

University of Diyala

College of Engineering

Chemical Engineering Department



Production of formaldehyde

A project report Submitted to the Engineering Department
of Chemical of the University of Diyala in a partial fulfillment
for the Degree of B.Sc in Chemical Engineering

By

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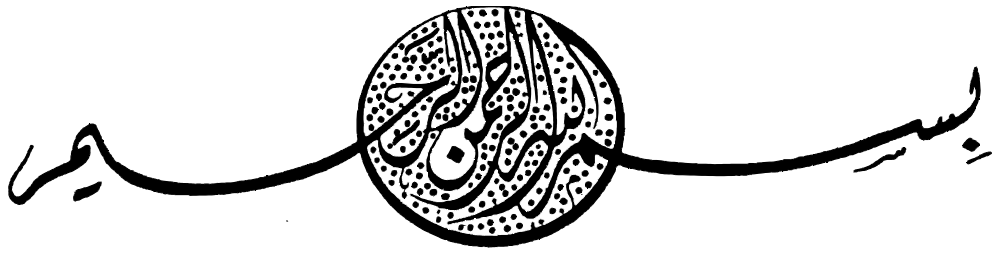
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(... وَأَنْزَلَ اللَّهُ عَلَيْكَ الْكِتَابَ وَالْحِكْمَةَ وَعَلَّمَكَ مَا

لَمْ تَكُن تَعْلَمُ وَكَانَ فَضْلُ اللَّهِ عَلَيْكَ عَظِيمًا)

صدق الله العظيم

سورة النساء (١١٣)

Dedication

To my beloved family

My parents .. My Father & My Mother

My Brothers

My Sisters

To my lovely friends



sajad, muhanad, Mohammed

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CHAPTER ONE

SUMMARY

1. Summary

1.1- Introduction

Formaldehyde is called Methyl aldehyde or Methylene glycol or Methylene oxide it is a colorless, flammable gas or liquid that has a pungent, suffocating odor. It is a volatile organic compound, which is an organic compound that easily becomes a vapor or gas. It is also naturally produced in small, harmless amounts in the human body. The chemical symbol for formaldehyde is CH_2O .

Formaldehyde is released into the air by burning wood, kerosene, or natural gas; from automobiles and diesel exhaust; and from cigarettes and other products. It is found in the air at home, at work, and outdoors, especially in smog. It is also found in some foods.

Formaldehyde occurs in forest fires, animal wastes, microbial products of biological systems, and plant volatiles. It can also be formed in seawater by photochemical processes.

Formaldehyde was discovered in 1859 by a Russian chemist named Aleksandr Butlerov. Then in 1869, it was ultimately identified by the German chemist August Hofmann. The manufacture of formaldehyde started in the beginnings of the twentieth century. Between 1958 and 1968, the annual growth rate for formaldehyde production averaged to 11.7%. In the mid-1970s, the production was 54% of capacity. Annual growth rate of formaldehyde was 2.7% per year from 1988 to 1997. In 1992, formaldehyde ranked 22nd among the top 50 chemicals produced in the United States. The total annual formaldehyde capacity in 1998 was estimated by 11.3 billion pounds. Since then and the production capacity around the globe is expanding exponentially reaching a world's production of 32.5 million metric tons by 2012. Due to its relatively low costs compared to other materials, and its receptivity for reaching high purities, formaldehyde is considered one of the most widely demanded and manufactured materials in the world. It is also the center of many chemical researches and alternative manufacture methods. This also explains the vast number of applications of this material including a building block for other organic compounds, photographing washing, glues, adhesives, paints, explosives, disinfecting, tissue preservation and drug testing. formaldehyde is most commonly produced in industry through the vapor- phase oxidation reaction between methanol and air (Oxygen).

1.2- Health effects

The most probable route of human exposure to formaldehyde is inhalation .Non-Cancer: Vapors are highly irritating to the eye and respiratory track. Acute effects include nausea, headaches, and difficulty breathing. Formaldehyde can also induce or exacerbate asthma, and throat irritation and Repeated exposure to it cause skin irritation

1.3- Sources

Formaldehyde is both directly emitted into the atmosphere and formed in the atmosphere as a result of photochemical oxidation of reactive organic gases in polluted atmospheres containing ozone and nitrogen oxides. Photochemical oxidation is the largest source (could be as high as 88 percent) of formaldehyde concentrations in California ambient air. A primary source of formaldehyde is vehicular exhaust Formaldehyde is a product of incomplete combustion. About 9 percent of direct formaldehyde emissions are estimated to come from the combustion of fossil fuels mobile sources.

The primary stationary sources that have reported emissions of formaldehyde are crude petroleum and natural gas extraction, manufacturers of miscellaneous nonmetallic mineral products, and gas production and distribution services.

1.4- Demand

Demand for formaldehyde will grow with the development of the manufacturing sector mainly the chemical industries such as disinfectants, cosmetics, pharmaceuticals, insecticide & fungicides and the like. The demand for the output of such establishments is in turn influenced by population growth, urbanization, income rise and expansion of health services and the like. Considering the combined effect of the above factors a growth rate of 10% is taken to forecast the future demand.

PROJECTED DEMAND FOR FORMALDEHYDE (KG)

Year	Projected Demand
2012	143,000
2013	157,300
2014	173,030
2015	190,333
2016	209,366

1.5- Use of formaldehyde

Formaldehyde is an important industrial chemical because of its versatility as a chemical intermediate (Gerberich et al. 1994). It primarily is used in the production of urea-formaldehyde, phenol-formaldehyde, and melamine-formaldehyde resins, which are used as adhesives in the production of particle board, fiber board, and plywood. Formaldehyde is also used in the manufacture of plastics, insulation, fertilizers, fungicides, biocides, corrosion inhibitors, embalming fluids, disinfectants, and household cleaners, and it is used in the textile industry .

1.6- Physical and chemical properties

Formaldehyde is a flammable, colorless gas at room temperature and has a pungent, suffocating odor (Budavari et al. 1989). Odor thresholds ranging from 0.5 to 1.0 parts per million (ppm) (ATSDR 1999) and 0.06 to 0.5 ppm (Gerberich et al. 1994) have been reported. Formaldehyde reacts readily with many substances and polymerizes easily, making it one of the world's most important industrial Compound. (Gerberich et al. 1994). Selected chemical and physical properties are listed in TABLE

1.6.1- Physical Properties of Formaldehyde

Properties	Formic aldehyde, methanal, methyl aldehyde, methylene oxide, Oxo methane, ox methylene
CAS registry number	50-00-0
Molecular formula	HCHO
Molecular weight	30.03
Boiling point	-19.5°C
Melting point	-92°C
Flash point	83°C (closed cup)
Explosive limits	7% to 73%
Specific gravity	1.067 with respect to air
Vapor pressure	3,890 mmHg at 25°C
Solubility	Very soluble in water; soluble in alcohol and ether
Conversion factors	1 ppm = 1.23 mg/m ³ ; 1 mg/m ³ = 0.81 ppm
Vapor Pressure	3284 mm Hg at 20 °C
Vapor Density	1.03 for aq. soln.; 1.08 for gas
Density/Specific Gravity	1.067 (air = 1)
Log Octanol/Water Partition Coefficient	0.35
Conversion Factor	1 ppm = 1.23 mg/m ³

1.6.2 - Chemical properties

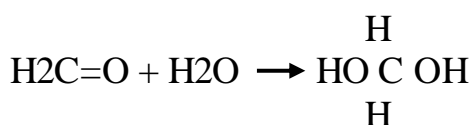
Formaldehyde is one of the most reactive organic compounds known. The various chemical properties are as follows:

Decomposition

At 150 °C formaldehyde undergoes heterogeneous decomposition to form methanol and CO₂ mainly. Above 350 °C it tends to decompose into CO and H₂.

Polymerization

Gaseous formaldehyde polymerizes slowly at temperatures below 100 °C, polymerization accelerated by traces of polar impurities such as acids, alkalis or water. In water solution formaldehyde hydrates to methylene glycol



Which in turn polymerizes to polymethylene glycols, HO (CH₂O)_nH, also called polyoxy methylenes.

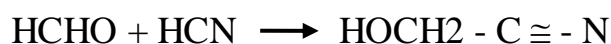
Reduction and Oxidation

Formaldehyde is readily reduced to methanol with hydrogen over many metal and metal oxide catalysts. It is oxidized to formic acid or CO₂ and H₂O. In the presence of strong alkalis or when heated in the presence of acids formaldehyde undergoes Cannizzaro reaction with formation of methanol and formic acid. In presence of aluminum or magnesium methylate, paraformaldehyde reacts to form methyl formate (Tishchenko reaction)



Addition reactions

The formation of sparingly water-soluble formaldehyde bisulphite is an important addition reaction. Hydrocyanic acid reacts with formaldehyde to give glyconitrile.



Resin formation

Formaldehyde condenses with urea, melamine, urethanes, cyanamide, aromatic sulfonamides and amines, and phenols to give wide range of resins.

Chemical reaction of Formaldehyde

Number	Reaction	$\Delta H_{R,973\text{ K}}$ (kJ/mol)
(1)	$\text{CH}_3\text{OH} + 1/2\text{O}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-156
(2)	$\text{CH}_3\text{OH} \rightarrow \text{HCHO} + \text{H}_2$	+85
(3)	$\text{CH}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	+12
(4)	$\text{CH}_3\text{OH} + 2/3\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-676
(5)	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	-519
(6)	$\text{CH}_2\text{O} + 1/2\text{O}_2 \rightarrow \text{CH}_2\text{O}_2$	-314
(7)	$\text{CH}_3\text{OH} \rightarrow \text{C} + \text{H}_2\text{O} + \text{H}_2$	-31
(8)	$\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$	-136
(9)	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	-35

1.7- Production methods

Today two main processes are in use for the production of formaldehyde from methanol, the silver process and the oxide process. The first can be divided in to two processes, the methanol ballast process and the BASF Badische Anilin& Soda-Fabrik process as shown in Figure 1.1.

