OPTIMIZATION OF FORMALDEHYDE PRODUCTION FROM METHANOL

A MASTER'S THESIS
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by
RUWIDA AB.M. IDRES

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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ABSTRACT

OPTIMIZATION OF FORMALDEHYDE PRODUCTION FROM METHANOL

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Formaldehyde is one of the chemicals that is regarded as very important in many chemical industries for the production of building materials and in polymeric resins like phenol formaldehyde.

The main purpose of this project is to investigate the process of formaldehyde production from methanol, from the viewpoint of chemical engineering, by studying the integrated design of the reactor which produces formaldehyde within a specific capacity and under certain operating conditions. In this project, formaldehyde is produced at a rate of 120000 tons/year and a production level of at least 99.1 wt% of formaldehyde and 99.1 wt% of nitrogen. The metal oxide process is developed in the production.

In this project, the process was simulated and optimized by the software Aspen Plus V9. The main focus is on the design and improvement of the reactor in the production process by studying the effect of temperature, pressure, number of tubes, diameter, and length of the reactor was also examined. In this project, formaldehyde is to be produced through a catalytic vapor-phase oxidation reaction.

Keywords: Formaldehyde, methanol, plug flow reactor, catalyst, Aspen Plus.

ÖZ

METANOLDEN FORMALDEHİT ÜRETİMİNİN OPTİMİZASYONU

IDRES, Ruwida AB.M.
Yüksek Lisans, Kimya Mühendisliği ve Uygulamalı Kimya
Danışman: Yrd. Doç. Dr. Enver GÜLER
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Formaldehit, yapı malzemelerinin ayrıca fenol formaldehit gibi polimerik reçinelerin üretimini içeren birçok kimya endüstrisinde oldukça önemli kabul edilen kimyasallardan birisidir.

Bu projenin başlıca amacı, kimya mühendisliği bakış açısından, belirli çalışma koşulları altında ve spesifik kapasite dahilinde formaldehit üreten entegre reaktör tasarımı üzerinde çalışma yapmak ve metanolden formaldehit üretim sürecini incelemektir. Bu projede, yılda 120000 ton seviyesinde formaldehit üretimi ve bunda en az ağırlıkça %99.1 formaldehit ve %99.1 azot üretimini sağlanmaktadır. Üretimde metal oksit işlemi kullanılmıştır.

Bu projede, süreç Aspen Plus V9 yazılımı kullanılarak simüle ve optimize edilmiştir. Başlıca odak noktası, üretim sürecinde reaktörün tasarımı ve geliştirilmesidir. Sıcaklık, basınç, boruların sayısı, reaktördeki çapı ve uzunluğu da incelenmiştir. Bu projede, formaldehit, katalitik buhar-fazlı oksidasyon reaksiyonu ile üretilmiştir.

Anahtar Kelimeler: Formaldehit, metanol, tıkaç akışlı reaktör, katalist, Aspen Plus.

To my husband and my kids

To my father and my mother

To my aunts

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Words of sentences are always never enough to express gratitude and thankfulness for what have been given.

First of all i would like to thank my supervisor Asst. Prof. Dr. Enver Güler, for his guidance and encouragement.

To those who helped me to those who planted optimism in my heart who gave me a hand and had patience with me throughout the period of my studies

My dear husband, Khaled.

My kids Ayhem, Haider and Makdad.

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CHAPTER 1

INTRODUCTION

1.1 Formaldehyde

Formaldehyde is indeed unarguably, considered of the most important chemicals in the world. Because it is used in many important production processes in daily life. Formaldehyde is one of the simplest and most clearly uncomplicated molecule in organic chemistry and formaldehyde is a popular building block for the synthesis of more complex compounds and materials. It has a holistic variety of applications in atmospheric chemical processes or in the incomplete combustion of organic materials [1].

Formaldehyde is a highly active aldehyde gas formed and created by the oxidation or incomplete combustion of hydrocarbons. Formaldehyde is found and developed in vegetables, meat, and fruits, as a metabolic intermediate for the use in many organisms, and as a tissue fixative and preservative. Formaldehyde is found in clouds, fog, and natural rainfall. Formaldehyde formation and oxidation are affected and overblown by temperature and catalyst. Formaldehyde the temperature range of oxidation are 600-700°C [2,3]. Endogenous formaldehyde occurs in the normal physiological system by DNA methylationis a crucial epigenetic modification that has been implicated in numerous cellular processes in mammals, including embryonic development, transcription, X chromosome inactivation, genomic imprinting and chromatin structure [4,5]. Formaldehyde mainly comes from natural and man-made industrial activities and the burning of biofuels [6,7].

In the most conventional physiological brain, formaldehyde is absorbed in the categories of 0.2 to 0.4 mmol/L. At this stage, formaldehyde is the key to memory formation through DNA demethylation cycles and cognitive abilities [6,7]. Formaldehyde reacts highly with proteins and with amino acids and amide side [8,11].

1.2 Physical Properties

Pure Formaldehyde is, at room temperature and atmospheric pressure, colorless, gas, with a brawny and tough displeasing odor, easily soluble in water and ethanol and ether, used pure formaldehyde in solution or in polymeric form (paraformaldehyde). Formaldehyde is a colorless gas under normal conditions and at room temperature and atmospheric pressure, but has a special odor that may displease or create anger as being categorized as possibly carcinogenic [12,15]. Formaldehyde becomes liquid at -19.2°C and cures to the white paste which melts easily in water at -118°C. It is commercially composed of 37% by weight [16,13]. A formaldehyde gas having an ignition temperature of 430°C [17]. Air mixtures are explosive, and they are stable at 80 to 100 % purity, they are quite easy to ignite at 50°C. For the preservation of formaldehyde solution, formaldehyde hydrate and methanol are added in order to maintain the stability, when the storage time is too long, the reaction may still occur. It is also the polymerization can occuras a paraformaldehyde because paraformaldehyde deposition as a clean powder. It is also important to consider the temperature at which HCHO is stored. Formic acid begins to form if the temperature is more than 60°C [12,15]. Formaldehyde is easily oxidized to carbon dioxide in sunlight under atmospheric conditions. It reacts with the trace substances and pollutants in the breeze, so its half-life in urban air under the influence of sunlight is very short. In the absence of nitrogen dioxide, the half-life of formaldehyde during the day is about 50 minutes; in the presence of nitrogen dioxide, it drops to 35 minutes [18]. According to physical properties formaldehyde is divided into three types.

Monomeric Formaldehyde: HCHO is a colorless gas with a foul, intense odor and irritating to the eyes, sense of smell, crag, and lacing. Monomeric HCHO liquefies at -19 °C and solidified at -80°C to give a blank paste. Liquid and vapor phases are easily polymerized at temperatures up to 80°C. further, pure formaldehyde gas does not polymerize between 80°C and 100°C [19,20].

Para-formaldehyde: This is, however, a colorless, granular solid with a piquant and annoying smell. Para-formaldehyde is made by the intensification of ethylene glycol ($HOCH_2OH$), and its composition is clearly understood and illustrated by the form HO-(HCHO)-OH .Paraformaldehyde which melts over an extended temperature scope area (120-170°C), which relies on the degree of polymerization has commonly alike uses of HCHO it is commonly and traditionally used as a exporter of formaldehyde for disinfecting broad areas [20].

Formalin: The main mart for formaldehyde is in aqueous parts, Formalin. It is a clear solution with the distinctive scent of formaldehyde. A methanol is mostly present, from 6-15%, to overpower by the force of polymerization. In watery phase, the predominant conformation of formaldehyde, which is ethylene glycol and polyoxymethylene [20].

1.3 Chemical Properties

Decomposition: At 150°C, formaldehyde, which experiences and undertakes a heterogeneous decomposition to develop CH_3OH and CO_2. Above 350°C, the reaction decomposes to develop carbon dioxide. In this reaction, methanol CH_3OH, methyl formate $C_2H_4O_2$, formic acid HCOOH, carbon dioxide CO_2 and methane CH_4 are produced [21].

Polymerization: The formaldehyde monomer vapor attempts to polymerize at an exact room temperature and at low pressure, when it is at a higher temperature the monomer formaldehyde can be easily preserve for several hours without being polymerized at an equilibrium vapor pressure. In the watery phase, formaldehyde moderate is simply oxidized, even with mild oxidants, such as silver(I) diamine $Ag(NH_3)_2$, and this property has been instrumentally useful in the development and improvement of multiple wet chemical analytical technique and system for formaldehyde [20].

Reduction and Oxidation: Formaldehyde is oxidized by HNO_3, $KMnO_4$ and O_2 to form HCOOH or CO_2 and H_2O. Reactions take place when formaldehyde reacts with basic acids. When the acid is heated, methanol and formic acid are shaped [20,21].

1.4 Applications

Formaldehyde is by no doubt a very relevant chemical used by many industries for the production and the constructions of building materials, textiles, sterilization products, plastics and cosmetics [22]. Formaldehyde is also used to manufacture a large number of chemicals that include; ethylene glycol, dyes, pharmaceuticals, plastics, pharmacy and perfumes [23, 25].

Furthermore, are use in the production of permanent adhesives in the carpet or plywood, and also used in lubricating the strong resin which is always added to sanitary paper products [24,26]. Formaldehyde is a core intermediate material in more than 50 chemical industries such as resins with urea, phenol and melamine [27]. It is, however utilized in industries that have water, minerals and liquids such as shampoos [28].

Formaldehyde is the simplest aldehyde and it is applied as an abrasion cleaner and as a preservative agent for nutrients [30,29] which includes the combination of resins and suntans for use in the undertaking of re-tanning leather. It is used as an antiseptic and to preserve biological samples. The formaldehyde environment has a disinfectant property that is utilized in soap as a bactericide.

Formaldehyde is applied in a very broad-range of hydraulic solution in the sterilization of surgical instruments. It is also utilized as a protective in cosmetics to accelerate its productivity to an extent up against other microorganisms. Small amounts of formaldehyde are also applied in the production of lubricants in leather tanning, paper coating, packaging, photographic chemicals, dyes, drilling wells, and providing wrinkle resistance of fabrics [30,29].

1.5 Alternative Production Methods of Formaldehyde

1.5.1 Production from methane and other hydrocarbon gases

This process is used to produce formaldehyde by oxidation of hydrocarbon gases. During this process hydrocarbon HCHO is generally a dilute solution that is economically advantageous chaperon by other aldehydes and by-products. Moreover, improvements have been made through the use of particular catalysts and better control methods. Wheelers have found out that methane is not oxidized, it just utilizes a temperature of not lessthan 600 degrees Celsius oxidation. The challenge is that the technique which lies in the control and management of the oxidation of the reaction. The oxidation of ethylene, ethane, and propane can control and manage formaldehyde production in a closely similar manner to methane. The upper hydrocarbon gas can be oxidized at a whole lot more and much lower temperature range than methane and ethane. These techniques have been labeled and illustrated by Bibb, as outlined and announced by Wesiewicz and Forlich, using Fe, Ni, Al and other metals as catalysts and pressures up to 135 atm [32,33,34,35,36].

1.5.2 Metal Oxide Process (Formox)

Another method of producing formaldehyde is through immediate catalytic oxidation of methanol and some other by-products like carbon monoxide CO and dimethyl ether C_2H_6O form the oxidation of H_3OH to HCHO with the vanadium pentoxide catalyst. The Formox process was developed by Reichwald Chemicals [32,33,34,35, 36].

There are two technical approaches and ways to manufacture; formaldehyde from methanol at the moment:

1.5.2.1 The Silver Process

Silver is used as a catalyst and the process is divided into two: the methanol ballast and BASF process, these are completely closely similar to one another. Both processes apply and operate with gauze or silver crystals as catalysts [12, 37,40].

1.5.2.2 Oxide Process

The process of oxide was noted to be first used by The Formox process (Metal oxide). The operation is run with an atmospherical pressure and temperatures range from 250 - 400°C with proper temperature control in it [12,37, 39,41].

The technique and procedure used in this project the oxide process. And methanol is converted to formaldehyde 99% in the reactor.

1.6 Methanol

Methanol is commonly known as one of the easiest types of alcohol. It is also called the "colorless" liquid, but oftentimes it is added to the color of the burden so in that case it can be easily identified to ensure that it will not be abused or misused as a beverage. Methanol in ethanol (also known as methanol) is a chemical of the formula CH_3OH. Methanol got named "wood alcohol" because it used to be a by-product of the destructive distillation of wood. Most recently, in today's world industrial methanol is produced and manufactured directly from CO, CO_2, and hydrogen.

Methanol is the easiest and most uncomplicated alcohol, directly connected to the hydroxyl on the methyl. It is a light, volatile, colorless, flammable liquid with a dynamic, distinctive odor that, similar to ethanol [42].

1.7 Scope of Study

1- To design the reactor and determine the temperature and pressure needed inside the reactor to convert the largest amount of methanol to formaldehyde. And also to reduce the oxidation of formaldehyde and the formation of carbon monoxide.

2- To selecting the appropriate property method for this process. This study is performed by using Aspen Plus.

1.8 Research Aims

This project studies carefully on how to improve the formaldehyde production of methanol and oxidation with air in the presence of a catalyst where the broadest possible amount of methanol is transformed and changed to formaldehyde and the lowest possible amount of carbon monoxide the production process.

In this project, formaldehyde is produced from methanol and oxidized with air and while in the presence of a catalyst is iron-molybdenum. Iron-molybdenum catalyst plays an important and irreplaceable role. Its benefits are the comparatively low investment cost, the rise yield, and the stable production. The strongly exothermic reaction is carried out beneath adiabatic conditions [47].

In this project, it is desired to produce about 120,000 tons/year of formaldehyde (1 year = 8000 operating hours), at least 99.1 wt% formaldehyde and 99.1 wt% nitrogen. Sensitivity analysis was also performed to see the effect of both functioning pressure, temperature inside the reactor and the length of the reactor on HCHO/CO.

