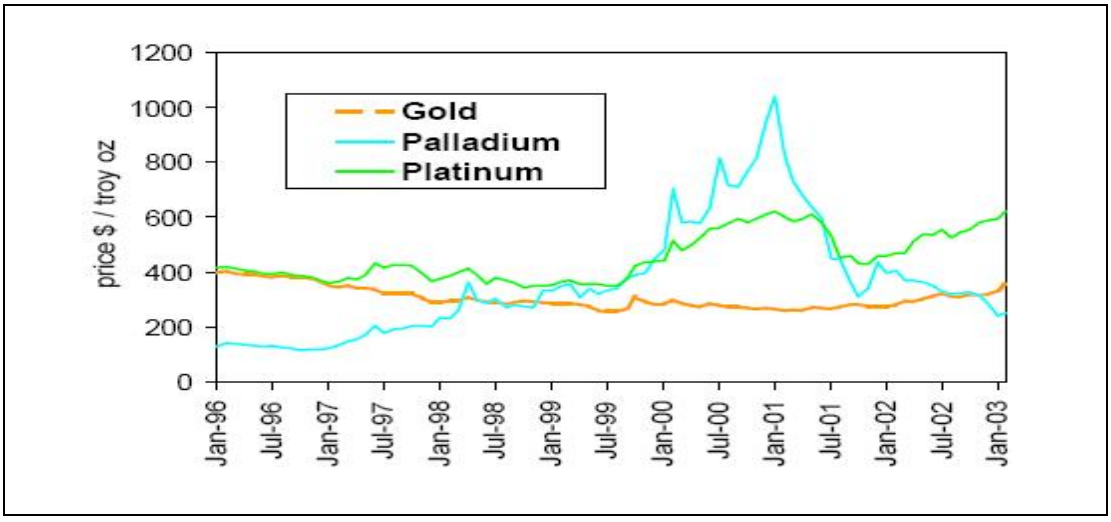

Figure 4-1: Precious metal prices[20]

4.2.4 Factors affecting the activity of gold catalysts

The activity of gold catalysts depends on a variety of factors. These include size and morphology of particles, method of preparation, oxide support, pretreatment conditions of catalysts and knowledge of reaction mechanism.

It is often observed that a metal deposited in thin layers or small clusters on the surface of an “inert” carrier or support exhibits not only an increase and stabilization of its own surface, but also a reduction of its characteristic activation energy for a certain reaction, a synergetic promotion. In a similar way, as the action of a simple catalyst, metal or semi-conductor can be understood by the electronic factor. It is feasible to explain the synergetic promotion by an electron transfer between support and catalysts. Since metals usually show a lower work function than semi-conductors, in electric contact, electrons must be emitted from the metal to the support. Provided the metal is, as usual, present in relatively small amounts, its Fermi level must be lowered to that of the support. The effect should be the same as an admixture of an electron-poor metal like palladium or nickel. This effect is indeed observable in many examples, and the technical importance of binary catalysts may often be due to this effect[46, 47].

In respect of size and morphology, Haruta[48] showed in his review that nanogold particles manifest high catalytic activity when deposited on suitable metallic oxide support and they should be hemispherical with diameter smaller than 5 nm.

Andreeva[49] had investigated the influence of preparation method and the nature of the support on gold dispersion and WGS activity and came up with the following conclusion. For high catalytic activity and stability for gold catalysts in WGS, the following factors have to be considered: suitable choice of support, the size of catalysts optimized at 3-5 nm, good choice of preparation method, knowledge of various aspects of the reaction mechanism.

4.2.5 Methods of preparation of gold-based catalysts

There are numerous methods for preparing gold-based catalysts, namely: Impregnation, Co-Precipitation, Deposition-Precipitation, Suspension Spray Reaction, Grafting, Ion Exchange, Chemical Vapour Deposition, Iwasawa, Self Assembly, etc. However, this study will focus mainly on the three first methods, as these are the most frequently used methods for preparing gold catalysts tested in hydrogenation of carbon monoxide.

4.2.5.1 Impregnation

The simplest and probably the most common method for dispersing a catalytic species on a carrier is by impregnating the pre-dried support to incipient wetness with an aqueous or non aqueous solution containing a salt (precursor) of the catalytic element or elements.

The precursor salt is dissolved in a volume of solvent equal to the catalyst pore volume, and this solution is slowly added (sometimes dropwise) to the support in which capillary forces of up to several hundred atmospheres draw the liquid into the pores. Addition of solution continues until the pores of the support are saturated as evident by the beading of the excess solvent.

For gold catalysts, $HAuCl_4$ (tetrachloroauric acid) is generally used as a source of gold which is dissolved in water. The aqueous solutions of chloroauric acid being acidic are capable of dissolving metallic oxides such as Al_2O_3, MgO, and ZnO.

The solution is dried and calcined at a specific temperature. Generally, the gold particles formed in the impregnation method are relatively large compared with those prepared by other methods.

4.2.5.2 Co-Precipitation

The Co-precipitation technique for catalyst preparation can be used when a very intimate contact is wanted between two or even three components. It involves the simultaneous precipitation of two hydroxides by addition of chloroauric acid ($HAuCl_4$) and a metal nitrate to a solution of sodium carbonate. After washing, the precipitate is dried and then calcined in air. Work done by Haruta and co-workers showed that catalyst materials made by the co-precipitation method have superior catalytic activity. That was the case for both Au/ZnO and Au/Fe_2O_3, and both catalysts manifested better catalytic activity for carbon monoxide hydrogenation when prepared by co-precipitation than by other methods [48].

4.2.5.3 Deposition-Precipitation[50]

This is a special method for the preparation of supported catalysts by adding, for instance urea to the slurry of metal salt solution and the support. The product obtained is heated to a certain temperature with decomposition of the urea to NH_3 and CO_2, and by homogeneous precipitation of metals on the surface of the support.

Deposition-precipitation thus permits the preparation of supported catalysts if precipitation from solution of active precursor is carried out in the presence of finely divided suspended support. Provided the interaction between the nuclei of the insoluble active precursor and the surface of the suspended support is strong enough, precipitation will occur exclusively at the support surface.

For a homogeneous distribution of the active precursor to be achieved within the pore system of the support, the pH and the valence state of the precursor have to be controlled and complexing agents may be added, which keep the active precursor in solution under conditions which would otherwise lead to precipitation away from the support surface.

When gold nanocatalysts are prepared in this way, the size distribution is narrow as reported by Haruta *et al*[51] and gave good results for CO oxidation not for CO hydrogenation.

4.2.6 Characterization of supported gold catalysts

A comparison of the activities of different preparation methods can be made on the basis of unit weight of catalyst or of unit weight of gold; although it should be noted that often the gold content is not determined analytically. More informative bases of comparison, for instance activity per unit area of gold or per superficial gold atom (i.e., turn-over frequency) depends on an accurate knowledge of how much gold the catalyst contains.

The estimation of particle size and surface area entirely relies on physical techniques because selective chemisorption is barely applicable to the metals of Groups 8-10. Transmission electron microscopy, when performed quantitatively, provides a particle size distribution, from which a mean size and a surface area can be derived. X-ray diffraction affords a mean size estimate from line broadening, but it only senses particles large enough to give coherent diffraction. Wide-angle x-ray scattering (WAXS) and small-angle x-ray scattering (SAXS) can also be used. Extended x-ray absorption fine structure (EXAFS) yields a mean gold-gold distance and a coordination number from which particle size can be obtained; other information such as gold-oxygen distances may also be obtained. X-ray photoelectron spectroscopy (XPS) can, in principle, identify the oxidation states of the active element and is often used for this purpose. Some other analysis techniques such as Raman spectroscopy, Atomic absorption spectroscopy can also be used for catalysts characteization.

4.3 Molecular sieves and zeolites

One of the components of the catalyst system used in this study being zeolite-Y, the following section is therefore devoted to an overview of the catalytic aspects of molecular sieves and zeolites.

4.3.1 Background

Zeolites are crystalline aluminosilicates having pores of molecular dimensions. The term molecular sieve refers to a class of crystalline materials having a range

of compositions that exhibit shape-selective adsorption and reaction properties, whereas the term zeolites refers to shape-selective materials composed only of aluminosilicates. The range of materials that make up molecular sieves includes carbon, silica, aluminosilicates, aluminophosphates, metallosilicates and metalloaluminates. In fact, the list of cations that can be incorporated into molecular sieve frameworks has been expanded to include 16 or more elements (Si, Al, Ga, Ge, Be, Li, Mg, Ti, Mn, Fe, Co, Zn, B, C, P, etc).

4.3.2 Composition and structure of zeolites [21, 52]

Zeolites or aluminosilicates have the general formula: $M_a(AlO_2)_x(SiO_2)_y.zH_2O$; the AlO_2 and SiO_2 species are the fundamental units that share oxygen ions to form tetrahedral AlO_4 and SiO_4 building blocks for the zeolites unit cell. Thus, the framework of zeolites is made up of an aluminum and silicon tetrahedral, while metal or hydrogen cations (M) occupy exchangeable cationic sites. Typical zeolites are A, X, Y, chabazite, erionite and mordenite, and a, being a valencial constant.

4.3.3 Pore structure of molecular sieves[21]

The zeolites listed in Table 4-2 are just a few of the many possible molecular sieve structures. The simplest level of classifying molecular sieve structure is in terms of pore diameter and ring size. By convention, ring size is specified by the number of T atoms or TO_4 units where T=Si, Al, P or B. Pore diameters of

aluminosilicate molecular sieves (A, erionite, pentasil, mordenite and faujasite) range from 3 to 8 Á, whereas ring sizes range from 8 Á for erionite to 12Á for Y-zeolite. The latter is the hydrating agent used in this study.

Table 4-2

Compositions and limiting pore diameters for common zeolites[21]

Type	Composition per unit cell				Aperture size (Á)
	Na	AlO_2	SiO_2	H_2O	
A	12	12	12	27	4.2
Faujasite X	86	86	106	264	8.0
Faujasite Y	56	56	136	264	8.0
Erionite	4.5	9	27	27	4.4
Mordenite	8	8	40	24	6.6
Pentasil (ZSM-5)	9	9	87	16	5.5
Pentasil (Silicate)	0	0	96	16	5.5

4.3.4 Preparation of molecular sieves

Most commercial zeolites are synthesized by crystallization at 90-180˚C, 1-10 atm and pH>10 (pH=3-6 for aluminophosphates) using reactive forms of silicon, aluminum, sodium, sodium hydroxide and an organic template[53]. Aluminophosphates sieves are also made by the conventional templating procedures, combining equimolar portions of reactive hydrated alumina, phosphoric acid and water to form a gel, to which the templating agent is added.

The reaction mixture is then maintained at 100-300˚C for periods of 2 hours to 2 weeks for the purpose of crystallizing out the molecular sieve[54].

4.3.5 Adsorption properties

Because of their high surface areas, molecular sieves can adsorb large quantities of species sufficiently small to negotiate the small pores. The quantity adsorbed is a function of the adsorbate size, aperture size, temperature and acidity. Due to the aperture or pore diameter of a molecular sieve which is of the order of molecular dimensions, molecules having diameters on the same order or larger than the pore diameter or aperture are excluded from pores or supercages. Since larger molecules are excluded, preferential adsorption and reaction are a basis for separation by exclusion or sieving, hence the term molecular sieve.

The adsorption properties of ALPOs (Aluminophosphates) differ from alumino-silicates; ALPOs are more hydrophilic and adsorb water preferentially over hydrocarbons and permanent gases. This suggests their potential use in high-volume drying of natural gas, other hydrocarbons and hydrogen[55].

4.3.6 Exchangeability

Most zeolites are synthesized in the alkali cation form (mostly Na^+) in which the positively charged cations balance the negatively charged framework system. In aluminosilicates, these cations are readily exchanged by other mono-, di- and

trivalent cations including NH_4^+, H^+, Ca^{2+}, and La^{3+}. Cations in ALPOs are not exchangeable. According to Ward [56] the rate and degree of cation exchange in zeolites depends on:

- The type of cation being exchanged, diameter and charge;
- The nature of size, strength of cation, coordination complex;
- Ion exchange temperature;
- Thermal treatment of the zeolites before or after exchange;
- The structural properties of the zeolites and its Si:Al ratio;
- The locations of cations in the zeolites;
- The concentration of the cation exchange solution;
- Any previous treatment of the zeolites

4.3.7 Aluminum content and acidity

Acidity in zeolites increases with decreasing Si:Al ratio since acid sites are associated with Al ions; acidity is also a function of the cation. H-sieves are strong acids but often too unstable for commercial use. The Brønsted and Lewis acidities of zeolites play important roles in their abilities to catalyze various hydrocarbon reactions, e.g., cracking and isomerization. Gates[57] explained that zeolites are grouped into families on the basis of composition, namely, the Si/Al ratio (Table 4-3). Since the ion exchange capacity is equal to the concentration of Al^{3+} ions in the zeolites, the structures with low Si/Al ratios can have higher concentrations of catalytic sites than the others. The zeolites with high concentrations of H^+ are hydrophilic, having strong affinities for polar molecules

small enough to enter the pores. The zeolites with low H^+ concentrations are hydrophobic, taking up organic compounds ratio near 10.

Table 4-3: Acid form zeolites classified by their Si/Al ratios[57]

Si/Al atomic ratio	Zeolites	Properties
Low (1-1.5)	A, X	Relatively low stability of framework; high stability in base; high concentration of acid groups with moderate acid strength
Intermediate (2-5)	Erionite, Chabazite, Clinoptilolite, Mordenite,	Relatively high stability of framework; high stability in acid; low stability in base; low concentration of acid groups with acid strength
High (~10 to ∞)	ZSM-5, Erionite, Mordenite, Y	

4.3.8 Thermal stability

The thermal stability of zeolites increases with increasing silica content and by exchange with rare earth cations**.** Most sieves are unchanged by dehydrating to

400˚C; high silica (ultra-stable forms prepared by steam pretreatment) and are earth-exchanged sieves are stable to 700-800˚C. Generally, extensive dehydration causes loss of Brønsted acidity due to the removal of OH or silanol surface groups. Gates[57] argued that the stability of the crystal framework also increases with increasing Si/Al ratios; decomposition temperatures of the different zeolites range from roughly 700 to 1300˚C. Zeolites with high Si/Al ratios are stable in the presence of concentrated acids, but those with low Si/Al ratios are not; the trend is reversed for basic solutions.

Thermal treatment of zeolites in the presence of water normally leads to dealumination. In fact, it is one of the recommended methods for preparing ultra-stable zeolites. Moderate dealumination generally increases catalytic activity or leaves it unchanged, whereas advanced dealumination leads to a decrease in activity due to a loss of active sites and ultimately collapse of zeolites structure.

4.3.9 Shape selectivity

Shape selectivity is a consequence of geometric restrictions on:

(1) access of reactants to the zeolites framework,
(2) diffusion of reactants in or products out,
(3) formation of transition states.

These geometric restrictions result in at least four kinds of shape selectivity: reactant selectivity, product selectivity, restricted transition state selectivity, and molecular traffic control.

4.3.10 Catalytic reactions and processes

As a result of their degree of acidity, zeolites find applications in cracking, isomerization, alkylation and aromatization reactions. Medium pore zeolites (pentasils) are finding wide application because of their ability to selectively perform these reactions, such as conversion of light hydrocarbons to mono-cyclic aromatics, while minimizing coke formation. Zeolites are also used in conversion of Methanol to Gasoline (MTG) or to other hydrocarbons like alkenes and ethers.

4.4 Conclusion

The literature survey conducted on catalysis showed that gold at nano-scale level has likely the potentiality to be used as catalysts for the synthesis of methanol and dimethyl ether. Because of its dehydrating properties, zeolite will be physically mixed with nano-gold precursor to make the catalysts that will be used in the experimental programme of this study.

4.5 References

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CHAPTER 5

STUDY OF CARBON MONOXIDE HYDROGENATION OVER SUPPORTED Au CATALYSTS

The first part of this experimental programme is the report of the paper that we submitted at the American Chemical Society, Division of Petroleum Chemistry in 2005. It was published *by the American Chemical Society, Division of Petroleum Chemistry*, 50(2), pp. 206-207, 2005, under the title given above with the following persons as co-authors and their respective organizations.

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Abstract

Recently, there has been a marked increase in the interest shown in catalysis by gold. It is now recognized that gold has unique properties as a catalyst for many reactions with pre-eminence in the oxidation of carbon monoxide. However, it is also known that supported gold catalysts can be used for other reactions involving carbon monoxide, for example the water gas shift reaction. Supported gold catalysts have also been shown to be effective for hydrogenation reactions. This paper reports the possible use of gold as a catalyst for the hydrogenation of carbon monoxide. In particular, it describes the preparation and characterization of Au/ZnO and Au/Fe_2O_3 as catalysts for CO hydrogenation and for the synthesis of alcohols in particular. Alcohols including methanol, ethanol, 1-propanol, 2-propanol and 1-butanol have been successfully synthesized at 300°C (573K) at a pressure of 25 atm over supported Au catalysts.

5.1 Introduction

Presently there is a great deal of interest in the use of gold as both heterogeneous and homogeneous catalysts. For many years gold was perceived as a relatively inert catalyst material; however the discovery in the 1980s that finely supported divided nanoparticles of gold could act as catalysts for reactions at low temperatures has stimulated considerable research effort on gold catalysts. Bond and co-workers [1] were amongst the first to demonstrate that very small gold particles supported on silica could give interesting catalytic performance for hydrogenation of butadiene. Subsequently, Hutchings *et al*. showed that Au/ZnO could be used for selective hydrogenation of α,β-

unsaturated aldehydes[2]. Haruta and co-workers discovered that supported Au catalysts are very active for low temperature CO oxidation [3]. In addition, there have been extensive studies on the oxidation of carbon monoxide which have been reviewed [4, 5]. Haruta and co-workers [6] have reported that gold supported on ZnO and Fe_2O_3 could be used as a catalyst for carbon monoxide hydrogenation, and a small amount of methanol was observed.

This paper extends this earlier study and explores the preparation and characterization of Au/ZnO and Au/Fe_2O_3 as catalysts for the hydrogenation of carbon monoxide, particularly for the synthesis of alcohols. Mixed alcohols are widely used as fuel additives in the petroleum industry. The introduction of mixed alcohols into the fuels decreases the unwanted CO, NO_x and hydrocarbon emissions. It is for this reason that this work intends to explore supported Au catalysts, which could function as CO hydrogenation catalysts and initial results are reported.

5.2 Experimental

5.2.1 Catalyst preparation

5wt%Au/ZnO catalysts used in this study were prepared by co-precipitation from $HAuCl_4 \cdot 3H_2O$ (Johnson-Matthey) and $Zn(NO_3)_2 \cdot 6H_2O$ (ACROS). An aqueous mixture of the precursors ($HAuCl_4$ 0.002M and Zn $(NO_3)_2 \cdot 6H_2O$, 0.1M) was introduced at the rate of 7.5 ml/min into an aqueous solution of 1M Na_2CO_3 (pH 9-11.5) under vigorous stirring (~600 rpm) for 90-120 min. The precipitation temperature was maintained at 70-80ºC. The co-precipitated sample obtained

was aged for about 24 h, filtered, washed several times with warm distilled water, and then dried. The powder obtained was calcined at 400ºC in air. ZnO catalyst was prepared in a similar way without adding the gold source.

5wt%Au/Fe_2O_3 catalyst was used as obtained, as a standard catalyst provided by the World Gold Council [7]. Fe_2O_3 catalyst was prepared by a precipitation method. An aqueous solution of iron nitrate (0.25M $Fe(NO_3)_3 \cdot 9H_2O$) was heated at 80 °C. Afterwards, a Na_2CO_3 solution (0.25M) was added dropwise to the nitrate solution until a pH value of 8.2 was reached. The precipitate was washed with distilled water and then dried. The dried brown colour catalyst was calcined in air at 400 °C for 6 h.

For the Au/ZrO_2 catalyst, $ZrO(NO_3)_2$ (35ml, 0.1M) solution was added dropwise to $HAuCl_4 \cdot 3H_2O$ (10ml, 0.025M) followed by the ammonia 4.98N (d:0.88) solution. The co-precipitate was filtered, washed with warm water, dried at 80 ºC and calcined at 300 ºC for 6h. The Au/SiO_2 catalyst was prepared by mixing gold solution ($HAuCl_4 \cdot 3H_2O$ 0.025M) with a silica suspension made by stirring SiO_2 powder (2.18g) in distilled water (100ml). The resulting solution was evaporated. The precursor obtained was calcined at 300 ºC under ammonia vapor for 6h.

5.2.2 Catalyst characterization

Catalysts were characterized by powder X-ray diffraction using an Enraf Nonius PSD120 diffractometer with a monochromatic $Cu_{K\alpha-1}$ source operated at 40 keV and 30 mA. Phases were identified by matching experimental patterns to the JCPDS powder diffraction file. BET surface areas were determined from the

nitrogen adsorption isotherm, using Micromeritics Gemini equipment. Raman spectroscopy characterization was undertaken using a Renishaw Ramanscope.

5.2.3 Catalyst testing procedure

The catalysts used in this study were evaluated in a stainless steel tubular reactor (0.25 in external diameter), which is shown in the set-up of Figure 5-1. The catalyst (ca. 0.2 gram) of catalyst was pre-treated with 1% H_2/N_2 (flow rate 10 ml/min) for 1 h at 250°C under atmospheric pressure. Then syngas ($CO/H_2/N_2$=47.5/47.5/5, BOC UK) was introduced in the reactor and the pressure was increased to 25 atm by using a back-pressure regulator (TESCOM 26-1700). The temperature of reactor (300°C) was adjusted and maintained with a Cole Parmer controller. The gas phase products were analyzed using an online gas chromatograph (Varian GC 3800). Concentrations of carbon monoxide, carbon dioxide and nitrogen were analyzed by a thermal conductivity detector and the other organic compounds such as hydrocarbons and oxygenates were determined by a flame ionization detector. Conversion was determined using nitrogen as internal standard. The liquid products were collected using a trap that was kept at room temperature and under catalytic test pressure. The liquid products were identified by GC-MS (Perkin Elmer, TurboMass). Oxygenates were quantified by a second gas chromatograph (Chrompack) equipped with capillary column (CP-Sil 8CB 30m, 0.32mm, 1μm) and FID detector.

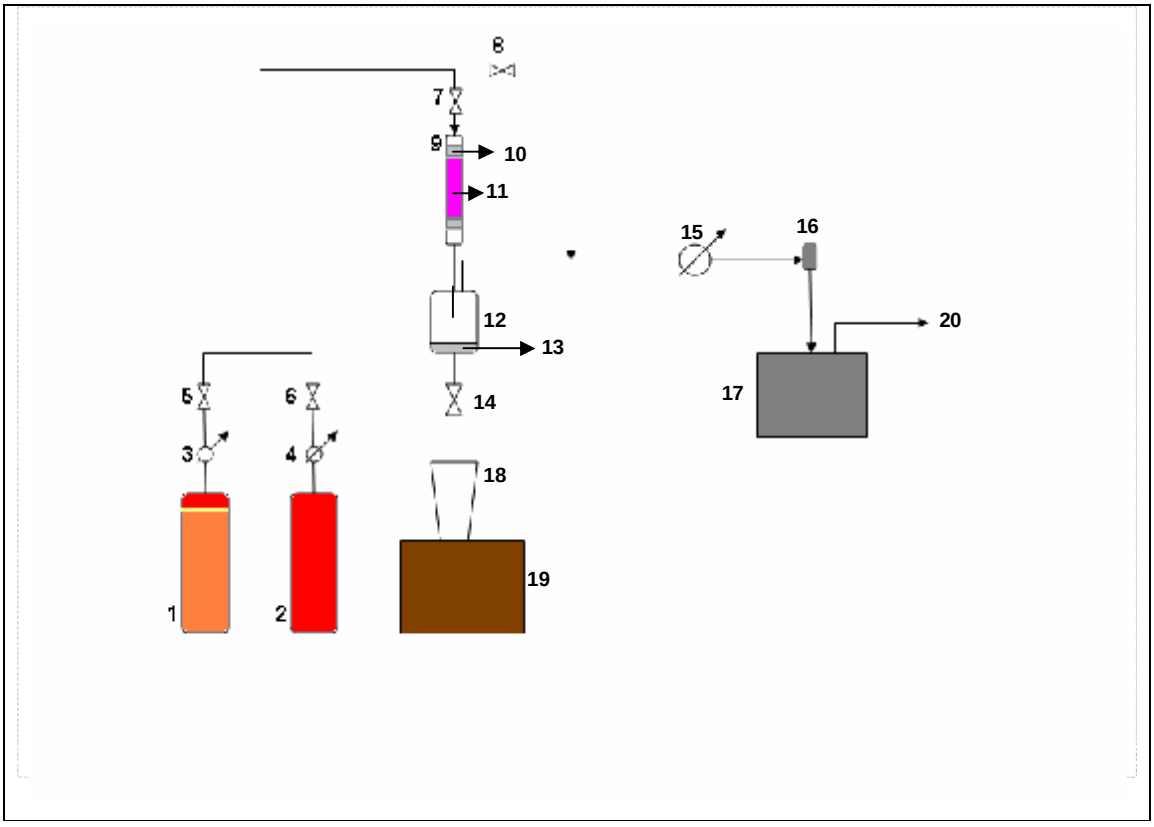

Figure 5-1: Set-up of the rig used for gold-based catalysts testing

Each number corresponds to a particular equipment of the rig as described below.

1: Syngas (mixture CO/H_2) cylinder; 2: Hydrogen (H_2) cylinder; 3: Pressure regulator for the syngas cylinder; 4: Pressure regulator for the hydrogen cylinder; 5, 6, 7, 8, 14: Shut off valves; 9: Stainless steel tubular reactor (PFR); 10: quartz wool; 11: catalytic bed; 12: Liquid trap; 13: condensed liquid; 15: Back pressure regulator; 16: GC sampling valve; 17: GC (TCD and FID); 18: Liquid collector; 19: Platform; 20: Gas venting.

5.3 Results and discussion

5.3.1 Characterization of the catalysts

The XRD pattern of the 5%Au/ZnO and 5%Au/Fe_2O_3 catalyst present only the diffraction lines characteristic to the support ZnO and Fe_2O_3 respectively (Figure 5-2). The amount of Au on the sample should be sufficient to provide an X-ray diffraction pattern of crystalline Au particles if they had been sufficiently large. The observed X-ray pattern may suggest that the Au particles are very small in the investigated catalysts.

The laser Raman spectra of the ZnO support and 5%Au-ZnO catalyst are presented in Figure 5-3. Unfortunately, significant fluorescence is observed for the ZnO support.

For the Au/ZnO sample, the fluorescence is decreased and new bands at 3224 and 3472 cm^{-1} were observed and these are assigned to hydroxyl groups, which, since they are absent in the ZnO support may be associated with the interface between the ZnO and the Au nanocrystals.

The measured BET surface areas are 35 m^2/g and 41 m^2/g for Fe_2O_3 and 5%Au/Fe_2O_3 catalysts respectively.