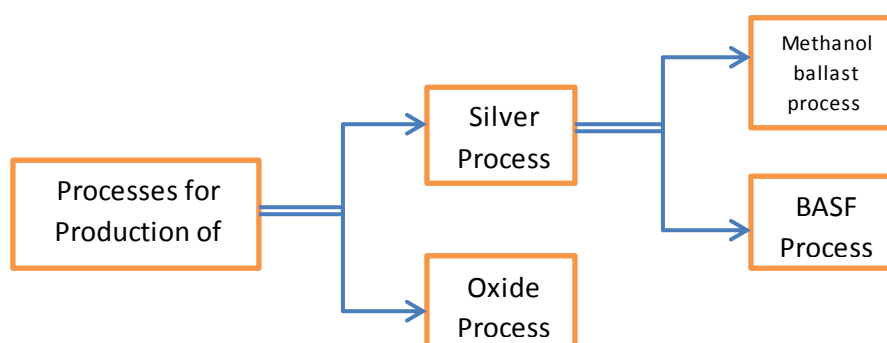


Figure 1.1. The different process types for production of formaldehyde from methanol.

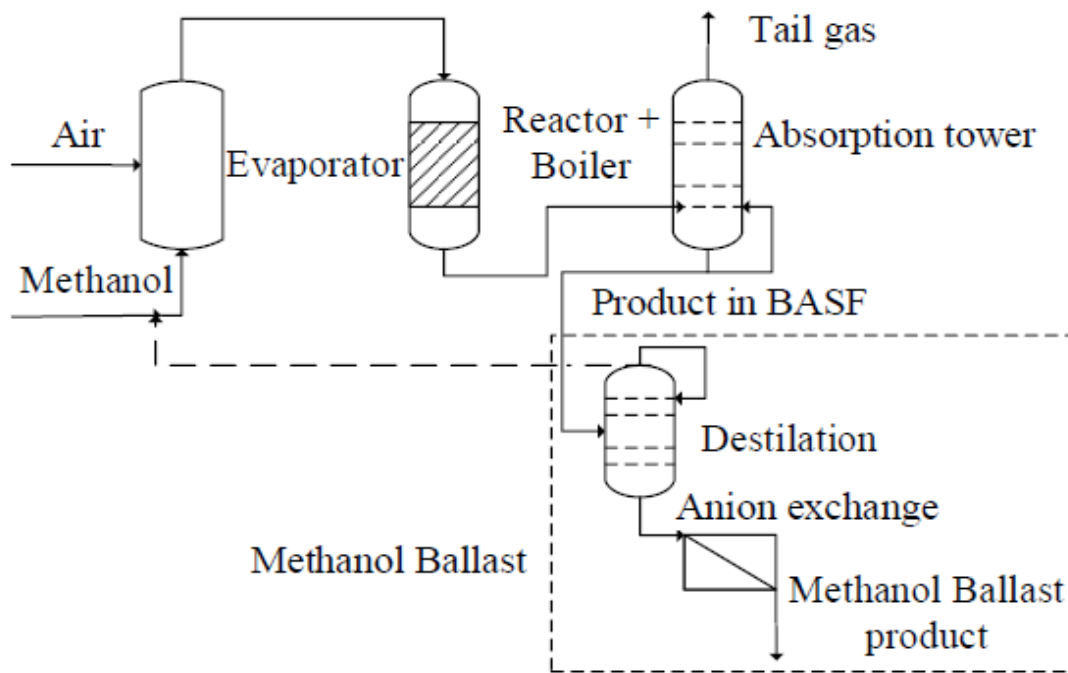


Figure 2.2. schematic overview of the silver process. The dashed square shows what only exist in the methanol ballast process

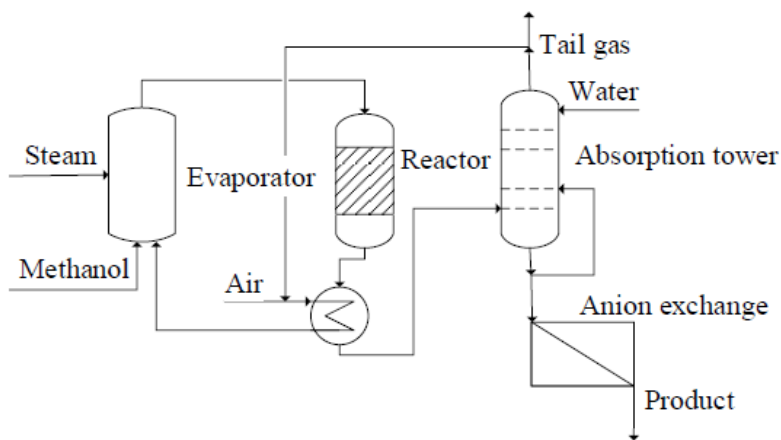


Figure 2.3. A schematic scheme over the oxidation process (Table 1.1.)

[%]	Methanol Ballast	BASF	Oxide
Conversion	77-88	97-98	95 – 98
Yield mol.	86-90	89.5-90.5	<92.5
Formaldehyde [wt]	42	40-55	<55
Methanol in product [wt]	< 1	< 1.3	0.5-1.5

1.7.1- From methanol by silver catalysts process

Feed mixture of pure methanol vapor and blown in air is generated in evaporator the mixture combined with steam and enter the reactor vapor passes through bed to silver catalyst or silver gauze. The conversion is in completed and the reaction takes place in 600-720 °C the reaction gases cooled in directly with water, the remaining heat of bottom of a formaldehyde absorption column. In the water cooled section of column, the bulk of a methanol, water, and formaldehyde separate out a 42% formaldehyde solution from the bottom absorption column is fed to distillation column, methanol recovered at top of column, and recycled to the bottom of evaporator A formaldehyde and less than 1%(wt) methanol product containing up 5 is taken from, the bottom of distillation column and cooled. Diagram(1) explains the process:

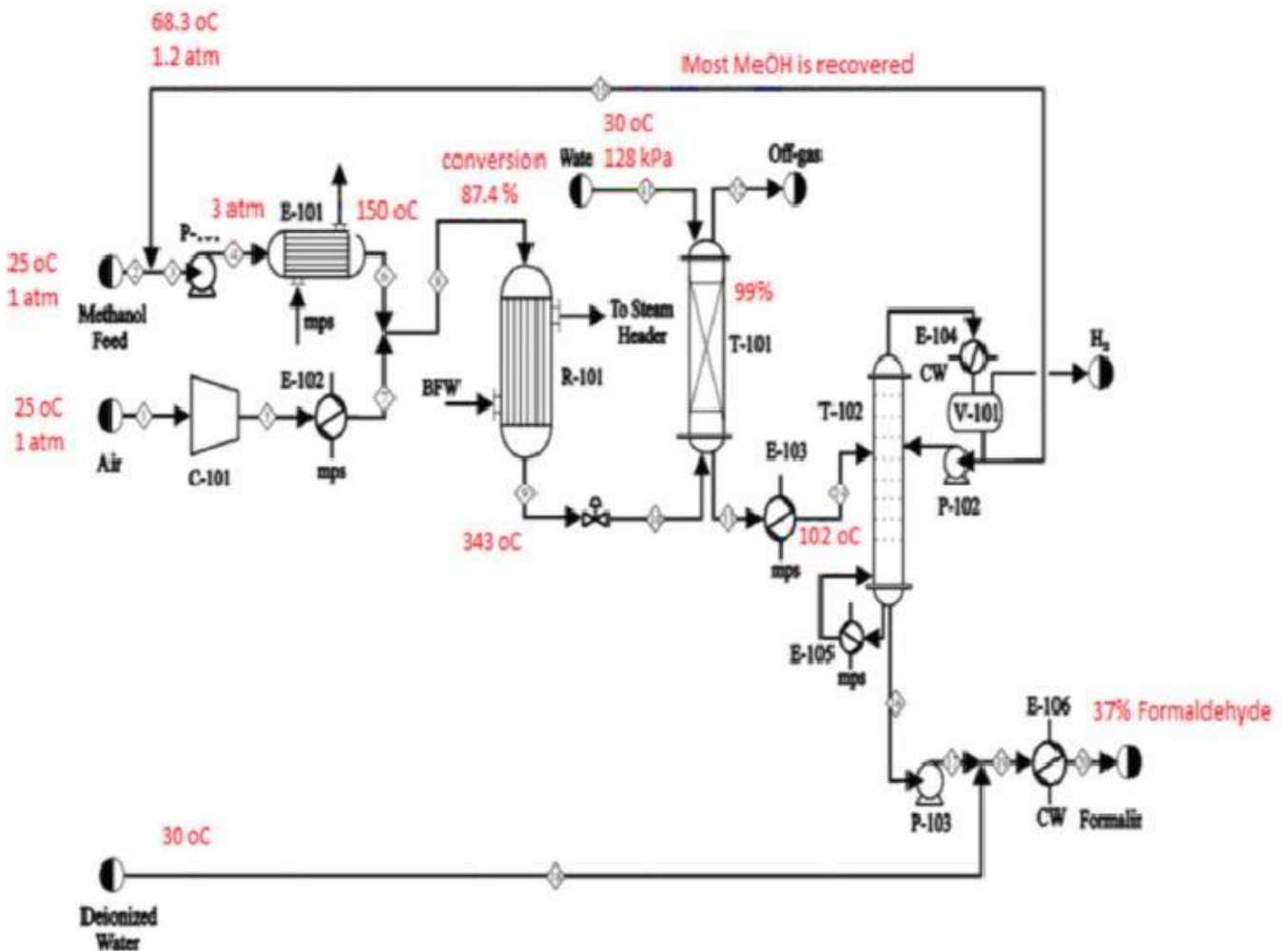


DIAGRAM 1

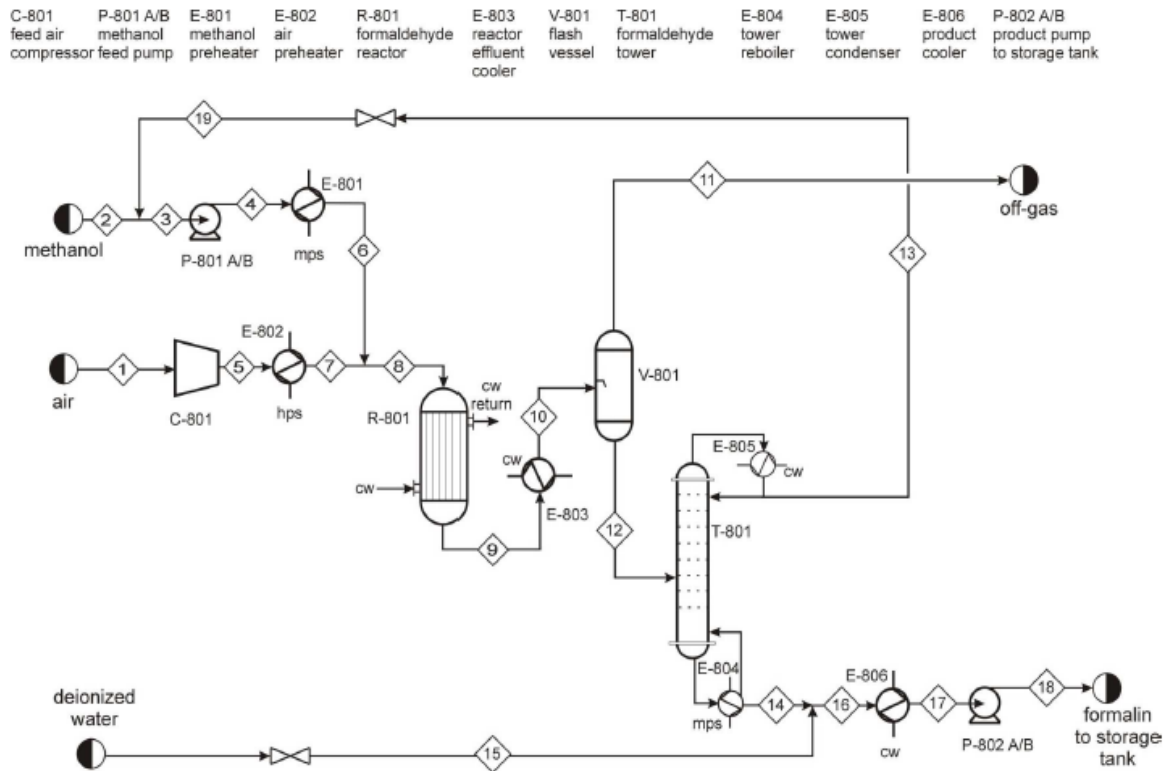


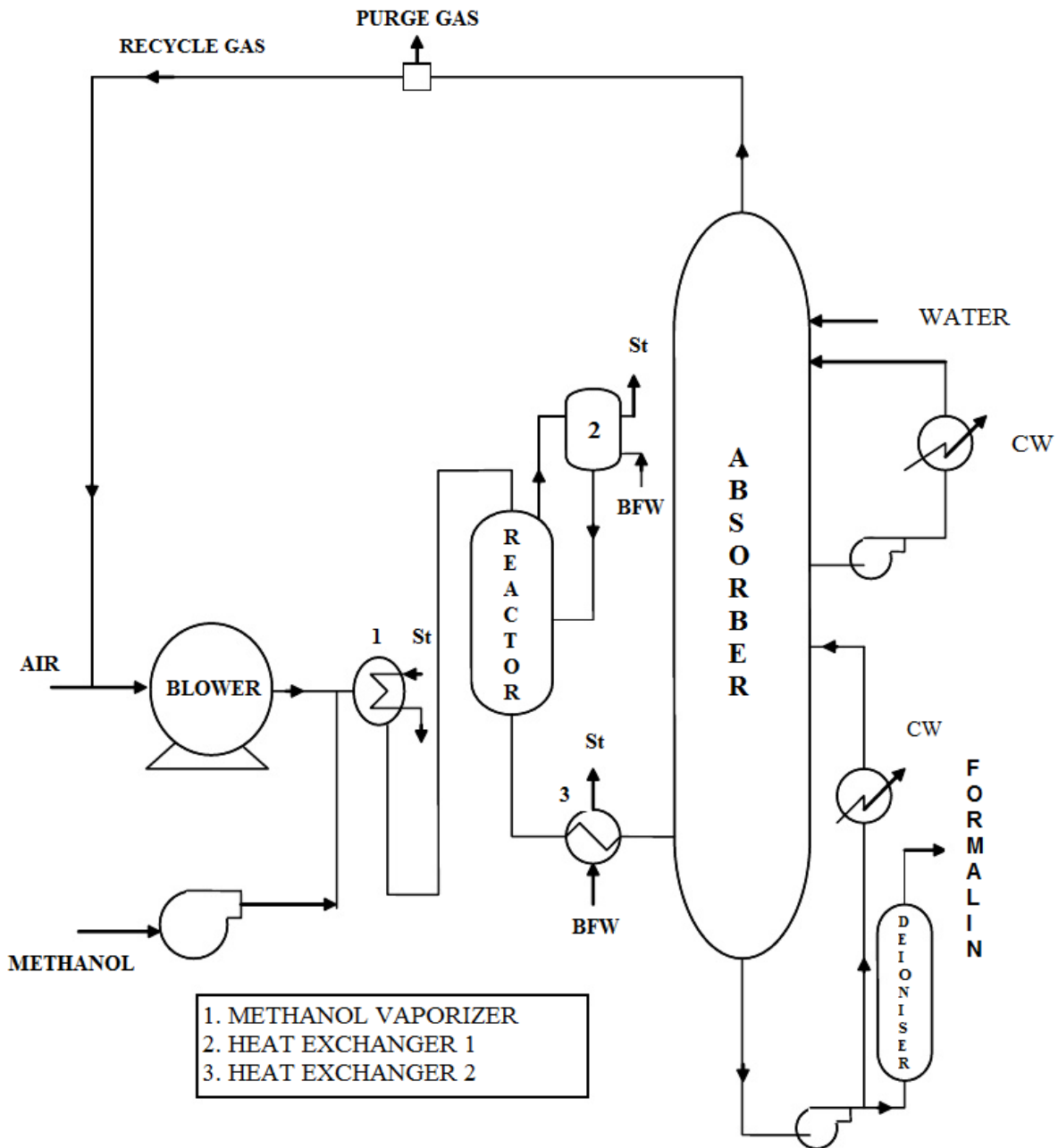
Figure 1: Unit 800 Formalin Production from Methanol

FORMALIN (FORMALDEHYDE 37 WT. % SOLUTION)

Flash point	64 °C
Autoignition temperature	430 °C
Explosive limits	36%
Lower Explosion Limit	6%
Upper Explosion Limit	36%
Products of Combustion	Carbon monoxide (CO) and Carbon

1.7.2- Metal Oxide Catalyst Process

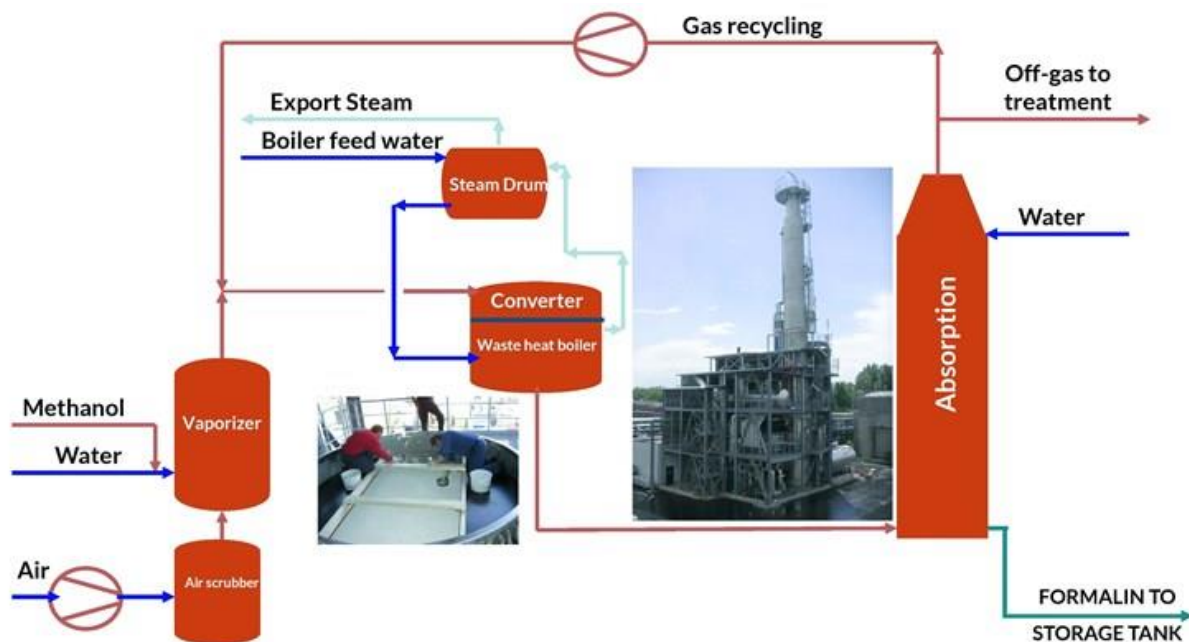
The Formax process developed by Reichhold chemicals to produce formaldehyde through direct catalytic oxidation of methanol and some other 7 by-products such as carbon monoxide and dimethyl ether forms. In 1921, the oxidation of methanol to formaldehyde with vanadium pentoxide catalyst was introduced to and patented. Then in 1933, the iron-molybdenum oxide catalyst was also patented and used till the early 1990's. Improvements to the metal oxide catalyst were done through the metal composition, inert carriers and preparation methods. The first commercial plant for the production of formaldehyde using the iron-molybdenum oxide catalyst was put into action in 1952. Unlike the silver based catalyst in this project, the iron-molybdenum oxide catalyst makes formaldehyde from the exothermic reaction (1) entirely. Under atmospheric pressure and 250 –350 °C, methanol conversion inside the reactor could reach 99% and a yield of 88% - 92%.



The process begins by mixing of vaporized methanol and air prior to entering the reactors. Inside the heat exchanger reactor, the feed is passed through the metal oxide catalyst filled tubes where heat is removed from the exothermic reaction to the outside of the tubes. Short tubes (1 – 1.5 m) and a shell diameter 2.5 m is the expected design of typical reactors. The bottom product leaving the reactors is cooled and passed to the absorber. The composition of formaldehyde in the absorber outlet is controlled by the amount of water addition. An almost methanol-free product can be achieved on this process design. The advantage of this process over the silver based catalyst is the absence of the distillation column to separate unreacted methanol and formaldehyde product. It also has a life span of 12 to 18 months, larger than the silver catalyst.

1.7.3- Production of formaldehyde from methane and other hydrocarbon gases

Another method of producing formaldehyde is through the oxidation of hydrocarbon gases. An increase in the amount produced of formaldehyde is expected in this process. However, the hydrocarbon formaldehyde is usually obtained as dilute solution which is not economically concentrated accompanied by other aldehydes and by-products. However, improvements have been effected by the use of special catalysts and better methods of control. Wheeler demonstrated that methane is not oxidized at an appreciable rate below 600°C. The difficulty in this method is in controlling the oxidation of reaction. Ethylene, ethane and propane oxidations can be controlled to yield formaldehyde under similar conditions to methane. Higher hydrocarbon gases can be oxidized at much lower temperatures than methane and ethane. These methods have been described by Bibb also reported by Wiezevich and Frolich, who used iron, nickel, aluminum, and other metals as catalysts and employed pressures up to 135 atmospheres. The Cities Service Oil Company has developed a commercial process using this method.