Sensitivity analysis is a gadget for determining how a process interact to varying key operating and design variables. It can be used to vary one or more flowsheet variables and study the impact of that variation on other variables. It isa valuable gadget for performing “what if” studies. Sensitivity analysis can be used to verify if the solution to a design specificationlies within the range of the manipulated variable. It can also be used to performsimple process optimization.

1.9 Outline

This thesis is divided into five chapters. The first chapter introduces the physical and chemical properties and uses of formaldehyde and defines the production methods of formaldehyde and its production principle. The second chapter briefly introduces the history of formaldehyde production and the theory of reaction kinetics and the influence of operating variables in the production process. The third chapter introduces the selection of production process used in the project, design parameters of the reactor, and sensitivity analysis. The fourth chapter includes the results that are discussed, and then finally, the fifth chapter gives the conclusion regarding the produced data. All these parameters are investigated in Aspen Plus software.

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CHAPTER 2

FORMALDEHYDE PRODUCTION FROM METHANOL

2.1 History

In 1859, Alexandra Mikhailovich Butlerov inadvertently found formaldehyde due to his proposed composition of methylene glycol [CH2(OH)2]. However, in 1869, the German chemist August Hofmann developed a more practical approach, technique, and method for the synthesis of formaldehyde from methanol [47]. In his lab experiments, Butlerov observed the special odor of HCHO solutions while hydrolyzes the methylacetate that decomposed to form formaldehyde and water [49].

The industry of formaldehyde began in the early twentieth century. From 1958 to 1968, the average yearly growth rate of HCHO production reached 11.7%. In the mid-1970s, production was 54% of capacity. From 1988 to 1997, the yearly growth rate of formaldehyde was 2.7% per annum. In 1992, HCHO grade 22nd among the top 50 chemicals in the United States. The yearly production of formaldehyde in 1998 is estimated at 11.3 billion pounds. Since then, global capacity has doubled to reach 32.5 million tonnes of world production by 2012 [17,27, 50, 51].

Formaldehyde is behold as one of the most widely used and manufactured materials in the world and at the center of many chemical research and alternative manufacturing methods due to its comparatively low cost compared to other materials and the acceptability of high purity [52,53].

2.2 Process Description

The series of formaldehyde production consists of 3 main phases the vapor reforming of naturalistic gas leads to the production of syngas, which is transformed to methanol CH_3OH by the methanol synthesis reaction (hydrogenation of CO carbon monoxide), and finally, the partial oxidation of CH3OH leads to HCHO production. Formaldehyde is produced industrially mainly by two main reactions: one is methanol dehydrogenation as shown in the equation (1) and the other is a partial oxidation of methanol as shown in the equation (2). At present, two major processes are being used for the commercial production of formaldehyde: one is the air-deficient process or the silver-contact process, and the formation of formaldehyde by dehydrogenation and the other one is partial oxidation by methanol removal. The latter involves excess air, which is also called the Formox process, where only partial methanol oxidation occurs [54,55].

$$CH_3OH \leftrightarrow HCHO + H_2 \tag{1}$$

$$CH_3OH + 1/2\ O_2 \longrightarrow HCHO + H_2O \tag{2}$$

$$CH_4 + O_2 \longrightarrow HCHO + H_2O \tag{3}$$

The immediate oxidation of methane CH_4 to form formaldehyde HCHO is other widely discussed method [56]. One of the advantages of this process is formaldehyde production in one stage; but, low selectivity and formaldehyde yield are the major case facing this process [57]. Several attempts have been made to improve general selectivity of HCHO up to an approximate value of 80% [58]. In some studies, the problem of low methane conversion (2%) remains unresolved. To date, the elevated CH_4 conversion (24.3%) and yield (9%) have been achieved in that study [59]. Carbon monoxide is a major byproduct of this process. Amongst the catalysts used to partially oxidize CH_4 to HCHO, iron oxide Fe_2O_3 , molybdenum oxide MoO_3 and vanadium oxide V_2O_5 are the most used catalysts [60,62].

Because of methane is chemically weak on the catalyst surface [63]. It is therefore tricky to activate the relatively inactive CH_4 on the catalyst surface used in HCHO production. Further oxidation of formaldehyde may result in the production of carbon dioxide, Where the amount of oxygen used in the reaction should be determined. This affects the transformation of CH_4 into HCHO significantly. A moreover consideration is that the metal oxygen bond on the surface of the catalyst This may increase the activity of the catalyst used but the selectivity to formaldehyde is low [64]. High temperatures increase the kinetics of methane activation and process, but also result in the perfect oxidation of CH_4 to CO_2 instead of HCHO [65].

In order to prevent formaldehyde oxidation with oxygen and carbon monoxide production, the need for is short stay time. A positive effect has been that it has been shown that the height surface area of the catalyst backing can increase CH_4 conversion. In this project in order to produce formaldehyde, a reactor plug flow is needed for the reaction process separation units to separate the formaldehyde from the other resulting materials, as shown in Figure 2.1.

The following figure shows the process diagram to formaldehyde production using metal oxide process

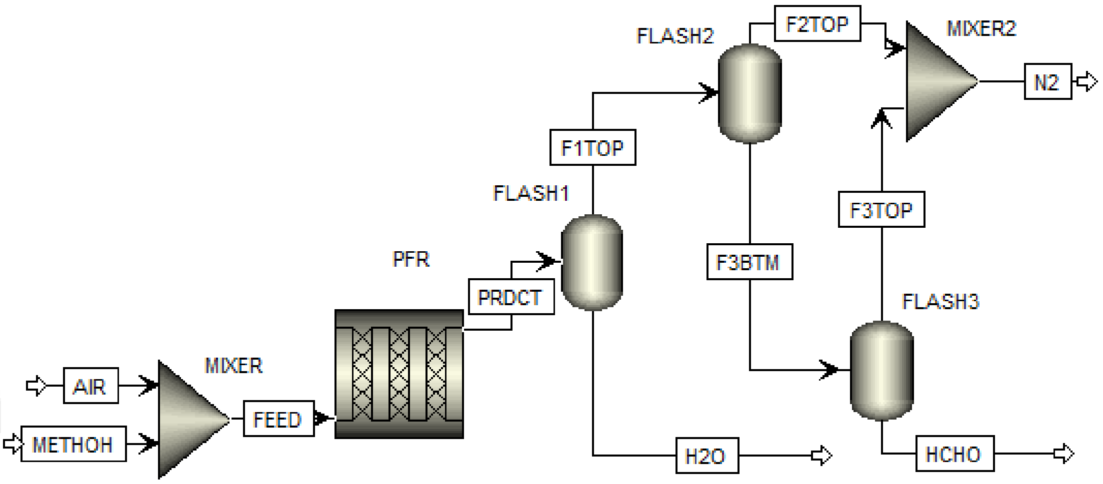

Figure 2.1 Process diagram to produce formaldehyde from methanol

2.2.1 Modeling using ASPEN PLUS

This project depends mainly on the control of the reactor and the type of reactor used. Chemical reactors are vessel that contain the chemical reactions of different types of biological, physical and chemical substances. These reactors play an important role in many chemical processes, such as material conversion, energy consumption, raw materials and environmental safety. In this process, a plug flow reactor was used. Because it bears the high temperature and pressure, reaction taking place at vapor phase, used when oxidation reaction, transfer temperature is good, high conversion rate.

2.2.1.1 Plug Flow Reactor

This is a tubular reactor, which means that it consists of a long cylindrical tube through which the reaction mixture can be used for this process. In this chemical reactor, the material used in the production flows into the pipe, and the reaction between the materials used in the production takes place within the length of the pipe. Reactors of this type are commonly used under adiabatic or non-thermal conditions.

The Merits of Plug Flow Reactor:

1- Flow is a laminar flow, the nature of the reaction medium ie pressure, temperature reactant and product concentration are the same across the flow cross-section.

2- The entire elemental volumes of the reaction medium are held in the reactor for the same amount of time, and the concentration, temperature, and pressure of each elemental volume are the same over time.

3- In addition, there are temperature and reactant concentration gradients along the length of the reactor.

4- The rate of chemical reaction varies along the length of the reactor.

Different reactor models were also found in Aspen Plus such as:

- **Stoichiometric Reactor (R stoic)**

This type is used by the Reaction kinetics which is unbeknown and unimportant, but its stoichiometry and extent are given and the purpose of this type Stoichiometric reactor with particular reaction conversion.

- **Yield Reactor (R Yield)**

These are the reaction stoichiometry and kinetics that are unbeknown and unimportant, but yield allocation is known.

- **Equilibrium Reactor (R Equil)**

simultaneous phase equilibrium and these are the single- and two-phase chemical equilibrium. The user must specify the reaction stoichiometry and the reactor conditions. If no additional specifications are given, “R Equil” model will assume that the reactions will reach equilibrium.

- **Equilibrium Reactor (R Gibbs)**

These are chemical or simultaneous phase and chemical equilibrium. Solid phase equilibrium may be included. This model does not require any sort of reaction stoichiometry; however, the user ought to specify the reactor pressure and enthalpy, or temperature and pressure, or pressure and enthalpy, and purpose of this type of chemical and phase equilibrium by Gibbs free energy minimization, subject to atom balance constraints.

- **Continuous Stirred-Tank Reactor (CSTR)**

These are with the 1, 2 or 3 phase stirred-tank reactor with reaction taking place in the vapor or liquid.

- **Batch Reactor (R Batch)**

In batch reactors, all the reactants are taken place in at the first and processed according to the predetermined route of work through which no material is fed into or removed from the reactor [66].

2.3 Catalyst Types

2.3.1 Silver Catalyst

There are currently two main processes using different catalysts. Silver process (as the name suggests) is an unsupported silver catalyst. The reactor is stuffed with a layer of silver crystals with a thickness of 11-50 mm or filled with silver gauze on a tray. Metallic catalysts are generally not used for catalytic reactions, but methanol dehydrogenation can be used if the reaction is strongly exothermic. Catalysts are very sensitive to metals or sulfur, resulting in catalyst deactivation. This leads to the need for all the tubing in touch with the catalyst to be made of an alloy. The catalyst deactivation time is usually 2 to 7 months [12,33,37,67]. Silver is used between 600°C and 650°C [68].

The catalyst has a significant effect on increasing the amount of formaldehyde produced by methanol. This is Advantages of using silver for the product. Formaldehyde has low investment costs and high yields conversion rates depend on the type of catalyst and the reaction temperature of the reactor at a constant operating pressure. Both catalysts produces high yields of formaldehyde, with different types of processes in terms of operating costs, capital, and process type [69,70].

2.3.2 Iron-Molybdate Catalyst

The iron-moblybdenum Fe-Mo catalyst was found in the year 1926. By the year 1931, Adkins and Perterson collectively wrote an essay were they had examined iron-moblybdenum and iron, moblybdenum [71]. The conclusions and assertions from their studies when molybdenum is used as a catalyst, a surplus of methanol is needed, and furthermore, when using iron as a catalyst, formaldehyde would not desorb and continuous reacting to carbon oxides. The found mixture between the two were in equal amounts, however, this gave perfect results and this is however acclaimed to be the most commonly used catalyst today [71].

2.3.3 Vanadium-Oxide Catalyst

The vanadium-oxide V_2O_5 catalyst could be applied as a replaceable, substitute to Fe-Mo catalyst while operating an oxidation [33,34,37,72,73]. This is, however, not the famous catalyst that is known to be used commercially, however, studies are being conducted on this catalyst. For example, in a paper that was written by Häggblad et al for instance the dispersal of vanadium has been looked at. They had arrived at an assertive derivation that is vanadium more volatile than molybdate when deterioration [72]. While Massa et al. They studied a catalyst a spinel-type that consists of Fe, Mo, V_2 and oxides. Where the conclusion was that the use of this system was more less volatile than the Fe-Mo and the V_2-O_2 catalyst [37].

2.4 Theory

2.4.1 Equations and reaction kinetics

Formaldehyde is produced from exothermic oxidative and removes hydrogen from methanol using heat.

$$CH_3OH + 1/2O_2 \rightarrow HCHO + H_2O \qquad (1)$$

$$-r_{CH3OH\left(\frac{kmol}{kg}cat.s\right)} = 4.762 \times 10^{-5} \times \exp\left[-17630 \times \left(\frac{1}{T} - \frac{1}{485}\right)\right] P_{CH3OH}^{0.5}\, P_{O2}^{0.1} \quad (1)$$

r: is rate (kmol/kg cat.s)

T: is temperature (k)

P: partial pressure (N/m^2)

The general law expression will be:

$$r = k' exp^{-E/R[\frac{1}{T}]}$$

k': is kinetic factor

E: is the activation energy (kJ/kmol)

T: is temperature (k)

R: is universal gas constant (cal/mol k)

Since the value of the kinetic data entered in the ASPEN PLUS in the first reaction can be known from the equation,

$k' = 4.762 \times 10^{-5}$

$T = 485\ K$

An unknown variable E can be calculated from this equation

$$-\frac{17630}{T} = -\frac{E}{R}[\frac{1}{T}]$$

$$-\frac{E}{R} = -17630$$

$$E = R \times 17630$$

$$E = 8.314 \times 17630 = 146576\ kJ/kmol$$

In this case is chosen POWERLAW, because it is reaction with simple kinetics

In addition formaldehyde may undergo a complete oxidation [66]:

$$HCHO + 1/2O_2 \rightarrow CO + H_2O \qquad (2)$$

$$-r_{HCHO} = 2.8246 \times 10^{-10} \exp[-8710 \times (\frac{1}{T} - \frac{1}{485})]\ ]\ P_{O2}\, P_{HCHO}\ /[1 + [212818.09 \exp[-5290\ (\frac{1}{T})]P_{HCHO}$$

So the general equation

r = (kinetic factor) (driving force expression)/(adsorption term)

Since the value of kinetic data input in ASPEN PLUS in the second reaction (R-2) can be known from the equation:

So kinetic factor;

$$r = k'\, exp^{-E/R(\frac{1}{T})}$$

$k' = 2.8246 \times 10^{-10}$

In order to find E,

$$-\frac{8710}{T} = -\frac{E}{R}(\frac{1}{T})$$

$$\frac{E}{R} = 8710$$

$$E = 8.314 \times 8710 = 72414.9\ kJ/kmol$$

$T = 485\ K$

Driving force for the Non-reversible is the power each reactant expression is given as

$$K_1 \pi_{i=1}^{N} C_i - K_2 \pi_{j=1}^{N} C_j \qquad (3)$$

Ci and C_j are the concentration terms

K_1 is the first term in driving force

K_2 is the second term in driving force

Adsorption term is reactions depends on the assumed adsorption mechanism

$$1 + \pi_{j=1}^{N} K_i C_i^{\alpha} \qquad (4)$$

Ci is the concentration terms

Thus, this explains the value of A in adsorption

$A = In\ (kt)$

$= In\ (212818.09) = 12.268$

And

$B = -5290$

To enter these equations in ASPEN PLUS, (Langmuir-Hinshelwood -Hougen-Watson) (LHHW) is chosen because here catalyst is used to enhance the reaction. And also that this model takes into account the adsorption process occurring over the sunfare and more accurate in concentration related to rate equation. In these casesa dsorption the different Reactive substances on the catalyst can be an important process that affects the reaction rate.