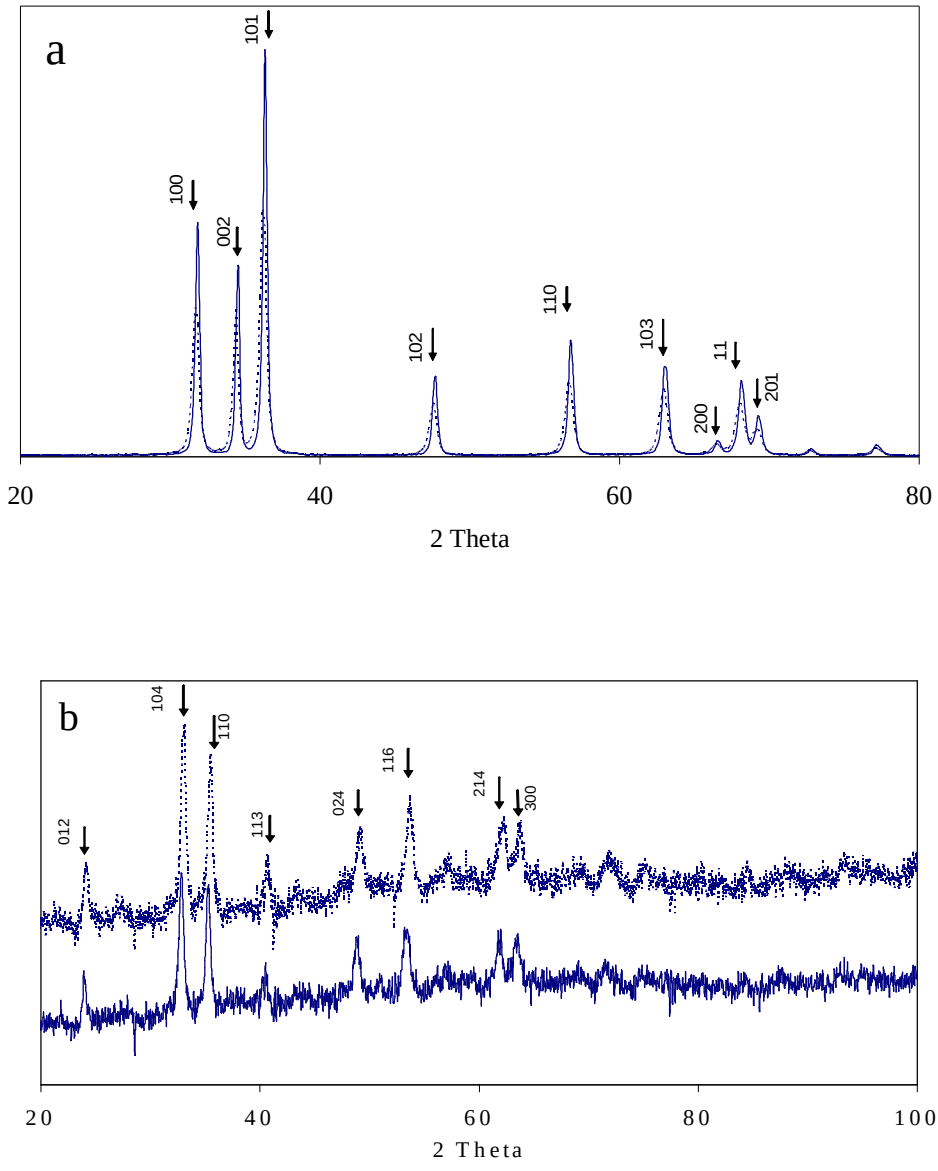

Figure 5-2: XRD diagram of a: 5%Au/ZnO catalyst (–) and ZnO support (-) b: 5%Au/Fe_2O_3 catalyst (–) and Fe_2O_3 support (- -)

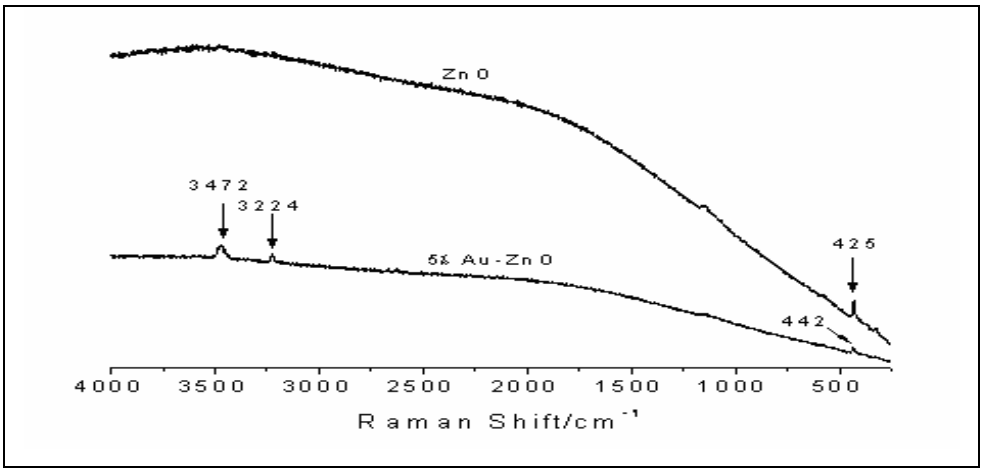

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Figure 5-3: Raman spectra of ZnO and 5%Au-ZnO catalysts

5.3.2 CO hydrogenation

5.3.2.1 Hydrogenation over Au/Fe_2O3

Two sets of experiments of CO hydrogenation were carried out to examine the effect of Au on the Fischer-Tropsch synthesis with Fe_2O_3 as support material. Figure 5-4 shows the online analysis data when Fe_2O_3 was used alone and when Au was supported on Fe_2O_3, i.e. these data are for the gas phase products only. Several features of the results for Au/Fe_2O_3 are noteworthy when compared with those obtained with use of Fe_2O_3 alone. First, for Au/Fe_2O_3 the conversion increases slightly in the first 10 h and then decreases rapidly until after 30 h when it reaches a steady state with a conversion of ca. 55%. This is significantly different from the catalytic behavior of Fe_2O_3. In the catalytic test for Fe_2O_3, a smooth but small increase in conversion was observed over the first 15 h and

then the reaction reached a steady state for the rest of the running time, giving a conversion of ca. 80%.

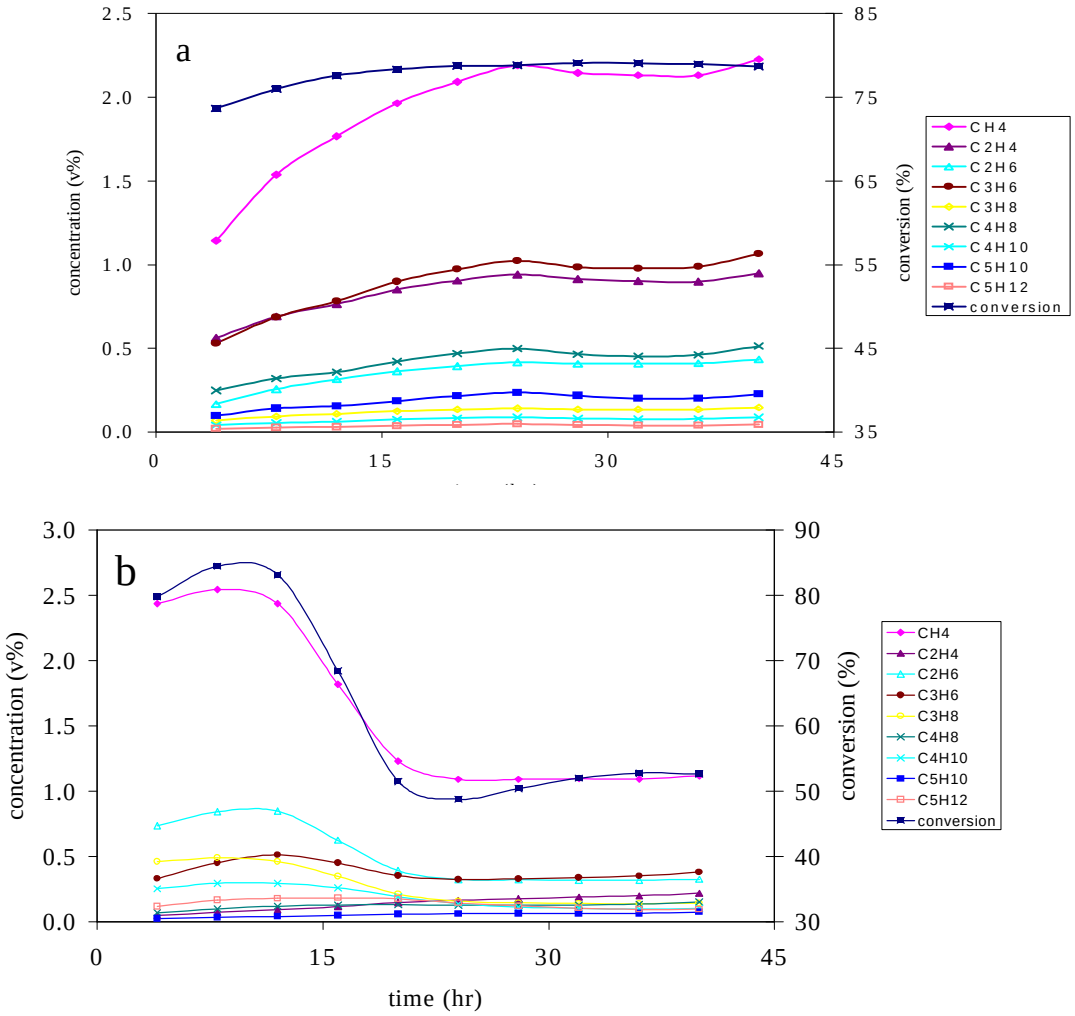

Figure 5-4: Hydrocabons produced over (a) 5%Fe_2O_3 and (b) 5%Au/Fe_2O_3 by operating the reactor at 300 °C (573K) and 25 atm

Second, the concentration of alkanes for bulk Au/Fe_2O_3 and Fe_2O_3 follows quite similar trends as the conversion. However, a different pattern was observed for alkene generation for Au/Fe_2O_3 which increased with time on stream. These results may indicate that for the Au/ Fe_2O_3 catalysts, the conversion and alkane synthesis rates are correlated. A detailed analysis data of the collected liquid is shown in Table 5-1. For the above two set experiments, both hydrocarbons and alcohols were synthesized. Two phases are collected in the trap, one (Phase I) being water rich. The decline in activity for Au/Fe_2O_3 could be related to addition effect of nano-gold particles on Fe_2O_3, which by interacting (after 15 hours) with iron oxide hinder the easy formation of light hydrocarbons (Fig. 5-4), whereas they contribute to keep the rate of formation of high hydrocarbons and alcohols almost at the same level (Table 5-1) as when iron oxide is tested alone.

From a detailed analysis of the products and the contributing reactions, total mass balances and carbon mass balances were assessed. Mass balances could be closed to within better than 5% which given the complexity of the product distribution is deemed sufficient for present purposes.

Table 5-1

Liquid phase analysis of catalyst (a) Fe_2O_3 (b) 5%Au/Fe_2O_3 by operating the reactor at 300°C (573K) and 25 atm

Phase I (wt%)	Fe_2O_3	5%$AuFe_2O_3$	Phase II (wt%)	Fe_2O_3	5%$AuFe_2O_3$
Methanol	0.34	0.74	C_5	1.56	2.6
Ethanol	3.9	1.5	C_6	2.09	6.5
2-Propanol	0.08	trace	C_7	9.6	8.8
1-Propanol	0.58	0.41	C_8	10.2	9.3
1-Butanol	0.18	0.16	C_9	9.44	8.5
Water	20.3	17.2	C_{10}	7.7	6.7
			$>C_{10}$	34.1	37.6

It was noticed that the addition of Au to the Fe_2O_3 catalyst did not give a distinct effect on the liquid product distribution. The percentage of alcohol produced is slightly lower for 5% Au/Fe_2O_3 than that for Fe_2O_3 alone system, and vice versa for hydrocarbons. A total distribution for the products combining liquid and gas phase products is shown in Table 5-2.

Table 5-2

Total products analysis of catalyst (a) Fe_2O_3 (b) 5%Au/Fe_2O_3 by operating the reactor at 300°C (573K) and 25 atm

Hydrocarbons (wt %)	Fe_2O_3	5%AuFe_2O_3	Alcohols (wt %)	Fe_2O_3	5%AuFe_2O_3
CO_2	73.2	73.5	Methanol	0.06	0.13
CH_4	2.0	2.0	Ethanol	0.7	0.3
C_2-C_5	8.0	6.9	2-Propanol	0.01	Trace
C_6-C	6.7	7.2	1-Propanol	0.1	0.07
>C_{10}	5.8	6.8	1-Butanol	0.03	0.03
			water	3.5	3.12

5.3.2.2 Hydrogenation over Au/ZnO catalyst

Two sets of gas-phase on-line data for the catalytic reaction of CO hydrogenation over ZnO and Au/ZnO are shown in Figure 5-5(a) and (b) respectively. An average conversion of ca. 20% was achieved with only ZnO powder as the catalyst in Figure 5-5(a), which is much higher than the ca. 6% conversion observed with 5%Au/ZnO as the catalyst. Meanwhile, the percentage

of hydrocarbons decreased from ca. 0.36% to ca. 0.26% for methane and from a maximum of *ca*. 0.17% to a maximum of *ca*. 0.07% for other hydrocarbons. The decreased conversion could be partially attributed to the decreased production of hydrocarbons.

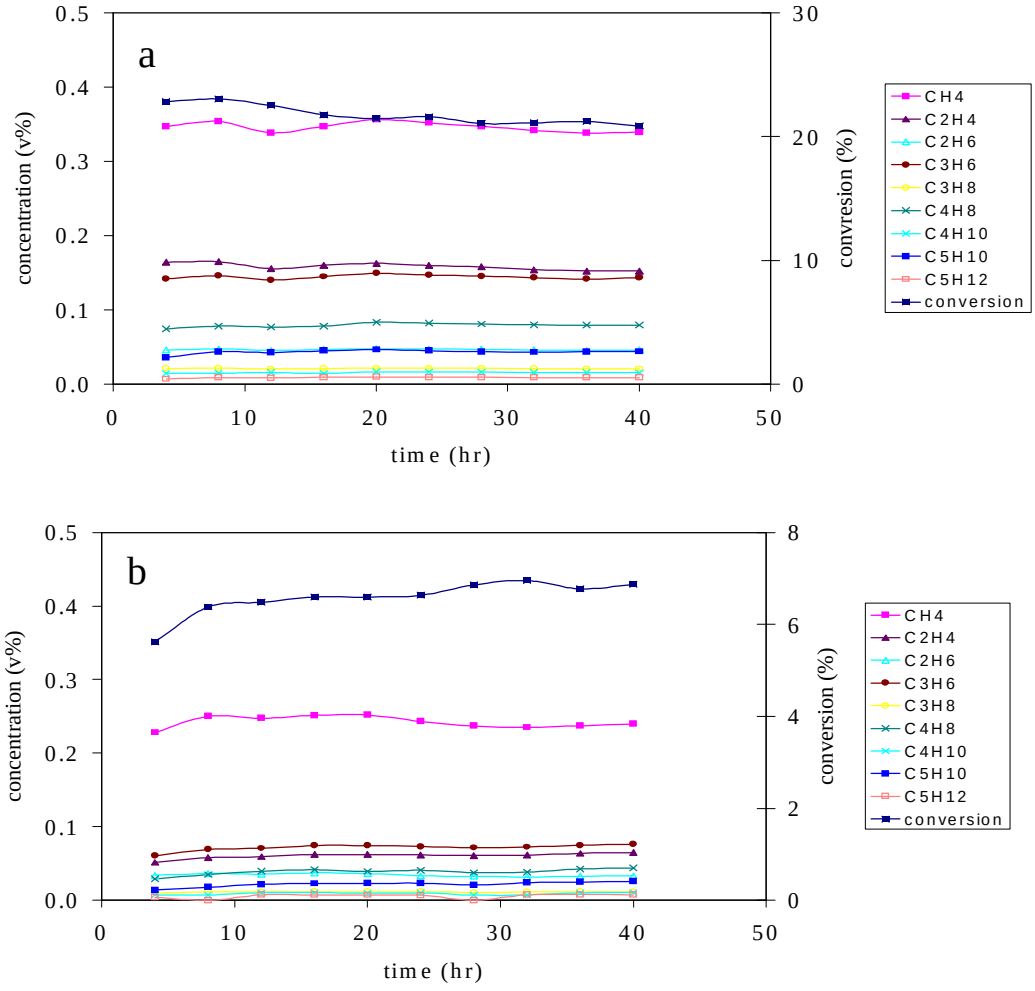

Figure 5-5: Gas phase online data of catalyst (a) ZnO (b) 5%Au/ZnO by operating the reactor at 300 °C and 25 atm

Table 5-3 presents the liquid phase results in the CO hydrogenation over ZnO and 5%Au-ZnO. Small quantities of liquid products were collected for both cases. For ZnO, the products include mixed alcohols, C_5 to C_{23} hydrocarbons and wax. The 5%Au/ZnO produces the mixed alcohol products only. The calculation of alcohol and hydrocarbon phases was carried out separately for the purpose of a direct comparison. The observed results suggest that the presence of Au suppresses the activity of the catalyst for the production of hydrocarbons, and also it shifts the selectivity towards higher alcohols.

Table 5-3

Liquid phase analysis of catalyst (a) ZnO (b) 5%Au/ZnO by operating the reactor at 300 °C (573K) and 25 atm

Phase I (wt %)	ZnO	5%AuZnO	Phase II (wt %)	ZnO	5%AuZnO
Methanol	75.8	62.9	C_5	7.4	0
Ethanol	17.9	26.2	C_6	0.5	0
2-Propanol	1.13	0.7	C_7	2.9	0
1-Propanol	3.8	7.5	C_8	7.4	0
1-Butanol	1.3	2.7	C_9	7.7	0
			C_{10}	51.7	0
			$>C_{10}$	34.1	0

Again, total mass and carbon balances could be closed to within better than 5%. It is known that ZnO alone is a methanol synthesis catalyst [8, 9, 10], however, the impurities (for example, alkaline residues) introduced to the catalyst during the preparation accelerate side reactions including higher alcohol synthesis and hydrocarbon synthesis [9]. In this paper, the support and the gold catalysts were prepared in a similar way, which enables us to investigate the function of gold over the supported catalysts. The results above show that the catalytic behavior is improved with the addition of Au to the catalyst, since the Au/ZnO selectivity produces alcohols as products and there is a distinct increase in the selectivity for higher alcohols for Au/ZnO when compared with ZnO alone.

5.3.2.3 Gold over other supported catalysts

Au/SiO_2 catalyst was also tested but no observable conversion or products were found. The CO hydrogenation over Au/ZrO_2 produced CH_4, C_2H_6 and C_3H_8 in our current system. It was reported by Baiker[11] in 1993 that methanol was synthesized over Au/ZrO_2 from hydrogenation of CO and CO_2, but our initial results show some differences in this respect.

5.4 Conclusions

Supported gold catalysts were studied in detail for CO hydrogenation to investigate the possibility of using gold as a higher alcohol synthesis catalyst.

The initial results, particularly for the Au/ZnO catalyst, are interesting and suggest that Au could play a role in the synthesis of mixed alcohols:
[i] by suppressing the side-reactions leading to hydrocarbon synthesis and [ii] shifting the product selectivity towards higher alcohols.

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CHAPTER 6

LOW-PRESSURE METHANOL/DIMETHYL ETHER SYNTHESIS FROM SYNGAS OVER GOLD-BASED CATALYSTS

This second part of the experimental programme is the paper submitted in the Gold Bulletin. The paper was published (Gold Bulletin, 40-3, 219-224, 2007) under the title given above with the following persons as co-authors with their respective academic institutions.

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Abstract

The hydrogenation of carbon monoxide over Au/ZnO catalysts has been re-examined and new data is presented on the way in which the product distribution can be manipulated by choice of co-added solids such as alumina or zeolite-Y.

This comparative study reveals that while ZnO itself leads to a high selectivity to methanol, the incorporation of gold drastically alters the product spectrum and leads to a very high selectivity to hydrocarbons. The hydrocarbon selectivity at a reaction temperature of 400˚C (673K) is in fact much higher than the case where alumina or zeolite-Y is introduced into a composite catalyst comprising the Au/ZnO and the acidic solid. In the latter case dimethyl ether is a major product. Significant light hydrocarbon formation on gold-based systems under these circumstances appears not to have been discussed before. The reactions taking place on these catalysts, the selectivities and absolute activities are discussed and significant role of gold highlighted.

6.1 Introduction

The current technology used for methanol synthesis requires high pressure (>120 atm) to reach an acceptable CO conversion. However, the transformation of methanol into DME (dimethyl ether) can be used to relieve the thermodynamic constraints for high operating pressure. If the methanol and DME synthesis take place in the same reactor at the same conditions, one should in principle be able to use a much lower operating pressure, making a potentially cheaper large scale process to produce methanol and DME which are becoming the preferred alternative clean fuels for diesel engines [1, 2].

The catalysts that are needed for this co-production have to be stable, selective and actively able to catalyse the main reactions (methanol and DME synthesis) involved in this process at the same temperature. Unfortunately existing commercial copper-based methanol catalysts are not able to function efficiently

in the presence of large concentrations of water or at high temperature [3]. PGM (Platinum Group Metals)-based catalysts usually suffer from the methanol selectivity that decreases when the operating temperature increases. Moreover, the PGM materials are relatively expensive and their market prices are relatively unstable [4, 5]. Therefore, it is of interest to develop a more satisfactory and competitive catalyst for methanol/dimethyl ether synthesis.

Catalytic studies done on metallic gold have shown that supported gold nano-particles can be used as catalyst for the hydrogenation of carbon oxides [6, 7]. Accordingly, this study investigates the possibility of using bifunctional based gold catalysts for the methanol and dimethyl co-production at low pressure.

6.2 Experimental

6.2.1. Catalyst preparation

The catalysts used in this study were: ZnO, 5%Au/ZnO, 5%Au/ZnO/γ-Al_2O_3 and 5%Au/ZnO/LZ-Y52 that were prepared as follows:

The 5%Au/ZnO samples were synthesised by co-precipitation method using dilute solutions of $HAuCl_4.xH_2O$ (Next Chimica) and $Zn(NO_3)_2.6H_2O$ (Aldrich) and concentrate solution of Na_2CO_3. An aqueous solution mixture of tetrachloro auric acid and zinc nitrate was introduced dropwise into the carbonate solution under vigorous stirring for 90-120 min. The precipitation temperature was maintained at 70-80ºC. The co-precipitated sample was aged for 24 h, filtered, washed several times with warm distilled water, and then dried in the oven. The powder obtained was calcined at 400ºC in air. ZnO catalyst was prepared in a similar way, but without adding the gold source. 5%Au/ZnO/γ-Al_2O_3 catalyst was made from a

physical mixture 1:1 (mass) of 5%Au/ZnO with gamma-alumina and 5%Au/ZnO/LZ-Y52 catalyst from the physical mixture 1:1 (mass) of 5%Au/ZnO with Y-zeolite.

6.2.2 Catalyst characterization

After preparation, catalysts were characterised by powder X-ray diffraction using an Enraf Nonius PSD120 diffractometer with a monochromatic $CuK_{\alpha 1}$ source operated at 40 keV and 30 mA. Phases were identified by matching experimental patterns to the JCPDS powder diffraction standard. The surface areas were determined by BET from the nitrogen adsorption isotherm, using Micrometrics Gemini equipment. Raman spectroscopy characterisation was made using a Renishaw Ramanscope spectrometer. The particle sizes were determined using the transmission electron microscope. ICP-AES was used to quantify impurities in catalyst samples.

6.2.3 Catalyst testing procedure

The catalysts used in this study were tested in a stainless steel tubular reactor with an external diameter of ¼ inch. For ZnO and 5%Au/ZnO, only 0.3 g was used, whereas 0.6g was considered in the case of 5%Au/ZnO/γ-Al_2O_3 and 5%Au/ZnO/LZ-Y52 in the ratio 1:1 (mass). The catalyst was pre-treated with pure hydrogen under atmospheric pressure at 250ºC for 2 h with a gas flow rate of 10 mL/min. After reduction, the gas was changed for syngas (H2/CO/Ar=60/30/10, Afrox) and the reactions conditions (10 mL/min, 300-

400ºC, 25 atm) were adjusted. In the operating conditions of this work the steady state was achieved after 4 hours of reaction. A gas chromatograph connected in line (Varian GC 4290), equipped with both a flame ionisation detector (FID) and a thermal conductivity detector (TCD) was used to analyze respectively hydrocarbon products and inorganic (carbon monoxide, carbon dioxide and nitrogen) products.

6.3 Results and discussion

6.3.1 Catalysts characterization

As shows Figure 6-1, the XRD pattern presents only the diffraction lines of the support ZnO. The gold particles are too small to give rise to well-defined lines.

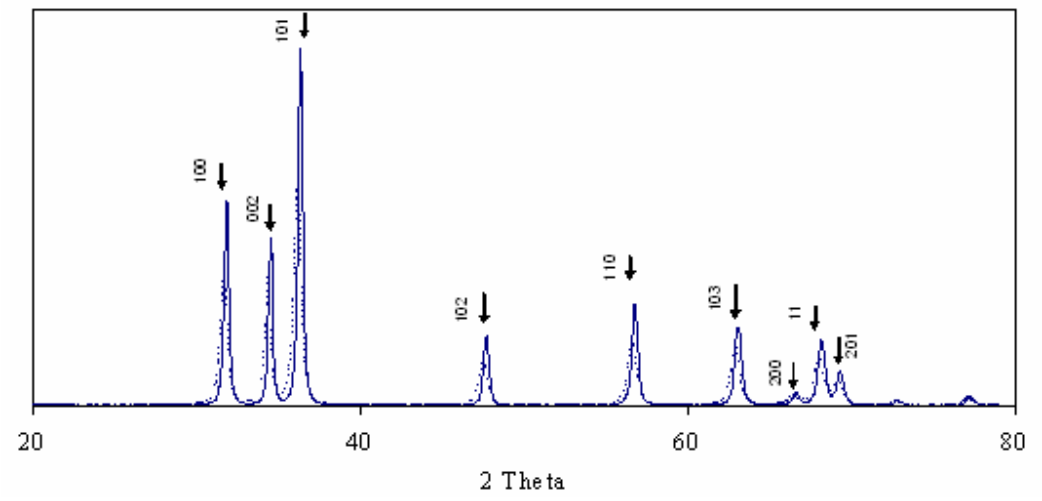

Figure 6-1: XRD diagram of 5%Au/ZnO catalyst and ZnO support

Raman spectroscopy analysis was associated and revealed new bands observed at 3230 and 3483 cm^{-1} for 5%Au/ZnO due to hydroxyl groups associated at the interface nanogold and ZnO (Figure 6-2).