1.8- Selection of process

The oxide process has to think about how to let out their tail gas, which mostly consist of nitrogen, oxygen, CO and other compounds from the absorption tower such as formaldehyde and methanol exist in the tail gas. Because of these compounds the tail gas cannot be released into the air as it is, compared to the silver processes that can let their tail gas go without consideration.

the disadvantage of The oxide process design is the need for significantly large equipment to accommodate the increased flow of gases (3 times larger) compared to the original silver catalyst process design. This increase in equipment sizing clashes with economic prospect behind the design costs.

silver catalysts process

In this project formaldehyde is to be produced through a catalytic vapor-phase oxidation reaction involving methanol and oxygen according to the following reactions.



The desired reaction is the first which is exothermic with a selectivity of 9, while the second is an endothermic reaction. Operate of the process at atmospheric pressure and very high temperatures (600°C – 650°C) .

CHAPTER TWO
MATERIAL AND ENERGY BALANCE

2.1-Mass balance

The amount of input basis of methanol is $10 \frac{\text{kmol}}{\text{h}}$

Definitions of all abbreviations used in our calculations:

n : is the molar flow-rate (kmol/hr)

m : methanol

water: deionized water

H_2 : hydrogen

N_2 : nitrogen

f : formaldehyde

O_2 : oxygen

x : is the mole fraction

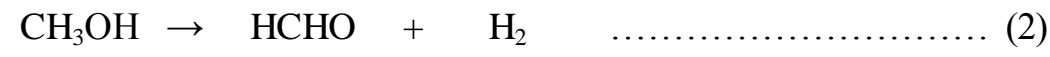
n_m : methanol flow rate, similarly for the rest components.

2.1.1-First run mass balance

2.1.1.1- Material balance on the reactor



10	$n_{\text{O}_2,8}$	0	0
$10 - \xi_1$	$-1/2\xi$	$+\xi$	$+\xi$
-----	-----	-----	-----
2.13	0	7.87	7.87



2.13	0	0
$2.13 - \varepsilon_2$	$+\varepsilon_2$	$+\varepsilon_2$
-----	-----	-----
1.26	0.87	0.87

From the conversion :-

$$87\% = \frac{\varepsilon_1 + \varepsilon_2}{n_{M,8}} = \frac{\varepsilon_1 + \varepsilon_2}{10}$$

$$\varepsilon_1 + \varepsilon_2 = 8.7 \dots\dots\dots(1)$$

FROM the selectivity :-

$$\varepsilon_1 = \varepsilon_2 * 9$$

$$\varepsilon_1 - \varepsilon_2 * 9 = 0 \dots\dots\dots(2)$$

FROM (1) and (2) we get :-

$$\varepsilon_1 = 7.87 \text{ kmol/hr}$$

$$\varepsilon_2 = 0.87 \text{ kmol/hr}$$

$$n_{O_2,8} = 1/2 \varepsilon_1$$

$$= 3.935 \text{ kmol/hr}$$

$$n_{N_2,9} = n_{O_2,8} * \frac{79}{21}$$

$$= 14.803 \text{ kmol/hr}$$

$$n_{H_2,9} = \varepsilon_2 = 0.87 \text{ kmol/hr}$$

$$n_{\text{water}} = \varepsilon_1 = 7.87 \text{ kmol/hr}$$

$$n_{F,9} = \varepsilon_1 + \varepsilon_2$$

$$7.87 + 0.87 = 8.74 \text{ kmol/hr}$$

$$N_{M,9} = n_{M,8} - \varepsilon_1 - \varepsilon_2$$

$$10 - 7.87 - 0.87 = 1.26 \text{ kmol/hr}$$

$$\text{STREM 8 } (n_8) = \sum n_i$$

$$= n_{M,8} + n_{O_2,8} + n_{H_2,8} + n_{H_2O,8} + n_{F,8} + n_{N_2,8}$$

$$10 + 3.935 + 0 + 0 + 0 + 14.803$$

$$= 28.738 \text{ kmol/hr}$$

$$n_{O_2,9} = 0 \text{ kmol/hr}$$

$$\text{STREAM 9 } (n_9) = \sum n_i$$

$$= n_{O_2,9} + n_{N_2,9} + n_{H_2,9} + n_{H_2O,9} + n_{F,9} + n_{M,9}$$

$$= 0 + 14.803 + 0.87 + 8.74 + 1.26$$

$$= 33.543 \text{ kmol/hr}$$

$$X_{i,8} = \frac{n_i}{\sum n}$$

$$X_{O_2,8} = \frac{3.935}{28.738} = 0.1369$$

$$X_{M,8} = \frac{10}{28.738} = 0.347$$

$$X_{N_2,8} = \frac{14.803}{28.738} = 0.515$$

$$X_{M,9} = \frac{1.26}{33.543} = 0.0357$$

$$X_{O_2,9} = \frac{0}{33.543} = 0$$

$$X_{H_2O,9} = \frac{7.87}{33.543} = 0.2346$$

$$X_{H_2,9} = \frac{0.87}{33.543} = 0.0259$$

$$X_{F,9} = \frac{8.74}{33.543} = 0.2605$$

$$X_{N_2,9} = \frac{14.803}{33.543} = 0.4413$$

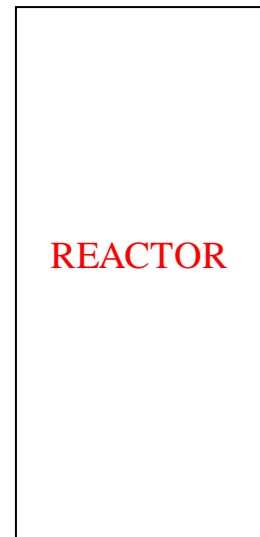
STREAM(8)

$$X_M = 0.347$$

$$X_{O_2} = 0.1369$$

$$X_W = 0$$

$$X_N = 0.515$$



STREAM (9)

$$X_M = 0.0375$$

$$X_F = 0.2605$$

$$X_W = 0.2346$$

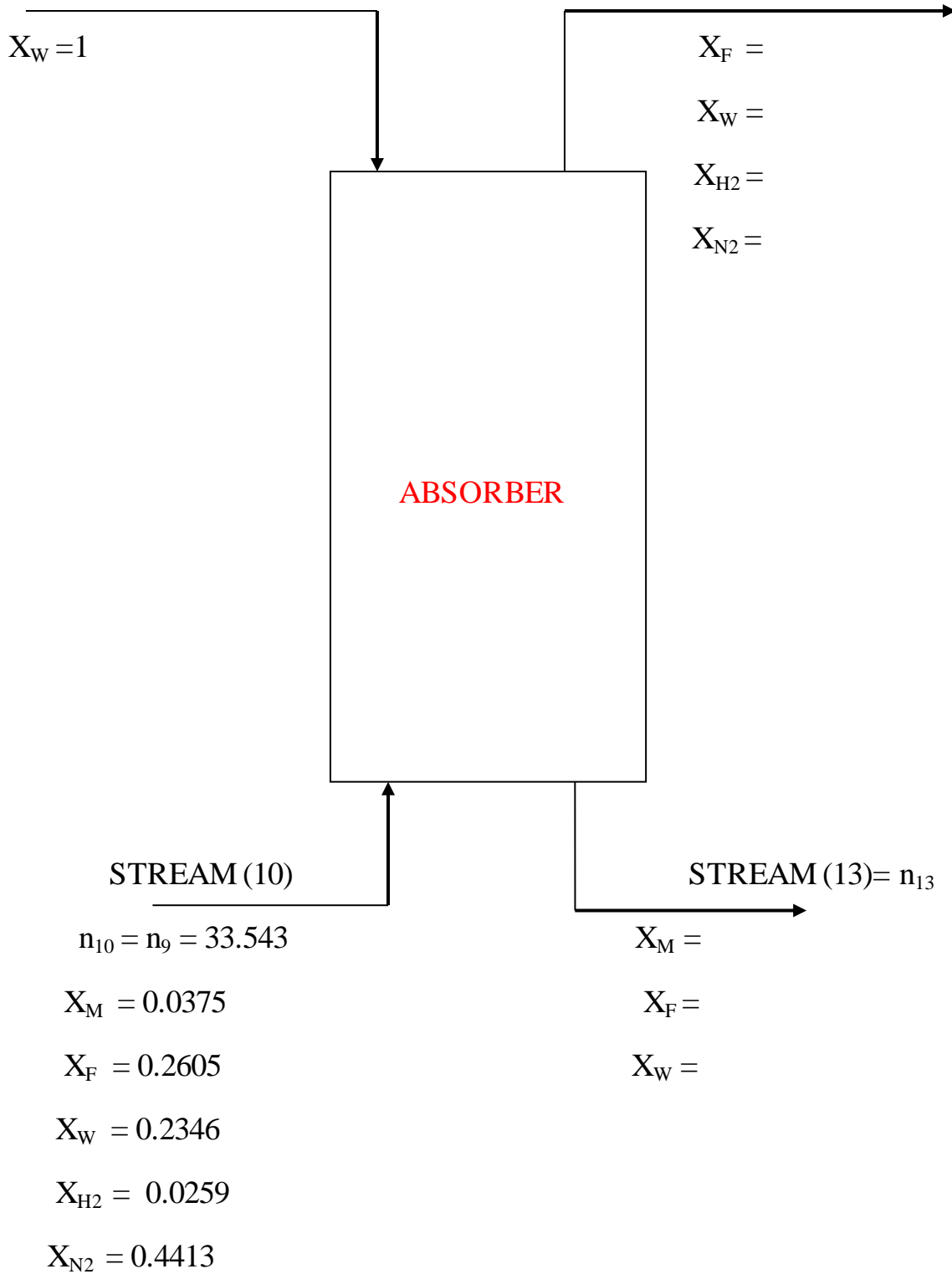
$$X_{H_2} = 0.0259$$

$$X_{N_2} = 0.4413$$

2.1.1.2- Material balance on the absorber

STREAM (11) = $n_{11} = ?$

STREAM (12) = $n_{12} = ?$



SOLUBILITY OF FORMALDEHYDE IN WATER AT T= 89.37C

EQUAL TO 0.78 KG F / KG WATER

$$= \frac{0.78 \text{ KG F}}{\text{KG WATER}} * \frac{1 \text{ Kmol F}}{30.02 \text{ KG F}} * \frac{18 \text{ KG WATER}}{1 \text{ KG WATER}}$$