2.4.2 Thermodynamic models

In processes, choice of a thermodynamic model is very important to attain precise process simulation. To choose the appropriate thermodynamic model for the system, must know the system and the mixture used in the simulation. Thermodynamic models can be classified into two types:

2.4.2.1 Equation of state

An equation of state is a relationship between molar volume, temperature, pressure, the fugacity, enthalpy, and is an algebraic equation. This equation is used to calculate these properties for any density and then properties can be determined for steam and liquid. This equation is used to polar materials as well as for materials near or above critical temperature and systems that carry light gases and hydrocarbons [84].

2.4.2.2 Liquid-state activity-coefficient model

Liquid state activity - the coefficient of the model is the better choice to most chemical systems which operate under critical temperature. This equation is only used when calculating liquid state fugacity and enthalpies of mix. This models grant algebraic equations for the activity coefficient (ɣi) uses as a function to composition and temperature [84].

2.4.3 Overall Selectivity

The overall selectivity is the ratio of the quantity of one component produced to the quantity of another component produced. Or telles us how one product is desired over another one is undesired when have multiple reactions. Through overall selectivity to know the ratio of formaldehyde produced to the quantity of carbon monoxide produced. Selectivity can be calculated from the following equation [83].

S_i = total amount of speies i / total amount of production of interest

S_{HCHO} = Overall selectivity =

Amount of HCHO formed /Amount of production of interest (CO formed)

Through this theory we can know the overall selectivity to formaldehyde produced

2.5 Operational Variables

In this section, the amount of temperature used, the pressure required, and the size of the reactor that contributes to the production will be clarified and the production amount of formaldehyde and also the fraction of formaldehyde over carbon monoxide (selectivity fraction of formaldehyde) will be investigated.

2.5.1 Temperature

Temperature plays a large role in oxidation of methanol with air, and formaldehyde production. In this The project, the process of metal oxide is used and with a iron-molybdenum precipitated agent. This process operates between temperature 250-400 °C. Until the catalytic agent is activated and produced formaldehyde.

2.5.2 Pressure

In this project, pressure is used in the reactor, and this pressure helps to activate the catalyst and obtain a high proportion of formaldehyde and a small amount of carbon monoxide.

2.5.3 The size and number of tubes

In this process, the component flow reactor is used. It contains a group of pipes where the reacting material moves through the tubes. The pipes help the speed of movement, ie, the entry of reactive materials on the one hand and the exit of the resulting materials on the other hand.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Process Description

In this work, a simplified reaction process, oxidation of methanol by air, to produce formaldehyde is considered. The simulation process flow diagram represented by the Aspen Plus flow is shown in Figure 3.2.

The first stage of the formaldehyde production process is to introduce air into the mixer at about 1195 kmol /hour shown as **AIR** in process flow diagram. The air contains oxygen and nitrogen with an oxygen content of 21% air, corresponding to 250.95 kg / hour and a nitrogen ratio of 79%, corresponding to 944.05 kg/hour. At this stage the temperature and pressure of air and methanol strong is 300°C and 42 bar.

In the meantime, methanol was introduced into the mixer at a flow rate of 500 k mol/hour at a flow rate **METHOH** of 300°C and 42 bar. 1195 kmol/hour of air is required per 500 kmol /hr of methanol. Air and methanol are mixed in a mixer at a temperature of 300°C and a pressure of 42 bar. The mixture of methanol and air flows from the mixer to the feed (the connector between the mixer and the reactor). There is no chemical reaction at this stage.

The mixture then flows into the reactor from the **FEED**, as shown in Figure 3.2. There methanol reaction and oxidation with oxygen and dehydrogenation reactions occurred at the reactor. The presence of an iron-molybdenum catalyst inside the reactor witha bed porosity of 0.5, the particle density of 2 g/cm^3. The temperature is not less than 300°C, the pressure is 42 bar. At this stage, the amount of methanol is completely converted to formaldehyde, with a few exceptions, among other gases so conversion is 100%. Most of the formaldehyde is formed in the reactor. A further reaction takes place between formaldehyde and the oxygen produced by the carbon monoxide and water vapor. As we observed in equation 2.

$CH_3OH + 1/2\ O_2 \rightarrow HCHO + H_2O$ (1)

$HCHO + 1/2\ O_2 \rightarrow CO + H_2O$ (2)

After that the flash separation process begins with the first unit FLASH 1 in the production process, as shown in the Figure 3.2. In this unit, formaldehyde and nitrogen are separated from the water and then formaldehyde and nitrogen are transferred to the second unit. FLASH 2 separates the nitrogen from formaldehyde as shown in Figure 3.2. Finally, the final stage of the production process enter formaldehyde into FLASH 3 and the remaining nitrogen is separated from the formaldehyde to yield 99% by weight of formaldehyde.

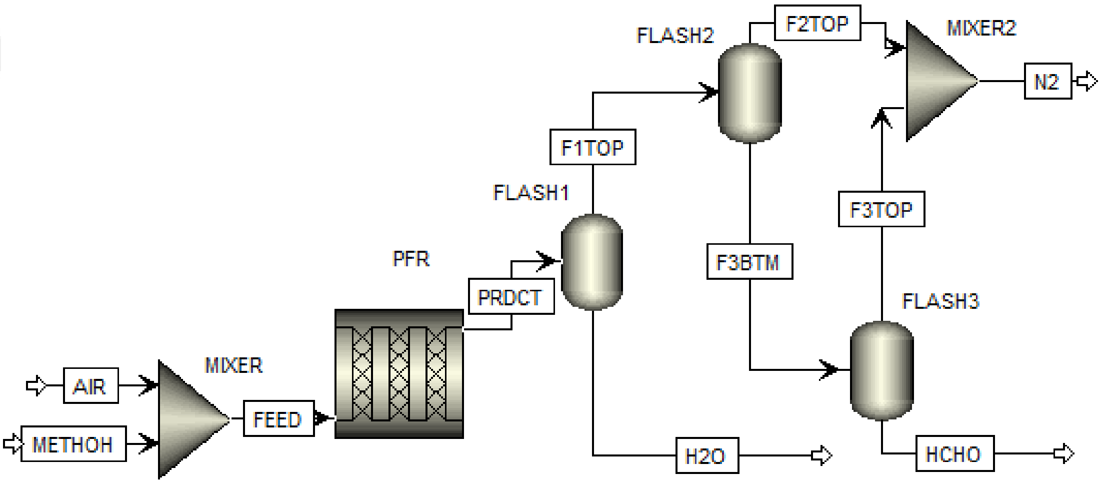

Figure 3.2: Process diagram to produce formaldehyde from methanol

3. 2 Methodology for Aspen Plus Modeling

The operation of producing formaldehyde from methanol is simulated using software ASPEN PLUS V9 which is a simulation software with an excellent reference and instruction manual that is used for the simulation of the process that ASPEN PLUS does not stay until each process condition is commenced the calculation. Any changes to the data are automatically propagated anywhere in the program and all necessary recalculations are performed immediately.

ASPEN is an abbreviation of Advanced Process Engineering System [66]. It is based on one flowchart simulation. Flowchart simulation is computer software for quantitative modeling of a chemical processing plant.

Therefore, the simulation of the whole chemical process from raw material to finished product is symbolically represented by different icons, where each icon represents a unit operation, a chemical process, an input/output material flow, an input/output energy flow. In flowchart notation, there is a block icon and stream icon. Aspen Plus allows us to predict the behavior of the process. This complex and broad package is available for nearly almost every aspect of the engineering process from the design phase through the cost and the benefit analysis. It has a built-in model library of distillation columns, separators, heat exchangers, reactors and more. The custom or appropriate models can extend its model library. These user models are often created by using Fortran subroutines or Excel worksheets and added to their model library.

It is important to note that Aspen plus has a built-in attribute database of thermodynamic and physical parameters. While calculating the flowchart, any missed-out parameters could be automatically estimated and evaluated by the various contribution methods.

The Merits of using Aspen Plus

The use of process simulators is beneficial in all phases of the plant: research and development, design and production. In research and development, they help reduce laboratory testing and pilot plant operations. In the design phase, there are a variety of alternatives to compare, the development can be more rapid. Finally, in the production phase, they can be used for risk-free analysis of various hypothetical scenarios [66].

The demerits of using Aspen Plus

Manually solving a problem often forces someone to think more deeply about the problem, find new ways to solve the problem, and more closely assess and reassess the assumptions. The shortcomings of the process flow simulator may be due to the lack of detailed interaction with the problem. On the one hand, it hides the complexity of a problem so you can focus on the real problem [66].

2.3.1 The Property Method

The attribute method is a set of models used to calculate thermodynamics, kinetics, and thermodynamics and transport properties. Aspen Plus includes a number of built-in attribute methods that are sufficient for most applications. An activity coefficient is used in thermodynamics to calculation for deviations from ideal conduct in a mixture of Chemicals.

The model based on the activity coefficient is "NRTL" (Non-Random-Two-Liquid), which describes the vapor-liquid equilibrium and the liquid-liquid equilibrium of strongly non-ideal solutions. The NRTL model can handle any combination of polar and non-polar compounds to achieve very strong nonidealities [74]. "UNIFAC" (UNIversal Functional Activity Coefficient) and "UNIQUAC" the universal QUASI Chemical Activity Coefficient. Models typically performs well in low pressure and polar compound systems far from the critical area. They are the best method of representing a highly non-ideal liquid mixture at low pressure [75].

The state equation model is Peng – Robinson (PENG-ROB). The state of the other cubic equations produce results that are not very accurate, but they provide sufficient vapor and liquid descriptions and are sufficient for thermodynamic calculations for non- Polar and hydrogen-free pure fluids and blends and PENG-ROB main fractionator for pressurizing applications up to several hundreds of atmospheres in refinery main fractionator and hydrogen-rich application reformer, hydrofiner, lubrication oil equipment, deasphalting equipment, gas processing cryogenic as processing air separation and hydrocarbon separation demethanizer separators, petrochemicals light hydrocarbon separation series quenching tower and substituted hydrocarbon units acrylonitrile units and chemical ammonia units.

The "PENG-ROB" was used in this process for the production of formaldehyde from methanol because it provides sufficient vapor and liquid descriptions. It is also suitable for all temperature and pressure.

PENG-ROBINSON used for different applications [76] :

- Refinery
- Gas Processing
- Petrochemicals
- Chemicals

The general equation for PENG-ROBINSON is:

$$p = \frac{RT}{V-b} - \frac{a}{V^{2+}\quad 2bv - b^2} \qquad [6]$$

Where:

P is pressure

T is temperatue

R is ideal gas constant

V is molar volume

a is measure of the attractive forces between the molecules

b is the related to the size of the molecules

3.3 Process Conditions and Reactions

3.3.1 Modeling assumptions

In this project, emphasis was on the reactor unit and it was designed for formaldehyde production with the specified capacity.

MIXER: Mixing of pure methanol with air,is performed in the mixer the components in mixer are in the vapor phase andliquid phase, input stream temperature is 300°C ,pressure is 42 bar, output temperature 293°C.

REACTOR: The type of reactor used in this process is reactor with specified temperature. The reaction takes place in the vapor phase, Input temperature is 300°C, and pressure is 42 bar, output temperature 300°C, and pressure 42 bar. Reactor length is 3.0480 m, and diameter is 0.0254 m. Catalystiron, molybdenum is present in the reactor, a bed voidage of 0.5, and particle density of 2 g/cm^3.

3.3.2 Reaction Conditions

Through this process, vaporized methanol is mixed with air in the reactor and formaldehyde is formed. The reaction is described by the reaction:

$CH_3OH + 1/2\ O_2 \rightarrow HCHO + H_2O$ (1)

From this equation (1) the reaction of oxygen with methanol produces formaldehyde as well as carbon monoxide and this is an exothermic reaction and converts the entire amount of methanol to formaldehyde

$HCHO + 1/2\ O_2 \rightarrow CO + H_2O$ (2)

The formation of carbon monoxide in the reaction between formaldehyde and oxygen as the equation (2) is an exothermic reaction. The formation of these by-products can occur when formaldehyde is desorbed from the catalyst at a slower rate. The desired condition is that formaldehyde is produced during this process with a large quantity and a small amount of byproducts [78].

3.4 Sensitivity Analysis

Sensitivity analysis allows users to study the effects of input variables on the changes of process output. Sensitivity analysis is a tool that helps to determine how the process responds to changes in key operations and design variables. It can be used to change one or more flowchart variables and study the effect of this change on other flowchart variables. This is a valuable tool for conducting "if" research. It can use sensitivity analysis to verify that the design specifications are within the controlled variables. it also be used it to perform simple process optimization. The result may be drawn to visualize the relationship between different variables. Sensitivity block changes in the inputs do not affect the simulation. Sensitivity studies run independently of the basic simulation.