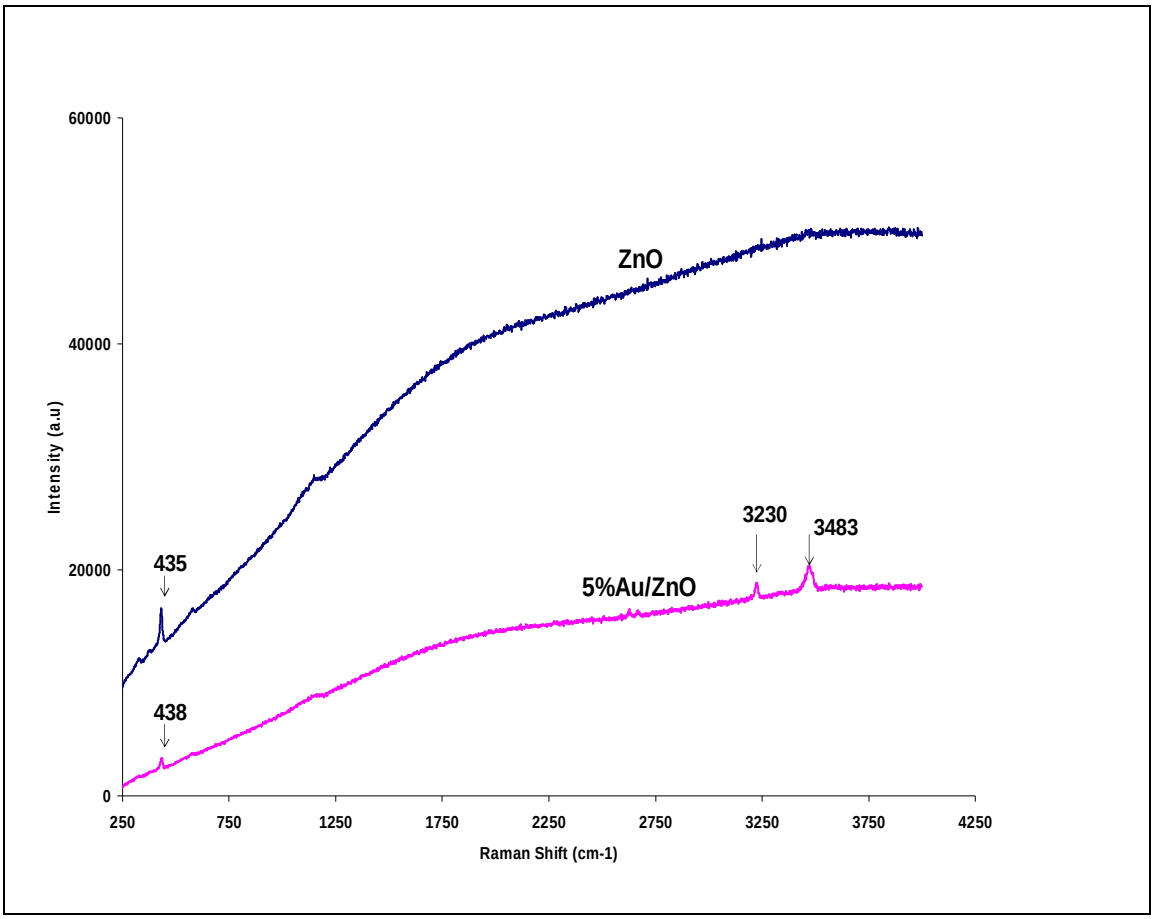

Figure 6-2: Raman spectra of ZnO and 5%Au-ZnO catalysts

For the size of gold particles transmission electron microscopy was used and a closer look on the micrograph from TEM (Figure 6-3) gave an average Au particle size of 6nm.

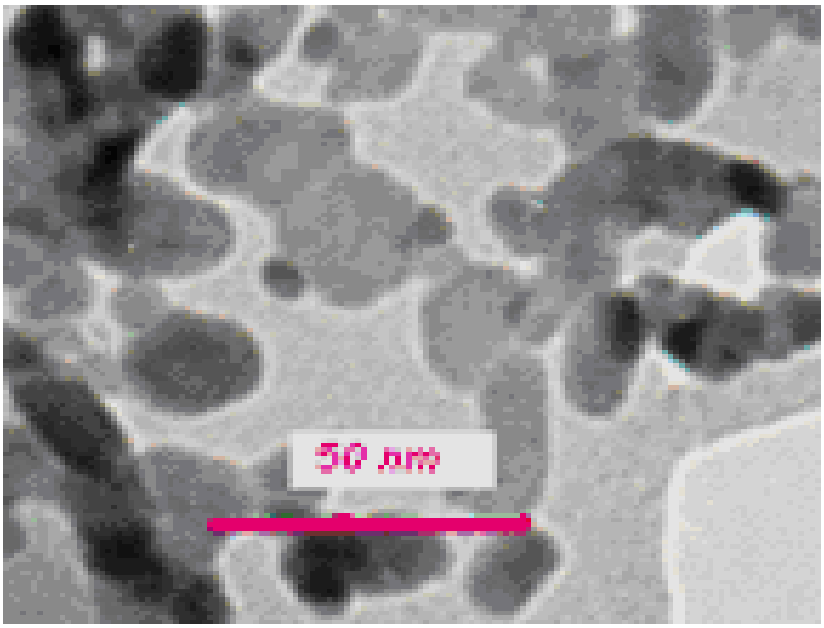

Figure 6-3: TEM micrograph of 5%Au/ZnO

The specific surface area of 5%Au/ZnO sample as determined from BET was 49 m^2/g and the ICPAES analysis done on both ZnO and 5%Au/ZnO catalysts showed that they contained 0.006, 0.00 and 0.022 ppm of nickel, iron and cobalt respectively.

6.3.2 CO hydrogenation

Amongst all hydrocarbon products, methanol was formed with high selectivity (Table 6-1) accompanied with some traces of FT products when ZnO was tested at 300˚C (573K) and 25 atm.

Table 6-1

Hydrocarbon products distribution (mole%) over gold-based catalysts tested at 300˚C (573K) and 25 atm

Product	Catalyst				Blank reactor
	ZnO	5%Au/ZnO	5%Au/ZnO/γ- Al_2O_3	5%Au/ZnO/LZ-Y52	
CH_4	3.0	50.9	31.4	23.6	nd
C_2H_4	0.6	2.2	2.3	26.4	nd
C_2H_6	0.2	6.9	8.5	8.6	nd
C_3H_6	0.5	6.6	2.3	17.1	nd
C_3H_8	nd	3.2	2.9	nd	nd
CH_3OCH_3	**nd**	**nd**	**48.2**	**26.9**	nd
CH_3OH	**95.0**	**3.0**	**nd**	**0**	nd
C_2H_5OH	nd	nd	nd	21.7	nd
C_4H_8	0.3	3.4	0.7	8.9	nd
C_4H_{10}	0.4	5.9	2.2	nd	nd
C_5H_{10}	nd	2.4	1.0	nd	nd
C_5H_{12}	nd	4.1	0.4	nd	nd
C_6	nd	4.8	nd	nd	nd
C_7	nd	3.8	nd	nd	nd
C_8	nd	2.6	nd	nd	nd

nd = not detected

The specific rate of formation of methanol (on ZnO) was 129 $\mu mol\ g_{cat}^{-1}h^{-1}$ and the total CO conversion was 1.2% *(the assessment of the CO conversion was done as detailed in Appendix D).* The production of hydrocarbons was remarkably higher in the case of the gold-containing catalyst and may reflect a tendency for Fischer-Tropsch activity to develop in the gold-based catalyst. An alternative source of hydrocarbons is the methanol and/or DME. The typical transformation of methanol into hydrocarbons is well known [8-10], and though this process is normally associated with the action of acid catalysts [8-10], other mechanisms have been proposed to account for hydrocarbon formation over composite catalysts comprising a methanol synthesis component and a zeolitic structure[11-14]. Significant acidity would not be expected to be exhibited by Au/ZnO and so further work is required in order to establish how the hydrocarbons are produced. (Blank runs with an empty reactor confirmed that no conversion of the synthesis gas took place under our reaction conditions). The formation of hydrocarbons in the presence of gold on zinc oxide is consistent with other work recently reported on gold-containing Fe/zinc oxide catalysts [15].

It can also be meanwhile noted that the hydrocarbon distributions obtained by us in this work differs somewhat from those reported for Cu-Zn/zeolite hybrid catalysts such as those recently described by Asami et al [11] in that the latter observe high selectivities to C_3 and C_4 hydrocarbons, with relatively little methane, C_2 or C_5 products. The specific net rate of formation of methanol; on Au/ZnO was 9.8 $\mu mol\ g_{cat}^{-1}h^{-1}$ and that of methane was 172.2 $\mu mol\ g_{cat}^{-1}h^{-1}$ with a CO conversion level of 3.0%. The reduction (by a factor of 13) in the observed rate of formation of methanol in the presence of gold suggests that methanol producing sites are eliminated by gold or that methanol transformation to hydrocarbons is accelerated by this metal, resulting in a lower net production of

the alcohol. Although methanol decomposition on gold surfaces has not yet been extensively described, there is clear evidence that decomposition to methane and carbon dioxide is not unexpected[15]. The incorporation of γ-alumina that acts as dehydrating agent did not greatly affect the relative distribution of hydrocarbon products, but the new product, dimethylether was formed and associated with an increase in CO conversion as shown in Figure 6-4. The observed CO conversion level was now 5.0%. This, results from the dehydration (reaction (2)) of methanol formed from reaction (1) in parallel with the water-gas shift reaction that takes place. These reactions lead to the direct synthesis of DME from syngas (reaction (4)) with a significant co-production of hydrocarbons. The relatively slight changes seen in the hydrocarbon distribution are in line with the expected catalytic action of alumina, acting largely as an acid catalyst, with slight decreases in propene and butene suggestive of some degree of further conversion of these alkenes, probably by oligomerization.

$$2CO + 4H_2 \leftrightarrow 2CH_3OH \quad (1)$$
(methanol formation)

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad (2)$$
(Methanol dehydration & DME formation)

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (3)$$
(Water gas shift reaction)

Overall reaction:

$$3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2 \quad (4)$$

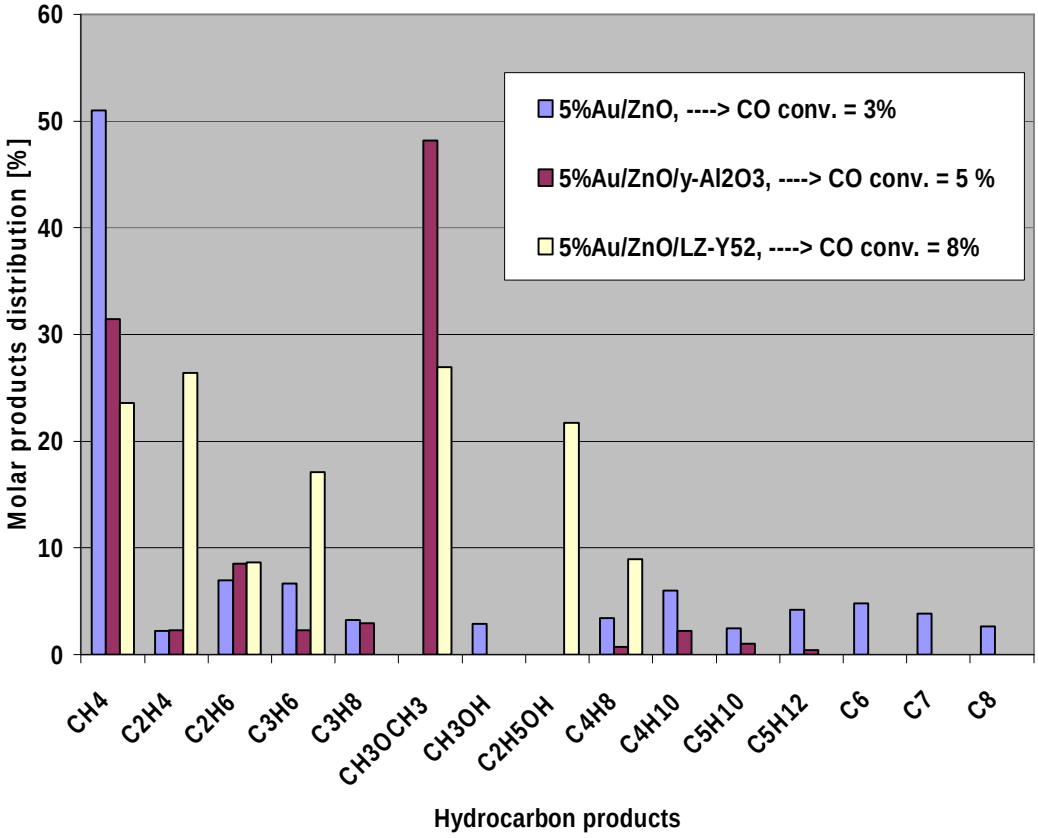

Figure 6-4: Hydrocarbon products distribution-CO conversion over gold-based catalysts tested at 300˚C (573K), 25 atm

The substitution for γ-alumina by zeolite-Y increased olefin formation, mainly ethylene and propylene, and the formation of DME (and water) increased the CO conversion significantly when compared with the CO conversions observed with 5%Au/ZnO/γ-Al_2O_3 and 5%Au/ZnO. The CO conversion level was now 8.0%.

At 400˚C, the formation of methanol over ZnO slightly decreased with respect to other hydrocarbons due to the exothermicity of reaction (1), which restricts the formation of methanol in favour of methane production. At such temperature, the 5%Au/ZnO become selectively more active towards methanol formation, conversely, the FT products were being less produced**,** future investigation could explained this observed phenomenon. Both 5%Au/ZnO/γ-Al_2O_3 and 5%Au/ZnO/LZ-Y52 exhibited a higher tendency for hydrocarbon formation compared with Au/ZnO (Table 6-2) but dimethyl ether is the main product for the bifunctional gold/ZnO-zeolite system.

Table 6-2

Hydrocarbon products distribution (mole%) over gold-based catalysts tested at 400˚C (673K) and 25 atm

Product	Catalyst				Blank reactor
	ZnO	5%Au/ZnO	5%Au/ZnO/y-Al_2O_3	5%Au/ZnO/LZ-Y52*	
CH_4	13.1	43.2	49.9	15.7	nd
C_2H_4	1.9	1.5	3.9	2.2	nd
C_2H_6	0.4	0.6	3.4	0.6	nd
C_3H_6	1.4	0.5	2.7	1.0	nd
C_3H_8	nd	nd	20.9	0.1	nd
CH_3OCH_3	**nd**	**nd**	**18.1**	**75.7**	nd
CH_3OH	**82.1**	**54.1**	**1.4**	**nd**	nd
C_2H_5OH	nd	nd	nd	3.8	nd
C_4H_8	0.7	nd	1.2	0.4	nd
C_4H_{10}	0.3	nd	1.0	0.2	nd
C_5H_{10}	nd	nd	0.3	0.1	nd
C_5H_{12}	nd	nd	0.5	0.2	nd

nd: not detected; (*) GC trace of hydrocarbons formed over 5%Au/ZnO/LZ-Y52 catalyst is presented in Appendix F

The formation of DME over both composite catalysts increased the CO conversion (Figure 6-5) respectively by 60% (over 5%Au/ZnO/γ-Al_2O_3) and 300% (over 5% Au/ZnO/LZ-Y52). Table 6-3 displays the selectivity and production rates of results obtained over bifunctional catalysts tested at 25 atm and 400˚C (673K). As can be seen, the 5% Au/ZnO/LZ-Y52 catalyst yields dimethylether with a relatively high selectivity of 75.7% and a production rate of 252.3 $mmol \cdot h^{-1} \cdot g_{cat}^{-1}$ (Figure 6-5 and Figure 6-6). This could be related to the acidity of zeolite-dehydrating agent, as the determining rate of direct DME depends on the acid properties of dehydrating catalyst [17]. Compared with γ-Al_2O_3, LZ-Y52 is more acidic and the higher DME rate observed is a reasonable finding.

The data discussed here reflect the characteristics of the different catalysts studied. It cannot be considered a definitive study of intrinsic kinetics, and it has not yet been attempted to compare product distributions on an isoconversion basis. Nevertheless, the work clearly demonstrates what may be achieved with gold-based catalysts. While the co-production of light hydrocarbons in general with DME may be considered acceptable from the viewpoint that these products could be considered as being compatible with the transportation of DME using LPG-facilities [18], the production of methane and C_2 hydrocarbons is generally less welcome. Future studies will focus on whether these specific products can be reduced, meanwhile we attempted in the section, which follows to give presumably what could be the source of hydrocarbons formation.

Finally, we are naturally led to consider whether the gold-based catalysts having the attractive feature of enabling syngas conversion under conditions where water is a co-product, display activities comparable with those found for copper-based systems, now used for the past 35 years or so for the commercial

synthesis of methanol. Direct comparison of the two catalyst systems is not entirely straightforward since, the desired products (and therefore operating conditions) are not identical, but a rough assessment can be made. The total specific rate conversion of CO on the Au/ZnO system, for example, at 300˚C (573K) is 840 $mmol\ g_{cat}^{-1}h^{-1}$. For copper-based catalysts of the Cu-Zn-Al type under the experimental conditions of temperature and pressure of this study, the rate is expected to be in the range 1200 – 3600 $mmol\ g_{cat}^{-1}h^{-1}$ [19, 20]. Given that the study did not yet attempt to optimize the gold catalyst composition or the catalyst synthesis procedures, the activities of the gold-containing catalysts can be considered very reasonable.

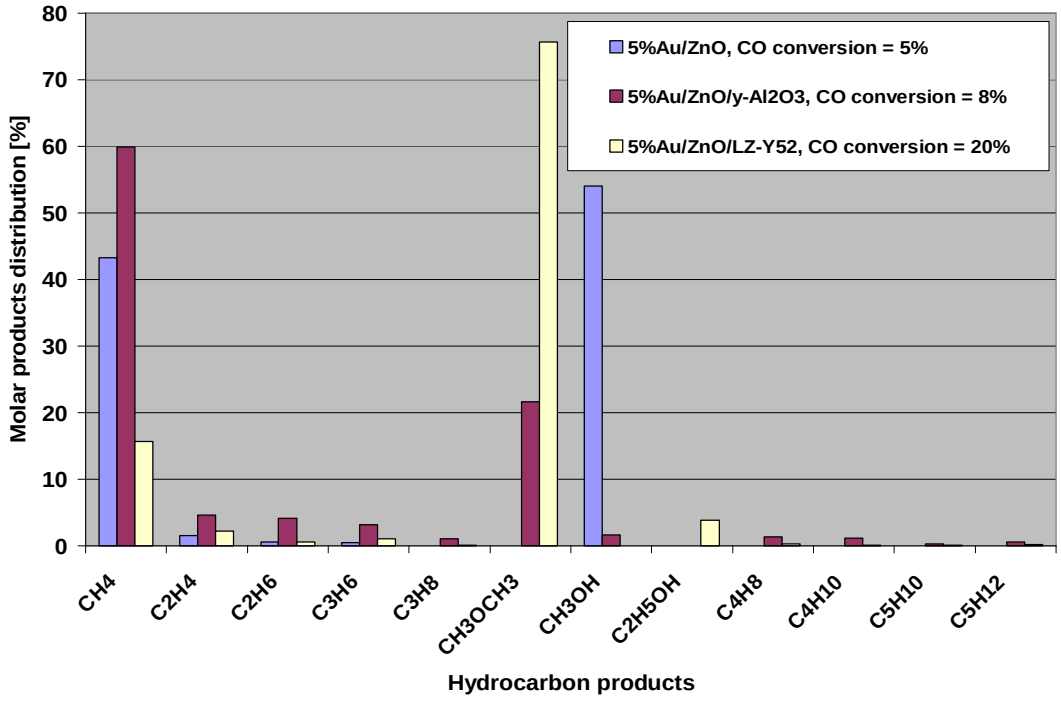

Figure 6-5: Hydrocarbon products distribution-CO conversion over gold-based catalysts tested at 400˚C (673K), 25 atm.

Table 6-3

Selectivity* and production rate of the selected hydrocarbons yielded for catalysts tested at 400˚C (673K) and 25 atm

Selected Product **à**	CH_3OH		CH_3OCH_3		CH_4	
Catalyst	Selectivity (%)	Production Rate ($\mu mol.h^{-1}.g_{cat}^{-1}$)	Select. (%)	Prod. rate ($\mu mol.h^{-1}.g_{cat}^{-1}$)	Select. (%)	Prod. rate ($\mu mol.h^{-1}.g_{cat}^{-1}$)
5%Au/ZnO/γ-Al_2O_3	13.9	35.0	0.4	5.12	83.9	210
5%Au/ZnO/LZ-Y52	-	-	75.7	252.3	15.6	52.2

***Selectivity of X = (moles of hydrocarbon X/ total moles of hydrocarbons produced)

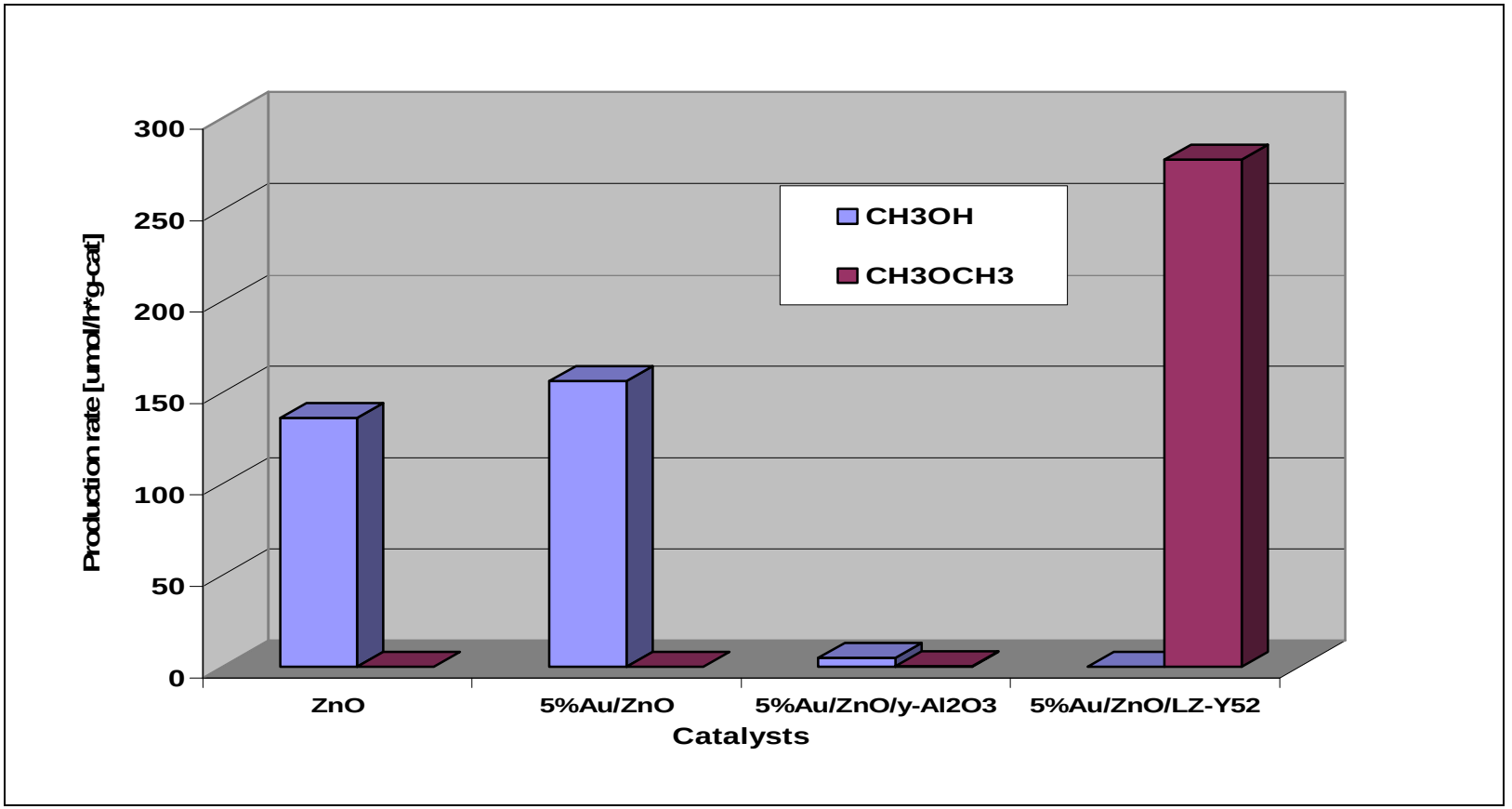

Figure 6-6: Production rate of methanol and dimethyl ether at 400˚C (673K), 25 atm over gold-based catalyst

6.3.3 Hydrocarbons formation over gold-based catalysts

When catalysts containing gold were tested, amongst products formed, we observed the presence of hydrocarbons. In the attempt to explain the presence of the hydrocarbons, methanol vapor with a purity of 99.8% was fed at about 1 atm in the reactor (stainless steel tube, ¼ inch diameter) running at 400˚C (Figure 6-7) in another experiment.

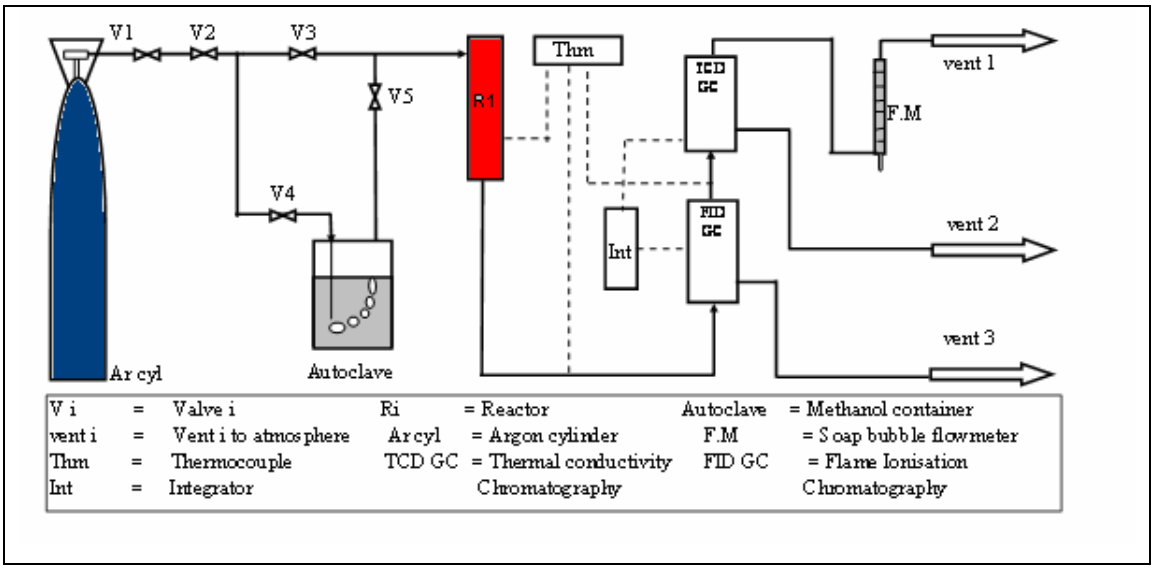

Figure 6-7: The overall set-up for the catalyst testing for the decomposition of methanol

Two runs were carried out; in the first, 0.3 g of 5%Au/ZnO catalyst was used; this was initially pretreated as described previously whereas, in the second run

the 5%Au/ZnO/LZ-Y52 catalyst was used. After reaching a steady state after 2 hours of run with a flow rate of 10 mL/min, the recorded results displayed in Tables E-1 and E-2 (Appendix E) are presented in Figures 6-8 and 6-9.