$$= 0.468 \frac{\text{Kmol F}}{\text{Kmol WATER}}$$

$$\frac{0.468 \text{ kmol f}}{8.7 \text{ kmol f}} = \frac{1 \text{ kmol water}}{x \text{ kmol water}}$$

$$X = 18.675 \text{ kmol water/hr}$$

$$n_{11} = 18.675 \text{ kmol / hr}$$

from the solubility of methanol we find the amount of methanol which dissolved in 18.675 of water

$$\text{s.of methanol} = \frac{p(\text{atm}) * \text{fraction} * \text{m.w}}{\text{Henry constant}}$$

$$= \frac{1.362 * 0.0375 * 32 \text{ gm/mol}}{4.55 * 10^{-6} \text{ atm} * \text{m}^3/\text{mol}}$$

$$= 359208.7912 \text{ g methanol/m}^3 \text{ water}$$

$$359208.7912 \text{ gm methanol/m}^3 * \frac{\text{kmol}}{33 \text{ kg}} * \frac{\text{kg}}{1000 \text{ gm}} * 1 \text{ m}^3 / 1000 \text{ liter}$$

$$= 0.011225 \text{ kmol methanol/ L of water}$$

$$\text{Molarity} = \text{kmol of water / volume}$$

$$\text{Molarity} = \text{weight / m.wt}$$

$$= 1/18$$

$$\frac{1}{18} = \frac{\text{mole of water}}{1 \text{ L}}$$

$$\text{Kmol of water} = 0.0555$$

Thus ,

$$\frac{0.011225 \text{ kmol methanol}}{x \text{ kmol methanol}} = \frac{0.0555}{18.675}$$

$$X = 3.777 \text{ kmol of methanol / hr}$$

So all the methanol dissolved in water because we have 1.26 kmol of methanol /hr in the stream (10)

$$n_{M,13} = n_{M,10} = 1.26 \text{ kmol methanol /hr}$$

all the kmoles of N₂ and H₂ out from stream (12)

$$\text{so } n_{2,12} = n_{N_2,10} = 14.803 \text{ kmol/hr}$$

$$n_{H_2,12} = n_{H_2,10} = 0.87 \text{ kmol/hr}$$

$$n_{F,12} = n_{F,10} * (1 - 0.99)$$

$$= 8.74 * 0.01$$

$$= 0.0874 \text{ kmol/hr}$$

$$n_{F,13} = n_{F10} * 0.99$$

$$= 8.74 * 0.99$$

$$= 8.6526 \text{ kmol/hr}$$

$$P^* (89.37c) = p * X_{H_2O,12}$$

$$X_{H_2O,12} = \frac{P^*_{H_2O,12}(89.37C)}{P} \dots\dots\dots(1)$$

$$P^*_{H_2O} = \exp(A - B/T + C) \quad A = 16.3872$$

$$P^*_{H_2O} = \exp(16.3872 - 3885.7/89.37 + 230.17) \quad B = 3885.7$$

$$P^*_{H_2O} = 68.5 \text{ kpa} \quad C = 230.17$$

$$P = 138 \text{ kpa}$$

Substituting $p^*_{H_2O}$ and p in equation (1)

$$X_{\text{H}_2\text{O},12} = 68.15/138 = 0.496$$

METERAIL BALANE FOR WATER

$$n_{\text{H}_2\text{O},10} + n_{\text{H}_2\text{O},11} = n_{\text{H}_2\text{O},12} + n_{\text{H}_2\text{O},13} \dots\dots\dots(2)$$

$$7.87 + 18.675 = n_{\text{H}_2\text{O},12}/X_{\text{H}_2\text{O},12}$$

$$n_{\text{H}_2\text{O},12} = 26.545 * 0.496$$

$$n_{\text{H}_2\text{O},12} = 13.116632 \text{ kmol/hr}$$

substituting $n_{\text{H}_2\text{O}}$ in equation (2)

$$n_{\text{H}_2\text{O},13} = 13.37868 \text{ kmol/hr}$$

$$\begin{aligned} n_{12} &= n_{\text{F},12} + n_{\text{N},12} + n_{\text{H}_2,12} + n_{\text{H}_2\text{O},12} \\ &= 0.0874 + 14.803 + 0.87 + 13.16632 \\ &= 28.92672 \text{ kmol/hr} \end{aligned}$$

$$\begin{aligned} n_{13} &= n_{\text{F},13} + n_{\text{M},13} + n_{\text{H}_2\text{O},13} \\ &= 8.6526 + 1.26 + 13.37868 \\ &= 23.29 \text{ kmol/hr} \end{aligned}$$

$$X_{\text{F},12} = \frac{n_{\text{F},12}}{n_{12}} = \frac{0.0874}{28.92672} = 0.00302$$

$$X_{\text{N}_2,12} = \frac{n_{\text{N}_2,12}}{n_{12}} = \frac{14.803}{28.92672} = 0.51174$$

$$X_{\text{H}_2,12} = \frac{n_{\text{H}_2,12}}{n_{12}} = \frac{0.87}{28.92672} = 0.03$$

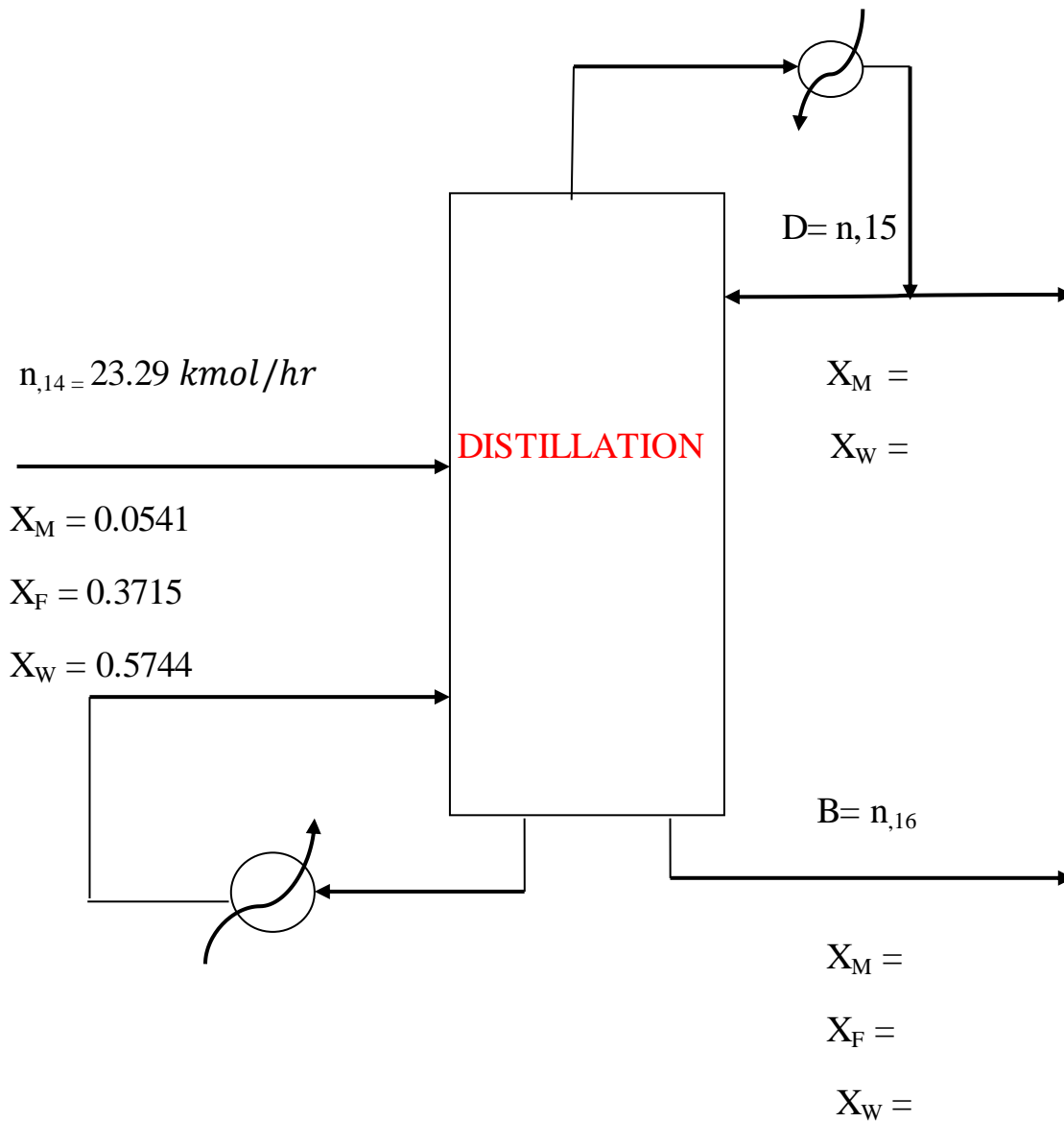
$$X_{\text{H}_2\text{O},12} = \frac{n_{\text{H}_2\text{O},12}}{n_{12}} = \frac{13.16632}{28.92672} = 0.45516$$

$$X_{\text{F},13} = \frac{n_{\text{F},13}}{n_{13}} = \frac{8.6526}{23.29} = 0.3715$$

$$X_{\text{M},13} = \frac{n_{\text{M},13}}{n_{13}} = \frac{1.26}{23.29} = 0.0541$$

$$X_{\text{H}_2\text{O},13} = \frac{n_{\text{H}_2\text{O},13}}{n_{13}} = \frac{13.37868}{23.29} = 0.5744$$

2.1.1.3- Material balance on the distillation column



from the boiling point of methanol and formaldehyde and water the assumption is :-