Only the quantities entered into the flow chart should be changed or manipulated. Multiple inputs can vary. It can also work on simulating each set of manipulated variables [79].

3.4.1 Effect of Temperature

Temperature is an important variable to the production process. The temperature significantly affects the production process of formaldehyde. The higher the temperature, the greater the amount of formaldehyde produced, and the lower the amount of carbon monoxide produced. Actually, sensitivity analysis is performed to determine the temperature the appropriate inside the reactor PFR to produce formaldehyde. In a simulation model the starting point is set to the temperature is 100°C and end point is 400°C. This is further clarified in Chapter IV.

3.4.2 Effect of Pressure

Pressure is one of the important variables that affect the production process. Increased pressure increases the amount of material being produced as it increases the selectivity to formaldehyde, but this high pressure affects the reactors and other machinery used in the production process and can cause explosion and damage of these tools. Sensitivity analysis is used to study the effect of pressure within the reactor on the production process and the starting point to the pressure is 1 bar and the end point is 42 bar, as described in Chapter 4.

3.4.3 Effect of the Length of Reactor

The length of the reactor is an important of variables affecting the production process. Sensitivity analysis are conducted to study the effect of reactor length on formaldehyde production. In a simulation model The starting point is determined as 0.1 m and end point as 6 m. Chapter IV explains more about this.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Temperature and Pressure

4.1.1 Effect of Temperature and Pressure on Formaldehyde Production

Temperature plays a major role in the oxidation of methanol by air as well as it activates the iron-molybdenum catalyst. The aim of this project is to produce about 15000 kg/hr and 99 wt% of formaldehyde and pure hydrogen 99.1 wt%. Therefore the appropriate temperature and pressure must be determined by the reaction in inside the reactor to obtain the required quantity of formaldehyde. As shown in Figure 4.1, the change is done in temperature and pressure only but, the other variables are constant, where the length of the reactor is 3m, the diameter of the pipes are 0.0025 m and their number is 500 pipes and total flow rate is 50497 kg/hr. As shown in Figure 4.1, there is a small amount of formaldehyde at 100°C because this temperature is not enough to oxidize the methanol with oxygen and stimulate the catalyst. After 200°C, we notice an increase in the amount of formaldehyde produced because the oxidation of methanol with oxygen and also the stimulation of the catalysts requires high temperature. So we deduce the best temperature to the production process is 300°C. According to the oxide process, the formaldehyde production is a mixture of methanol and oxygen they interact at a temperature ranging from 250-400°C with the present catalyst of iron oxide as well as molybdenum [81].

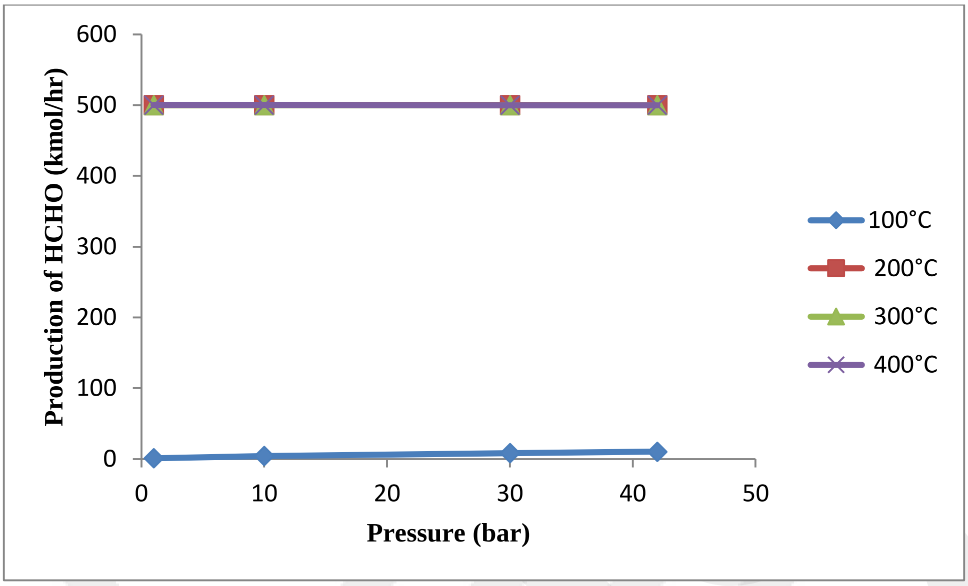

Figure 4.1 Effect of temperature and pressure on formaldehyde production

4.1.2 Effect of Temperature and Pressure on Carbon Monoxide Production

The carbon monoxide is formed when formaldehyde absorbs the catalyst and reacts with the oxygen. Therefore, this interaction should be minimized until 99.1%wt of formaldehyde is obtained. Therefore, it is necessary to determine the appropriate temperature within the reactor where this interaction does not occur. As shown in Figure 4.2 the temperature and pressure are changed only and the rest of the variables are constant. In Figure 4.2 the amount of carbon monoxide produced is the highest at 100°C and it decreases while increasing the temperature. So when the temperature increase the amount of carbon monoxide produced decreases. In temperature ranges of 200 – 400°C the conversion of methanol to formaldehyde is almost complete. In other words, the undesired side reactions do not occur at high temperatures [78].

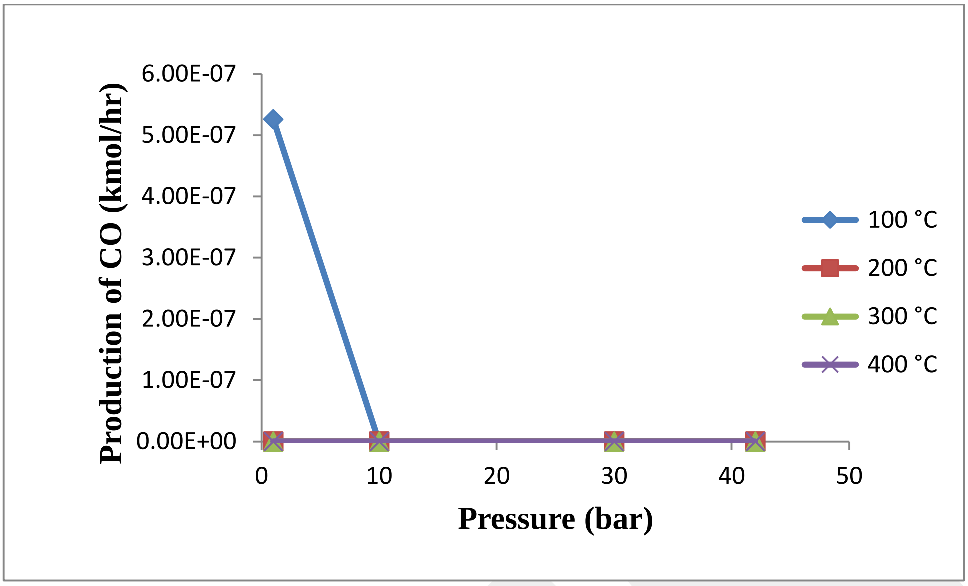

Figure 4.2 Effect of temperature and pressure on carbon monoxide production

4.1.3 Effect of Temperature and Pressure on the Overall Selectivity

The overall selectivity is the ratio of the quantity of one component produced to the quantity of another component produced. So molar flow rate of formaldehyde over the molar flow rate of carbon monoxide. Figure 4.3 is related to previous graphs 4.1 and 4.2 since selectivity is the ratio of these graphs.

There is an increase in overall selectivity when increasing the temperature and pressure as shown in Figure 4.3 and Table A3 in Appendix. The proportion of formaldehyde is increasing and the amount of carbon monoxide is reducing in production with increasing temperature and pressure. This shows that the best temperatures for the formaldehyde production process are at 300°C and 400°C.

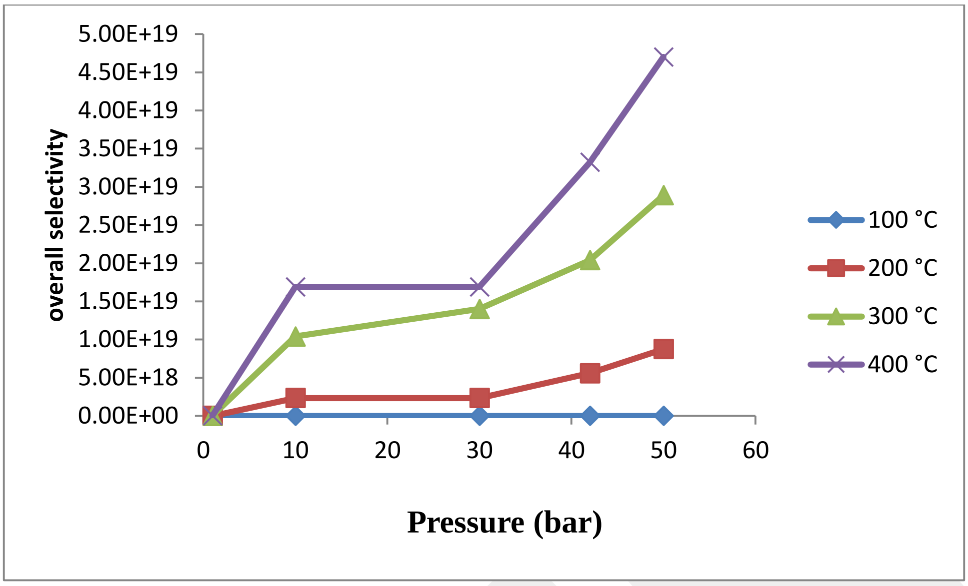

Figure 4.3 Effect of temperature on and pressure the overall selectivity

4.2 Effect of the Length of Reactor

4.2.1 Effect of The Length of Reactor on Formaldehyde Production

The length of the reactor is one of the important variables affecting the production process. Therefore, the appropriate length must be determined for the reactor to obtain the required quantity of formaldehyde. As shown in Figure 4.4, the length of the reactor is changed only and the other variables are constant as the temperature is 300 °C, the pressure is 42 bar, the diameter is 0.0025 meters, the number of pipes is 500 and total flow rate are 50497 kg/hr. The effect of the length of the reactor on the process of formaldehyde production from methanol as shown in Figure 4.4, starts from 2.72 meters obtain the same amount of formaldehyde as the reactor length increases. In this process, the length of the reactor is 3.0480 meters. This length is suitable to obtain the required quantity of production. The metal oxide process needs a large equipment space because the oxidation takes place with excess air and also expands to the resulting gases [16].

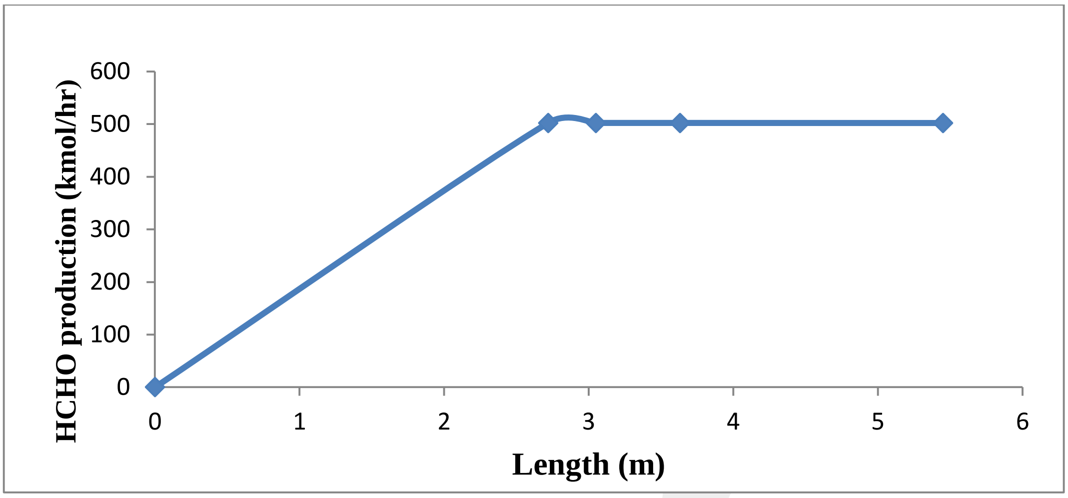

Figure 4.4 Effect of reactor length on formaldehyde production

4.2.2 Effect of The Length of Reactor on Carbon Monoxide

As mentioned above, carbon monoxide is formed by the formaldehyde uptake of the catalyst and the reaction with oxygen. Therefore, the length of the appropriate reactor should be chosen so that the time of formaldehyde retention within the reactor is minimized. Effect of the length of the reactor on carbon monoxide formation as shown in Figure 4.5 there is an increase in the amount of carbon monoxide but in small amounts. The amount of carbon monoxide produced at 3.04 m is 9.32E-18 kmol/hr and increasing at 5.45 m is 1.67E-17 kmol/hr and the increase is small.

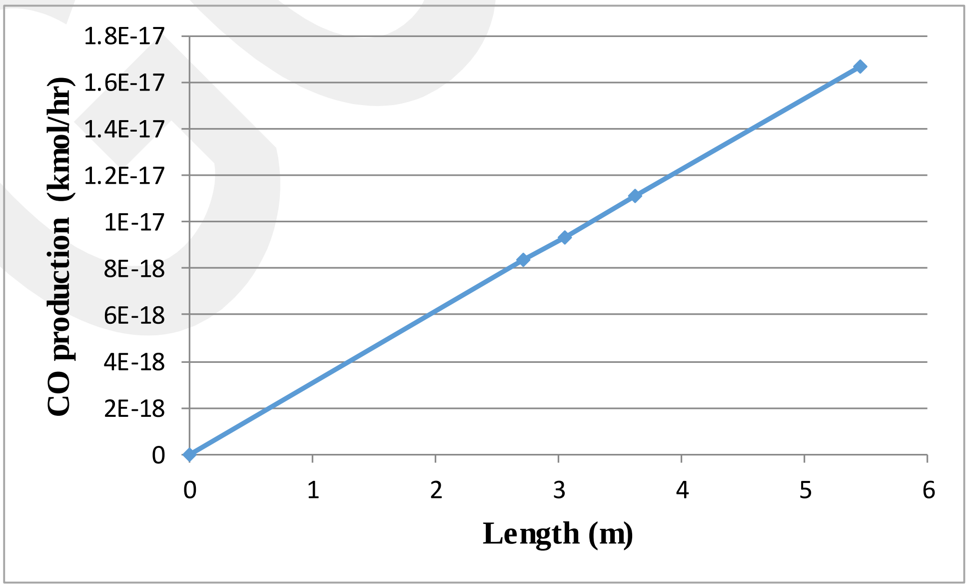

Figure 4.5 Effect of reactor length on carbon monoxide production

4.2.3 Effect of Reactor Length on The Overall Selectivity

The overall selectivity is the molar flow rate of formaldehyde over the molar flow rate of carbon monoxide. Figure 4.6 is linked to previous graphs 4.4 and 4.5 since selectivity is the ratio of these graphs.