It results from the trends obtained in both cases that the methanol vapor when passing over gold-based catalysts in the operating conditions, reacts on the catalytic sites of the catalysts, producing the hydrocarbons, with relatively high distribution percentage of olefins and paraffins in the case of 5%Au/ZnO (Figure 6-8) than presents the catalyst 5%Au/ZnO/LZ-Y52. Over this later dimethyl ether is the main product (Figure 6-9), this can be explained by the direct conversion of methanol into DME as underlined previously.

Although, all experiments were not done exactly at same operating conditions, but one can see, that to a certain extend gold-based catalyst has the ability of converting methanol to hydrocarbons. However, future investigations need to be done to understand in depth the chemistry of this transformation over this particular catalyst and eventually the optimization of this latter by considering the effect of Au addition on different types of support.

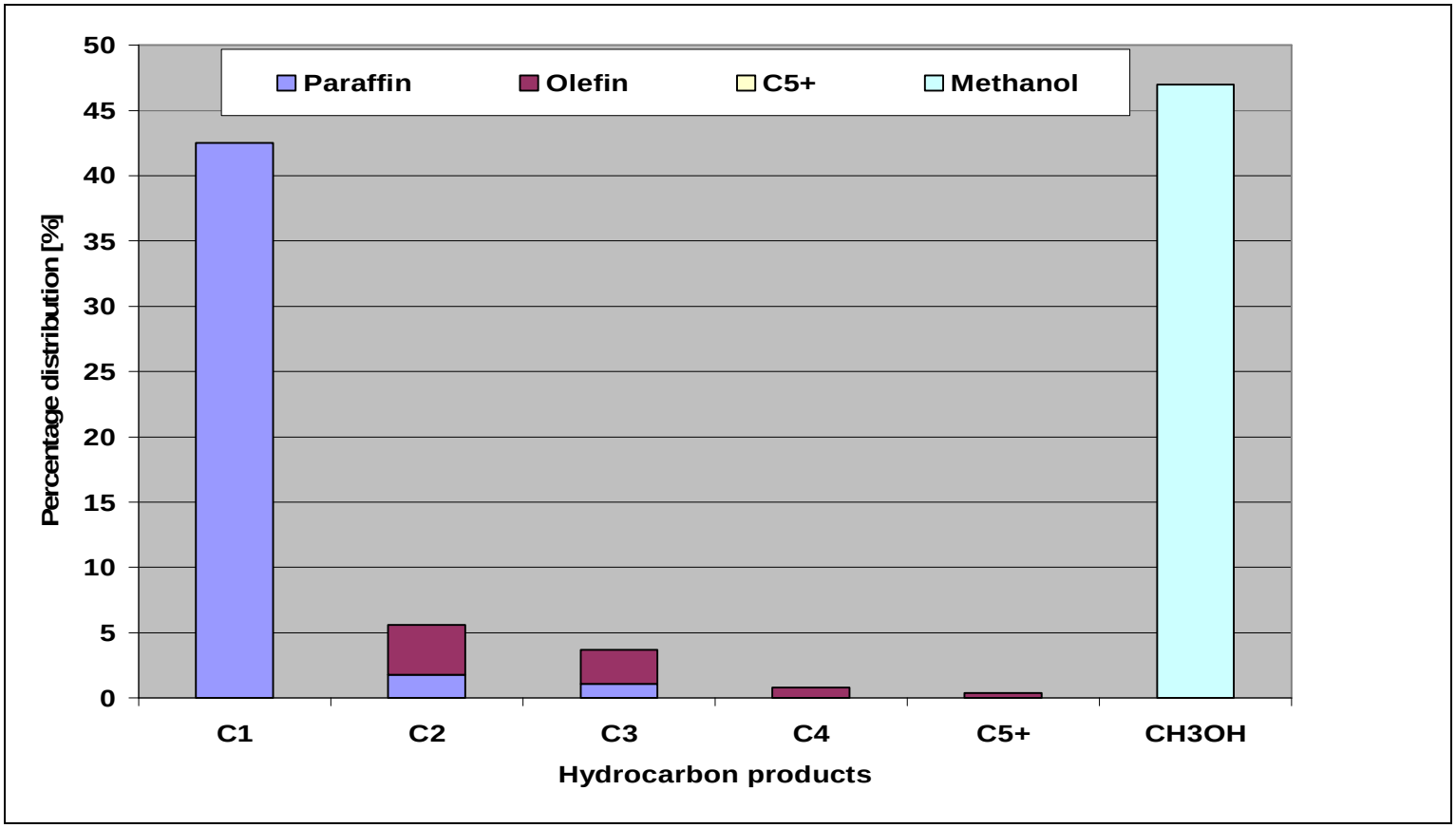

Figure 6-8: Products distribution in methanol conversion reaction over 5%Au/ZnO at 400˚C, 1 atm

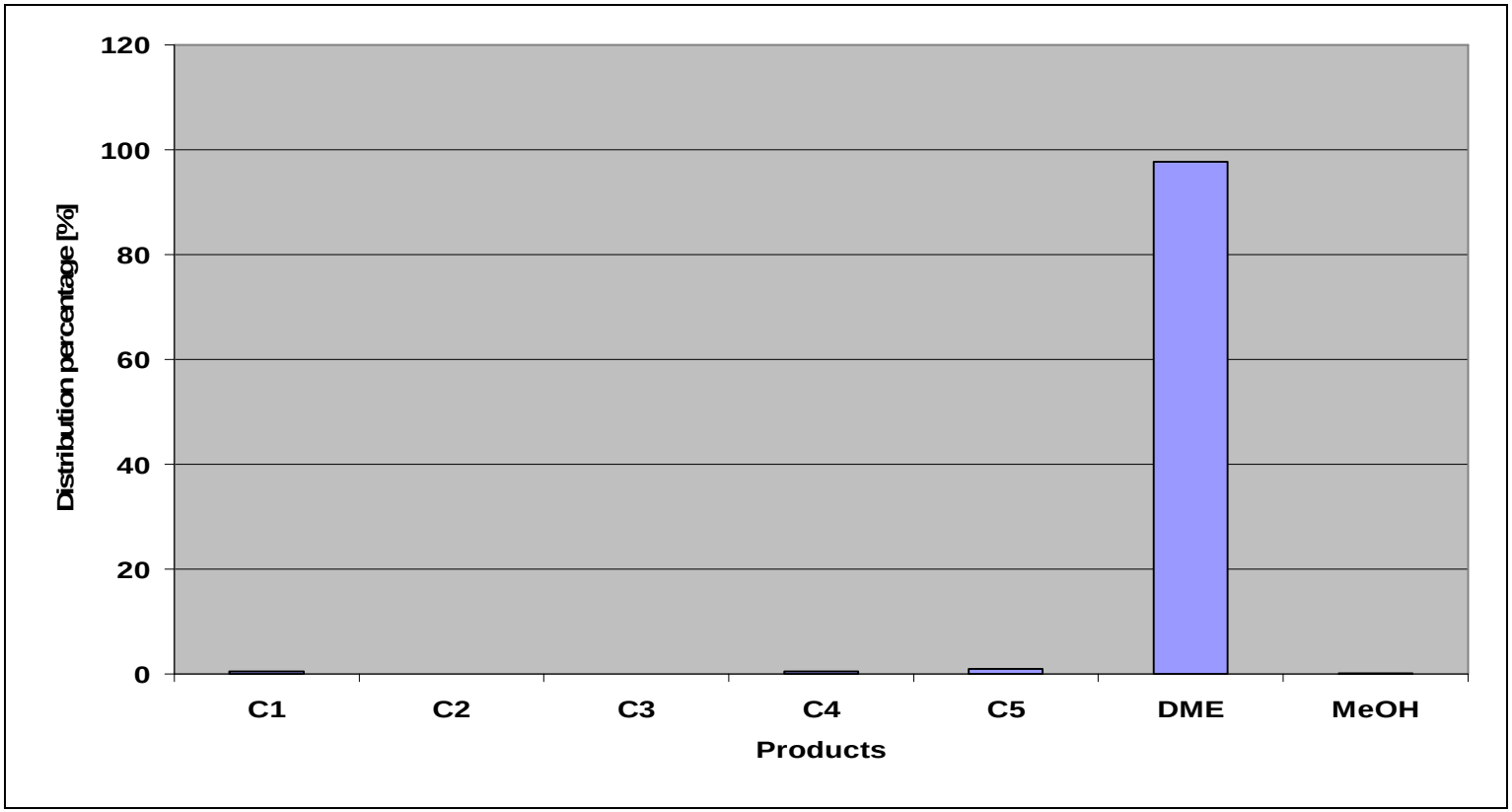

Figure 6-9: Products distribution in methanol conversion reaction over 5% Au/ZnO/LZ-Y52 at 400˚C, 1 atm

6.4 Conclusions

At low pressure methanol can be synthesized over gold-based catalyst with a CO conversion relatively low; however by combining this latter with a DME catalyst one is able to produce either products or mainly the dimethylether by enhancing significantly the CO conversion. This study has shown that this can be achieved by using 5%Au/ZnO/ LZ-Y52 which manifests good catalytic activity towards direct dimethylether synthesis at moderately high temperature. Gold-based catalysts are clearly also capable of producing mixtures of methanol, DME and hydrocarbons, which could be attractive in a scenario where the synthesis of both fuel and petrochemical feedstocks is desired. The exact mode of hydrocarbon formation needs to be investigated in more detail, but initial work suggests that methanol (and/or DME) conversion may be the dominant pathway. Lower selectivities to methane might be achievable through a programme of catalysts design and process optimization

6.5 References

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CHAPTER 7
GENERAL CONCLUSIONS AND RECOMMENDATIONS

In view of developing a new catalyst system for the co-production of methanol and dimethyl ether at low pressure in the same reactor, the main objectives of this study were to: (i) make use of process synthesis approach in order to show that is convenient to co-produce methanol and dimethyl ether in the same reactor than making them in different units; (ii) setting operating conditions for testing catalysts; (iii) identify a catalyst system, which is water tolerant for the synthesis of methanol and DME and (iv) prepare, characterize and test the identified catalyst system to simultaneously making methanol and dimethyl ether.

The following are the outcomes of the study:

1. Through a process synthesis approach, we have shown that it is more convenient producing simultaneously methanol and dimethyl ether in the same reactor than making them separately. The process thermodynamic analysis has been used to set operating conditions within which the chosen catalysts were tested. Considering the compressor work load per

unit of oxygenate yielded as objective function, we have shown that methanol and dimethyl ether can be produced at pressure lower than 25 atm within a temperature range of 500-700K. This study also showed that for a particular pressure, there is a temperature range that has to be considered for a minimum compressor work load per unit of oxygenate (CH_3OH and CH_3OCH_3) generated.

2. After having theoretically identified gold at nano scale as the potential and more tolerant water catalysts, we have prepared by co-precipitation a set of gold-based catalysts, which were characterized by different analysis techniques (XRD, Raman spectroscopy, TEM and ICPAES) and then tested through two experimental programmes. In the first one, gold nanoparticles were supported on different types of supports, and when tested at 300˚C (573K) and 25 atm, we were able to make methanol, mixture of alcohols and some Fischer-Tropsch products using Au/ZnO catalysts. During the second experimental programme, when tested at low temperature 300˚C (573K) and 25 atm, both $Au/ZnO/\gamma\text{-}Al_2O_3$ and Au/ZnO/LZ-Y-52 catalysts were less active, while, when tested at 400˚C (673K), both catalysts were more active, in particular, the gold-based catalyst mixed with zeolite-Y gave high selectivity (75.7%) and production rate (252.3 $\mu mol.h^{-1}.g_{cat}^{-1}$) for dimethyl ether. To the best of our knowledge, no other study on making dimethyl ether via methanol from syngas over gold-based catalysts has been reported in the literature to date. This study can be considered as a nurturing milestone in the field of chemical processing of bulk and speciality chemicals, using gold based catalysts.

3. The present work (through its experimental results) has sufficiently shown that when supported on metal oxides and/or zeolites, gold at the nano-scale can be used as based catalytic metal for the production of hydrocarbons, in particular methanol and dimethyl ether. The technical approach exploited in this work (use of a process synthesis to set operating conditions, and then exploit those conditions for testing the prepared catalysts) is a valuable tool for chemical engineers and chemists working together in the catalysis field when it is question of developing new catalytic systems for industrial applications.

4. The presence of Fischer-Tropsch products in the process suggests that further investigations be done to gain more insight for the formation of these hydrocarbons alongside with methanol and dimethyl ether. The gold-based catalysts optimization study is also requested in order of generating kinetic data that shall be used for a reactor design, which, incorporated into a complete process design shall lead to methanol and dimethyl ether co-production on a large scale.

APPENDICES

Appendix A
Evaluation of equilibrium constant (K_{eq})

Considering the chemical reactions below involved in the methanol/dimethyl ether synthesis:

$CO_{(g)}$ + 2 $H_{2(g)}$	**=**	**$CH_3OH_{(g)}$**	**(1)**
2 $CH_3OH_{(g)}$	**=**	**$CH_3OCH_{3(g)}$ + $H_2O_{(g)}$**	**(2)**
$CO_{(g)}$ + $H_2O_{(g)}$	**=**	**$CO_{2(g)}$ + $H_{2(g)}$**	**(3)**

the equilibrium constant corresponding to each chemical reaction was computed using the following expressions

$$\Delta G_{rxn} = \Sigma \Delta G^{o}_{products} - \Sigma \Delta G^{o}_{reac\,tan\,ts} \qquad [A.1]$$

$$\Delta H_{rxn} = \Sigma \Delta H^{o}_{products} - \Sigma \Delta H^{o}_{reac\,tan\,ts} \qquad [A.2]$$

$$K_0 = exp[-\frac{\Delta G_{rxn}}{RT}] \qquad [A.3]$$

$$\frac{d \ln K_{eq}(T)}{dT} = \frac{\Delta H_{rxn}}{RT^2} \qquad [A.4]$$

The integration of equation [A.4] from T_o = 298K to T led to the expression given afterwards that enabled to calculate K_{eqj}, which is the equilibrium constant for j^{th} reaction at temperature T.

$$K_{eqj} = K_o \exp\left[\frac{\Delta H}{R}\left(\frac{1}{298} - \frac{1}{T}\right)\right] \qquad \text{[A.5]}$$

Results of calculations done using above equations and thermodynamic constants of Table A-1 are displayed in Table A-2.

Table A-1
Heats and Free Energies of Formation of Inorganic and Organic Compounds in gas phase

Compound	CO	CO_2	H_2O	CH_3OH	CH_3OCH_3
Heat of formation ΔH (@ 25˚C), kJ/mole	-110.551*	-393.61	-241.893	-200.94	-184.1
Free energy of formation ΔG (@ 25˚C), kJ/mole	-137.301	-394.418	-228.668	-162.32	-112.8

*Values of energies used in this table were originally extracted from R.H. Perry and D.W. Green, Perry's Chemical Engineers' Handbook, 7th ed., 1997, and then converted from kcal to kJ by multiplying initial values by a factor of 4.185.

Table A-2
Equilibrium constant for reactions involved in methanol/DME synthesis at different temperatures

Chemical reaction		$CO + 2H_2 = CH_3OH$	$2CH_3OH = CH_3OCH_3 + H_2O$	$CO + H_2O = CO_2 + H_2$
ΔH_{rxn}, kJ/mol		-9.0389E+01	-2.4113E+01	-4.1166E+01
ΔG_{rxn}, kJ/mol		-2.5019E+01	-1.6828E+01	-2.8449E+01
Ko		2.4299E+04	8.9081E+02	9.7014E+04
Equilibrium constant (***Keq***)	Temperature [K]	***Keq1***	***Keq2***	***Keq3***
	400	2.2146E+00	7.4466E+01	1.4020E+03
	450	1.0808E-01	3.3272E+01	3.5435E+02
	500	9.6490E-03	1.7465E+01	1.1792E+02
	550	1.3366E-03	1.0308E+01	4.7929E+01
	600	2.5740E-04	6.6422E+00	2.2635E+01
	650	6.3868E-05	4.5796E+00	1.1998E+01
	700	1.9338E-05	3.3297E+00	6.9629E+00
	750	6.8667E-06	2.5261E+00	4.3450E+00
	800	2.7751E-06	1.9837E+00	2.8760E+00

Appendix B

Equilibrium calculations for System I (MeOH only)

Using the flowsheet (Figure B-1), calculations of molar flow rates at equilibrium for species involved in System I were done as follows:

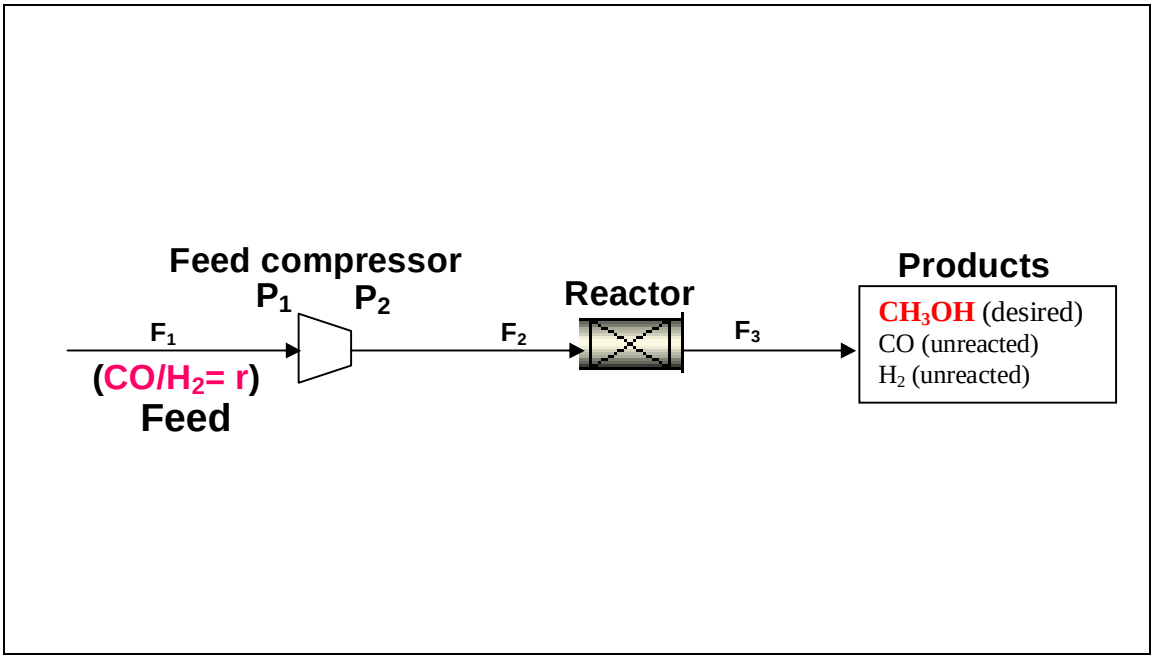

Figure B-1: Flow-diagram for methanol production in System I

- **Preliminary assumptions**

$F_1 = N_{CO,1} + N_{H2,1}$ *(kmol/day); ratio* $CO:H_2 = r$

$N_{CO,1}$ = 32500 kmol/day

$N_{H2,1}$ = 325000; 65000; 975000 kmol/day, for r = 1:1, 1:2, and 1:3 respectively.

$N_{X,j}$*: molar flow rate of the chemical component X in stream j (kmol/day)*

F_j*: total molar flow rate for stream j (kmol/day)*

- **Chemical reaction**:

$CO + 2\ H_2 = CH_3OH$ e_1 [1]

(e_1: extent 1 represents the number of kmoles/day of CO consumed at equilibrium**)**

- **Number of mole at equilibrium** (kmol/day):

$N_{CO,3} = N_{CO,2} - e_1$ [B-1]

$N_{H2,3} = N_{H2,2} - 2\ e_1$ [B-2]

$N_{CH3OH,3} = e_1$ [B-3]

- **Equilibrium constants:**

$$Keq_1 = \frac{\left(N_{CH3OH,3}\right) * \left(N_{CO,3} + N_{H2,3} + N_{CH3OH,3}\right)^2}{\left(N_{CO,3}\right) * \left(N_{H2,3}\right)^2 * P^2} \quad \text{[B-4]}$$

Equation B-4 is solved in terms of e_1 by setting values of P (pressure: 1-100 atm) and T (temperature: 400-800K). Each temperature value yields an equilibrium constant value (K_{eq}) which is substituted in A1-5 for the computation of e_1. Replacing e_1 values in equations (B-1, B-2, and B-3) gives molar flow rate values of components in stream 3 as displayed in Tables A1.

The carbon monoxide conversion (X_{CO}) is calculated as follows:

$$X_{CO}\ (\%) \ = \frac{moles.(CO).reacted}{moles.(CO).fed} \times 100$$

$$X_{CO}\ (\%) \ = \frac{e_1(kmol/day)}{32500.(kmol/day)} \times 100 \qquad \text{[B-6]}$$

The Carbon Efficiency (CE) is given by the following expression

$$\text{CE} = \frac{moles \cdot of \cdot carbon \cdot in \cdot (CH_3OH)}{moles \cdot of \cdot CO \cdot fed \cdot to \cdot reactor}$$

$$\text{CE} = \frac{N_{CH3OH,3}(kmol/day)}{32500 \cdot (kmol/day)} \qquad \text{[B-7]}$$

The Hydrogen Efficiency (HE) was evaluated using the following expression:

$$HE = \frac{moles \cdot of \cdot hydrogen \cdot in \cdot (CH_3OH)}{moles \cdot of \cdot hydrogen \cdot in \cdot the \cdot feed}$$

- The compressor work load for the feed compressor is given by the following expression:

$$\text{Pad} = \frac{g}{g-1} F_1 RT \left[\left(\frac{P_2}{P_1} \right)^{\frac{(g-1)}{g}} - 1 \right] \qquad \text{[B-8]}$$

where $g = 1.4$, R = 8.314 *kJ.kmol*$^{-1}$*.K*$^{-1}$, T = 313*K*, P1 = 1 *atm*, P2 = P (compressor exit pressure, atm)

- Mass of oxygenate yielded is computed as follows

m(MeOH+DME) = moles(MeOH)**M*$_W$(MeOH) + moles (DME)**M*$_W$(DME)

M$_W$(MeOH): methanol molecular weight, 32.0424
M$_W$(DME): dimethyl ether molecular weight, 46.069

Table B-1.1
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 400K for CO:H_2 = 1:2

Reactor temperature [K]	400				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.2933E+04	2.8771E+04	3.0560E+04	3.1302E+04	3.1755E+04
$N_{CH3OH,3}$ [kmol/day]	1.2933E+04	2.8771E+04	3.0560E+04	3.1302E+04	3.1755E+04
$N_{CO,3}$ [kmol/day]	1.9567E+04	3.7290E+03	1.9400E+03	1.1980E+03	7.4500E+02
$N_{H2,3}$ [kmol/day]	3.9134E+04	7.4580E+03	3.8800E+03	2.3960E+03	1.4900E+03
X_{CO} [%]	3.9794E+01	8.8526E+01	9.4031E+01	9.6314E+01	9.7708E+01
F_1 [kmol/day]	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad} [kW]	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	2.2146E+00	2.2148E+00	2.2158E+00	2.2169E+00	2.2181E+00
CE	3.9794E-01	8.8526E-01	9.4031E-01	9.6314E-01	9.7708E-01
HE	3.9794E-01	8.8526E-01	9.4031E-01	9.6314E-01	9.7708E-01
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	8.5468E-01	1.3042E+00	1.7370E+00	2.2694E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-1.2
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 450K for CO:H_2 = 1:2

Reactor temperature [K]	450				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.4460E+03	2.1069E+04	2.6733E+04	2.9030E+04	3.0383E+04
$N_{CH3OH,3}$ [kmol/day]	1.4460E+03	2.1069E+04	2.6733E+04	2.9030E+04	3.0383E+04
$N_{CO,3}$ [kmol/day]	3.1054E+04	1.1431E+04	5.7670E+03	3.4700E+03	2.1170E+03
$N_{H2,3}$ [kmol/day]	6.2108E+04	2.2862E+04	1.1534E+04	6.9400E+03	4.2340E+03
X_{CO} [%]	4.4492E+00	6.4828E+01	8.2255E+01	8.9323E+01	9.3486E+01
F_1 [kmol/day]	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad} [kW]	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	1.0805E-01	1.0808E-01	1.0810E-01	1.0808E-01	1.0803E-01
CE	4.4492E-02	6.4828E-01	8.2255E-01	8.9323E-01	9.3486E-01
HE	4.4592E-02	6.4828E-01	8.2355E-01	8.9323E-01	9.3486E-01
P_{ad}/m*(MeOH+DME)* [kJ/g]	0.0000E+00	1.1671E+00	1.4909E+00	1.8729E+00	2.3719E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-1.3
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 500K for CO:H_2 = 1:2

Ractor temperature [K]	500				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.3800E+02	8.3360E+03	1.8387E+04	2.4024E+04	2.7446E+04
$N_{CH3OH,3}$ [kmol/day]	1.3800E+02	8.3360E+03	1.8387E+04	2.4024E+04	2.7446E+04
$N_{CO,3}$ [kmol/day]	3.2362E+04	2.4164E+04	1.4113E+04	8.4760E+03	5.0540E+03
$N_{H2,3}$ [kmol/day]	6.4724E+04	4.8328E+04	2.8226E+04	1.6952E+04	1.0108E+04
X_{CO} [%]	4.2462E-01	2.5649E+01	5.6575E+01	7.3920E+01	8.4449E+01
F_1 [kmol/day]	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad} [kW]	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	9.6219E-03	9.6497E-03	9.6486E-03	9.6481E-03	9.6493E-03
CE	4.2462E-03	2.5649E-01	5.6575E-01	7.3920E-01	8.4449E-01
HE	4.2562E-03	2.5649E-01	5.6575E-01	7.3920E-01	8.4449E-01
P_{ad}/m(MeOH+DME) [kJ/g]	0.0000E+00	2.9498E+00	2.1676E+00	2.2632E+00	2.6257E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-1.4
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 550K for CO:H_2 = 1:2

Reactor temperature [K]	550				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.9000E+01	1.7590E+03	7.6110E+03	1.5262E+04	2.1933E+04
$N_{CH3OH,3}$ [kmol/day]	1.9000E+01	1.7590E+03	7.6110E+03	1.5262E+04	2.1933E+04
$N_{CO,3}$ [kmol/day]	3.2481E+04	3.0741E+04	2.4889E+04	1.7238E+04	1.0567E+04
$N_{H2,3}$ [kmol/day]	6.4962E+04	6.1482E+04	4.9778E+04	3.4476E+04	2.1134E+04
X_{CO} [%]	5.8462E-02	5.4123E+00	2.3418E+01	4.6960E+01	6.7486E+01
F_1 [kmol/day]	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad} [kW]	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	1.3167E-03	1.3370E-03	1.3367E-03	1.3366E-03	1.3368E-03
CE	5.8462E-04	5.4123E-02	2.3418E-01	4.6960E-01	6.7486E-01
HE	5.8462E-04	5.4123E-02	2.3418E-01	4.6960E-01	6.7486E-01
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	1.3980E+01	5.2366E+00	3.5625E+00	3.2857E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-1.5
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 600K for CO:H_2 = 1:2