1- light key : methanol

2- heavy key :H₂O

$$n_{14} = D + B$$

Fractional(1) recovery for methanol = 99.7 %

Fraction (2) recovery for water = 99%

$$n_{M,D} = n_{M,W} + \text{frac } 1$$

$$\begin{aligned} n_{M,D} &= 1.26 * 0.977 \\ &= 1.25622 \text{ kmol / hr} \end{aligned}$$

$$n_{M,B} = n_{,14} * (1 - \text{frac } 1)$$

$$\begin{aligned} n_{M,B} &= 1.26 * (1 - 0.997) \\ &= 0.00378 \text{ kmol/hr} \end{aligned}$$

$$n_{H_2O,B} = n_{H_2O,14} * \text{frac } 2$$

$$n_{H_2O,B} = 13.37868 * 0.99$$

$$n_{H_2O,B} = 13.2558 \text{ kmol/hr}$$

$$n_{H_2O,D} = n_{H_2O,14} * (1 - \text{frac } 2)$$

$$n_{H_2O,D} = 13.37868 * (1 - 0.99)$$

$$n_{H_2O,D} = 0.1337 \text{ kmol / hr}$$

$$n_{F,B} = n_{F,14} = 8.6526 \text{ kmol/hr}$$

$$D = \sum n_{i,D} = n_{W,D} + n_{M,D}$$

$$D = 0.1337 + 1.25622$$

$$D = 1.38992 \text{ kmol/hr}$$

$$B = \sum n_{i,B} = n_{M,B} + n_{F,B} + n_{W,B}$$

$$= 0.00378 + 8.6526 + 13.2448$$

$$B = 21.9 \text{ kmol/hr}$$

$$X_{M,D} = \frac{n_{M,D}}{D} = \frac{1.25622}{1.38992} = 0.903$$

$$X_{W,D} = \frac{n_{W,D}}{D} = \frac{0.1337}{1.38992} = 0.0961$$

$$X_{M,B} = \frac{n_{M,B}}{B} = \frac{0.00378}{21.9} = 0.00017$$

$$X_{F,B} = \frac{n_{F,B}}{B} = \frac{8.6526}{21.9} = 0.395$$

$$X_{W,B} = \frac{n_{W,B}}{B} = \frac{13.2448}{21.9} = 0.6047$$

MATERIAL	MOLE FRACTION	n_i	M.wt	Mass = $n_i * M.wt$	Mass fraction
Methanol	0.00017	0.00378	32.042	0.1211	0.000243
Formaldehyde	0.395	8.6526	30.02	259.751	0.5212
Water	0.6047	13.2448	18	238.4064	0.4784
Σ				498.2785	

$$\text{Formaldehyde to water ratio} = \frac{0.5212}{0.4784} = 1.089$$

Mass balance at mixing point of stream 2,3 and 15 : (second run)

$$n_{M,3} = n_{M,2} + n_{M,15}$$

$$10 = n_{M,2} + 1.25622$$

$$n_{M,2} = 10 - 1.25622 = 8.74378 \text{ kmol/hr}$$

$$n_{W,3} = n_{W,15} = 0.1337 \text{ kmol / hr}$$

$$n_3 = n_{W,3} + n_{M,3}$$

$$n_3 = 0.1337 + 10 = 10.1337 \text{ kmol/hr}$$

Mass balance at mixing point of stream 6 , 7 and 8 :

$$n_7 = n_5 = n_1 = n_{O_2,1} + n_{N_2,1}$$

$$= 3.935 + 14.803$$

$$= 18.738 \text{ kmol/hr}$$

$$n_3 = n_4 = n_6 = 10.1337 \text{ kmol/hr}$$

$$n_8 = n_6 + n_7$$

$$= 10.1337 + 18.738$$

$$= 28.8717 \text{ kmol/hr}$$

2.2- Second run mass balance

2.1.2.1- Mass balance on the reactor

The feed to the reactor is $n_8 = 28.8717 \text{ kmol/hr}$

Its composition is :-

$$X_{M,8} = 10$$

$$X_{N_2,8} = 14.803$$

$$X_{O_2,8} = 3.935$$

$$X_{W,8} = 0.1067$$

$$n_{M,9} \text{ (second run) } = n_{M,9} \text{ (first run) } = 1.26 \text{ kmol/hr}$$

$$n_{O_2,9} \text{ (second run) } = n_{O_2,9} \text{ (first run) } = 3.935 \text{ kmol/hr}$$

$$n_{N_2,9} \text{ (second run) } = n_{N_2,9} \text{ (first run) } = 14.803 \text{ kmol/hr}$$

$$n_{H_2,9} \text{ (second run)} = n_{H_2,9} \text{ (first run)} = 0.87 \text{ kmol/hr}$$

$$n_{F,9} \text{ (second run)} = n_{F,9} \text{ (first run)} = 8.74 \text{ kmol/hr}$$

$$\begin{aligned} n_{W,9} \text{ (second run)} &= 0.1067 + \varepsilon_1 \\ &= 0.1607 + 7.87 = 7.9767 \text{ kmol/hr} \end{aligned}$$

$$n_9 \text{ (second run)} = \sum n_{i,9} = 37.5847 \text{ kmol/hr}$$

2.1.2.2- Mass balance on the absorber

$$n_{F,10} \text{ (second run)} = n_{F,10} \text{ (first run)} = 8.74 \text{ kmol/hr}$$

$$n_{f,12} \text{ (second run)} = n_{F10} \text{ (second run)} * (1-0.99)$$

$$n_{F,12} = 0.0874 \text{ kmol/hr}$$

$$n_{F,13} \text{ (second run)} = n_{F,10} * 0.99$$

$$n_{F,13} = 8.6526 \text{ kmol/hr}$$

$$n_{N_2,13} = 14.803 \text{ kmol/hr}$$

$$n_{H_2,13} = 0.87 \text{ kmol/hr}$$

$$X_{H_2O,12} \text{ (second run)} = X_{H_2O,12} \text{ (first run)} = 0.496$$

$$\begin{aligned} n_{H_2O,12} &= [n_{H_2O,10} \text{ (second run)} + n_{H_2O,11} \text{ (second run)}] * X_{H_2O,12} \\ &= [7.9767 + 18.675] * 0.496 \end{aligned}$$

$$\begin{aligned} n_{12} &= \sum n_{i,12} = n_{F,12} + n_{N_2,12} + n_{H_2,12} + n_{H_2O,12} \\ &= 0.6874 + 14.803 + 0.87 + 13.219 \\ &= 28.988 \text{ kmol/hr} \end{aligned}$$

$$\begin{aligned} n_{H_2O,13} &= n_{H_2O,11} + n_{H_2O,10} - n_{H_2O,12} \\ &= 18.675 + 7.9767 - 13.219 \\ &= 13.432 \text{ kmol/hr} \end{aligned}$$

$$n_{M,13} = n_{M,10} - n_{m,12}$$

$$= 1.26 - 0 = 1.26 \text{ kmol/hr}$$

$$n_{13} = \sum n_{i,13} = n_{M,13} + n_{H_2O,13} + n_{F,13}$$

$$= 1.26 + 13.432 + 8.6526$$

$$= 23.344 \text{ kmol/hr}$$

2.1.2.3- Mass balance on the distillation column

$$n_{,14} = n_{13} = D + B$$

$$23.44 = D + B \quad \dots\dots\dots (1)$$

$$n_{M,D} = n_{M,14} * \text{frac .1}$$

$$= 1.26 * 0.997$$

$$= 1.256 \text{ kmol/hr}$$

$$n_{M,B} = n_{M,14} * (1 - \text{frac .1})$$

$$= 1.26 * (1 - 0.997)$$

$$= 0.00378 \text{ kmol/hr}$$

$$n_{H_2O,B} = n_{H_2O,14} * \text{frac .2}$$

$$= 13.432 * 0.99$$

$$= 13.297 \text{ kmol/hr}$$

$$n_{H_2O,D} = n_{H_2O,14} * (1 - \text{frac.2})$$

$$= 13.432 * (1 - 0.99)$$

$$= 0.13432 \text{ kmol/hr}$$

$$n_{F,B} = n_{F14} = 8.6526 \text{ kmol/hr}$$

$$D = \sum n_{i,D} = n_{H_2O,D} + n_{M,D}$$

$$= 0.13432 + 1.256$$

$$= 1.39 \text{ kmol/hr}$$

$$B = \sum n_{i,B} = n_{H_2O} + n_{M,B} + n_{F,B}$$

$$= 13.297 + 0.00378 + 8.6526$$

$$B = 21.953 \text{ kmol/hr}$$

$$X_{M,D} = \frac{n_{M,D}}{D} = \frac{1.256}{1.39} = 0.903$$

$$X_{W,D} = \frac{n_{W,D}}{D} = \frac{0.13432}{1.39} = 0.0966$$

$$X_{M,B} = \frac{n_{M,B}}{B} = \frac{0.00378}{21.953} = 0.000172$$

$$X_{F,B} = \frac{n_{F,B}}{B} = \frac{8.6526}{21.953} = 0.3941$$

$$X_{W,B} = \frac{n_{W,B}}{B} = \frac{13.297}{21.953} = 0.6057$$

MATERIAL	MOLE FRACTION	n_i	M.wt	Mass = $n_i * M.wt$	Mass fraction
Methanol	0.000172	0.00398	32.042	0.12118	0.000242
Formaldehyde	0.3941	8.6526	30.02	259.751	0.5203
Water	0.6057	13.297	18	239.346	0.4794
Σ				499.218	