There is an increase in overall selectivity at 2.7 m is 6.02E+19 as shown in Figure 4.6 and Table A6 in Appendix after that the quantity overall selectivity decreased but by a small percentage.

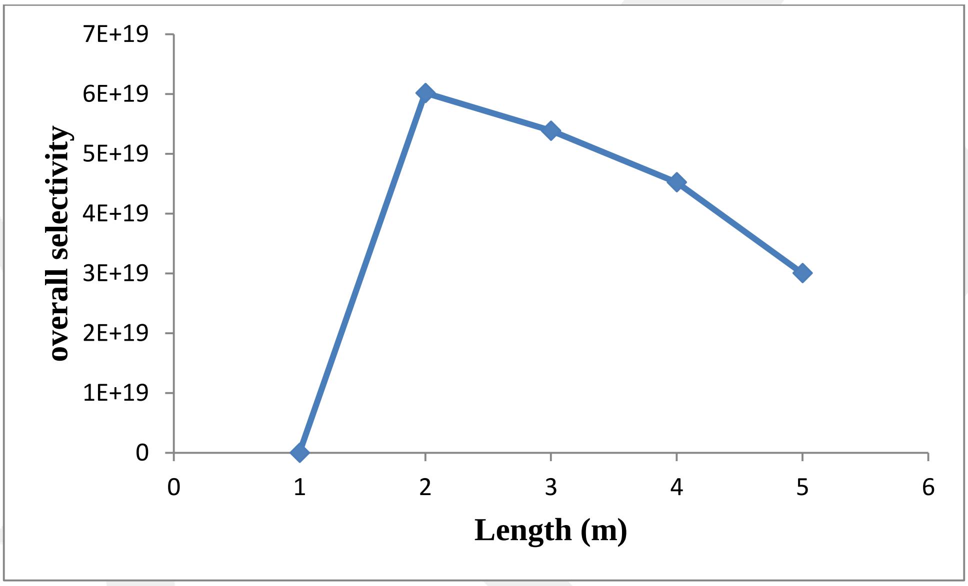

Figure 4.6 Effect of reactor lengthon the overall selectivity

4.3 Effect of Pipe Diameter

4.3.1 Effect of Pipe Diameter on Formaldehyde Production

The diameter of the pipes used within the reactor is also considered as a variable that affects the production process. As shown in figure 4.7 where the diameter of the pipe is changed only and the other variables are constant as the temperature is 300°C, the pressure is 42 bar, the length of the reactor is 3 meters, the number of pipe 500 and total flow rate are 50497 kg/hr. Appropriate diameter is determined by the pipe and produces about 15000 kg/hr.

Whereas the effect of pipe diameter on process production of formaldehyde from methanol as shown in Figure 4.7 starts from 0.0010 meters obtain the same amount of formaldehyde as the pipe diameter increases. And the pipe diameter used in this process is 0.025 meters. This pipe diameter is suitable to obtain the required quantity of production. Because the small diameter helps to transfer the temperature and also suitable for high pressure and quick-stay interactions.

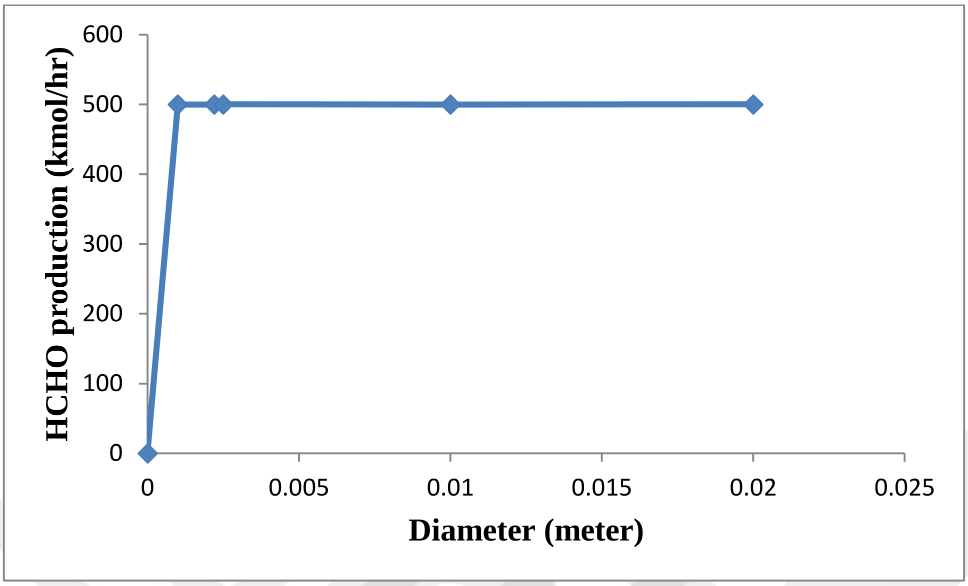

Figure 4.7 Effect of pipe diameter on formaldehyde production

4.3.2 Effect of Pipe Diameter on Carbon Monoxide Production

Effect of pipe diameter on carbon monoxide production is shown in Figure 4.8. There is a small amount of carbon monoxide at 0.001, 0.0022 and 0.0025 meters but at 0.01 meter there is an increase in the amount of carbon monoxide. This is because when increasing the pipe diameter, this will increase the size of the reactor and also decrease the flowrate of the material and thus allow the formaldehyde to interact with the oxygen.

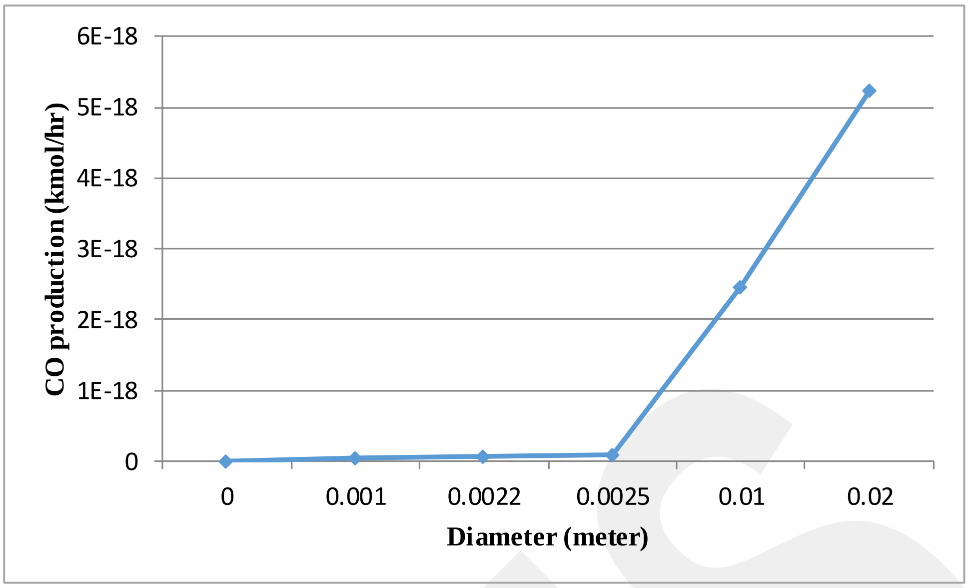

Figure 4.8 Effect of Pipe Diameter on Carbon Monoxide production

4.3.3 Effect of Pipe Diameter on The Overall Selectivity

Figure 4.9 is linked to the previous graphs 4.7 and 4.8 since selectivity is the ratio of these graphs.

There is an increase in overall selectivity from 0.001 to 0.0025 meter as shown in Figure 4.9. After that, the quantity overall selectivity decreased, because there is an increase in the amount of carbon monoxide when increasing the diameter as shown in Figure 4.8.

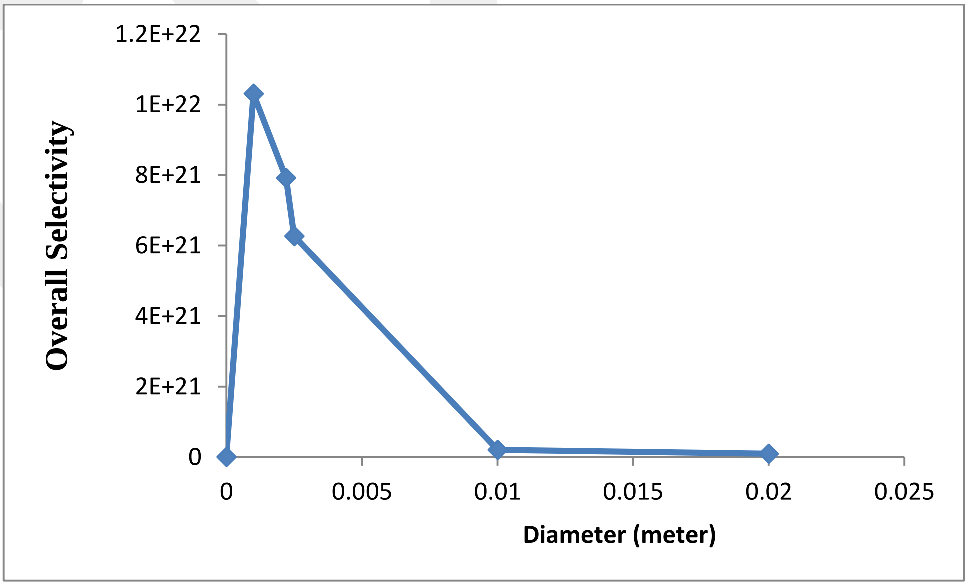

Figure 4.9 Effect of pipe diameter on the overall selectivity

4.4 Effect of Number of Pipes

4.4.1 Effect of Number of Pipes on Formaldehyde Production

The number of pipes used within the reactor PFR is one of the variables that affect the production process. Therefore, the number of suitable pipes is determined by changing their number and the other variables are constant where the temperature is 300°C, the pressure is 42 bar, the length of the reactor is 3 meter, its diameter is 0.0025 meter and total flow rate are 50497 kg/hr. Until the appropriate number of the pipe is selected and the required quantity of formaldehyde is produced.

As shown in Figure 4.10 effect of the number of pipes on formaldehyde production, starts from 300 pipes and then increase the amount of production at 400 pipes obtain the same amount of formaldehyde as the number of pipes increases. The number of pipes used in this process is 500. This number is suitable to obtain the required quantity of production.

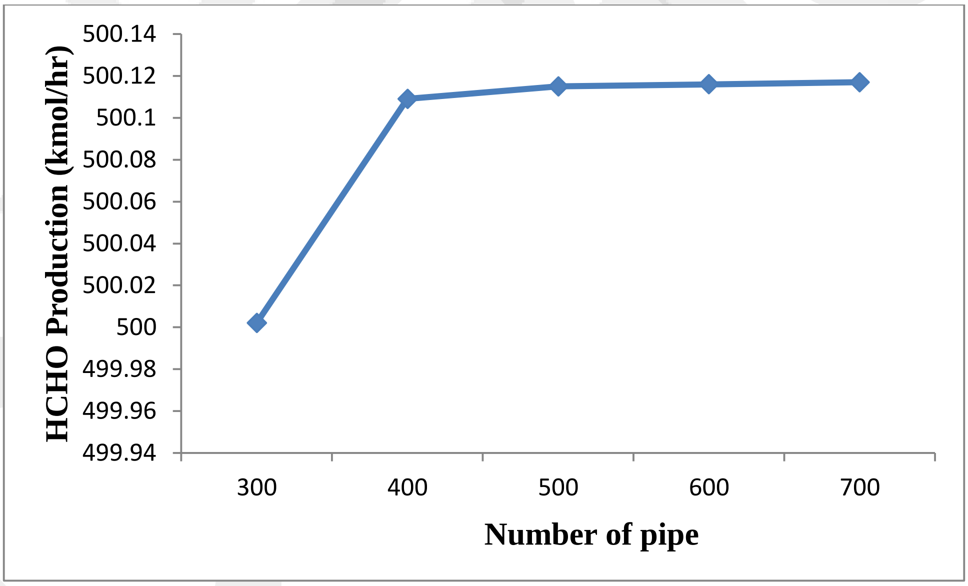

Figure 4.10 Effect of number of pipes on formaldehyde

4.4.2 Effect of Number of Pipes on Carbon Monoxide

Effect of the number of pipes on carbon monoxide production as shown in Figure 4.11 there is a small increase in the amount of carbon monoxide when increasing the number of the pipe. Because when increasing the number of pipes increases the size of the reactor and also increases the survival of the resulting materials decrease speed the flow of the material and thus allow the formaldehyde to interact with the oxygen.

The number of pipes used in this process is 500. In this number, the amount of carbon monoxide produced is 1.51E-17 kmol/hr it is a small amount.