Reactor temperature [K]	600				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	4.0000E+00	3.6500E+02	2.0790E+03	6.3860E+03	1.3792E+04
$N_{CH3OH,3}$ [kmol/day]	4.0000E+00	3.6500E+02	2.0790E+03	6.3860E+03	1.3792E+04
$N_{CO,3}$ [kmol/day]	3.2496E+04	3.2135E+04	3.0421E+04	2.6114E+04	1.8708E+04
$N_{H2,3}$ [kmol/day]	6.4992E+04	6.4270E+04	6.0842E+04	5.2228E+04	3.7416E+04
X_{CO} [%]	1.2308E-02	1.1231E+00	6.3969E+00	1.9649E+01	4.2437E+01
F_1 [kmol/day]	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad} [kW]	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	2.7698E-04	2.5750E-04	2.5736E-04	2.5743E-04	2.5742E-04
CE	1.23E-04	1.12E-02	6.39E-02	1.96E-01	4.24E-01
HE	1.23E-04	1.12E-02	6.40E-02	1.96E-01	4.24E-01
P_{ad}/m*(MeOH+DME)* [kJ/g]	0.0000E+00	6.7370E+01	1.9171E+01	8.5141E+00	5.2252E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-1.6
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 650K for CO:H_2 = 1:2

Reactor temperature [K]	650				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	9.2000E-01	9.1820E+01	5.6000E+02	2.0650E+03	6.3520E+03
$N_{CH3OH,3}$ [kmol/day]	9.2000E-01	9.1820E+01	5.6000E+02	2.0650E+03	6.3520E+03
$N_{CO,3}$ [kmol/day]	3.2499E+04	3.2408E+04	3.1940E+04	3.0435E+04	2.6148E+04
$N_{H2,3}$ [kmol/day]	6.4998E+04	6.4816E+04	6.3880E+04	6.0870E+04	5.2296E+04
X_{CO} [%]	2.8308E-03	2.8252E-01	1.7231E+00	6.3538E+00	1.9545E+01
F_1 [kmol/day]	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad} [kW]	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	6.3695E-05	6.3868E-05	6.3858E-05	6.3858E-05	6.3868E-05
CE	2.8308E-05	2.8252E-03	1.7231E-02	6.3538E-02	1.9545E-01
HE	2.8308E-05	2.8352E-03	1.7231E-02	6.3538E-02	1.9545E-01
P_{ad}/m*(MeOH+DME)* [kJ/g]	0.0000E+00	2.6781E+02	7.1171E+01	2.6330E+01	1.1345E+01

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-1.7
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 700K for CO:H_2 = 1:2

Reactor temperature [K]	700				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	3.0000E-01	2.8000E+01	1.7300E+02	6.7400E+02	2.4480E+03
$N_{CH3OH,3}$ [kmol/day]	3.0000E-01	2.8000E+01	1.7300E+02	6.7400E+02	2.4480E+03
$N_{CO,3}$ [kmol/day]	3.2500E+04	3.2472E+04	3.2327E+04	3.1826E+04	3.0052E+04
$N_{H2,3}$ [kmol/day]	6.4999E+04	6.4944E+04	6.4654E+04	6.3652E+04	6.0104E+04
X_{CO} [%]	9.2308E-04	8.6154E-02	5.3231E-01	2.0738E+00	7.5323E+00
F_1 [kmol/day]	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad} [kW]	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	2.0770E-05	1.9412E-05	1.9334E-05	1.9330E-05	1.9337E-05
CE	9.2308E-06	8.6154E-04	5.3231E-03	2.0738E-02	7.5323E-02
HE	9.2308E-06	8.6154E-04	5.3231E-03	2.0738E-02	7.5323E-02
P_{ad}/m*(MeOH+DME)* [kJ/g]	0.0000E+00	8.7821E+02	2.3038E+02	8.0669E+01	2.9439E+01

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-1.8
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 750K for CO:H_2 = 1:2

Reactor temperature [K]	750				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.0000E-01	9.9200E+00	6.1800E+01	2.4500E+02	9.4400E+02
$N_{CH3OH,3}$ [kmol/day]	1.0000E-01	9.9200E+00	6.1800E+01	2.4500E+02	9.4400E+02
$N_{CO,3}$ [kmol/day]	3.2500E+04	3.2490E+04	3.2438E+04	3.2255E+04	3.1556E+04
$N_{H2,3}$ [kmol/day]	6.5000E+04	6.4980E+04	6.4876E+04	6.4510E+04	6.3112E+04
X_{CO} [%]	3.0769E-04	3.0523E-02	1.9015E-01	7.5385E-01	2.9046E+00
F_1 [kmol/day]	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad} [kW]	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	6.9231E-06	6.8712E-06	6.8673E-06	6.8708E-06	6.8658E-06
CE	3.0769E-06	3.0523E-04	1.9015E-03	7.5385E-03	2.9046E-02
HE	3.0769E-06	3.0523E-04	1.9015E-03	7.5385E-03	2.9046E-02
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	2.4788E+03	6.4491E+02	2.2192E+02	7.6341E+01

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-1.9
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 800K for CO:H_2 = 1:2

Reactor temperature [K]	800				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	4.0000E-02	4.0100E+00	2.5000E+01	1.0000E+02	3.9300E+02
$N_{CH3OH,3}$ [kmol/day]	4.0000E-02	4.0100E+00	2.5000E+01	1.0000E+02	3.9300E+02
$N_{CO,3}$ [kmol/day]	3.2500E+04	3.2496E+04	3.2475E+04	3.2400E+04	3.2107E+04
$N_{H2,3}$ [kmol/day]	6.5000E+04	6.4992E+04	6.4950E+04	6.4800E+04	6.4214E+04
X_{CO} [%]	1.2308E-04	1.2338E-02	7.6923E-02	3.0769E-01	1.2092E+00
F_1 [kmol/day]	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad} [kW]	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	2.7692E-06	2.7767E-06	2.7728E-06	2.7835E-06	2.7766E-06
CE	1.2308E-06	1.2338E-04	7.6923E-04	3.0769E-03	1.2092E-02
HE	1.2308E-06	1.2338E-04	7.6923E-04	3.0769E-03	1.2092E-02
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	6.1322E+03	1.5942E+03	5.4371E+02	1.8337E+02

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-2.1
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 400K for CO:H_2 = 1:1

Reactor temperature [K]	400				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	7.1866E+03	1.5161E+04	1.5813E+04	1.6032E+04	1.6131E+04
$N_{CH3OH,3}$ [kmol/day]	7.1866E+03	1.5161E+04	1.5813E+04	1.6032E+04	1.6131E+04
$N_{CO,3}$ [kmol/day]	2.5313E+04	1.7340E+04	1.6687E+04	1.6468E+04	1.6369E+04
$N_{H2,3}$ [kmol/day]	1.8127E+04	2.1790E+03	8.7320E+02	4.3680E+02	2.3800E+02
X_{CO} [%]	2.2113E+01	4.6648E+01	4.8657E+01	4.9328E+01	4.9634E+01
F_1 [kmol/day]	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad} [kW]	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	2.2146E+00	2.2146E+00	2.2149E+00	2.2140E+00	1.8646E+00
CE	2.2113E-01	4.6648E-01	4.8657E-01	4.9328E-01	4.9634E-01
HE	4.4225E-01	9.3295E-01	9.7313E-01	9.8656E-01	9.9268E-01
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	1.0813E+00	1.6802E+00	2.2610E+00	2.9784E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-2.2
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 450K for CO:H_2 = 1:1

Reactor temperature [K]	450				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	8.1280E+02	1.1521E+04	1.4287E+04	1.5263E+04	1.5756E+04
$N_{CH3OH,3}$ [kmol/day]	8.1280E+02	1.1521E+04	1.4287E+04	1.5263E+04	1.5756E+04
$N_{CO,3}$ [kmol/day]	3.1687E+04	2.0979E+04	1.8213E+04	1.7237E+04	1.6744E+04
$N_{H2,3}$ [kmol/day]	3.0874E+04	9.4580E+03	3.9254E+03	1.9736E+03	9.8800E+02
X_{CO} [%]	2.5009E+00	3.5449E+01	4.3961E+01	4.6964E+01	4.8480E+01
F_1 [kmol/day]	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad} [kW]	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	1.0808E-01	1.0808E-01	1.0808E-01	1.0807E-01	1.0811E-01
CE	2.5009E-02	3.5449E-01	4.3961E-01	4.6964E-01	4.8480E-01
HE	5.0018E-02	7.0898E-01	8.7922E-01	9.3927E-01	9.6960E-01
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	1.4229E+00	1.8597E+00	2.3748E+00	3.0492E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-2.3
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 500K for CO:H_2 = 1:1

Ractor temperature [K]	500				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	7.7800E+01	4.6573E+03	1.0122E+04	1.3008E+04	1.4604E+04
$N_{CH3OH,3}$ [kmol/day]	7.7800E+01	4.6573E+03	1.0122E+04	1.3008E+04	1.4604E+04
$N_{CO,3}$ [kmol/day]	3.2422E+04	2.7843E+04	2.2379E+04	1.9492E+04	1.7896E+04
$N_{H2,3}$ [kmol/day]	3.2344E+04	2.3185E+04	1.2257E+04	6.4840E+03	3.2916E+03
X_{CO} [%]	2.3938E-01	1.4330E+01	3.1143E+01	4.0025E+01	4.4936E+01
F_1 [kmol/day]	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad} [kW]	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	9.6446E-03	9.6489E-03	9.6491E-03	9.6494E-03	9.6488E-03
CE	2.3938E-03	1.4330E-01	3.1143E-01	4.0025E-01	4.4936E-01
HE	4.7877E-03	2.8660E-01	6.2286E-01	8.0049E-01	8.9872E-01
P_{ad}/m*(MeOH+DME)* [kJ/g]	0.0000E+00	3.5199E+00	2.6251E+00	2.7865E+00	3.2897E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-2.4
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 550K for CO:H_2 = 1:1

Reactor temperature [K]	550				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.0800E+01	9.8800E+02	4.2553E+03	8.4510E+03	1.1963E+04
$N_{CH3OH,3}$ [kmol/day]	1.0800E+01	9.8800E+02	4.2553E+03	8.4510E+03	1.1963E+04
$N_{CO,3}$ [kmol/day]	3.2489E+04	3.1512E+04	2.8245E+04	2.4049E+04	2.0537E+04
$N_{H2,3}$ [kmol/day]	3.2478E+04	3.0524E+04	2.3989E+04	1.5598E+04	8.5746E+03
X_{CO} [%]	3.3231E-02	3.0400E+00	1.3093E+01	2.6003E+01	3.6808E+01
F_1 [kmol/day]	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad} [kW]	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	1.3306E-03	1.3366E-03	1.3366E-03	1.3366E-03	1.3366E-03
CE	3.3231E-04	3.0400E-02	1.3093E-01	2.6003E-01	3.6808E-01
HE	6.6462E-04	6.0800E-02	2.6186E-01	5.2006E-01	7.3617E-01
P_{ad}/m*(MeOH+DME)* [kJ/g]	0.0000E+00	1.6592E+01	6.2441E+00	4.2891E+00	4.0161E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-2.5
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 600K for CO:H_2 = 1:1

Reactor temperature [K]	600				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	2.1000E+00	2.0500E+02	1.1680E+03	3.5744E+03	7.6544E+03
$N_{CH3OH,3}$ [kmol/day]	2.1000E+00	2.0500E+02	1.1680E+03	3.5744E+03	7.6544E+03
$N_{CO,3}$ [kmol/day]	3.2498E+04	3.2295E+04	3.1332E+04	2.8926E+04	2.4846E+04
$N_{H2,3}$ [kmol/day]	3.2496E+04	3.2090E+04	3.0164E+04	2.5351E+04	1.7191E+04
X_{CO} [%]	6.4615E-03	6.3077E-01	3.5938E+00	1.0998E+01	2.3552E+01
F_1 [kmol/day]	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad} [kW]	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	2.5851E-04	2.5716E-04	2.5741E-04	2.5740E-04	2.5740E-04
CE	6.4615E-05	6.3077E-03	3.5938E-02	1.0998E-01	2.3552E-01
HE	1.2923E-04	1.2615E-02	7.1877E-02	2.1996E-01	4.7104E-01
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	7.9967E+01	2.2749E+01	1.0141E+01	6.2766E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-2.6
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 650K for CO:H_2 = 1:1

Reactor temperature [K]	650				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	5.2000E-01	5.1600E+01	3.1490E+02	1.1600E+03	3.5560E+03
$N_{CH3OH,3}$ [kmol/day]	5.2000E-01	5.1600E+01	3.1490E+02	1.1600E+03	3.5560E+03
$N_{CO,3}$ [kmol/day]	3.2499E+04	3.2448E+04	3.2185E+04	3.1340E+04	2.8944E+04
$N_{H2,3}$ [kmol/day]	3.2499E+04	3.2397E+04	3.1870E+04	3.0180E+04	2.5388E+04
X_{CO} [%]	1.6000E-03	1.5877E-01	9.6892E-01	3.5692E+00	1.0942E+01
F_1 [kmol/day]	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad} [kW]	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	6.4003E-05	6.3811E-05	6.3861E-05	6.3861E-05	6.3874E-05
CE	1.6000E-05	1.5877E-03	9.6892E-03	3.5692E-02	1.0942E-01
HE	3.2000E-05	3.1754E-03	1.9378E-02	7.1385E-02	2.1883E-01
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	3.1770E+02	8.4377E+01	3.1248E+01	1.3511E+01

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-2.7
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 700K for CO:H_2 = 1:1

Reactor temperature [K]	700				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.6000E-01	1.5700E+01	9.7320E+01	3.7900E+02	1.3750E+03
$N_{CH3OH,3}$ [kmol/day]	1.6000E-01	1.5700E+01	9.7320E+01	3.7900E+02	1.3750E+03
$N_{CO,3}$ [kmol/day]	3.2500E+04	3.2484E+04	3.2403E+04	3.2121E+04	3.1125E+04
$N_{H2,3}$ [kmol/day]	3.2500E+04	3.2469E+04	3.2305E+04	3.1742E+04	2.9750E+04
X_{CO} [%]	4.9231E-04	4.8308E-02	2.9945E-01	1.1662E+00	4.2308E+00
F_1 [kmol/day]	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad} [kW]	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	1.9693E-05	1.9351E-05	1.9338E-05	1.9332E-05	1.9342E-05
CE	4.9231E-06	4.8308E-04	2.9945E-03	1.1662E-02	4.2308E-02
HE	9.8462E-06	9.6615E-04	5.9889E-03	2.3323E-02	8.4615E-02
P_{ad}/m*(MeOH+DME)* [kJ/g]	0.0000E+00	1.0442E+03	2.7302E+02	9.5640E+01	3.4941E+01

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-2.8
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 750K for CO:H_2 = 1:1

Reactor temperature [K]	750				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	6.0000E-02	5.6000E+00	3.4760E+01	1.3800E+02	5.3100E+02
$N_{CH3OH,3}$ [kmol/day]	6.0000E-02	5.6000E+00	3.4760E+01	1.3800E+02	5.3100E+02
$N_{CO,3}$ [kmol/day]	3.2500E+04	3.2494E+04	3.2465E+04	3.2362E+04	3.1969E+04
$N_{H2,3}$ [kmol/day]	3.2500E+04	3.2489E+04	3.2430E+04	3.2224E+04	3.1438E+04
X_{CO} [%]	1.8462E-04	1.7231E-02	1.0695E-01	4.2462E-01	1.6338E+00
F_1 [kmol/day]	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad} [kW]	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	7.3847E-06	6.8959E-06	6.8671E-06	6.8814E-06	6.8703E-06
CE	1.8462E-06	1.7231E-04	1.0695E-03	4.2462E-03	1.6338E-02
HE	3.6923E-06	3.4462E-04	2.1391E-03	8.4923E-03	3.2677E-02
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	2.9274E+03	7.6440E+02	2.6266E+02	9.0478E+01

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-2.9
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 800K for CO:H_2 = 1:1

Reactor temperature [K]	800				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	2.0000E-02	2.2500E+00	1.4070E+01	5.6000E+01	2.2100E+02
$N_{CH3OH,3}$ [kmol/day]	2.0000E-02	2.2500E+00	1.4070E+01	5.6000E+01	2.2100E+02
$N_{CO,3}$ [kmol/day]	3.2500E+04	3.2498E+04	3.2486E+04	3.2444E+04	3.2279E+04
$N_{H2,3}$ [kmol/day]	3.2500E+04	3.2496E+04	3.2472E+04	3.2388E+04	3.2058E+04
X_{CO} [%]	6.1538E-05	6.9231E-03	4.3292E-02	1.7231E-01	6.8000E-01
F_1 [kmol/day]	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad} [kW]	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	2.4615E-06	2.7698E-06	2.7743E-06	2.7712E-06	2.7765E-06
CE	6.1538E-07	6.9231E-05	4.3292E-04	1.7231E-03	6.8000E-03
HE	1.2308E-06	1.3846E-04	8.6585E-04	3.4462E-03	1.3600E-02
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	7.2859E+03	1.8884E+03	6.4728E+02	2.1739E+02

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-3.1
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 400K for CO:H_2 = 1:3

Reactor temperature [K]	400				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.6140E+04	3.1942E+04	3.2407E+04	3.2477E+04	3.2494E+04
$N_{CH3OH,3}$ [kmol/day]	1.6140E+04	3.1942E+04	3.2407E+04	3.2477E+04	3.2494E+04
$N_{CO,3}$ [kmol/day]	1.6360E+04	5.5800E+02	9.3000E+01	2.3000E+01	6.0000E+00
$N_{H2,3}$ [kmol/day]	6.5220E+04	3.3616E+04	3.2686E+04	3.2546E+04	3.2512E+04
X_{CO} [%]	4.9662E+01	9.8283E+01	9.9714E+01	9.9929E+01	9.9982E+01
F_1 [kmol/day]	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad} [kW]	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	2.2148E+00	2.2144E+00	2.2175E+00	2.2561E+00	2.1655E+00
CE	4.9662E-01	9.8283E-01	9.9714E-01	9.9929E-01	9.9982E-01
HE	3.3108E-01	6.5522E-01	6.6476E-01	6.6619E-01	6.6654E-01
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	1.0264E+00	1.6398E+00	2.2322E+00	2.9571E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-3.2
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 450K for CO:H_2 = 1:3

Reactor temperature [K]	450				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.8290E+03	2.5626E+04	3.0839E+04	3.2039E+04	3.2381E+04
$N_{CH3OH,3}$ [kmol/day]	1.8290E+03	2.5626E+04	3.0839E+04	3.2039E+04	3.2381E+04
$N_{CO,3}$ [kmol/day]	3.0671E+04	6.8740E+03	1.6610E+03	4.6100E+02	1.1900E+02
$N_{H2,3}$ [kmol/day]	9.3842E+04	4.6248E+04	3.5822E+04	3.3422E+04	3.2738E+04
X_{CO} [%]	5.6277E+00	7.8849E+01	9.4889E+01	9.8582E+01	9.9634E+01
F_1 [kmol/day]	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad} [kW]	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	1.0809E-01	1.0808E-01	1.0806E-01	1.0815E-01	1.0805E-01
CE	5.6277E-02	7.8849E-01	9.4889E-01	9.8582E-01	9.9634E-01
HE	3.7518E-02	5.2566E-01	6.3259E-01	6.5721E-01	6.6423E-01
P_{ad}/m*(MeOH+DME)* [kJ/g]	0.0000E+00	1.2794E+00	1.7232E+00	2.2627E+00	2.9674E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-3.3
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 500K for CO:H_2 = 1:3

Ractor temperature [K]	500				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.7500E+02	1.0473E+04	2.2628E+04	2.8624E+04	3.1291E+04
$N_{CH3OH,3}$ [kmol/day]	1.7500E+02	1.0473E+04	2.2628E+04	2.8624E+04	3.1291E+04
$N_{CO,3}$ [kmol/day]	3.2325E+04	2.2027E+04	9.8720E+03	3.8760E+03	1.2090E+03
$N_{H2,3}$ [kmol/day]	9.7150E+04	7.6554E+04	5.2244E+04	4.0252E+04	3.4918E+04
X_{CO} [%]	5.3846E-01	3.2225E+01	6.9625E+01	8.8074E+01	9.6280E+01
F_1 [kmol/day]	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad} [kW]	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	9.6418E-03	9.6486E-03	9.6495E-03	9.6499E-03	9.6482E-03
CE	5.3846E-03	3.2225E-01	6.9625E-01	8.8074E-01	9.6280E-01
HE	3.5897E-03	2.1483E-01	4.6416E-01	5.8716E-01	6.4187E-01
P_{ad}/m*(MeOH+DME)* [kJ/g]	0.0000E+00	3.1306E+00	2.3485E+00	2.5327E+00	3.0708E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-3.4
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 550K for CO:H_2 = 1:3

Reactor temperature [K]	550				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	2.4000E+01	2.2130E+03	9.5400E+03	1.8921E+04	2.6524E+04
$N_{CH3OH,3}$ [kmol/day]	2.4000E+01	2.2130E+03	9.5400E+03	1.8921E+04	2.6524E+04
$N_{CO,3}$ [kmol/day]	3.2476E+04	3.0287E+04	2.2960E+04	1.3579E+04	5.9760E+03
$N_{H2,3}$ [kmol/day]	9.7452E+04	9.3074E+04	7.8420E+04	5.9658E+04	4.4452E+04
X_{CO} [%]	7.3846E-02	6.8092E+00	2.9354E+01	5.8218E+01	8.1612E+01
F_1 [kmol/day]	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad} [kW]	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	1.3141E-03	1.3300E-03	1.3300E-03	1.3300E-03	1.3301E-03
CE	7.3846E-04	6.8092E-02	2.9354E-01	5.8218E-01	8.1612E-01
HE	4.9231E-04	4.5395E-02	1.9569E-01	3.8812E-01	5.4408E-01
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	1.4815E+01	5.5703E+00	3.8314E+00	3.6227E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-3.5
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 600K for $CO:H_2 = 1:3$

Reactor temperature [K]	600				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	5.0000E+00	4.6200E+02	2.6280E+03	8.0400E+03	1.7183E+04
$N_{CH3OH,3}$ [kmol/day]	5.0000E+00	4.6200E+02	2.6280E+03	8.0400E+03	1.7183E+04
$N_{CO,3}$ [kmol/day]	3.2495E+04	3.2038E+04	2.9872E+04	2.4460E+04	1.5317E+04
$N_{H2,3}$ [kmol/day]	9.7490E+04	9.6576E+04	9.2244E+04	8.1420E+04	6.3134E+04
X_{CO} [%]	1.5385E-02	1.4215E+00	8.0862E+00	2.4738E+01	5.2871E+01
F_1 [kmol/day]	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad} [kW]	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	2.7356E-04	2.5759E-04	2.5742E-04	2.5739E-04	2.5741E-04
CE	1.5385E-04	1.4215E-02	8.0862E-02	2.4738E-01	5.2871E-01
HE	1.0256E-04	9.4769E-03	5.3908E-02	1.6492E-01	3.5247E-01
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	7.0967E+01	2.0221E+01	9.0168E+00	5.5920E+00

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-3.6
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 650K for CO:H_2 = 1:3

Reactor temperature [K]	650				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.2000E+00	1.1600E+02	7.0900E+02	2.6100E+03	7.9980E+03
$N_{CH3OH,3}$ [kmol/day]	1.2000E+00	1.1600E+02	7.0900E+02	2.6100E+03	7.9980E+03
$N_{CO,3}$ [kmol/day]	3.2499E+04	3.2384E+04	3.1791E+04	2.9890E+04	2.4502E+04
$N_{H2,3}$ [kmol/day]	9.7498E+04	9.7268E+04	9.6082E+04	9.2280E+04	8.1504E+04
X_{CO} [%]	3.6923E-03	3.5692E-01	2.1815E+00	8.0308E+00	2.4609E+01
F_1 [kmol/day]	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad} [kW]	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	6.5644E-05	6.3756E-05	6.3906E-05	6.3863E-05	6.3865E-05
CE	3.6923E-05	3.5692E-03	2.1815E-02	8.0308E-02	2.4609E-01
HE	2.4615E-05	2.3795E-03	1.4544E-02	5.3538E-02	1.6406E-01
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	2.8264E+02	7.4952E+01	2.7776E+01	1.2014E+01

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-3.7
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 700K for $CO:H_2$ = 1:3

Reactor temperature [K]	700				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	3.0000E-01	3.5000E+01	2.1900E+02	8.5300E+02	3.0930E+03
$N_{CH3OH,3}$ [kmol/day]	3.0000E-01	3.5000E+01	2.1900E+02	8.5300E+02	3.0930E+03
$N_{CO,3}$ [kmol/day]	3.2500E+04	3.2465E+04	3.2281E+04	3.1647E+04	2.9407E+04
$N_{H2,3}$ [kmol/day]	9.7499E+04	9.7430E+04	9.7062E+04	9.5794E+04	9.1314E+04
X_{CO} [%]	9.2308E-04	1.0769E-01	6.7385E-01	2.6246E+00	9.5169E+00
F_1 [kmol/day]	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad} [kW]	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	1.6410E-05	1.9173E-05	1.9341E-05	1.9338E-05	1.9337E-05
CE	9.2308E-06	1.0769E-03	6.7385E-03	2.6246E-02	9.5169E-02
HE	6.1538E-06	7.1795E-04	4.4923E-03	1.7497E-02	6.3446E-02
P_{ad}/m*(MeOH+DME)* [kJ/g]	0.0000E+00	9.3676E+02	2.4265E+02	8.4988E+01	3.1066E+01

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-3.8
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 750K for CO:H_2 = 1:3

Reactor temperature [K]	750				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	1.2000E-01	1.2500E+01	7.8200E+01	3.1000E+02	1.1940E+03
$N_{CH3OH,3}$ [kmol/day]	1.2000E-01	1.2500E+01	7.8200E+01	3.1000E+02	1.1940E+03
$N_{CO,3}$ [kmol/day]	3.2500E+04	3.2488E+04	3.2422E+04	3.2190E+04	3.1306E+04
$N_{H2,3}$ [kmol/day]	9.7500E+04	9.7475E+04	9.7344E+04	9.6880E+04	9.5112E+04
X_{CO} [%]	3.6923E-04	3.8462E-02	2.4062E-01	9.5385E-01	3.6738E+00
F_1 [kmol/day]	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad} [kW]	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	6.5641E-06	6.8411E-06	6.8662E-06	6.8702E-06	6.8658E-06
CE	3.6923E-06	3.8462E-04	2.4062E-03	9.5385E-03	3.6738E-02
HE	2.4615E-06	2.5641E-04	1.6041E-03	6.3590E-03	2.4492E-02
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	2.6229E+03	6.7955E+02	2.3385E+02	8.0475E+01