$$n_{F,19} = n_{F,17}/n_{17} + n_{18}$$

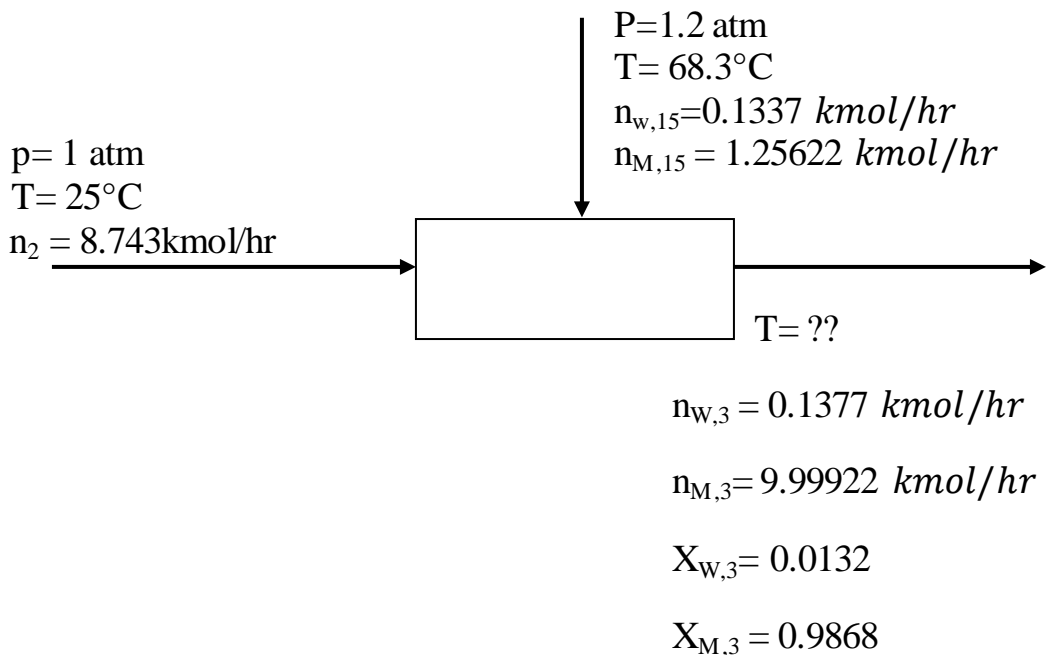
$$n_{F,19} = 0.00378 \text{ kmol/hr}$$

2.2- Energy balance

Table of (cp) for each compound in the system :-

Component	Phase	A	B	C	D
Methanol	Liquid	$75.86 \cdot 10^{-3}$	$16.83 \cdot 10^{-5}$	0	0
	Gas	$42.93 \cdot 10^{-3}$	$8.301 \cdot 10^{-5}$	$-1.87 \cdot 10^{-8}$	$-8.03 \cdot 10^{-12}$
Water	Liquid	$75.4 \cdot 10^{-3}$	0	0	0
	Gas	$33.46 \cdot 10^{-3}$	$0.688 \cdot 10^{-5}$	$0.7604 \cdot 10^{-8}$	$-3.593 \cdot 10^{-12}$
Formaldehyde	Gas	$34.28 \cdot 10^{-3}$	$4.268 \cdot 10^{-5}$	0	$-8.694 \cdot 10^{-12}$
N2	Gas	$29 \cdot 10^{-3}$	$0.2199 \cdot 10^{-5}$	$0.5723 \cdot 10^{-8}$	$-2.871 \cdot 10^{-12}$
O2	Gas	$29.1 \cdot 10^{-3}$	$1.158 \cdot 10^{-5}$	$0.6076 \cdot 10^{-8}$	$1.311 \cdot 10^{-12}$
H2	Gas	$28.84 \cdot 10^{-3}$	$0.00765 \cdot 10^{-5}$	$0.3288 \cdot 10^{-8}$	$-0.8698 \cdot 10^{-12}$
$CP = A + BT + CT^2 + DT^3$					

2.2.1- Mixing point between streams 2,3 and 15



at $T = 68.3 \text{ }^\circ\text{C}$ and $P = 1.2$ Methanol is in liquid phase

$$E_{in} = E_{out}$$

$$n_2 \int_{25}^{25} cp_1 m_2 dt + n_{w,15} \int_{25}^{68.3} cp_{W,15} dt + n_{w,15} \int_{25}^{68.3} cp_{M,15} dt$$

$$= n_3 \int_{25}^T cp_3 dt$$

$$E_{in} = 0.1337 [75.4 * 10^{-3} T]_{25}^{68.3} + 1.25622 [75.86 * 10^{-3} T + 16.83 * 10^{-3} / 2]_{25}^{68.3}$$

$$E_{in} = 48.89 = E_{out}$$

$$E_{out} = n_3 \int_{25}^T cp_3 dt = \int_{25}^T (n_{W,3} cp_{wi} + n_{M,3} cp_{Mi}) dt$$

$$= \int_{25}^T 7.517 + 0.01646 T dt$$

$$= [7.517 T + \frac{0.01646}{2} T^2]_{25}^T$$

$$E_{out} = 7.517 T + 8.32 * 10^{-3} T^2 - [7.517 (25) + 8.32 * 10^{-3} (25)^2]$$

$$48.89 = 7.517 T + 8.32 * 10^{-3} T^2 - 193.06875$$

$$T = 31.13^\circ C$$

2.2.2- Energy balance on the heat exchanger E-101

$$Q = \sum n cp \Delta T$$

$$= (n cp \Delta T)_M + (n cp \Delta T)_W$$

$$= n_{M,4} [\int_{31.13}^{64.7} cp_{M,Liq} dt + \Delta H_V + \int_{64.7}^{150} CP_{M,gas} dt]$$

$$+ n_{W,4} [\int_{31.13}^{100} CP_{W,liq} dt + \Delta H_V + \int_{100}^{150} cp_{W,gas} dt]$$

$$= 9.99922 [\int_{31.13}^{64.4} (75.86 * 10^{-3} + 16.83 * 10^{-5} T) dt + 35.27$$

$$+ \int_{64.7}^{150} (42.93 * 10^{-3} dt + 8.301 * 10^{-3} T - 1.87 * 10^{-8} T^2 - 8.03 * 10^{-12} T^3) dt]$$

$$+ 0.1337 [\int_{31.13}^{100} 75.4 * 10^{-3} dt + 40.6565$$

$$+ \int_{100}^{150} (33.46 * 10^{-3} + 0.0688 * 10^{-5} T + 0.7604 * 10^{-8} T^2 - 3.593 * 10^{-12} T^3) dt]$$

$$= 4155051.3 + 6231729 = 4217368.59 \text{ kJ/hr}$$

$$Q = m \text{ cp } \Delta T$$

$$-4217368.59 \text{ KJ/hr} = m \int_{150}^{110} \text{cp}_w \text{ dt}$$

$$-4217368.59 = m \int_{150}^{110} (33.46 * 10^{-3} + 0.688 * 10^{-5} T + 0.7604 * 10^{-8} T^2 - 3.593 * 10^{-12} T^3) \text{ dt}$$

$$-4217368.59 = m [33.46 * 10^{-3} T + 0.688 * 10^{-5} / 2 T^2 + 0.7774 * 10^{-8} T^3 / 3 - 3.593 * 10^{-12} T^4 / 4]_{150}^{110}$$

$$-4217368.59 = m [(3.7004 * 10^{-3} T + 0.041624 + 3.373364 * 10^{-3} - 1.3151 * 10^{-4}) - (5.019 * 10^{-3} + 0.0774 + 8.5545 * 10^{-3} - 4.547 * 10^{-4})]$$

$$-4217368.59 = m [(0.0596) - (0.0905)]$$

$$-4217368.59 = m (-0.03453)$$

$$m = 12262971.04 \text{ mol/hr}$$

$$= 12202.97104 \text{ kmol/hr}$$

2.2.3- Energy balance on the heat exchanger E-102

$$Q = \sum n \text{ cp } \Delta T$$

$$= (n \text{ cp } \Delta T)_{\text{N}_2} + (n \text{ cp } \Delta T)_{\text{O}_2}$$

$$= 14.803 \left[\int_{25}^{150} (29 \cdot 10^{-3} + 0.2199 \cdot 10^{-5} T + 0.5723 \cdot 10^{-8} T^2 - 2.871 \cdot 10^{-12} T^3) dt \right] \\ + 3.935 \left[\int_{25}^{150} (29.1 \cdot 10^{-3} + 1.158 \cdot 10^{-5} T - 0.6676 \cdot 10^{-8} T^2 + 1.311 \cdot 10^{-12} T^3) dt \right]$$

$$= 14.803 \left[(29 \cdot 10^{-3} T + 0.2199 \cdot 10^{-5} T^2/2 + 0.5723 \cdot 10^{-8} T^3/3 \right. \\ \left. - 2.87 \cdot 10^{-12} T^4/4) \right]_{25}^{150} + 3.935 \left[(29.1 \cdot 10^{-3} T + 1.158 \cdot 10^{-5} T^2/2 \right. \\ \left. - 0.6076 \cdot 10^{-8} T^3 + 1.311 \cdot 10^{-12} T^4/4) \right]_{25}^{150}$$

$$= 14.803 \left[(4.35 + 0.0247 + 6.4383 \cdot 10^{-3} - 3.6336 \cdot 10^{-4}) - \right. \\ \left. (0.725 + 2.4738 \cdot 10^{-4} + 2.9807 \cdot 10^{-5} - 2.8037 \cdot 10^{-7}) \right]$$

$$+ 3.935 \left[(4.365 + 0.1302 - 6.8355 \cdot 10^{-3} + 1.6592 \cdot 10^{-4}) - \right. \\ \left. (0.7275 + 3.6187 \cdot 10^{-3} - 3.1645 \cdot 10^{-5} + 1.2802 \cdot 10^{-7}) \right]$$

$$= 14.803 (4.3808 - 0.72276) + 3.935 (4.4885 - 0.731)$$

$$= 54112.7 + 147857$$

$$= 68898.4 \text{ KJ/hr}$$

$$Q = m \text{ cp } \Delta T$$

$$-68898.4 = m \int_{150}^{110} \text{ cp } dt$$

$$3.593 \cdot 10^{-12} \cdot -68898.4 = m \int_{150}^{110} (33.46 \cdot 10^{-3} + 0.688 \cdot 10^{-5} T + 0.7604 \cdot 10^{-8} T^2 - \\ T^3) dt$$

$$-68898.4 = m \left[33.46 \cdot 10^{-3} T + 0.688 \cdot 10^{-5} T^2/2 + 0.7604 \cdot 10^{-8} T^3/3 \right. \\ \left. - 3.593 \cdot 10^{-12} T^4/4 \right]_{150}^{110}$$

$$-68898.4 = m \left[(3.7004 \cdot 10^{-3} + 0.041624 + 3.37364 \cdot 10^{-3} - 1.13151 \cdot 10^{-4}) \right. \\ \left. - (5.019 \cdot 10^{-3} + 0.0774 + 8.5545 \cdot 10^{-3} - 4.547 \cdot 10^{-4}) \right]$$

$$-68898.4 = m [(0.0596) - (0.0905)]$$

$$-68898.4 = m (-0.03453)$$

$$m = 1995320.012 \text{ kmol/hr}$$

2.2.4- Mixing point between streams 6, 7 Since the temperature of 6,7

are the same (150 °C) so the stream 8 also have the same temperature.