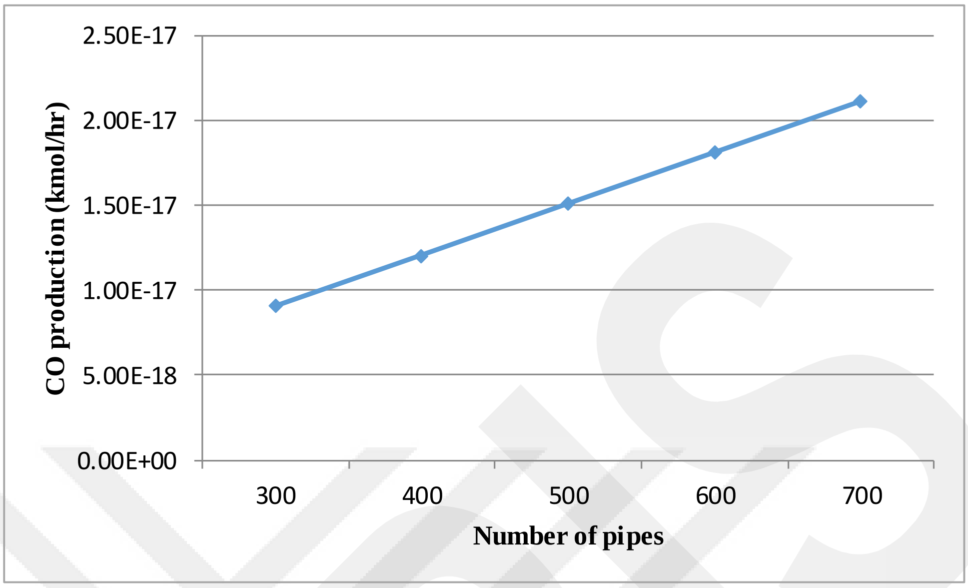

Figure 4.11 Effect of number of pipes on carbon monoxide production

4.4.3 Effect of Number of Pipes on Overall Selectivity

Figure 4.12 is linked to previous graphs 4.10 and 4.11 since selectivity is the ratio of these graphs.

As shown in Figure 4.12 the overall selectivity is highest for 300 pipes. After that, the quantity overall selectivity decreased, because there is an increase in the amount of carbon monoxide produced as shown in Figure 4.11.

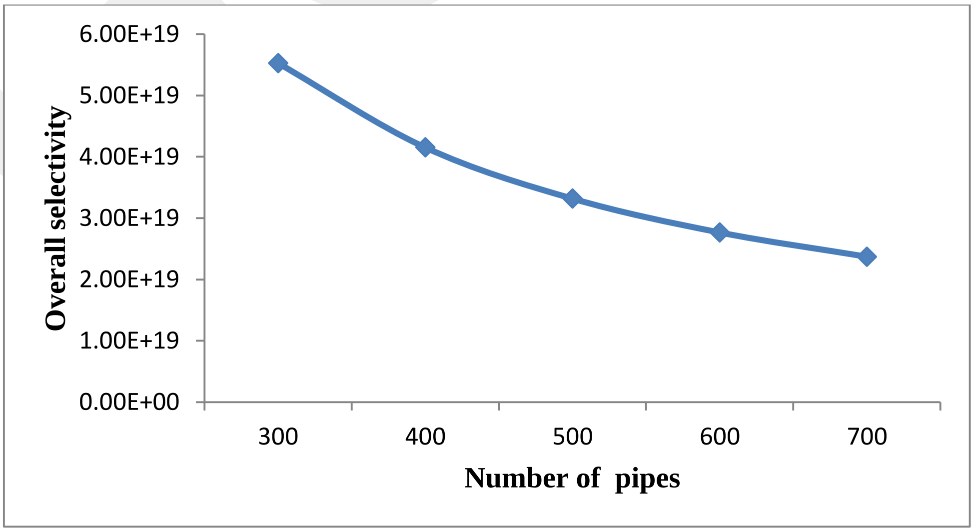

Figure 4.12 Effect of number of pipes on overall selectivity

4.5 Methanol Conversion

Conversion is a fraction of a component that has been converted to products by the reaction network. And the general equation for the conversion is

XA = Mole of A reacted / mole of A in fed

So,

XCH3OH = mole of methanol in fed – mole of methanol in production/mole of methanol in fed

XCH3OH = 500 -0 / 500 x 100 = 1 x 100 = 100%

The conversion of methanol to formaldehyde is highly dependent on the temperature the presence of the catalyst and the transformation of methanol into formaldehyde in the entire reactor. As shown in Figure 4.13 we observe at temperatures below 100°C there is a very small amount of formaldehyde but after 100°C, The conversion of methanol to formaldehyde is improved along with increased temperature. at 150°C obtain the same amount of formaldehyde as the temperature increases. Methanol oxidation with oxygen is a sensitive structure, when using iron molybdenum catalyst the ratio of conversion of methanol to formaldehyde is high could reach 99% [82].

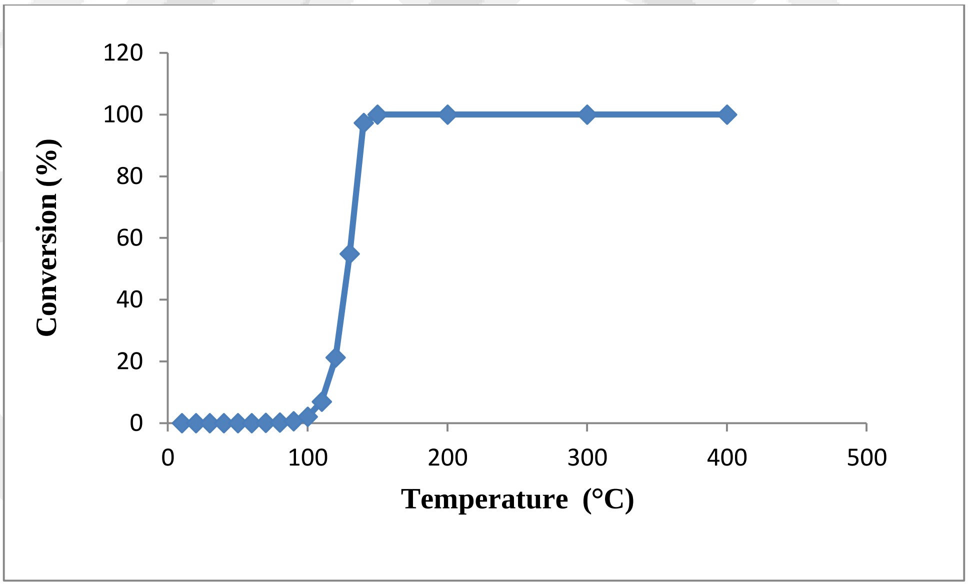

Figure 4.13 Methanol Conversion

4.6 Overall Selectivity of Formaldehyde

The results of overall selectivity of formaldehyde in different operating conditions as shown in Figure 4.14. At temperatures less than 150°C overall selectivity is 0. Because formaldehyde does not form at temperatures below 150°C. But when increasing the temperature to 150°C and pressure is 20 bar the overall selectivity is 1.22e+16 and when the temperature increases to 200°C the overall selectivity is 1.78e+18 and when increasing the pressure to 42 bar the overall selectivity is 5.62e+18. When the temperature increases to 300°C and the pressure is 20 bar the overall selectivity is 12.41e+18 and when increasing pressure to 42 bar the overall selectivity is 1.00e+19. Thus, here we note that when increasing temperature and pressure, the general selectivity increases. When increasing the temperature and pressure to 400°C and 20 bar the overall selectivity is 8.14e+18 and when increasing the pressure to 42 bar the overall selectivity is 3.32e+19, i.e. there is an increase in the amount of formaldehyde and decrease in the amount of carbon monoxide. But when increasing pressure and temperature to 60 bar and 400°C bar there is a slight increase in the overall selectivity, that the increase in pressure more than 42 does not have a significant impact on the production process.

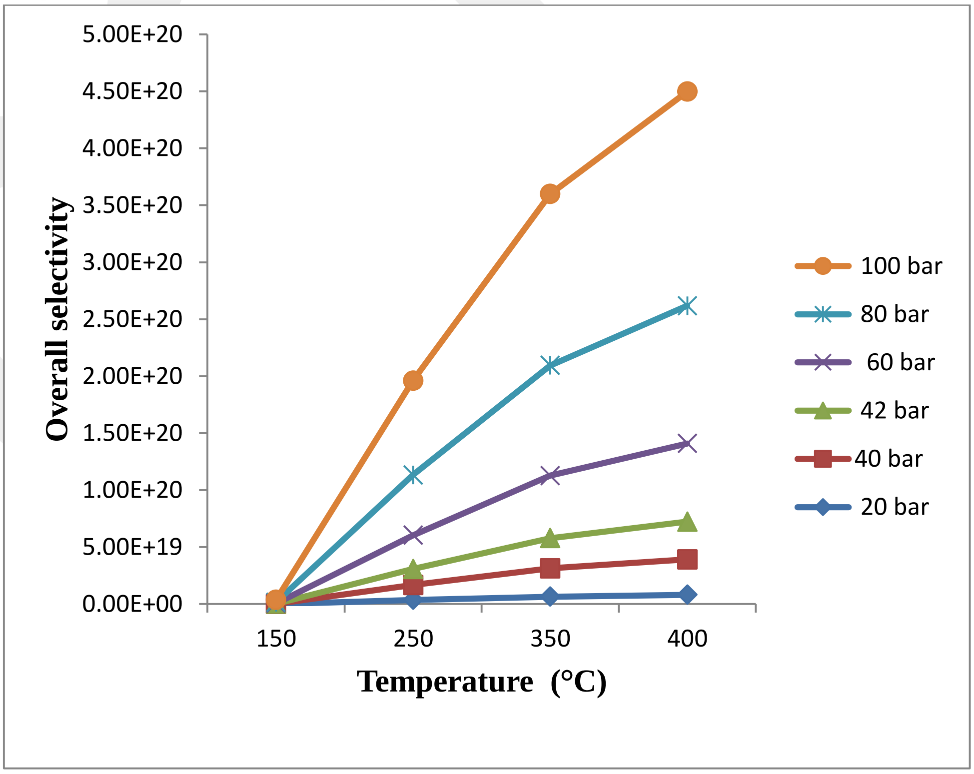

Figure 4.14 Overall selectivity of formaldehyde over carbon monoxide

4.7 Streams Results

Table 4.1 shows stream results of the process. The flow rate to feed the reactor is 50497 kg/hr and this mixture consists of methanol and air. A reaction occurs within the reactor between methanol and air, the production of formaldehyde is 15437 kg/hr. And also by-products are water and carbon monoxide. The total outflow from the reactor in stream PRDCT is 50497 kg/hr. After that, a process begins where the flow rate to feed flash 1 in stream PRDCT. In this unit, water is separated from formaldehyde and nitrogen and the total flow rate to water in stream H2O is 9268 kg/hr and the total outflow rate from flash 1 to formaldehyde and nitrogen in stream F1TOP is 42657 kg/hr. After that the second unit flash 2 is utilized. The total flow rate to flash 2 in stream F1TOP. In this unit, formaldehyde is separated from nitrogen. And the total outflow rate from flash 2 to nitrogen in stream F2TOP is 26905 kg/hr. And the total outflow rate from flash 2 to formaldehyde and remaining nitrogen in stream F3BTM is 15752 kg/hr. The final stage of the production process is flash 3. The flow to the flash 3 in called stream F3BTM. In this unit, the remaining nitrogen is separated from the formaldehyde. And total flow rate to formaldehyde in stream HCHO is 15351 kg/hr and total flow rate to nitrogen in stream N2 is 27230 kg/hr.

Table 4. 1 Mass flow

Materials	Units	Air	METHOH	FEED	PRDCT
Temperature	°C	300	300	293	300
Pressure	bar	40	40	40	42
Phase	-	Vapor	Vapor	Mixed	Vapor
CH_3OH	kg/hr	-	16021.1	16021.1	0
O_2	kg/hr	8030.1	-	8030.1	30.3
HCHO	kg/hr	-	-	-	15437
H_2O	kg/hr	-	-	-	9262.1
CO	kg/hr	-	-	-	4.2232E-16
N_2	kg/hr	26446.1	-	26446.1	26446.1
Mass flows	kg/hr	34476.2	16021.1	50497.3	50497.5

Materials	Units	F1TOP	H_2O	F2TOP	F3BTM
CH_3OH	kg/hr	-	-	-	-
O_2	kg/hr	32.902	0.000445	30.9246	1.9
HCHO	kg/hr	15428	9.3224	201.232	15226
H_2O	kg/hr	3.15228	9258.97	0.000919	3.1
CO	kg/hr	-	-	-	-
N_2	kg/hr	27193	0.00742	26673	520.2
Mass flows	kg/hr	42657	9268.3	26905.2	15752.1

Materials	Units	F3TOP	HCHO	N_2
CH_3OH	kg/hr	-	-	-
O_2	kg/hr	0.9372	1.0404	31.8619
HCHO	kg/hr	6.7905	15220	208.0220
H_2O	kg/hr	2.873e-5	3.14933	0.00094
CO	kg/hr	-	-	-
N_2	kg/hr	392.838	127.421	27065.8
Mass flows	kg/hr	400.566	15351	27230.5

Table 4.2 Mole flows

Material	Units	Air	METHOH	FEED	PRDCT
Temperature	°C	300	300	293	300
Pressure	bar	40	40	40	42
Phase	-	Vapor	Vapor	Mixed	Vapor
CH_3OH	kmol/hr	-	500	500	0
O_2	kmol/hr	250.95	-	250.95	0.94
HCHO	kmol/hr	-	-	-	500
H_2O	kmol/hr	-	-	-	500
CO	kmol/hr	-	-	-	1.5077E-17
N_2	kmol/hr	944.05	-	944.05	944.05
Mole flow	kmol/hr	1195	500	1695	1945.01

Material	Units	F1TOP	H_2O	F2TOP	F3BTM
CH_3OH	kmol/hr	-	-	-	-
O_2	kmol/hr	1.0282	1.3927e-5	0.9664	0.061
HCHO	kmol/hr	513.815	0.310	6.70186	507.113
H_2O	kmol/hr	0.1748	513.951	5.1016e-5	0.1748
CO	kmol/hr	-	-	-	-
N_2	kmol/hr	970.72	0.000264	952.149	18.571
Mole flow	kmol/hr	1485.74	514.261	959.817	525.922