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Table B-3.9
Values of thermodynamic variables calculated at equilibrium for Methanol synthesis @ 800K for CO:H_2 = 1:3

Reactor temperature [K]	800				
Pressure [atm]	1	10	25	50	100
ε_1 [kmol/day]	5.0000E-02	5.0000E+00	3.2000E+01	1.2600E+02	4.9700E+02
$N_{CH3OH,3}$ [kmol/day]	5.0000E-02	5.0000E+00	3.2000E+01	1.2600E+02	4.9700E+02
$N_{CO,3}$ [kmol/day]	3.2500E+04	3.2495E+04	3.2468E+04	3.2374E+04	3.2003E+04
$N_{H2,3}$ [kmol/day]	9.7500E+04	9.7490E+04	9.7436E+04	9.7248E+04	9.6506E+04
X_{CO} [%]	1.5385E-04	1.5385E-02	9.8462E-02	3.8769E-01	1.5292E+00
F_1 [kmol/day]	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad} [kW]	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	2.7350E-06	2.7356E-06	2.8044E-06	2.7712E-06	2.7751E-06
CE	1.5385E-06	1.5385E-04	9.8462E-04	3.8769E-03	1.5292E-02
HE	1.0256E-06	1.0256E-04	6.5641E-04	2.5846E-03	1.0195E-02
$P_{ad}/m(MeOH+DME)$ [kJ/g]	0.0000E+00	6.5573E+03	1.6607E+03	5.7536E+02	1.9334E+02

CE : Carbon Efficiency (≡carbon in methanol/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol/hydrogen in feed stream)

Appendix C

Equilibrium calculations for System II

(MeOH + DME + WGSR)

Using the flowsheet (Figure C-3), the calculations of equilibrium conversion of carbon monoxide and other component flow rates (kmol/day) were done as follows:

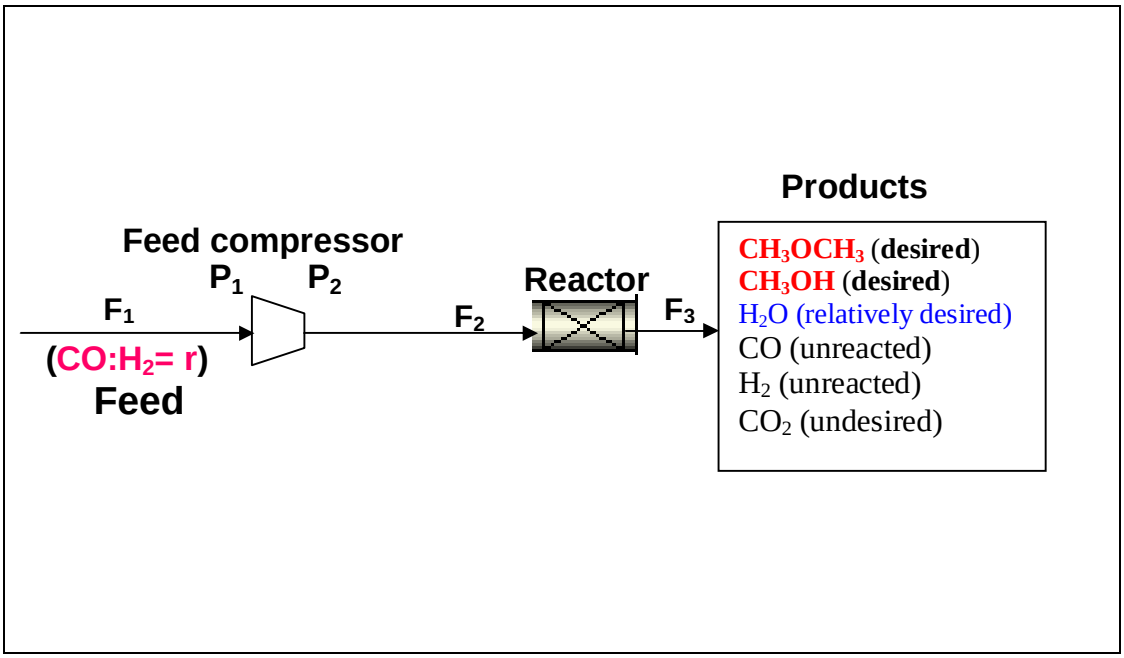

Figure C-3: Flow-diagram for methanol/DME production in System II

- **Preliminary assumptions**

$F_1 = N_{CO,1} + N_{H2,1}$ *(kmol/day); ratio CO:H_2 = r*

$N_{CO,1}$ = 32500 kmol/day

$N_{H2,1}$ = 325000; 65000; 975000 kmol/day, for r = 1:1, 1:2, and 1:3 respectively.

$N_{X,j}$: molar flow rate of the chemical component X in stream j (kmol/day)
F_j: total molar flow rate for stream j (kmol/day)

- **Chemical reactions**:

$CO + 2\ H_2$	=	CH_3OH	e_1	[1]
$2\ CH_3OH$	=	$CH_3OCH_3 + H_2O$	e_2	[2]
$CO + H_2O$	=	$CO_2 + H_2$	e_3	[3]

e_1: extent 1 is the number of kmoles/day of CO consumed at equilibrium in reaction [1]**;**

e_2: extent 2 is the number of kmoles/day of CH3OCH3 generated at equilibrium in reaction [2];

e_3: extent 3 is the number of kmoles/day of CO consumed at equilibrium in reaction [3]

- **Number of moles at equilibrium** (kmol/day):

$N_{CO,3} = N_{CO,2} - e_1 - e_3$ [C-1]

$N_{H2,3} = N_{H2,2} - 2\,e_1 + e_3$ [C-2]

$N_{CH3OH,3} = e_1 - 2e_2$ [C-3]

$N_{CH3OCH3,3} = e_2$ [C-4]

$N_{H2O,3} = e_2 - e_3$ [C-5]

$N_{CO2,3} = e_3$ [C-6]

- **Equilibrium constants:**

$$K_{eq1} = \frac{N_{CH_3OH,3} * \left(N_{CO,3} + N_{H_2,3} + N_{CH_3OH,3} + N_{CH_3OCH_3,3} + N_{H_2O,3} + N_{CO_2,3}\right)^3}{N_{CO,3} * N_{H_2,3}^2 * P^2} \quad [C\text{-}7]$$

$$K_{eq2} = \frac{N_{CH_3OCH_3,3} * N_{H_2O,3}}{N_{CH_3OH,3}^2} \quad [C\text{-}8]$$

$$K_{eq3} = \frac{N_{CO_2,3} * N_{H_2,3}}{N_{CO,3} * N_{H_2O,3}} \quad [C\text{-}9]$$

K_{eq1}, K_{eq2}, and K_{eq3} represent equilibrium constant respectively for the chemical reaction [1], [2], and [3]. The corresponding values of equilibrium constants were taken from Table A-2. After setting pressure values, replacing equations C-1, C-2, C-3, C-4, C5, and C-6 in C-7, C-8 and C-9, a system of three equations and three unknowns were generated and solved by the computer programme Maple 6. The results obtained are displayed in Tables C1-C9 below.

The **Carbon Efficiency** (CE) was computed using the following expression

$$\text{CE} = \frac{moles \cdot of \cdot carbon \cdot in \cdot (CH_3OH + CH_3OCH_3)}{moles \cdot of \cdot CO \cdot fed \cdot to \cdot reactor}$$

The Hydrogen Efficiency (HE) was evaluated using the following expression:

$$HE = \frac{moles \cdot of \cdot hydrogen \cdot in \cdot (CH_3OH + CH_3OCH_3)}{moles \cdot of \cdot hydrogen \cdot in \cdot the \cdot feed}$$

All other variables (CO conversion, compressor work load, etc) were calculated in the same way as previously described.

Table C-1.1
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 400K for CO:H_2 = 1:2

Reactor temperature [K]	400				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	2.1901E+04	2.5443E+04	2.7437E+04	2.8731E+04	2.9755E+04
ε_2 *[kmol/day]*	1.0804E+04	1.2258E+04	1.3122E+04	1.3690E+04	1.4142E+04
ε_3 *[kmol/day]*	1.0212E+04	7.0368E+03	5.0565E+03	3.7663E+03	2.7440E+03
$N_{CH3OCH3}$ *[kmol/day]*	1.0804E+04	1.2258E+04	1.3122E+04	1.3690E+04	1.4142E+04
N_{CH3OH} *[kmol/day]*	2.9300E+02	9.2706E+02	1.1922E+03	1.3507E+03	1.4712E+03
N_{CO} *[kmol/day]*	3.8667E+02	2.0333E+01	6.7892E+00	3.0602E+00	1.4140E+00
N_{H2} *[kmol/day]*	3.1410E+04	2.1151E+04	1.5183E+04	1.1305E+04	8.2347E+03
N_{CO2} *[kmol/day]*	1.0212E+04	7.0368E+03	5.0565E+03	3.7663E+03	2.7440E+03
N_{H2O} *[kmol/day]*	5.9169E+02	5.2211E+03	8.0657E+03	9.9237E+03	1.1398E+04
X_{CO} *[%]*	9.8810E+01	9.9937E+01	9.9979E+01	9.9991E+01	9.9996E+01
$M_{(feed)}$ *[kmol/day]*	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad}*(feed) [kW]*	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	2.2146E+00	2.2146E+00	2.2146E+00	2.2146E+00	2.2146E+00
K_{eq2}	7.4466E+01	7.4466E+01	7.4466E+01	7.4466E+01	7.4466E+01
K_{eq3}	1.4020E+03	1.4020E+03	1.4020E+03	1.4020E+03	1.4020E+03
CE	6.7388E-01	7.8286E-01	8.4421E-01	8.8402E-01	9.1553E-01
HE	5.0766E-01	5.9428E-01	6.4231E-01	6.7341E-01	6.9798E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.3258E+00	1.9873E+00	2.5854E+00	3.3058E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-1.2
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 450K for CO:H_2 = 1:2

Reactor temperature [K]	450				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	1.8279E+04	2.3344E+04	2.5242E+04	2.6790E+04	2.8194E+04
ε_2 *[kmol/day]*	9.0307E+03	1.1226E+04	1.1964E+04	1.2586E+04	1.3160E+04
ε_3 *[kmol/day]*	8.8569E+03	8.8678E+03	7.1669E+03	5.6702E+03	4.2887E+03
$N_{CH3OCH3}$ *[kmol/day]*	9.0307E+03	1.1226E+04	1.1964E+04	1.2586E+04	1.3160E+04
N_{CH3OH} *[kmol/day]*	2.1719E+02	8.9199E+02	1.3134E+03	1.6175E+03	1.8732E+03
N_{CO} *[kmol/day]*	5.3646E+03	2.8845E+02	9.1419E+01	3.9539E+01	1.7601E+01
N_{H2} *[kmol/day]*	3.7300E+04	2.7180E+04	2.1683E+04	1.7090E+04	1.2901E+04
N_{CO2} *[kmol/day]*	8.8569E+03	8.8678E+03	7.1669E+03	5.6702E+03	4.2887E+03
N_{H2O} *[kmol/day]*	1.7379E+02	2.3582E+03	4.7973E+03	6.9162E+03	8.8715E+03
X_{CO} *[%]*	8.3494E+01	9.9112E+01	9.9719E+01	9.9878E+01	9.9946E+01
$M_{(feed)}$ *[kmol/day]*	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad}*(feed) [kW]*	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	1.0808E-01	1.0808E-01	1.0808E-01	1.0808E-01	1.0808E-01
K_{eq2}	3.3272E+01	3.3272E+01	3.3272E+01	3.3272E+01	3.3272E+01
K_{eq3}	3.5435E+02	3.5435E+02	3.5435E+02	3.5435E+02	3.5435E+02
CE	5.6242E-01	7.1827E-01	7.7667E-01	8.2432E-01	8.6750E-01
HE	4.2348E-01	5.4557E-01	5.9260E-01	6.3066E-01	6.6502E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.4440E+00	2.1530E+00	2.7585E+00	3.4662E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-1.3
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 500K for CO:H_2 = 1:2

Reactor temperature [K]	500				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	5.9318E+03	2.1013E+04	2.3288E+04	2.4917E+04	2.6538E+04
ε_2 *[kmol/day]*	2.9170E+03	1.0120E+04	1.1010E+04	1.1609E+04	1.2212E+04
ε_3 *[kmol/day]*	2.8597E+03	9.0893E+03	8.4566E+03	7.2647E+03	5.8244E+03
$N_{CH3OCH3}$ *[kmol/day]*	2.9170E+03	1.0120E+04	1.1010E+04	1.1609E+04	1.2212E+04
N_{CH3OH} *[kmol/day]*	9.7811E+01	7.7286E+02	1.2687E+03	1.6993E+03	2.1135E+03
N_{CO} *[kmol/day]*	2.3708E+04	2.3976E+03	7.5503E+02	3.1811E+02	1.3723E+02
N_{H2} *[kmol/day]*	5.5996E+04	3.2063E+04	2.6880E+04	2.2430E+04	1.7748E+04
N_{CO2} *[kmol/day]*	2.8597E+03	9.0893E+03	8.4566E+03	7.2647E+03	5.8244E+03
N_{H2O} *[kmol/day]*	5.7280E+01	1.0308E+03	2.5532E+03	4.3442E+03	6.3880E+03
X_{CO} *[%]*	2.7051E+01	9.2623E+01	9.7677E+01	9.9021E+01	9.9578E+01
$M_{(feed)}$ *[kmol/day]*	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad}*(feed) [kW]*	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	9.6490E-03	9.6490E-03	9.6490E-03	9.6490E-03	9.6490E-03
K_{eq2}	1.7465E+01	1.7465E+01	1.7465E+01	1.7465E+01	1.7465E+01
K_{eq3}	1.1792E+02	1.1792E+02	1.1792E+02	1.1792E+02	1.1792E+02
CE	1.8252E-01	6.4656E-01	7.1656E-01	7.6668E-01	8.1657E-01
HE	1.3764E-01	4.9086E-01	5.4719E-01	5.8809E-01	6.2866E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.6050E+00	2.3314E+00	2.9570E+00	3.6639E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-1.4
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 550K for CO:H_2 = 1:2

Reactor temperature [K]	550				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	6.1475E+02	1.4594E+04	2.0225E+04	2.2775E+04	2.4790E+04
ε_2 *[kmol/day]*	2.9803E+02	7.0048E+03	9.5501E+03	1.0571E+04	1.1304E+04
ε_3 *[kmol/day]*	2.8593E+02	6.5015E+03	8.1838E+03	7.9710E+03	6.9612E+03
$N_{CH3OCH3}$ *[kmol/day]*	2.9803E+02	7.0048E+03	9.5501E+03	1.0571E+04	1.1304E+04
N_{CH3OH} *[kmol/day]*	1.8699E+01	5.8483E+02	1.1251E+03	1.6329E+03	2.1823E+03
N_{CO} *[kmol/day]*	3.1599E+04	1.1404E+04	4.0909E+03	1.7540E+03	7.4850E+02
N_{H2} *[kmol/day]*	6.4056E+04	4.2313E+04	3.2733E+04	2.7421E+04	2.2381E+04
N_{CO2} *[kmol/day]*	2.8593E+02	6.5015E+03	8.1838E+03	7.9710E+03	6.9612E+03
N_{H2O} *[kmol/day]*	1.2094E+01	5.0330E+02	1.3662E+03	2.6000E+03	4.3428E+03
X_{CO} *[%]*	2.7713E+00	6.4910E+01	8.7412E+01	9.4603E+01	9.7697E+01
$M_{(feed)}$ *[kmol/day]*	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad}*(feed) [kW]*	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	1.3366E-03	1.3366E-03	1.3366E-03	1.3366E-03	1.3366E-03
K_{eq2}	1.0308E+01	1.0308E+01	1.0308E+01	1.0308E+01	1.0308E+01
K_{eq3}	4.7929E+01	4.7929E+01	4.7929E+01	4.7929E+01	4.7929E+01
CE	1.8915E-02	4.4906E-01	6.2231E-01	7.0077E-01	7.6278E-01
HE	1.4331E-02	3.4129E-01	4.7539E-01	5.3814E-01	5.8887E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	2.3080E+00	2.6833E+00	3.2308E+00	3.9099E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-1.5
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 600K for CO:H_2 = 1:2

Reactor temperature [K]	600				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	7.0678E+01	5.0331E+03	1.3283E+04	1.8715E+04	2.2305E+04
ε_2 *[kmol/day]*	3.3487E+01	2.3776E+03	6.2178E+03	8.6371E+03	1.0100E+04
ε_3 *[kmol/day]*	3.0764E+01	2.1621E+03	5.4502E+03	7.0408E+03	7.1879E+03
$N_{CH3OCH3}$ *[kmol/day]*	3.3487E+01	2.3776E+03	6.2178E+03	8.6371E+03	1.0100E+04
N_{CH3OH} *[kmol/day]*	3.7046E+00	2.7776E+02	8.4766E+02	1.4408E+03	2.1044E+03
N_{CO} *[kmol/day]*	3.2399E+04	2.5305E+04	1.3766E+04	6.7442E+03	3.0071E+03
N_{H2} *[kmol/day]*	6.4889E+04	5.7096E+04	4.3884E+04	3.4611E+04	2.7578E+04
N_{CO2} *[kmol/day]*	3.0764E+01	2.1621E+03	5.4502E+03	7.0408E+03	7.1879E+03
N_{H2O} *[kmol/day]*	2.7222E+00	2.1553E+02	7.6757E+02	1.5963E+03	2.9123E+03
X_{CO} *[%]*	3.1213E-01	2.2139E+01	5.7642E+01	7.9249E+01	9.0748E+01
$M_{(feed)}$ *[kmol/day]*	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad}*(feed) [kW]*	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	2.5740E-04	2.5740E-04	2.5740E-04	2.5740E-04	2.5740E-04
K_{eq2}	6.6422E+00	6.6422E+00	6.6422E+00	6.6422E+00	6.6422E+00
K_{eq3}	2.2635E+01	2.2635E+01	2.2635E+01	2.2635E+01	2.2635E+01
CE	2.1747E-03	1.5486E-01	4.0872E-01	5.7585E-01	6.8631E-01
HE	1.6595E-03	1.1828E-01	3.1306E-01	4.4297E-01	5.3090E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	6.6538E+00	4.0728E+00	3.9238E+00	4.3351E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-1.6
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 650K for CO:H_2 = 1:2

Reactor temperature [K]	650				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	1.1361E+01	1.0665E+03	5.0768E+03	1.1383E+04	1.7701E+04
ε_2 *[kmol/day]*	5.2193E+00	4.8963E+02	2.3235E+03	5.1700E+03	7.9237E+03
ε_3 *[kmol/day]*	4.4734E+00	4.1846E+02	1.9592E+03	4.2070E+03	5.9385E+03
$N_{CH3OCH3}$ *[kmol/day]*	5.2193E+00	4.8963E+02	2.3235E+03	5.1700E+03	7.9237E+03
N_{CH3OH} *[kmol/day]*	9.2199E-01	8.7230E+01	4.2991E+02	1.0427E+03	1.8533E+03
N_{CO} *[kmol/day]*	3.2484E+04	3.1015E+04	2.5464E+04	1.6910E+04	8.8607E+03
N_{H2} *[kmol/day]*	6.4982E+04	6.3285E+04	5.6805E+04	4.6442E+04	3.5537E+04
N_{CO2} *[kmol/day]*	4.4734E+00	4.1846E+02	1.9592E+03	4.2070E+03	5.9385E+03
N_{H2O} *[kmol/day]*	7.4588E-01	7.1169E+01	3.6429E+02	9.6301E+02	1.9852E+03
X_{CO} *[%]*	4.8720E-02	4.5690E+00	2.1649E+01	4.7968E+01	7.2736E+01
$M_{(feed)}$ *[kmol/day]*	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad}*(feed) [kW]*	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	6.3868E-05	6.3868E-05	6.3868E-05	6.3868E-05	6.3868E-05
K_{eq2}	4.5796E+00	4.5796E+00	4.5796E+00	4.5796E+00	4.5796E+00
K_{eq3}	1.1998E+01	1.1998E+01	1.1998E+01	1.1998E+01	1.1998E+01
CE	3.4956E-04	3.2815E-02	1.5621E-01	3.5023E-01	5.4464E-01
HE	2.6926E-04	2.5282E-02	1.2047E-01	2.7070E-01	4.2273E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	3.1085E+01	1.0572E+01	6.4159E+00	5.4415E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-1.7
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 700K for CO:H_2 = 1:2

Reactor temperature [K]	700				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	2.4371E+00	2.4042E+02	1.4033E+03	4.5672E+03	1.0799E+04
ε_2 *[kmol/day]*	1.0789E+00	1.0642E+02	6.2058E+02	2.0144E+03	4.7273E+03
ε_3 *[kmol/day]*	8.3813E-01	8.2599E+01	4.7958E+02	1.5350E+03	3.4536E+03
$N_{CH3OCH3}$ *[kmol/day]*	1.0789E+00	1.0642E+02	6.2058E+02	2.0144E+03	4.7273E+03
N_{CH3OH} *[kmol/day]*	2.7930E-01	2.7589E+01	1.6210E+02	5.3851E+02	1.3447E+03
N_{CO} *[kmol/day]*	3.2497E+04	3.2177E+04	3.0617E+04	2.6398E+04	1.8247E+04
N_{H2} *[kmol/day]*	6.4996E+04	6.4602E+04	6.2673E+04	5.7401E+04	4.6855E+04
N_{CO2} *[kmol/day]*	8.3813E-01	8.2599E+01	4.7958E+02	1.5350E+03	3.4536E+03
N_{H2O} *[kmol/day]*	2.4075E-01	2.3817E+01	1.4099E+02	4.7936E+02	1.2737E+03
X_{CO} *[%]*	1.0078E-02	9.9391E-01	5.7933E+00	1.8776E+01	4.3855E+01
$M_{(feed)}$ *[kmol/day]*	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad}*(feed) [kW]*	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	1.9339E-05	1.9338E-05	1.9339E-05	1.9338E-05	1.9338E-05
K_{eq2}	3.3297E+00	3.3297E+00	3.3297E+00	3.3297E+00	3.3297E+00
K_{eq3}	6.9629E+00	6.9629E+00	6.9629E+00	6.9629E+00	6.9629E+00
CE	7.4987E-05	7.3976E-03	4.3177E-02	1.4053E-01	3.3229E-01
HE	5.8389E-05	5.7606E-03	3.3630E-02	1.0954E-01	2.5956E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.3619E+02	3.7807E+01	1.5832E+01	8.8531E+00

CE : Carbon Efficieny (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-1.8
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 750K for CO:H_2 = 1:2

Reactor temperature [K]	750				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	6.6073E-01	6.5835E+01	4.0379E+02	1.5152E+03	4.8881E+03
ε_2 *[kmol/day]*	2.8077E-01	2.7975E+01	1.7154E+02	6.4316E+02	2.0691E+03
ε_3 *[kmol/day]*	1.9227E-01	1.9152E+01	1.1727E+02	4.3747E+02	1.3824E+03
$N_{CH3OCH3}$ *[kmol/day]*	2.8077E-01	2.7975E+01	1.7154E+02	6.4316E+02	2.0691E+03
N_{CH3OH} *[kmol/day]*	9.9182E-02	9.8850E+00	6.0710E+01	2.2885E+02	7.4994E+02
N_{CO} *[kmol/day]*	3.2499E+04	3.2415E+04	3.1979E+04	3.0547E+04	2.6229E+04
N_{H2} *[kmol/day]*	6.4999E+04	6.4887E+04	6.4310E+04	6.2407E+04	5.6606E+04
N_{CO2} *[kmol/day]*	1.9227E-01	1.9152E+01	1.1727E+02	4.3747E+02	1.3824E+03
N_{H2O} *[kmol/day]*	8.8503E-02	8.8233E+00	5.4274E+01	2.0569E+02	6.8664E+02
X_{CO} *[%]*	2.6246E-03	2.6150E-01	1.6033E+00	6.0081E+00	1.9294E+01
$M_{(feed)}$ *[kmol/day]*	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad}*(feed) [kW]*	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	6.8667E-06	6.8667E-06	6.8667E-06	6.8667E-06	6.8667E-06
K_{eq2}	2.5261E+00	2.5261E+00	2.5261E+00	2.5261E+00	2.5261E+00
K_{eq3}	4.3450E+00	4.3450E+00	4.3450E+00	4.3450E+00	4.3450E+00
CE	2.0330E-05	2.0257E-03	1.2424E-02	4.6620E-02	1.5040E-01
HE	1.6010E-05	1.5953E-03	9.7852E-03	3.6726E-02	1.1857E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	4.9082E+02	1.2970E+02	4.7140E+01	1.9350E+01

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-1.9
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 800K for CO:H_2 = 1:2

Reactor temperature [K]	800				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	2.1639E-01	2.1614E+01	1.3427E+02	5.2569E+02	1.9404E+03
ε_2 *[kmol/day]*	8.8152E-02	8.8050E+00	5.4693E+01	2.1409E+02	7.8948E+02
ε_3 *[kmol/day]*	5.1995E-02	5.1929E+00	3.2240E+01	1.2597E+02	4.6131E+02
$N_{CH3OCH3}$ *[kmol/day]*	8.8152E-02	8.8050E+00	5.4693E+01	2.1409E+02	7.8948E+02
N_{CH3OH} *[kmol/day]*	4.0084E-02	4.0040E+00	2.4881E+01	9.7518E+01	3.6139E+02
N_{CO} *[kmol/day]*	3.2500E+04	3.2473E+04	3.2333E+04	3.1848E+04	3.0098E+04
N_{H2} *[kmol/day]*	6.5000E+04	6.4962E+04	6.4764E+04	6.4075E+04	6.1581E+04
N_{CO2} *[kmol/day]*	5.1995E-02	5.1929E+00	3.2240E+01	1.2597E+02	4.6131E+02
N_{H2O} *[kmol/day]*	3.6158E-02	3.6120E+00	2.2453E+01	8.8118E+01	3.2817E+02
X_{CO} *[%]*	8.2580E-04	8.2483E-02	5.1233E-01	2.0051E+00	7.3897E+00
$M_{(feed)}$ *[kmol/day]*	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04	9.7500E+04
P_{ad}*(feed) [kW]*	0.0000E+00	9.1074E+03	1.4761E+04	2.0137E+04	2.6691E+04
K_{eq1}	2.7751E-06	2.7751E-06	2.7751E-06	2.7751E-06	2.7751E-06
K_{eq2}	1.9837E+00	1.9837E+00	1.9837E+00	1.9837E+00	1.9837E+00
K_{eq3}	2.8760E+00	2.8760E+00	2.8760E+00	2.8760E+00	2.8760E+00
CE	6.6581E-06	6.6504E-04	4.1313E-03	1.6175E-02	5.9703E-02
HE	5.3019E-06	5.2958E-04	3.2899E-03	1.2882E-02	4.7557E-02
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.4759E+03	3.8507E+02	1.3416E+02	4.8164E+01

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-2.1
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 400K for CO:H_2 = 1:1

Reactor temperature [K]	400				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	2.0310E+04	2.1387E+04	2.1515E+04	2.1571E+04	2.1606E+04
ε_2 *[kmol/day]*	1.0140E+04	1.0678E+04	1.0742E+04	1.0771E+04	1.0789E+04
ε_3 *[kmol/day]*	1.0132E+04	1.0670E+04	1.0736E+04	1.0765E+04	1.0784E+04
$N_{CH3OCH3}$ *[kmol/day]*	1.0140E+04	1.0678E+04	1.0742E+04	1.0771E+04	1.0789E+04
N_{CH3OH} *[kmol/day]*	3.0000E+01	3.1000E+01	3.1000E+01	2.9000E+01	2.8000E+01
N_{CO} *[kmol/day]*	2.0580E+03	4.4300E+02	2.4900E+02	1.6400E+02	1.1000E+02
N_{H2} *[kmol/day]*	2.0120E+03	3.9600E+02	2.0600E+02	1.2300E+02	7.2000E+01
N_{CO2} *[kmol/day]*	1.0132E+04	1.0670E+04	1.0736E+04	1.0765E+04	1.0784E+04
N_{H2O} *[kmol/day]*	8.0000E+00	8.0000E+00	6.0000E+00	6.0000E+00	5.0000E+00
X_{CO} *[%]*	9.3668E+01	9.8637E+01	9.9234E+01	9.9495E+01	9.9662E+01
$M_{(feed)}$ *[kmol/day]*	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad}*(feed) [kW]*	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	2.1404E+00	2.2044E+00	2.2657E+00	2.2337E+00	2.3310E+00
K_{eq2}	9.0133E+01	8.8891E+01	6.7068E+01	7.6844E+01	6.8807E+01
K_{eq3}	1.2382E+03	1.1922E+03	1.4803E+03	1.3456E+03	1.4117E+03
CE	6.2492E-01	6.5806E-01	6.6200E-01	6.6372E-01	6.6480E-01
HE	9.3785E-01	9.8757E-01	9.9348E-01	9.9603E-01	9.9763E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.0658E+00	1.7173E+00	2.3367E+00	3.0922E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-2.2
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 450K for CO:H_2 = 1:1

Reactor temperature [K]	450				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	1.5596E+04	2.0527E+04	2.1060E+04	2.1287E+04	2.1427E+04
ε_2 *[kmol/day]*	7.7630E+03	1.0218E+04	1.0485E+04	1.0600E+04	1.0672E+04
ε_3 *[kmol/day]*	7.7410E+03	1.0192E+04	1.0460E+04	1.0576E+04	1.0651E+04
$N_{CH3OCH3}$ *[kmol/day]*	7.7630E+03	1.0218E+04	1.0485E+04	1.0600E+04	1.0672E+04
N_{CH3OH} *[kmol/day]*	7.0000E+01	9.1000E+01	9.0000E+01	8.7000E+01	8.3000E+01
N_{CO} *[kmol/day]*	9.1630E+03	1.7810E+03	9.8000E+02	6.3700E+02	4.2200E+02
N_{H2} *[kmol/day]*	9.0490E+03	1.6380E+03	8.4000E+02	5.0200E+02	2.9700E+02
N_{CO2} *[kmol/day]*	7.7410E+03	1.0192E+04	1.0460E+04	1.0576E+04	1.0651E+04
N_{H2O} *[kmol/day]*	2.2000E+01	2.6000E+01	2.5000E+01	2.4000E+01	2.1000E+01
X_{CO} *[%]*	7.1806E+01	9.4520E+01	9.6985E+01	9.8040E+01	9.8702E+01
$M_{(feed)}$ *[kmol/day]*	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad}*(feed) [kW]*	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	1.0663E-01	1.0920E-01	1.0902E-01	1.0903E-01	1.0936E-01
K_{eq2}	3.4854E+01	3.2082E+01	3.2361E+01	3.3611E+01	3.2532E+01
K_{eq3}	3.4749E+02	3.6053E+02	3.5863E+02	3.4728E+02	3.5696E+02
CE	4.7988E-01	6.3160E-01	6.4800E-01	6.5498E-01	6.5929E-01
HE	7.2089E-01	9.4880E-01	9.7338E-01	9.8382E-01	9.9022E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.1092E+00	1.7524E+00	2.3653E+00	3.1149E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-2.3
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 500K for CO:H_2 = 1:1

Reactor temperature [K]	500				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	4.7270E+03	1.7966E+04	1.9764E+04	2.0497E+04	2.0938E+04
ε_2 *[kmol/day]*	2.3380E+03	8.8880E+03	9.7810E+03	1.0148E+04	1.0371E+04
ε_3 *[kmol/day]*	2.3180E+03	8.8180E+03	9.7080E+03	1.0077E+04	1.0306E+04
$N_{CH3OCH3}$ *[kmol/day]*	2.3380E+03	8.8880E+03	9.7810E+03	1.0148E+04	1.0371E+04
N_{CH3OH} *[kmol/day]*	5.1000E+01	1.9000E+02	2.0200E+02	2.0100E+02	1.9600E+02
N_{CO} *[kmol/day]*	2.5455E+04	5.7160E+03	3.0280E+03	1.9260E+03	1.2560E+03
N_{H2} *[kmol/day]*	2.5364E+04	5.3860E+03	2.6800E+03	1.5830E+03	9.3000E+02
N_{CO2} *[kmol/day]*	2.3180E+03	8.8180E+03	9.7080E+03	1.0077E+04	1.0306E+04
N_{H2O} *[kmol/day]*	2.0000E+01	7.0000E+01	7.3000E+01	7.1000E+01	6.5000E+01
X_{CO} *[%]*	2.1677E+01	8.2412E+01	9.0683E+01	9.4074E+01	9.6135E+01
$M_{(feed)}$ *[kmol/day]*	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad}*(feed) [kW]*	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	9.6088E-03	9.6819E-03	9.6421E-03	9.6001E-03	9.6478E-03
K_{eq2}	1.7978E+01	1.7234E+01	1.7499E+01	1.7834E+01	1.7548E+01
K_{eq3}	1.1549E+02	1.1870E+02	1.1770E+02	1.1665E+02	1.1740E+02
CE	1.4545E-01	5.5280E-01	6.0812E-01	6.3068E-01	6.4425E-01
HE	2.1895E-01	8.3212E-01	9.1529E-01	9.4911E-01	9.6938E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.2643E+00	1.8630E+00	2.4510E+00	3.1808E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-2.4
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 550K for CO:H_2 = 1:1

Reactor temperature [K]	550				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	4.8000E+02	1.1740E+04	1.6597E+04	1.8630E+04	1.9817E+04
ε_2 *[kmol/day]*	2.3500E+02	5.7440E+03	8.1250E+03	9.1260E+03	9.7170E+03
ε_3 *[kmol/day]*	2.3000E+02	5.6300E+03	7.9730E+03	8.9660E+03	9.5620E+03
$N_{CH3OCH3}$ *[kmol/day]*	2.3500E+02	5.7440E+03	8.1250E+03	9.1260E+03	9.7170E+03
N_{CH3OH} *[kmol/day]*	1.0000E+01	2.5200E+02	3.4700E+02	3.7800E+02	3.8300E+02
N_{CO} *[kmol/day]*	3.1790E+04	1.5130E+04	7.9300E+03	4.9040E+03	3.1210E+03
N_{H2} *[kmol/day]*	3.1770E+04	1.4650E+04	7.2790E+03	4.2060E+03	2.4280E+03
N_{CO2} *[kmol/day]*	2.3000E+02	5.6300E+03	7.9730E+03	8.9660E+03	9.5620E+03
N_{H2O} *[kmol/day]*	5.0000E+00	1.1400E+02	1.5200E+02	1.6000E+02	1.5500E+02
X_{CO} *[%]*	2.1846E+00	5.3446E+01	7.5600E+01	8.4911E+01	9.0397E+01
$M_{(feed)}$ *[kmol/day]*	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad}*(feed) [kW]*	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	1.2781E-03	1.3378E-03	1.3368E-03	1.3411E-03	1.3394E-03
K_{eq2}	1.1750E+01	1.0311E+01	1.0257E+01	1.0219E+01	1.0268E+01
K_{eq3}	4.5971E+01	4.7819E+01	4.8148E+01	4.8062E+01	4.7992E+01
CE	1.4769E-02	3.6123E-01	5.1068E-01	5.7323E-01	6.0975E-01
HE	2.2308E-02	5.4572E-01	7.7135E-01	8.6566E-01	9.2052E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.9266E+00	2.2093E+00	2.6857E+00	3.3477E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-2.5
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 600K for CO:H_2 = 1:1

Reactor temperature [K]	600				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	5.4000E+01	3.8840E+03	1.0375E+04	1.4748E+04	1.7527E+04
ε_2 *[kmol/day]*	2.6000E+01	1.8680E+03	4.9930E+03	7.1050E+03	8.4560E+03
ε_3 *[kmol/day]*	2.5000E+01	1.7900E+03	4.7910E+03	6.8330E+03	8.1600E+03
$N_{CH3OCH3}$ *[kmol/day]*	2.6000E+01	1.8680E+03	4.9930E+03	7.1050E+03	8.4560E+03
N_{CH3OH} *[kmol/day]*	2.0000E+00	1.4800E+02	3.8900E+02	5.3800E+02	6.1500E+02
N_{CO} *[kmol/day]*	3.2421E+04	2.6826E+04	1.7334E+04	1.0919E+04	6.8130E+03
N_{H2} *[kmol/day]*	3.2417E+04	2.6522E+04	1.6541E+04	9.8370E+03	5.6060E+03
N_{CO2} *[kmol/day]*	2.5000E+01	1.7900E+03	4.7910E+03	6.8330E+03	8.1600E+03
N_{H2O} *[kmol/day]*	1.0000E+00	7.8000E+01	2.0200E+02	2.7200E+02	2.9600E+02
X_{CO} *[%]*	2.4308E-01	1.7458E+01	4.6665E+01	6.6403E+01	7.9037E+01
$M_{(feed)}$ *[kmol/day]*	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad}*(feed) [kW]*	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	2.4720E-04	2.5690E-04	2.5696E-04	2.5674E-04	2.5758E-04
K_{eq2}	6.5000E+00	6.6519E+00	6.6652E+00	6.6768E+00	6.6177E+00
K_{eq3}	2.4997E+01	2.2689E+01	2.2633E+01	2.2632E+01	2.2684E+01
CE	1.6615E-03	1.1951E-01	3.1923E-01	4.5378E-01	5.3929E-01
HE	2.5231E-03	1.8154E-01	4.8483E-01	6.8895E-01	8.1840E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	5.7860E+00	3.5116E+00	3.3714E+00	3.7621E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-2.6
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 650K for CO:H_2 = 1:1

Reactor temperature [K]	650				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	8.5000E+00	8.0000E+02	3.8190E+03	8.6020E+03	1.3424E+04
ε_2 *[kmol/day]*	4.0000E+00	3.7600E+02	1.7940E+03	4.0450E+03	6.3260E+03
ε_3 *[kmol/day]*	3.7000E+00	3.4700E+02	1.6590E+03	3.7500E+03	5.8960E+03
$N_{CH3OCH3}$ *[kmol/day]*	4.0000E+00	3.7600E+02	1.7940E+03	4.0450E+03	6.3260E+03
N_{CH3OH} *[kmol/day]*	5.0000E-01	4.8000E+01	2.3100E+02	5.1200E+02	7.7200E+02
N_{CO} *[kmol/day]*	3.2488E+04	3.1353E+04	2.7022E+04	2.0148E+04	1.3180E+04
N_{H2} *[kmol/day]*	3.2487E+04	3.1247E+04	2.6521E+04	1.9046E+04	1.1548E+04
N_{CO2} *[kmol/day]*	3.7000E+00	3.4700E+02	1.6590E+03	3.7500E+03	5.8960E+03
N_{H2O} *[kmol/day]*	3.0000E-01	2.9000E+01	1.3500E+02	2.9500E+02	4.3000E+02
X_{CO} *[%]*	3.7538E-02	3.5292E+00	1.6855E+01	3.8006E+01	5.9446E+01
$M_{(feed)}$ *[kmol/day]*	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad}*(feed) [kW]*	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	6.1580E-05	6.3027E-05	6.3986E-05	6.4014E-05	6.3933E-05
K_{eq2}	4.8000E+00	4.7326E+00	4.5387E+00	4.5520E+00	4.5642E+00
K_{eq3}	1.2333E+01	1.1925E+01	1.2061E+01	1.2017E+01	1.2014E+01
CE	2.6154E-04	2.4615E-02	1.1751E-01	2.6468E-01	4.1305E-01
HE	4.0000E-04	3.7662E-02	1.7982E-01	4.0489E-01	6.3145E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	2.7856E+01	9.4561E+00	5.7293E+00	4.8698E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-2.7
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 700K for CO:H_2 = 1:1

Reactor temperature [K]	700				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	1.7600E+00	1.7500E+02	1.0220E+03	3.3300E+03	7.8870E+03
ε_2 *[kmol/day]*	8.0000E-01	8.0000E+01	4.6600E+02	1.5190E+03	3.6050E+03
ε_3 *[kmol/day]*	6.5000E-01	7.0000E+01	4.0800E+02	1.3330E+03	3.1810E+03
$N_{CH3OCH3}$ *[kmol/day]*	8.0000E-01	8.0000E+01	4.6600E+02	1.5190E+03	3.6050E+03
N_{CH3OH} *[kmol/day]*	1.6000E-01	1.5000E+01	9.0000E+01	2.9200E+02	6.7700E+02
N_{CO} *[kmol/day]*	3.2498E+04	3.2255E+04	3.1070E+04	2.7837E+04	2.1432E+04
N_{H2} *[kmol/day]*	3.2497E+04	3.2220E+04	3.0864E+04	2.7173E+04	1.9907E+04
N_{CO2} *[kmol/day]*	6.5000E-01	7.0000E+01	4.0800E+02	1.3330E+03	3.1810E+03
N_{H2O} *[kmol/day]*	1.5000E-01	1.0000E+01	5.8000E+01	1.8600E+02	4.2400E+02
X_{CO} *[%]*	7.4154E-03	7.5385E-01	4.4000E+00	1.4348E+01	3.4055E+01
$M_{(feed)}$ *[kmol/day]*	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad}*(feed) [kW]*	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	1.9695E-05	1.8723E-05	1.9284E-05	1.9341E-05	1.9315E-05
K_{eq2}	4.6875E+00	3.5556E+00	3.3368E+00	3.3136E+00	3.3350E+00
K_{eq3}	4.3333E+00	6.9924E+00	6.9878E+00	6.9957E+00	6.9685E+00
CE	5.4154E-05	5.3846E-03	3.1446E-02	1.0246E-01	2.4268E-01
HE	8.3692E-05	8.3077E-03	4.8554E-02	1.5818E-01	3.7443E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.2610E+02	3.4967E+01	1.4642E+01	8.1997E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-2.8
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 750K for CO:H_2 = 1:1

Reactor temperature [K]	750				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	4.7000E-01	4.6000E+01	2.8500E+02	1.0680E+03	3.4470E+03
ε_2 *[kmol/day]*	2.1000E-01	2.0000E+01	1.2500E+02	4.7000E+02	1.5200E+03
ε_3 *[kmol/day]*	1.7000E-01	1.7000E+01	1.0200E+02	3.8300E+02	1.2440E+03
$N_{CH3OCH3}$ *[kmol/day]*	2.1000E-01	2.0000E+01	1.2500E+02	4.7000E+02	1.5200E+03
N_{CH3OH} *[kmol/day]*	5.0000E-02	6.0000E+00	3.5000E+01	1.2800E+02	4.0700E+02
N_{CO} *[kmol/day]*	3.2499E+04	3.2437E+04	3.2113E+04	3.1049E+04	2.7809E+04
N_{H2} *[kmol/day]*	3.2499E+04	3.2425E+04	3.2032E+04	3.0747E+04	2.6850E+04
N_{CO2} *[kmol/day]*	1.7000E-01	1.7000E+01	1.0200E+02	3.8300E+02	1.2440E+03
N_{H2O} *[kmol/day]*	4.0000E-02	3.0000E+00	2.3000E+01	8.7000E+01	2.7600E+02
X_{CO} *[%]*	1.9692E-03	1.9385E-01	1.1908E+00	4.4646E+00	1.4434E+01
$M_{(feed)}$ *[kmol/day]*	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad}*(feed) [kW]*	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	6.1541E-06	7.4122E-06	7.0553E-06	6.8932E-06	6.8543E-06
K_{eq2}	3.3600E+00	1.6667E+00	2.3469E+00	2.4957E+00	2.5326E+00
K_{eq3}	4.2500E+00	5.6646E+00	4.4236E+00	4.3595E+00	4.3518E+00
CE	1.4462E-05	1.4154E-03	8.7692E-03	3.2862E-02	1.0606E-01
HE	2.2462E-05	2.2154E-03	1.3692E-02	5.1262E-02	1.6535E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	4.7175E+02	1.2376E+02	4.5105E+01	1.8535E+01

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-2.9
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 800K for CO:H_2 = 1:1

Reactor temperature [K]	800				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	1.5000E-01	1.4700E+01	9.1600E+01	3.5900E+02	1.3240E+03
ε_2 *[kmol/day]*	6.2000E-02	6.2000E+00	3.8800E+01	1.5200E+02	5.6100E+02
ε_3 *[kmol/day]*	5.0000E-02	4.6000E+00	2.8800E+01	1.1300E+02	4.1800E+02
$N_{CH3OCH3}$ *[kmol/day]*	6.2000E-02	6.2000E+00	3.8800E+01	1.5200E+02	5.6100E+02
N_{CH3OH} *[kmol/day]*	2.6000E-02	2.3000E+00	1.4000E+01	5.5000E+01	2.0200E+02
N_{CO} *[kmol/day]*	3.2500E+04	3.2481E+04	3.2380E+04	3.2028E+04	3.0758E+04
N_{H2} *[kmol/day]*	3.2500E+04	3.2475E+04	3.2346E+04	3.1895E+04	3.0270E+04
N_{CO2} *[kmol/day]*	5.0000E-02	4.6000E+00	2.8800E+01	1.1300E+02	4.1800E+02
N_{H2O} *[kmol/day]*	1.2000E-02	1.6000E+00	1.0000E+01	3.9000E+01	1.4300E+02
X_{CO} *[%]*	6.1538E-04	5.9385E-02	3.7046E-01	1.4523E+00	5.3600E+00
$M_{(feed)}$ *[kmol/day]*	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04	6.5000E+04
P_{ad}*(feed) [kW]*	0.0000E+00	6.0716E+03	9.8409E+03	1.3425E+04	1.7794E+04
K_{eq1}	3.2000E-06	2.8342E-06	2.7779E-06	2.7901E-06	2.7866E-06
K_{eq2}	1.1006E+00	1.8752E+00	1.9796E+00	1.9597E+00	1.9661E+00
K_{eq3}	4.1667E+00	2.8745E+00	2.8770E+00	2.8854E+00	2.8767E+00
CE	4.6154E-06	4.5231E-04	2.8185E-03	1.1046E-02	4.0738E-02
HE	7.3231E-06	7.1385E-04	4.4431E-03	1.7415E-02	6.4215E-02
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.4621E+03	3.8080E+02	1.3253E+02	4.7642E+01

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-3.1
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 400K for CO:H_2 = 1:3

Reactor temperature [K]	400				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	2.2384E+04	2.8183E+04	3.0718E+04	3.1832E+04	3.2302E+04
ε_2 *[kmol/day]*	1.0980E+04	1.3449E+04	1.4568E+04	1.5063E+04	1.5272E+04
ε_3 *[kmol/day]*	9.7590E+03	4.3020E+03	1.7780E+03	6.6700E+02	1.9800E+02
$N_{CH3OCH3}$ *[kmol/day]*	1.0980E+04	1.3449E+04	1.4568E+04	1.5063E+04	1.5272E+04
N_{CH3OH} *[kmol/day]*	4.2400E+02	1.2850E+03	1.5820E+03	1.7060E+03	1.7580E+03
N_{CO} *[kmol/day]*	3.5700E+02	1.5000E+01	4.0000E+00	1.0000E+00	0.0000E+00
N_{H2} *[kmol/day]*	6.2491E+04	4.5436E+04	3.7842E+04	3.4503E+04	3.3094E+04
N_{CO2} *[kmol/day]*	9.7590E+03	4.3020E+03	1.7780E+03	6.6700E+02	1.9800E+02
N_{H2O} *[kmol/day]*	1.2210E+03	9.1470E+03	1.2790E+04	1.4396E+04	1.5074E+04
X_{CO} *[%]*	9.8902E+01	9.9954E+01	9.9988E+01	9.9997E+01	1.0000E+02
$M_{(feed)}$ *[kmol/day]*	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad}*(feed) [kW]*	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	2.2094E+00	2.2499E+00	2.0774E+00	2.5225E+00	6.2407E+00
K_{eq2}	7.4574E+01	7.4501E+01	7.4449E+01	7.4507E+01	7.4489E+01
K_{eq3}	1.3991E+03	1.4246E+03	1.3152E+03	1.5986E+03	3.9495E+03
CE	6.8874E-01	8.6717E-01	9.4517E-01	9.7945E-01	9.9391E-01
HE	3.4654E-01	4.4017E-01	4.8070E-01	4.9847E-01	5.0597E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.5902E+00	2.3594E+00	3.1035E+00	4.0524E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-3.2
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 450K for CO:H_2 = 1:3

Reactor temperature [K]	450				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	1.8603E+04	2.4944E+04	2.7897E+04	2.9980E+04	3.1434E+04
ε_2 *[kmol/day]*	9.1490E+03	1.1837E+04	1.3036E+04	1.3890E+03	1.4506E+04
ε_3 *[kmol/day]*	8.8110E+03	7.3070E+03	4.5340E+03	2.4950E+03	1.0580E+03
$N_{CH3OCH3}$ *[kmol/day]*	9.1490E+03	1.1837E+04	1.3036E+04	1.3890E+03	1.4506E+04
N_{CH3OH} *[kmol/day]*	3.0500E+02	1.2700E+03	1.8250E+03	2.7202E+04	2.4220E+03
N_{CO} *[kmol/day]*	5.0860E+03	2.4900E+02	6.9000E+01	2.5000E+01	8.0000E+00
N_{H2} *[kmol/day]*	6.9105E+04	5.4919E+04	4.6240E+04	4.0035E+04	3.5690E+04
N_{CO2} *[kmol/day]*	8.8110E+03	7.3070E+03	4.5340E+03	2.4950E+03	1.0580E+03
N_{H2O} *[kmol/day]*	3.3800E+02	4.5300E+03	8.5020E+03	-1.1060E+03	1.3448E+04
X_{CO} *[%]*	8.4351E+01	9.9234E+01	9.9788E+01	9.9923E+01	9.9975E+01
$M_{(feed)}$ *[kmol/day]*	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad}*(feed) [kW]*	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	1.0813E-01	1.0853E-01	1.0899E-01	1.0685E-01	1.0711E-01
K_{eq2}	3.3242E+01	3.3245E+01	3.3277E+01	3.3291E+01	3.3255E+01
K_{eq3}	3.5419E+02	3.5577E+02	3.5738E+02	3.5036E+02	3.5098E+02
CE	5.7240E-01	7.6751E-01	8.5837E-01	9.2246E-01	9.6720E-01
HE	2.8776E-01	3.9027E-01	4.3854E-01	6.0073E-01	4.9602E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.7930E+00	2.5841E+00	2.4828E+00	4.1285E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-3.3
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 500K for CO:H_2 = 1:3

Reactor temperature [K]	500				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	6.1510E+03	2.1916E+04	2.5055E+04	2.7476E+04	2.9680E+04
ε_2 *[kmol/day]*	3.0120E+03	8.3930E+03	1.1631E+04	1.2556E+04	1.3409E+04
ε_3 *[kmol/day]*	2.9190E+03	4.3020E+03	6.7990E+03	4.7780E+03	2.7310E+03
$N_{CH3OCH3}$ *[kmol/day]*	3.0120E+03	8.3930E+03	1.1631E+04	1.2556E+04	1.3409E+04
N_{CH3OH} *[kmol/day]*	1.2700E+02	5.1300E+03	1.7930E+03	2.3640E+03	2.8620E+03
N_{CO} *[kmol/day]*	2.3430E+04	6.2820E+03	6.4600E+02	2.4600E+02	8.9000E+01
N_{H2} *[kmol/day]*	8.8117E+04	5.7970E+04	5.4189E+04	4.7326E+04	4.0871E+04
N_{CO2} *[kmol/day]*	2.9190E+03	4.3020E+03	6.7990E+03	4.7780E+03	2.7310E+03
N_{H2O} *[kmol/day]*	9.3000E+01	4.0910E+03	4.8320E+03	7.7780E+03	1.0678E+04
X_{CO} *[%]*	2.7908E+01	8.0671E+01	9.8012E+01	9.9243E+01	9.9726E+01
$M_{(feed)}$ *[kmol/day]*	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad}*(feed) [kW]*	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	9.6705E-03	9.6432E-03	9.6523E-03	9.6661E-03	9.6062E-03
K_{eq2}	1.7367E+01	1.7480E+01	1.7482E+01	1.7475E+01	1.7480E+01
K_{eq3}	1.1804E+02	1.1787E+02	1.1803E+02	1.1818E+02	1.1745E+02
CE	1.8926E-01	6.7434E-01	7.7092E-01	8.4542E-01	9.1323E-01
HE	9.5282E-02	3.6348E-01	3.9466E-01	4.3483E-01	4.7129E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.9068E+00	2.8705E+00	3.5514E+00	4.3405E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-3.4
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 550K for CO:H_2 = 1:3

Reactor temperature [K]	550				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	6.4600E+02	1.5263E+04	2.1423E+04	2.4648E+04	2.7428E+04
ε_2 *[kmol/day]*	3.1000E+02	7.2360E+03	9.9260E+03	1.1180E+04	1.2204E+04
ε_3 *[kmol/day]*	2.9200E+02	6.3450E+03	7.3620E+03	6.3530E+03	4.4980E+03
$N_{CH3OCH3}$ *[kmol/day]*	3.1000E+02	7.2360E+03	9.9260E+03	1.1180E+04	1.2204E+04
N_{CH3OH} *[kmol/day]*	2.6000E+01	7.9100E+02	1.5710E+03	2.2880E+03	3.0200E+03
N_{CO} *[kmol/day]*	3.1562E+04	1.0892E+04	3.7150E+03	1.4990E+03	5.7400E+02
N_{H2} *[kmol/day]*	9.6500E+04	7.3319E+04	6.2016E+04	5.4557E+04	4.7142E+04
N_{CO2} *[kmol/day]*	2.9200E+02	6.3450E+03	7.3620E+03	6.3530E+03	4.4980E+03
N_{H2O} *[kmol/day]*	1.8000E+01	8.9100E+02	2.5640E+03	4.8270E+03	7.7060E+03
X_{CO} *[%]*	2.8862E+00	6.6486E+01	8.8569E+01	9.5388E+01	9.8234E+01
$M_{(feed)}$ *[kmol/day]*	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad}*(feed) [kW]*	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	1.4654E-03	1.3368E-03	1.3363E-03	1.3360E-03	1.3368E-03
K_{eq2}	8.2544E+00	1.0304E+01	1.0312E+01	1.0309E+01	1.0311E+01
K_{eq3}	4.9599E+01	4.7936E+01	4.7932E+01	4.7902E+01	4.7939E+01
CE	1.9877E-02	4.6963E-01	6.5917E-01	7.5840E-01	8.4394E-01
HE	1.0072E-02	2.3887E-01	3.3764E-01	3.9093E-01	4.3746E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	2.9293E+00	3.3549E+00	3.9487E+00	4.6728E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-3.5
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 600K for CO:H_2 = 1:3