Material	Units	F3TOP	HCHO	N_2
CH_3OH	kmol/hr	-	-	-
O_2	kmol/hr	0.0292	0.03251	0.995
HCHO	kmol/hr	0.2261	506.887	6.928
H_2O	kmol/hr	1.5951e-6	0.1748	5.2611e-5
CO	kmol/hr	-	-	-
N_2	kmol/hr	14.0232	4.5486	966.172
Mole flow	kmol/hr	14.2786	511.643	974.069

Table 4.3 Mole fractions

Materials	Units	Air	METHOH	FEED	PRDCT
Temperature	°C	300	300	293	300
Pressure	bar	40	40	40	42
Phase	-	Vapor	Vapor	Mixed	Vapor
CH_3OH	-	-	1	0.294	0
O_2	-	0.21	-	0.148	0.00048
HCHO	-	-	-	-	0.257
H_2O	-	-	-	-	0.257
CO	-	-	-	-	7.751E-21
N_2	-	0.79	-	0.556	0.485

Materials	Units	F1TOP	H_2O	F2TOP	F3BTM
CH_3OH	-	-	-	-	-
O_2	-	0.00069	2.708e-8	0.0010	0.000117
HCHO	-	0.345	0.000603	0.0069	0.964
H_2O	-	0.000117	0.999	5.315e-8	0.000332
CO	-	-	-	-	-
N_2	-	0.653	5.151e-7	0.992	0.035

Materials	Units	F3TOP	HCHO	N_2
CH_3OH	-	-	-	-
O_2	-	0.00205	6.355e-5	0.0010
HCHO	-	0.0158	0.991	0.0071
H_2O	-	1.117e-7	0.000341	5.401e-8
CO	-	-	-	-
N_2	-	0.982	0.0088	0.991

Table 4.4 Mass fractions

Materials	**Units**	**Air**	**METHOH**	**FEED**	**PRDCT**
Temperature	**°C**	**300**	**300**	**293**	**300**
Pressure	**bar**	**40**	**40**	**40**	**42**
Phase	**-**	**Vapor**	**Vapor**	**Mixed**	**Vapor**
CH_3OH	**-**	**-**	**1**	**0.31**	**0**
O_2	**-**	**0.23**	**-**	**0.15**	**0.0005**
HCHO	**-**	**-**	**-**		**0.29**
H_2O	**-**	**-**	**-**		**0.17**
CO	**-**	**-**	**-**		**1.36e-20**
N_2	**-**	**0.76**	**-**	**0.52**	**0.52**

Materials	**Units**	**F1TOP**	**H_2O**	**F2TOP**	**F3BTM**
CH_3OH	**-**	**-**	**-**	**-**	**-**
O_2	**-**	**0.0007**	**4.80e-8**	**0.001**	**0.0001**
HCHO	**-**	**0.36**	**0.001**	**0.007**	**0.96**
H_2O	**-**	**7.83e-5**	**0.99**	**3.41e-8**	**0.0001**
CO	**-**	**-**	**-**	**-**	**-**
N_2	**-**	**0.63**	**8.00e-7**	**0.99**	**0.03**

Materials	**Units**	**F3TOP**	**HCHO**	**N_2**
CH_3OH	**-**	**-**	**-**	**-**
O_2	**-**	**0.002**	**6.77e-5**	**0.001**
HCHO	**-**	**0.01**	**0.99**	**0.007**
H_2O	**-**	**7.17e-8**	**0.0002**	**3.47e-8**
CO	**-**	**-**	**-**	**-**
N_2	**-**	**0.98**	**0.008**	**0.99**

In the Tables 4.1 to 4.4, the feed stream temperature of the reactor is 293°C and the temperature outside the reactor is 300°C. This means that the reaction is releasing heat. The following Table 4.4 shows mass and enthalpy balance to the reactor where the mol number increased at the outlet conserving the mass balance.

Table 4.5 Mass and Enthalpy Balance of Plug Flow Reactor

Total	**Units**	**In**	**Out**
Mole-flow	**kmol/hr**	**1695**	**1945.04**
Mass-flow	**kg/hr**	**50497**	**50498**
Enthalpy	**cal/sec**	**-5.60e+6**	**-1.05e+7**

CHAPTER 5

CONCLUSIONS

In this project, the process of metal oxide was chosen to produce formaldehyde. Raw materials used in the production process were formaldehyde, methanol, and air. This project produces about 120,000 tons/year of formaldehyde. In this project, much emphasis was placed on the reactor PFR and a complete study was carried out in terms of the length, diameter and the number of pipes used with a reactor. The property method used in this process was PENG-Robinson. We came up with the appropriate design to the reactor to produce at least 99.1 wt% formaldehyde and 99.1 wt% nitrogen. The optimal results to achieve the desired production of formaldehyde are using a temperature between 300-400°C and pressure 42 bar inside the plug flow reactor, the number of pipes used within the reactor is 500, the diameter of these pipes is 0.0025 meter, with the length of 3.0480 meter. The Aspen Plus program was used to simulate formaldehyde production through this program which could easily calculate the energy and material needed for the production process.

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APPENDIX

Table A1: Effect of temperature and pressure on formaldehyde production

Formaldehyde production (kmol/hr)				
Pressure (bar)	100 °C	200 °C	300 °C	400 °C
1	1.1	500.02	500.03	500.09
10	4.37	500.16	500.033	500.16
30	8.425	500.093	500.052	500.02
42	10.297	500.029	500.026	500

Table A2: Effect of temperature and pressure on carbon monoxide

Carbon monoxide production (kmol/hr)				
Pressure (bar)	100 °C	200 °C	300 °C	400 °C
1	5.26E-7	7.12E-13	4.38E-14	2.65E-14
10	1.38E-10	2.13E-16	4.81E-17	2.96E-17
30	1.04E-9	2.14E-16	4.81E-17	2.96E-17
42	5.29E-11	8.96E-17	2.46E-17	1.51E-17

Table A3: Effect of temperature and pressure on overall selectivity

Pressure (bar)	100 °C	200 °C	300 °C	400 °C
1	2.09E+6	7.02E+14	1.14E+16	1.88E+16
10	3.16E+10	2.34E+18	1.04E+19	1.69E+19
30	6.10E+10	2.34E+18	1.04E+19	1.69E+19
42	1.95E+11	5.58E+18	2.04E+19	3.32E+19

Table A4: Effect of reactor length on formaldehydeproduction

Length (m)	HCHO (kmol/hr)
0	0
2.72	502.04
3.048	502.04
3.63	502.04
5.45	501.9

Table A5: Effect of reactor length on Carbon Monoxideproduction

Length (m)	CO (kmol/hr)
0	0
2.72	8.34E-18
3.048	9.32E-18
3.63	1.11E-17
5.45	1.67E-17

Table A6: Effect of reactor length onOverall selectivity

Length (m)	Overall selectivity
0	0
2.72	6.02e+19
3.048	5.39e+19
3.63	4.52e+19
5.45	3.01e+19

Table A7: Effect of pipe Diameter on formaldehyde production

Diameter (meter)	HCHO (kmol/hr)
0	0
0.0010	500.032
0.0022	500.038
0.0025	500.095
0.010	500.038
0.020	500.48

Table A8 : Effect of pipe Diameter on Carbon Monoxide production

Diameter (meter)	CO (kmol/hr)
0	0
0.0010	4.8537E-20
0.0022	6.31918E-20
0.0.025	7.97993E-20
0.010	2.46621E-18
0.020	5.24699E-18

Table A9: Effect of pipe Diameter on Overall selectivity

Diameter (meter)	Overall selectivity
0	0
0.0010	1.03E+22
0.0022	7.91E+21
0.0025	6.27E+21
0.010	2.03E+20
0.020	9.93E+19

Table A10: Effect of number of pipes on formaldehyde production

Number of pipes	HCHO (kmol/hr)
300	500.002
400	500.109
500	500. 115
600	500.116
700	500.117

Table A11: Effect of number of pipes on Carbon Monoxide production

Number of pipes	CO (kmol/hr)
300	9.046E-18
400	1.205E-17
500	1.507E-17
600	1.809E-17
700	2.110E-17

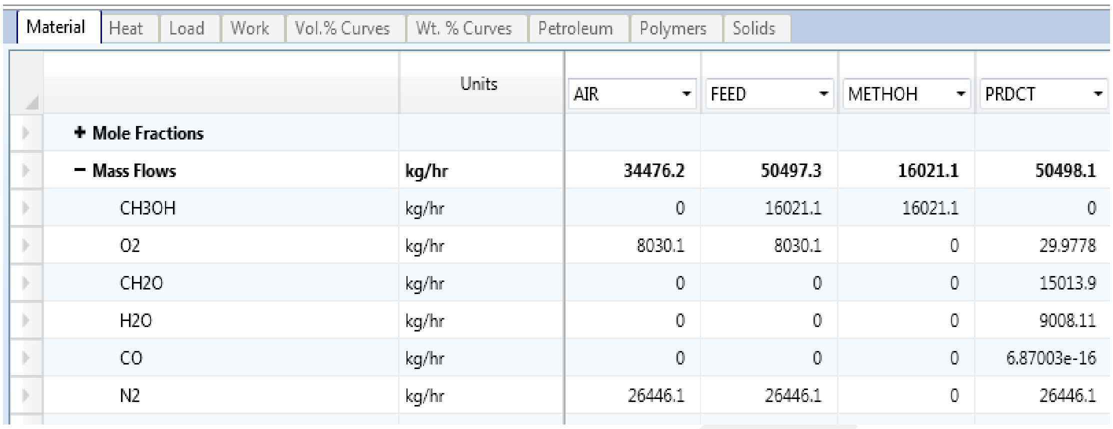
Table A12: Effect of number of pipes on Overall selectivity

Number of pipes	Overall selectivity
300	5.53E+19
400	4.15E+19
500	3.32E+19
600	2.76E+19
700	2.37E+19

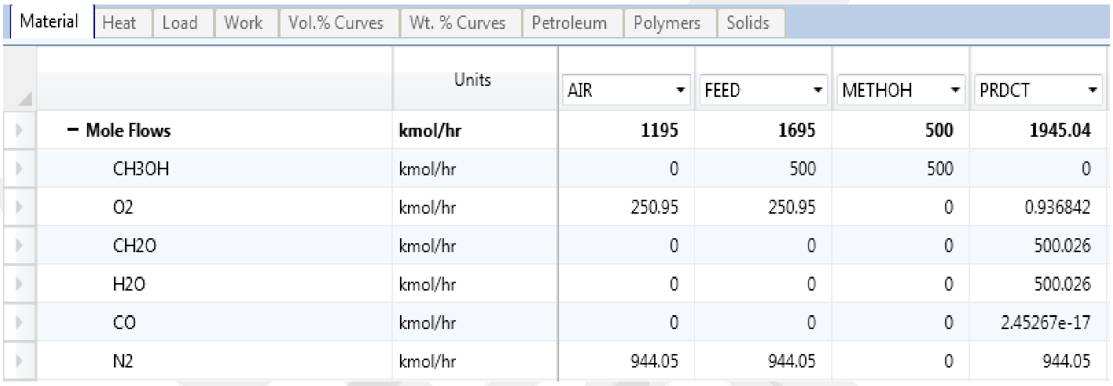
Table A13: Overall Selectivity

Temperatue °C	20 bar	40 bar	42 bar	60 bar	80 bar	100 bar
150	1.22E+16	1.06E+17	1.19E+17	3.93E+17	9.93E+17	2.10E+18
250	3.62E+18	1.31E+19	1.40E+19	2.97E+19	5.29E+19	8.28E+19
350	6.51E+18	2.48E+19	2.65E+19	5.49E+19	9.68E+19	1.50E+20
400	8.14E+18	3.10E+19	3.32E+19	6.86E+19	1.21E+20	1.88E+20

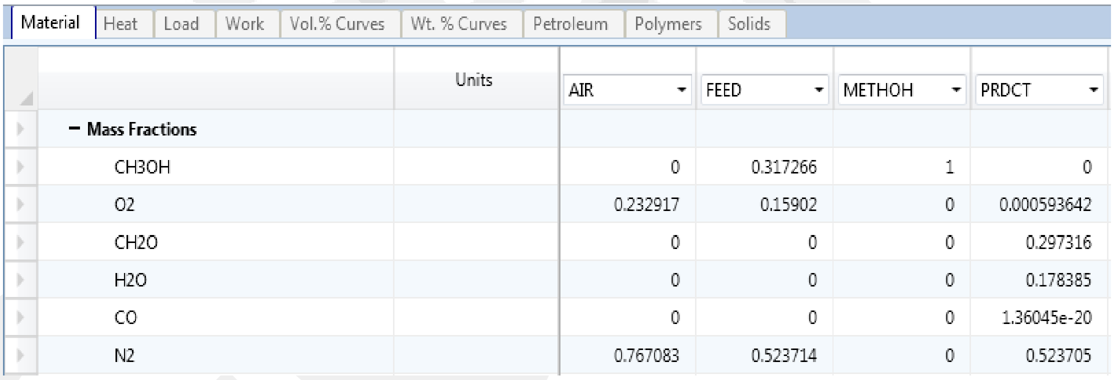
Tables A14: Streams Results from ASPEN PLUS