Reactor temperature [K]	600				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	7.5000E+01	5.3570E+03	1.4158E+04	2.0136E+04	2.4430E+04
ε_2 *[kmol/day]*	3.5000E+01	2.5000E+03	6.5140E+03	9.0810E+03	1.0760E+04
ε_3 *[kmol/day]*	3.1000E+01	2.1600E+03	5.2100E+03	6.2320E+03	5.5350E+03
$N_{CH3OCH3}$ *[kmol/day]*	3.5000E+01	2.5000E+03	6.5140E+03	9.0810E+03	1.0760E+04
N_{CH3OH} *[kmol/day]*	5.0000E+00	3.5700E+02	1.1300E+03	1.9740E+03	2.9100E+03
N_{CO} *[kmol/day]*	3.2394E+04	2.4983E+04	1.3132E+04	6.1320E+03	2.5350E+03
N_{H2} *[kmol/day]*	9.7381E+04	8.8946E+04	7.4394E+04	6.3460E+04	5.4175E+04
N_{CO2} *[kmol/day]*	3.1000E+01	2.1600E+03	5.2100E+03	6.2320E+03	5.5350E+03
N_{H2O} *[kmol/day]*	4.0000E+00	3.4000E+02	1.3040E+03	2.8490E+03	5.2250E+03
X_{CO} *[%]*	3.2615E-01	2.3129E+01	5.9594E+01	8.1132E+01	9.2200E+01
$M_{(feed)}$ *[kmol/day]*	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad}*(feed) [kW]*	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	2.7444E-04	2.5701E-04	2.5722E-04	2.5743E-04	2.5751E-04
K_{eq2}	5.6000E+00	6.6693E+00	6.6522E+00	6.6394E+00	6.6392E+00
K_{eq3}	2.3298E+01	2.2618E+01	2.2634E+01	2.2638E+01	2.2639E+01
CE	2.3077E-03	1.6483E-01	4.3563E-01	6.1957E-01	7.5169E-01
HE	1.1795E-03	8.4246E-02	2.2361E-01	3.1991E-01	3.9077E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	8.2988E+00	5.0640E+00	4.8240E+00	5.2285E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-3.6
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 650K for CO:H_2 = 1:3

Reactor temperature [K]	650				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	1.2220E+01	1.1580E+03	5.5130E+03	1.2388E+04	1.9419E+04
ε_2 *[kmol/day]*	5.9500E+00	5.2400E+02	2.4800E+03	5.5090E+03	8.4600E+03
ε_3 *[kmol/day]*	5.0000E+00	4.1600E+02	1.9170E+03	3.9480E+03	5.0830E+03
$N_{CH3OCH3}$ *[kmol/day]*	5.9500E+00	5.2400E+02	2.4800E+03	5.5090E+03	8.4600E+03
N_{CH3OH} *[kmol/day]*	3.2000E-01	1.1000E+02	5.5300E+02	1.3700E+03	2.4990E+03
N_{CO} *[kmol/day]*	3.2483E+04	3.0926E+04	2.5070E+04	1.6164E+04	7.9980E+03
N_{H2} *[kmol/day]*	9.7481E+04	9.5600E+04	8.8391E+04	7.6672E+04	6.3745E+04
N_{CO2} *[kmol/day]*	5.0000E+00	4.1600E+02	1.9170E+03	3.9480E+03	5.0830E+03
N_{H2O} *[kmol/day]*	9.5000E-01	1.0800E+02	5.6300E+02	1.5610E+03	3.3770E+03
X_{CO} *[%]*	5.2985E-02	4.8431E+00	2.2862E+01	5.0265E+01	7.5391E+01
$M_{(feed)}$ *[kmol/day]*	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad}*(feed) [kW]*	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	1.7514E-05	6.3449E-05	6.3941E-05	6.3854E-05	6.3903E-05
K_{eq2}	5.5200E+01	4.6770E+00	4.5657E+00	4.5818E+00	4.5748E+00
K_{eq3}	1.5795E+01	1.1907E+01	1.2005E+01	1.1997E+01	1.1996E+01
CE	3.7600E-04	3.5631E-02	1.6963E-01	3.8117E-01	5.9751E-01
HE	1.8964E-04	1.8379E-02	8.7651E-02	1.9761E-01	3.1157E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	3.7980E+01	1.2905E+01	7.8042E+00	6.5543E+00

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-3.7
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 700K for CO:H_2 = 1:3

Reactor temperature [K]	700				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	3.0000E+00	2.6700E+02	1.5570E+03	5.0720E+03	1.2018E+04
ε_2 *[kmol/day]*	1.2000E+00	1.1600E+02	6.7600E+02	2.1910E+03	5.1330E+03
ε_3 *[kmol/day]*	8.0000E-01	8.1000E+01	4.6700E+02	1.4690E+03	3.1410E+03
$N_{CH3OCH3}$ *[kmol/day]*	1.2000E+00	1.1600E+02	6.7600E+02	2.1910E+03	5.1330E+03
N_{CH3OH} *[kmol/day]*	6.0000E-01	3.5000E+01	2.0500E+02	6.9000E+02	1.7520E+03
N_{CO} *[kmol/day]*	3.2496E+04	3.2152E+04	3.0476E+04	2.5959E+04	1.7341E+04
N_{H2} *[kmol/day]*	9.7495E+04	9.7047E+04	9.4853E+04	8.8825E+04	7.6605E+04
N_{CO2} *[kmol/day]*	8.0000E-01	8.1000E+01	4.6700E+02	1.4690E+03	3.1410E+03
N_{H2O} *[kmol/day]*	4.0000E-01	3.5000E+01	2.0900E+02	7.2200E+02	1.9920E+03
X_{CO} *[%]*	1.1692E-02	1.0708E+00	6.2277E+00	2.0126E+01	4.6643E+01
$M_{(feed)}$ *[kmol/day]*	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad}*(feed) [kW]*	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	3.2825E-05	1.9373E-05	1.9259E-05	1.9358E-05	1.9331E-05
K_{eq2}	1.3333E+00	3.3143E+00	3.3619E+00	3.3226E+00	3.3311E+00
K_{eq3}	6.0004E+00	6.9854E+00	6.9545E+00	6.9620E+00	6.9656E+00
CE	9.2308E-05	8.2154E-03	4.7908E-02	1.5606E-01	3.6978E-01
HE	4.9231E-05	4.2872E-03	2.5005E-02	8.1569E-02	1.9388E-01
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.6251E+02	4.5159E+01	1.8881E+01	1.0524E+01

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-3.8
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 750K for CO:H_2 = 1:3

Reactor temperature [K]	750				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	7.5000E-01	7.5000E+01	4.5800E+02	1.7200E+03	5.5510E+03
ε_2 *[kmol/day]*	3.1000E-01	3.1000E+01	1.9100E+02	7.1500E+02	2.2960E+03
ε_3 *[kmol/day]*	1.8000E-01	1.8000E+01	1.1200E+02	4.1600E+02	1.2850E+03
$N_{CH3OCH3}$ *[kmol/day]*	3.1000E-01	3.1000E+01	1.9100E+02	7.1500E+02	2.2960E+03
N_{CH3OH} *[kmol/day]*	1.3000E-01	1.3000E+01	7.6000E+01	2.9000E+02	9.5900E+02
N_{CO} *[kmol/day]*	3.2499E+04	3.2407E+04	3.1930E+04	3.0364E+04	2.5664E+04
N_{H2} *[kmol/day]*	9.7499E+04	9.7368E+04	9.6696E+04	9.4476E+04	8.7683E+04
N_{CO2} *[kmol/day]*	1.8000E-01	1.8000E+01	1.1200E+02	4.1600E+02	1.2850E+03
N_{H2O} *[kmol/day]*	1.3000E-01	1.3000E+01	7.9000E+01	2.9900E+02	1.0110E+03
X_{CO} *[%]*	2.8615E-03	2.8615E-01	1.7538E+00	6.5723E+00	2.1034E+01
$M_{(feed)}$ *[kmol/day]*	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad}*(feed) [kW]*	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	7.1113E-06	7.1344E-06	6.7868E-06	6.8557E-06	6.8709E-06
K_{eq2}	2.3846E+00	2.3846E+00	2.6124E+00	2.5420E+00	2.5240E+00
K_{eq3}	4.1539E+00	4.1601E+00	4.2934E+00	4.3290E+00	4.3425E+00
CE	2.3077E-05	2.3077E-03	1.4092E-02	5.2923E-02	1.7080E-01
HE	1.2205E-05	1.2205E-03	7.4359E-03	2.7949E-02	9.0318E-02
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	5.6958E+02	1.5159E+02	5.5011E+01	2.2558E+01

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Table C-3.9
Values of thermodynamic variables calculated at equilibrium for Methanol/DME Synthesis @ 800K for CO:H_2 = 1:3

Reactor temperature [K]	800				
Pressure [atm]	1	10	25	50	100
ε_1 *[kmol/day]*	2.5000E-01	2.5000E+01	1.5600E+02	6.0900E+02	2.2480E+03
ε_2 *[kmol/day]*	1.0000E-01	1.0000E+01	6.2000E+01	2.4300E+02	8.9500E+02
ε_3 *[kmol/day]*	5.0000E-02	5.0000E+00	3.0000E+01	1.1800E+02	4.2800E+02
$N_{CH3OCH3}$ *[kmol/day]*	1.0000E-01	1.0000E+01	6.2000E+01	2.4300E+02	8.9500E+02
N_{CH3OH} *[kmol/day]*	5.0000E-02	5.0000E+00	3.2000E+01	1.2300E+02	4.5800E+02
N_{CO} *[kmol/day]*	3.2500E+04	3.2470E+04	3.2314E+04	3.1773E+04	2.9824E+04
N_{H2} *[kmol/day]*	9.7500E+04	9.7455E+04	9.7218E+04	9.6400E+04	9.3432E+04
N_{CO2} *[kmol/day]*	5.0000E-02	5.0000E+00	3.0000E+01	1.1800E+02	4.2800E+02
N_{H2O} *[kmol/day]*	5.0000E-02	5.0000E+00	3.2000E+01	1.2500E+02	4.6700E+02
X_{CO} *[%]*	9.2308E-04	9.2308E-02	5.7231E-01	2.2369E+00	8.2338E+00
$M_{(feed)}$ *[kmol/day]*	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05	1.3000E+05
P_{ad}*(feed) [kW]*	0.0000E+00	1.2143E+04	1.9682E+04	2.6850E+04	3.5588E+04
K_{eq1}	2.7351E-06	2.7380E-06	2.8196E-06	2.7635E-06	2.7709E-06
K_{eq2}	2.0000E+00	2.0000E+00	1.9375E+00	2.0077E+00	1.9925E+00
K_{eq3}	3.0000E+00	3.0014E+00	2.8205E+00	2.8641E+00	2.8712E+00
CE	7.6923E-06	7.6923E-04	4.8000E-03	1.8738E-02	6.9169E-02
HE	4.1026E-06	4.1026E-04	2.5641E-03	1.0000E-02	3.6933E-02
P_{ad}*/m(MeOH+DME) [kJ/g]*	0.0000E+00	1.6922E+03	4.3873E+02	1.5349E+02	5.5078E+01

CE : Carbon Efficiency (≡carbon in methanol and dimethyl ether/carbon in feed stream)
HE : Hydrogen Efficiency (≡hydrogen in methanol and dimethyl ether/hydrogen in feed stream)

Appendix D
Calculations of moles of hydrocarbons produced and CO conversion

The volume percentage of each component was calculated as follows:
The calibration gas whose the volume composition is known (2.42%CH_4, 0.20%C_2H_4, 0.50C_2H_6, 10%CO, 5.01%CO_2, balance Ar) was sent through the GC system (FID and TCD), then analyzed (Table D-2).

The molar percentage of a compound E (x_E) in the gas was calculated as follows.

$$x_{E,gas}(\%) = x_{P,cal}(\%) \times \left(\frac{A_{E,gas}}{A_{P,cal}} \right) \qquad [D\text{-}1]$$

where,

$x_{E,gas}(\%)$: is the molar percentage of compound E in the analyzed gas;

$x_{P,cal}(\%)$: is the molar percentage of compound P in the calibration mixture;

$A_{E,gas}$: is the integrated area of the GC peak corresponding to compound E in the analyzed gas;

$A_{P,cal}$: is the integrated area of the GC peak corresponding to compound P in the calibration mixture.

The following expression was used to evaluate the molar percentage of compounds whose calibration data could not be obtained directly from the calibration mixture.

$$x_{B,gas}(\%) = x_{R,cal}(\%) \times RF_{B/R} \times \left(\frac{A_{B,gas}}{A_{R,cal}} \right) \qquad \text{[D-2]}$$

where,

$x_{B,gas}(\%)$: is the molar percentage of compound B in the analyzed gas;

$x_{R,cal}(\%)$: is the molar percentage of the reference compound R in the calibration mixture;

$A_{B,gas}$: is the integrated area of the GC peak corresponding to compound E in the analyzed gas;

$A_{R,cal}$: is the integrated area of the GC peak corresponding to the reference compound P in the calibration mixture.

$RF_{B/R}$: is the relative response factor of the compound B with respect to the reference compound R

The simplest olefin and paraffin in the mixture gas can be taken as reference gas for olefins and paraffins respectively. Table D-2 displays molar response factors for some hydrocarbons. For methanol, ethanol and dimethyl ether, methane is taken as reference compound and the molar response factor for both is likely taken as unit.

The volume of gas entering and reacting in the reactor was assessed using the following expression

$$V_r = \frac{P_{out} V_{out}}{P_{in} T_{out}} T_r \qquad \text{[D-3]}$$

where,

V_e: *is the volume flow rate of gas entering and reacting in the reactor on the catalytic bed (mL/min)*

P_{out}: *is the pressure at which gas exits the GC (~ 1 atm)*

V_{out}: *is the volume flow rate of gas exiting the GC (~10 mL/min)*

T_{out}: *is the temperature at which gas exits the GC (~298K)*

T_r: *is the temperature at which the reactor operates (K)*

P_{in}: *is the pressure at which the reactor operates (atm)*

Knowing the volume flow rate of gas entering/reacting into the reactor (V_r) and the molar fraction or the volume fraction of each compound, we were able to calculate the molar flow rate using the following equation:

$$\dot{N}_E = \left(\frac{x_E}{100}\right) \times \left(\frac{PV_r}{RT} \times 1000\right) \qquad \text{[D-4]}$$

where,

$\dot{N}_E$: is the molar flow rate of compound E [µmol/min]

x_E: is the molar fraction of compound E [%]

P: is the pressure at which the reactor is operating [atm]

R: is the ideal gas constant [=0.082 atm.L/mol/K]

T_r: is the temperature at which the reactor operates [K]

For the CO conversion, we use the following expression to evaluate it:

$$\text{CO conversion (\%)} = 100 \times \left[1 - \frac{A_{CO}^{out}(\%) \times A_{Ar}^{in}(\%)}{A_{CO}^{in}(\%) \times A_{Ar}^{out}(\%)}\right] \qquad \text{[D-5]}$$

with,

$A_{CO}^{out}(\%)$: Percentage area value (displayed by the GC spread sheet) of CO exiting the reactor (measured before loading the catalyst);

A_{CO}^{in}: Percentage area value (displayed by the GC spread sheet) of CO entering the reactor (measured before loading the catalyst);

A_{Ar}^{out}: Percentage area (displayed by the GC spread sheet) of Ar entering the reactor (measured after testing the catalyst);

A_{Ar}^{in}: Percentage area value (as displayed by the GC integrator) of Ar entering the reactor (measured before loading the catalyst).

Table D-1

Results displayed by the GC integrator (Channel A-FID) for hydrocarbons analyzed from the calibration gas

Compound	Area (%)	RT*	Area
CH_4	50.852	0.47	7790981
C_2H_4	12.657	2.21	1675618
C_2H_6	28.427	3.24	3763286

*RT: retention time [minutes]

Table D-2 Molar response factors for hydrocarbon products*

Carbon number	Olefin	Paraffin
2	1.00	1.00
3	0.70	0.74
4	0.78	0.55
5	0.47	0.47
6	0.40	0.40
7	0.35	0.35
8	0.32	0.32

* From J.G. Price, PhD thesis, 1994, University of the Witwatersrand, Johannesburg, South Africa.

Table D-3

Production rate of hydrocarbons over ZnO catalyst @ 573K and 25 atm (experimental programme 2)

Compound	$x_E(\%)$	$\dot{N}_E\left(mmol \cdot \min^{-1}\right)$	$\dot{N}_r\left(mmol \cdot h^{-1} \cdot g_{cat}^{-1}\right)$*
CH_4	0.0050	0.0205	4.1059
C_2H_4	0.0010	0.0044	0.8902
C_2H_6	0.0002	0.0011	0.2315
C_3H_6	0.0009	0.0037	0.7406
CH_3OH	0.1577	0.6453	129.0635
C_4H_8	0.0004	0.0019	0.3858
C_4H_{10}	0.0006	0.0025	0.5138

* $\dot{N}_r = 60 * \dot{N}_E / 0.300 g(catalyst)$

Table D-4

Production rate of hydrocarbons over ZnO catalyst @ 673K and 25 atm (experimental programme 2)

Compound	$x_E(\%)$	$\dot{N}_E\left(mmol \cdot \min^{-1}\right)$	$\dot{N}_r\left(mmol \cdot h^{-1} \cdot g_{cat}^{-1}\right)$
CH_4	0.0266	0.1088	21.7729
C_2H_4	0.0038	0.0159	3.1812
C_2H_6	0.0008	0.0033	0.6777
C_3H_6	0.0027	0.0113	2.2756
CH_3OH	0.1663	0.6802	136.0445
C_4H_8	0.0014	0.0061	1.2233
C_4H_{10}	0.0007	0.0028	0.5756

Table D-5

Production rate of hydrocarbons over 5%Au/ZnO @ 573K and 25 atm (experimental programme 2)

Compound	$x_E(\%)$	$\dot{N}_E\left(mmol \cdot \min^{-1}\right)$	$\dot{N}_r\left(mmol \cdot h^{-1} \cdot g_{cat}^{-1}\right)$
CH_4	0.2105	0.8613	172.2615
C_2H_4	0.0090	0.0368	7.3698
C_2H_6	0.0286	0.1173	23.4671
C_3H_6	0.0274	0.1120	22.4185
C_3H_8	0.01322	0.0540	10.8177
CH_3OH	0.01197	0.0489	9.7976
C_4H_8	0.01399	0.0572	11.4501
C_4H_{10}	0.02462	0.1007	20.1463
C_5H_{10}	0.01006	0.0411	8.2331
C_5H_{12}	0.0173	0.0707	14.1545
C_6	0.0197	0.0807	16.1553
C_7	0.0158	0.0646	12.9289
C_8	0.0109	0.0445	8.9177

Table D-6

Production rate of hydrocarbons over 5 %Au/ZnO @ 673K and 25 atm (experimental programme 2)

Compound	$x_E(\%)$	$\dot{N}_E\left(mmol \cdot \min^{-1}\right)$	$\dot{N}_r\left(mmol \cdot h^{-1} \cdot g_{cat}^{-1}\right)$
CH_4	0.1527	0.6249	124.9816
C_2H_4	0.0053	0.0219	4.3957
C_2H_6	0.0022	0.0091	1.8378
C_3H_6	0.0018	0.0075	1.5189
CH_3OH	0.1909	0.7810	156.2114

Table D-7.1

Signal obtained from the GC-FID (Channel A) of hydrocarbons produced over 5%Au/ZnO/g -Al_2O_3 catalyst @ 573K and 25 atm

Compound	Area (%)	RT	Area
CH_4	21.547	0.57	92535
C_2H_4	4.125	2.16	17714
C_2H_6	13.657	3.03	58648
C_3H_6	5.873	11.16	25222
C_3H_8	6.403	12.05	27495
CH_3OCH_3	34.646	14.16	141993
C_4H_8	1.518	18.41	6517
C_4H_{10}	6.499	19.11	27910
C_5H_{10}	3.804	23.91	16336
C_5H_{12}	1.562	28.1	5933

Table D-7.2

Hydrocarbon - products distribution over 5%Au/ZnO/γ-Al_2O_3 and 5%Au/ZnO/LZ-Y52 catalysts @ 573K and 25 atm

5%Au/ZnO/g -Al_2O_3		**5%Au/ZnO/LZ-Y52**	
Product	Mole distribution (%)	Product	Mole distribution (%)
CH_4	31.4	CH_4	23.6
C_2H_4	2.3	C_2H_4	26.4
C_2H_6	8.5	C_2H_6	8.6
C_3H_6	2.3	C_3H_6	17.1
C_3H_8	2.9	**CH_3OCH_3**	**26.9**
CH_3OCH_3	**48.2**	C_2H_5OH	21.7
CH_3OH	0	C_4H_8	8.9
C_4H_8	0.7		
C_4H_{10}	2.2		
C_5H_{10}	1.0		
C_5H_{12}	0.4		

Table D-8

Signal obtained from the GC-FID (Channel A) of hydrocarbons produced over 5%Au/ZnO/g -Al_2O_3 @ 673K and 25 atm

Compound	Area (%)	RT	Area
CH_4	41.557	0.49	147053
C_2H_4	8.422	2.3	29801
C_2H_6	6.693	3.39	23682
C_3H_6	8.291	11.23	29339
C_3H_8	2.372	11.92	8395
CH_3OCH_3	15.061	**13.77**	**53293**
CH_3OH	1.152	15.08	4077
C_4H_8	3.296	17.48	11664
C_4H_{10}	3.525	18.08	12472
C_5H_{10}	1.461	22.32	5170
C5H12	2.269	22.85	8029

Table D-9

Production rate of hydrocarbons over 5%Au/ZnO/g -Al_2O_3 @ 673K and 25 atm

Compound	$x_E(\%)$	$\dot{N}_E\left(mmol \cdot \min^{-1}\right)$	$\dot{N}_r\left(mmol \cdot h^{-1} \cdot g_{cat}^{-1}\right)$*
CH_4	0.0456	0.1868	18.6818
C_2H_4	0.0035	0.0145	1.4548
C_2H_6	0.0031	0.0128	1.2868
C_3H_6	0.0024	0.0100	1.0025
C_3H_8	0.0008	0.0033	0.3375
CH_3OCH_3	0.0165	0.0677	6.7704
CH_3OH	0.0012	0.0051	0.5179
C_4H_8	0.0010	0.0044	0.4441
C_4H_{10}	0.0009	0.0037	0.3727
C_5H_{10}	0.0002	0.0011	0.1186
C_5H_{12}	0.0005	0.0020	0.2050

* $\dot{N}_r = 60 * \dot{N}_E / 0.600g(catalyst)$

Table D-10

Signal obtained from the GC-FID (Channel A) of hydrocarbons produced over 5%Au/ZnO/LZ Y-52 @ 673K and 25 atm

Compound	Area (%)	RT	Area
CH_4	14.219	0.55	411629
C_2H_4	5.226	2.72	151288
C_2H_6	1.202	4.02	34788
C_3H_6	3.535	11.78	102335
C_3H_8	0.291	12.44	8430
CH_3OCH_3	68.659	**13.97**	**1987581**
C_2H_5OH	3.478	17.73	100687
C_4H_8	1.125	18.47	32563
C_4H_{10}	0.582	18.98	16860
C_5H_{10}	0.672	22.6	19444
C5H12	0.931	23.25	26959

Table D-11

Production rate of hydrocarbons over 5%Au/ZnO/LZ-Y52 @ 673K and 25 atm

Compound	$x_E(\%)$	$\dot{N}_E\left(mmol \cdot \min^{-1}\right)$	$\dot{N}_r\left(mmol \cdot h^{-1} \cdot g_{cat}^{-1}\right)$*
CH_4	0.1278	0.5229	52.2554
C_2H_4	0.0181	0.0738	7.38008
C_2H_6	0.0046	0.0189	1.8890
C_3H_6	0.0085	0.0349	3.4944
C_3H_8	0.0008	0.0033	0.3387
CH_3OCH_3	0.6174	2.5250	252.3191
C_2H_5OH	0.0313	0.1279	12.7820
C_4H_8	0.0030	0.0123	1.2390
C_4H_{10}	0.0012	0.0050	0.5035
C_5H_{10}	0.0011	0.0044	0.4458
C_5H_{12}	0.0016	0.0068	0.6880

* $\dot{N}_r = 60 * \dot{N}_E / 0.600 g(catalyst)$

Table D-12.1

Signal obtained from the GC-TCD (Channel B) of inorganic compounds detected for the 5%Au/ZnO catalyst tested @ 673K and 25 atm

Compound	Area percentage symbol	Value	CO conversion, % (calculated)
CO	A_{CO}^{in} (%)	95.15	5.0
	A_{CO}^{out} (%)	92.68	
Ar	A_{Ar}^{in} (%)	1.32	
	A_{Ar}^{out} (%)	1.35	

Table D-12.2

Signal obtained from the GC-TCD (Channel B) of inorganic compounds detected for the 5%Au/ZnO/g -Al_2O_3 catalyst tested @ 673K and 25 atm

Compound	Area percentage symbol	Value	CO conversion, % (calculated)
CO	A_{CO}^{in} (%)	95.27	8.0
	A_{CO}^{out} (%)	93.32	
Ar	A_{Ar}^{in} (%)	1.31	
	A_{Ar}^{out} (%)	1.39	

Table D-12.3

Signal obtained from the GC-TCD (Channel B) of inorganic compounds detected for the 5%Au/ZnO/LZ Y-52 catalyst tested @ 673K and 25 atm

Compound	Area percentage symbol	Value	CO conversion, % (calculated)
CO	$A_{CO}^{in}(\%)$	95.12	20.2
	$A_{CO}^{out}(\%)$	92.28	
Ar	$A_{Ar}^{in}(\%)$	1.33	
	$A_{Ar}^{out}(\%)$	1.62	

Appendix E

Hydrocarbons formation

Table E-1

Hydrocarbon products distribution for methanol conversion over 5%Au/ZnO @ 400˚C and 1 atm

Product	%
CH_4	42.0
C_2H_4	3.7
C_2H_6	1.6
C_3H_6	2.6
C_3H_8	1.2
C_4H_8	1
C_5+	0.9
CH_3OH	47

Table E-2

Hydrocarbon products distribution for methanol conversion over 5%Au/ZnO/LZ-Y52 @ 400˚C and 1 atm

Product	%
C_1	0.5
C_2	0
C_3	0
C_4	0.5
C_5	1.0
DME	97.8
CH_3OH	0.2

Appendix F

GC trace of hydrocarbons produced

Figure F-1: GC (FID) trace of hydrocarbons produced over 5%Au/ZnO/LZ-Y52 catalyst at 25 atm, 400°C