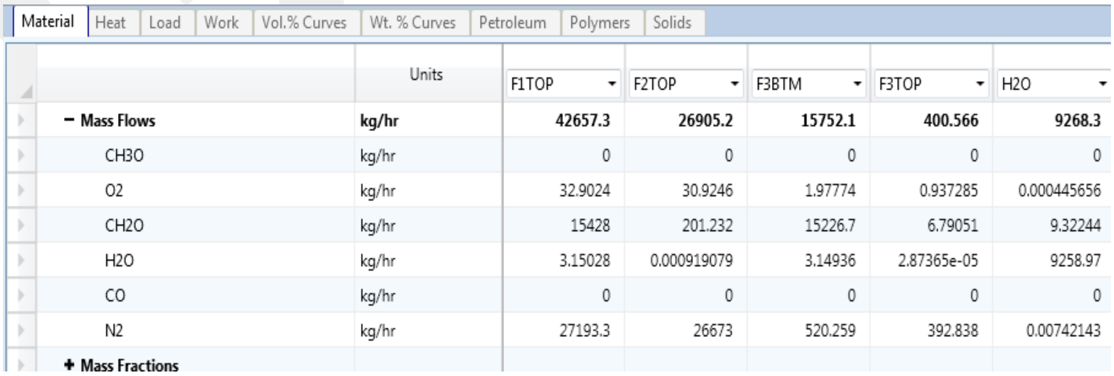
	Units	AIR	FEED	METHOH	PRDCT
+ **Mole Fractions**					
− **Mass Flows**	**kg/hr**	**34476.2**	**50497.3**	**16021.1**	**50498.1**
CH3OH	kg/hr	0	16021.1	16021.1	0
O2	kg/hr	8030.1	8030.1	0	29.9778
CH2O	kg/hr	0	0	0	15013.9
H2O	kg/hr	0	0	0	9008.11
CO	kg/hr	0	0	0	6.87003e-16
N2	kg/hr	26446.1	26446.1	0	26446.1



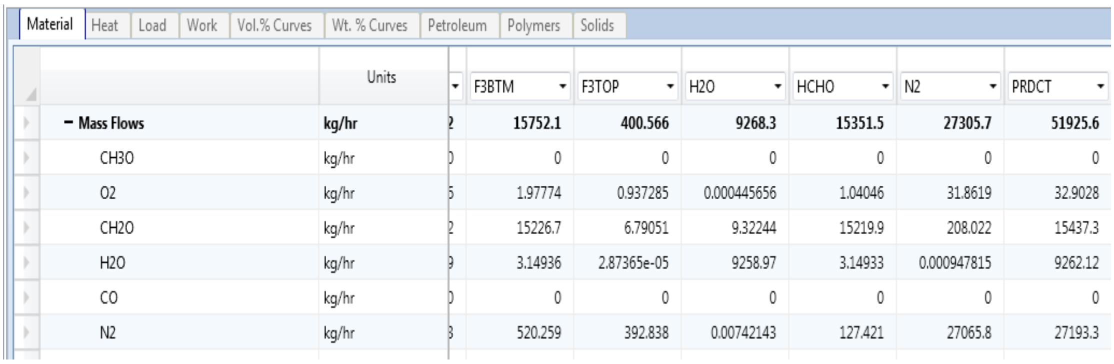
	Units	AIR	FEED	METHOH	PRDCT
− **Mole Flows**	**kmol/hr**	**1195**	**1695**	**500**	**1945.04**
CH3OH	kmol/hr	0	500	500	0
O2	kmol/hr	250.95	250.95	0	0.936842
CH2O	kmol/hr	0	0	0	500.026
H2O	kmol/hr	0	0	0	500.026
CO	kmol/hr	0	0	0	2.45267e-17
N2	kmol/hr	944.05	944.05	0	944.05



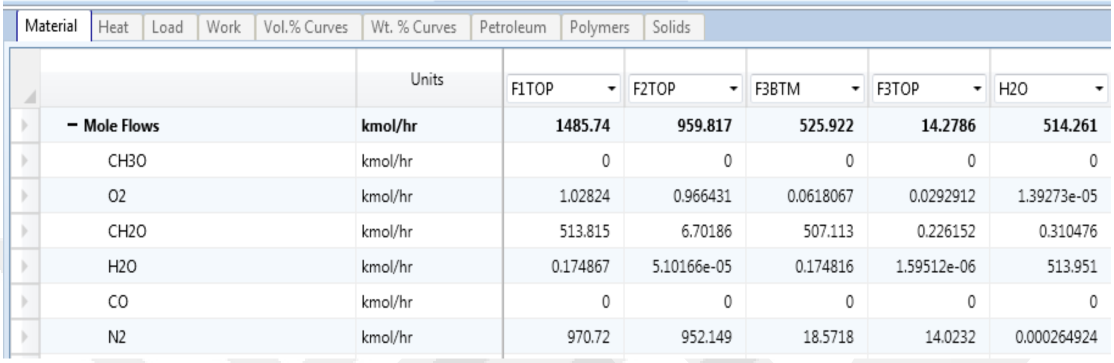
	Units	AIR	FEED	METHOH	PRDCT
− **Mass Fractions**					
CH3OH		0	0.317266	1	0
O2		0.232917	0.15902	0	0.000593642
CH2O		0	0	0	0.297316
H2O		0	0	0	0.178385
CO		0	0	0	1.36045e-20
N2		0.767083	0.523714	0	0.523705



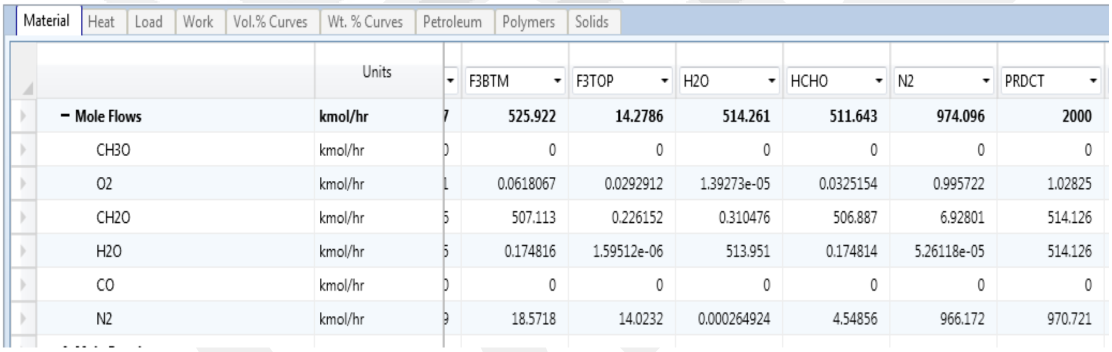
	Units	F1TOP	F2TOP	F3BTM	F3TOP	H2O
− **Mass Flows**	**kg/hr**	**42657.3**	**26905.2**	**15752.1**	**400.566**	**9268.3**
CH3O	kg/hr	0	0	0	0	0
O2	kg/hr	32.9024	30.9246	1.97774	0.937285	0.000445656
CH2O	kg/hr	15428	201.232	15226.7	6.79051	9.32244
H2O	kg/hr	3.15028	0.000919079	3.14936	2.87365e-05	9258.97
CO	kg/hr	0	0	0	0	0
N2	kg/hr	27193.3	26673	520.259	392.838	0.00742143
+ **Mass Fractions**						



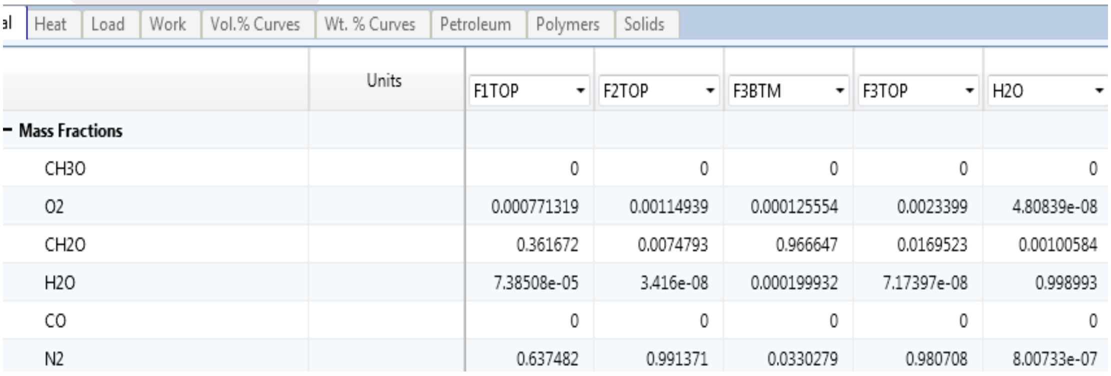
	Units	F3BTM	F3TOP	H2O	HCHO	N2	PRDCT
− Mass Flows	**kg/hr**	**15752.1**	**400.566**	**9268.3**	**15351.5**	**27305.7**	**51925.6**
CH3O	kg/hr	0	0	0	0	0	0
O2	kg/hr	1.97774	0.937285	0.000445656	1.04046	31.8619	32.9028
CH2O	kg/hr	15226.7	6.79051	9.32244	15219.9	208.022	15437.3
H2O	kg/hr	3.14936	2.87365e-05	9258.97	3.14933	0.000947815	9262.12
CO	kg/hr	0	0	0	0	0	0
N2	kg/hr	520.259	392.838	0.00742143	127.421	27065.8	27193.3



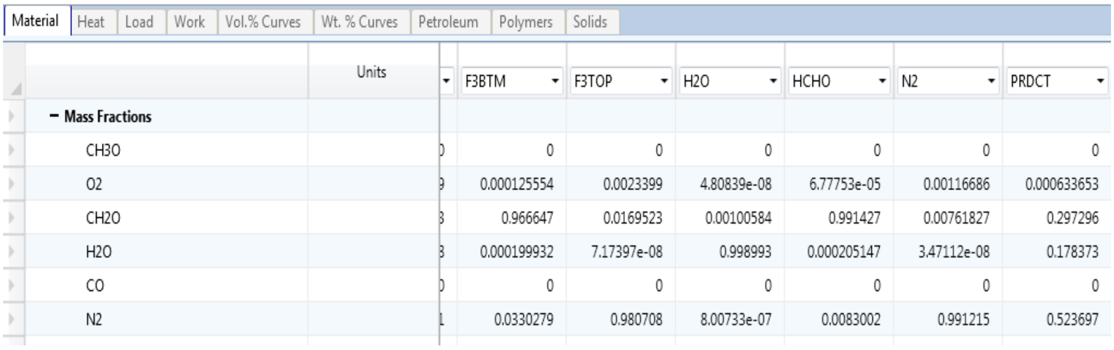
	Units	F1TOP	F2TOP	F3BTM	F3TOP	H2O
− Mole Flows	**kmol/hr**	**1485.74**	**959.817**	**525.922**	**14.2786**	**514.261**
CH3O	kmol/hr	0	0	0	0	0
O2	kmol/hr	1.02824	0.966431	0.0618067	0.0292912	1.39273e-05
CH2O	kmol/hr	513.815	6.70186	507.113	0.226152	0.310476
H2O	kmol/hr	0.174867	5.10166e-05	0.174816	1.59512e-06	513.951
CO	kmol/hr	0	0	0	0	0
N2	kmol/hr	970.72	952.149	18.5718	14.0232	0.000264924



	Units	F3BTM	F3TOP	H2O	HCHO	N2	PRDCT
− Mole Flows	**kmol/hr**	**525.922**	**14.2786**	**514.261**	**511.643**	**974.096**	**2000**
CH3O	kmol/hr	0	0	0	0	0	0
O2	kmol/hr	0.0618067	0.0292912	1.39273e-05	0.0325154	0.995722	1.02825
CH2O	kmol/hr	507.113	0.226152	0.310476	506.887	6.92801	514.126
H2O	kmol/hr	0.174816	1.59512e-06	513.951	0.174814	5.26118e-05	514.126
CO	kmol/hr	0	0	0	0	0	0
N2	kmol/hr	18.5718	14.0232	0.000264924	4.54856	966.172	970.721

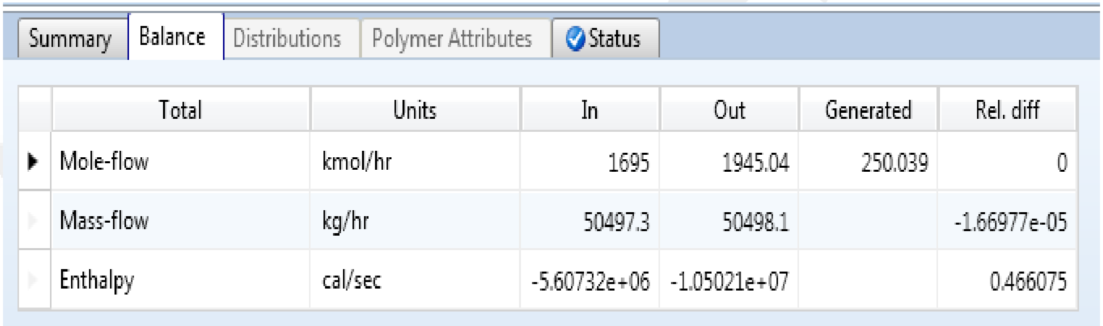


	Units	F1TOP	F2TOP	F3BTM	F3TOP	H2O
− Mass Fractions						
CH3O		0	0	0	0	0
O2		0.000771319	0.00114939	0.000125554	0.0023399	4.80839e-08
CH2O		0.361672	0.0074793	0.966647	0.0169523	0.00100584
H2O		7.38508e-05	3.416e-08	0.000199932	7.17397e-08	0.998993
CO		0	0	0	0	0
N2		0.637482	0.991371	0.0330279	0.980708	8.00733e-07



	Units	F3BTM	F3TOP	H2O	HCHO	N2	PRDCT
Mass Fractions							
CH3O		0	0	0	0	0	0
O2		0.000125554	0.0023399	4.80839e-08	6.77753e-05	0.00116686	0.000633653
CH2O		0.966647	0.0169523	0.00100584	0.991427	0.00761827	0.297296
H2O		0.000199932	7.17397e-08	0.998993	0.000205147	3.47112e-08	0.178373
CO		0	0	0	0	0	0
N2		0.0330279	0.980708	8.00733e-07	0.0083002	0.991215	0.523697

Table A15 Mass and Enthalpy Balance of Plug Flow Reactor from ASPEN PLUS



Total	Units	In	Out	Generated	Rel. diff
Mole-flow	kmol/hr	1695	1945.04	250.039	0
Mass-flow	kg/hr	50497.3	50498.1		-1.66977e-05
Enthalpy	cal/sec	-5.60732e+06	-1.05021e+07		0.466075