2.2.5- Energy balance on the reactor

Species	n_i (mole)	\hat{H}_{in}	n_{out} (mole)	\hat{H}_{out}
CH ₃ OH	10000	H ₁	1260	H ₅
O ₂	3935	H ₂	0	H ₆
N ₂	14803	H ₃	14803	H ₇
HCHO	0	-	8740	H ₈
H ₂	0	-	870	H ₉
H ₂ O	1310	H ₄	7976.7	H ₁₀

$$H_1 = \int_{25}^{150} CP_{m, \text{gas}} dt = 6.2522 \text{ kJ/mol}$$

$$H_2 = \int_{25}^{150} CP_{O_2, \text{gas}} dt = 3.7575 \text{ KJ/mol}$$

$$H_3 = \int_{25}^{150} CP_{N_2, \text{gas}} dt = 3.6551 \text{ KJ/mol}$$

$$H_4 = \int_{25}^{150} CP_{H_2O, \text{gas}} dt = 4.266 \text{ KJ/mol}$$

$$H_5 = \int_{25}^{343} CP_{M, \text{gas}} dt = 18.2296 \text{ kJ/mol}$$

$$H_6 = \int_{25}^{343} CP_{O_2, \text{gas}} dt = 9.854 \text{ kJ/mol}$$

$$H_7 = \int_{25}^{343} CP_{N_2, \text{gas}} dt = 9.418 \text{ kJ/mol}$$

$$H_8 = \int_{25}^{343} CP_{F, \text{gas}} dt = 13.368 \text{ kJ/mol}$$

$$H_9 = \int_{25}^{343} CP_{H_2, \text{gas}} dt = 9.2168 \text{ kJ/mol}$$

$$H_{10} = \int_{25}^{343} CP_{H_2O, \text{gas}} dt = 11.133 \text{ kJ/mol}$$

The standard of the reaction (298 °C, 1 atm) for the two reaction are given as :-

$$\Delta H_{f1} = -156 \text{ kJ/mol methanol}$$

$$\Delta H_{f2} = -85 \text{ kJ/mol methanol}$$

$$\Delta H = \sum \epsilon \Delta H_f + \sum \hat{H}_{i, \text{out}} - \sum \hat{H}_{i, \text{in}}$$

$$= (156 \times 7.87 \times 1000 - 85 \times 0.87 \times 1000) + 3679029.286 - 1290397.518$$

$$= -1301386 + 3679029.286 - 1290397.518 = 1087245.768 \text{ kJ/hr.}$$

2.2.6- Energy balance on the heat exchanger inside the reactor

Heat exchanger is joined with the reactor to cool down the product

From 343 °C to 200 °C.

The enthalpies entering to the cooling section are :-

$$\hat{H}_5 = \int_{25}^{343} CP_{M, \text{gas}} dt = 18.2296 \text{ kJ/mol}$$

$$\hat{H}_6 = \int_{25}^{343} CP_{O_2, \text{gas}} dt = 9.854 \text{ kJ/mol}$$

$$\hat{H}_7 = \int_{25}^{343} CP_{N_2, \text{gas}} dt = 9.418 \text{ kJ/mol}$$

$$\hat{H}_8 = \int_{25}^{343} CP_{F, \text{gas}} dt = 13.368 \text{ kJ/mol}$$

$$\hat{H}_9 = \int_{25}^{343} CP_{H_2, \text{gas}} dt = 9.2168 \text{ kJ/mol}$$

$$\hat{H}_{10} = \int_{25}^{343} CP_{H_2O, \text{gas}} dt = 11.133 \text{ kJ/mol}$$

The enthalpies out from the cooling section :-

$$\hat{H}_{M,9} = \int_{25}^{200} CP_{M, \text{gas}} dt = 9.0946 \text{ kJ/mol}$$

$$\hat{H}_{O_2,9} = \int_{25}^{200} CP_{O_2,gas} dt = 5.3048 \text{ kJ/mol}$$

$$\hat{H}_{N_2,9} = \int_{25}^{200} CP_{N_2,gas} dt = 5.13238 \text{ kJ/mol}$$

$$\hat{H}_{F,9} = \int_{25}^{200} CP_{F,gas} dt = 6.8358 \text{ kJ/mol}$$

$$\hat{H}_{H_2,9} = \int_{25}^{200} CP_{H_2,gas} dt = 5.0569 \text{ kJ/mol}$$

$$\hat{H}_{H_2O,9} = \int_{25}^{200} CP_{H_2O,gas} dt = 6.01 \text{ kJ/mol}$$

$$n_m = 1260 \text{ moles} , \quad n_{O_2} = 0 \text{ moles} , \quad n_{N_2} = 14803 \text{ moles}$$

$$n_F = 8740 \text{ moles} , \quad n_{H_2} = 870 \text{ moles} , \quad n_{H_2O} = 7976.7 \text{ moles}$$

$$Q = \Delta H = \sum n_i \hat{H}_{i,out} - \sum n_i \hat{H}_{i,in}$$

$$= [(1260 * 9.0940) + (14803 * 5.13238) + (8740 * 6.8358) + (7976.7 * 6.01) + (870 * 5.0569)] - [(1260 * 18.2296) + (14803 * 9.418) + (8740 * 13.368) + (7976.7 * 11.133) + (870 * 9.2168)]$$

$$= 199517.4231 - 376043.4871$$

$$= -176526.064 \text{ kJ/hr}$$

This is the heat required to remove from the system using the heat exchanger or using cold water .

$$Q = m c_p \Delta T$$

$$Q = \int c_p dt$$

$$176526.064 = m \int_{25}^{65} 75.4 * 10^{-3} dt$$

$$176526.064 = m [75.4 * 10^{-3} T]_{25}^{65}$$

$$176526.064 = m [75.4 * 10^{-3} (65) - 75.4 * 10^{-3} (25)]$$

$$176526.064 = m [4.901 - 1.885]$$

$$176526.064 = m [3.016]$$

$m = 58259.862607 \text{ kmol/hr}$ (amount of water that used).

2.2.7- Energy balance on the absorber

Energy in = Energy out

$$\sum n_i \hat{H}_{n10}(200^\circ\text{C}) + \sum n_i \hat{H}_{n11}(30^\circ\text{C}) = \sum n_i \hat{H}_{n12}(T^\circ\text{C}) + \sum n_i \hat{H}_{n13}(T^\circ\text{C})$$

Reference Temp. is 25°C

Heat in stream 10 : $\Delta T = (200-25)^\circ\text{C}$

$$Q_{n10} = (n \text{ cp } \Delta T)_{nM,10} + (n \text{ cp } \Delta T)_{nW,10} + (n \text{ cp } \Delta T)_{nF,10} + (n \text{ cp } \Delta T)_{nH2,10} + (n \text{ cp } \Delta T)_{nN2,10}$$

$$Q_{n10} = 4080729.58 \text{ kj/hr}$$

Heat in the stream 11 : $\Delta T = (30-25)^\circ\text{C}$

$$Q_{n11} = (n \text{ cp } \Delta T)_{nW,11} = -126730 \text{ kj/hr}$$

$$Q_{in} = Q_{n10} + Q_{n11} = \int_{25}^{200} \sum n_{i,10} \text{ cp}_{i,10} dt + \int_{25}^{30} \sum n_{i,11} \text{ cp}_{i,11}$$

$$Q_{in} = 3954000 \text{ kj/hr}$$

$$Q_{out} = Q_{in} = \int_{25}^T \sum n_{i,B} \text{ cp}_{i,13} dt + \int_{25}^T \sum n_{i,12} \text{ cp}_{i,12} dt$$

$$= \int_{25}^T [1260 (75.86 * 10^{-3} + 16.83 * 10^{-5} T)$$

$$+ 8652.6 (34.28 * 10^{-3} + 4.268 * 10^{-5} T) + 13378.68 (75.4 * 10^{-3})] dt$$

$$+ \int_{25}^T [13166.32 (75.4 * 10^{-3}) + 87.4 (34.28 * 10^{-3} + 4.268 * 10^{-5} T)$$

$$+ 870 (28.84 * 10^{-3} + 0.00765 * 10^{-5} T + 0.3288 * 10^{-8} T^2$$

$$- 0.8698 * 10^{-12} T^3) + 14803 (29 * 10^{-3} + 0.2199 * 10^{-5} T + 0.5723 * 10^{-8} T^2 - 2.871 * 10^{-12} T^3)] dt$$

$$T = 89.31^\circ\text{C}$$

2.2.8 - Energy balance on the heat exchanger E-103

$$n_F = 8652.6 \text{ moles}, n_W = 13378.68 \text{ moles}, n_M = 1260 \text{ moles}$$

$$\hat{H}_{M,13} = \int_{25}^{89.31} c_{p_{M,gas}} dt = 3.0615 \text{ kJ/mol}$$

$$\hat{H}_{H_2O,13} = \int_{25}^{89.31} c_{p_{H_2O,gas}} dt = 2.1788 \text{ kJ/mol}$$

$$\hat{H}_{F,13} = \int_{25}^{89.31} c_{p_{F,gas}} dt = 2.3613 \text{ kJ/mol}$$

$$\hat{H}_{M,14} = \int_{25}^{102} c_{p_{M,gas}} dt = 3.7048 \text{ kJ/mol}$$

$$\hat{H}_{H_2O,14} = \int_{25}^{102} c_{p_{H_2O,gas}} dt = 2.6126 \text{ kJ/mol}$$

$$\hat{H}_{F,14} = \int_{25}^{102} c_{p_{F,gas}} dt = 2.8480 \text{ kJ/mol}$$

$$\begin{aligned} Q &= \Delta H = \sum n_i \hat{H}_{i,14} - \sum n_i \hat{H}_{i,13} \\ &= [(1260 * 3.7048) + (13378.68 * 2.6126) + (8652.6 * 2.848)] \\ &\quad - [(1260 * 3.0615) + (13378.68 * 2.1788) +] \\ &= 64263.79 - 53438.3423 \\ &= 10825.4477 \text{ kJ/hr} \end{aligned}$$

$$Q = m \text{ cp } \Delta T$$

$$Q = m \int_{150}^{110} c_p dt$$

$$-10825.4477 = m \int_{150}^{110} c_p dt$$

$$\begin{aligned} -10825.4477 &= m \int_{150}^{110} (33.46 * 10^{-3} + 0.688 * 10^{-5} T + 0.7664 * 10^{-8} T^2 \\ &\quad - 3.593 * 10^{-12} T^3) dt \end{aligned}$$

$$\begin{aligned} -10825.4477 &= m [33.46 * 10^{-3} T + 0.688 * 10^{-5} T^2 / 2 \\ &\quad + 0.7664 * 10^{-8} T^3 / 3 - 3.593 * 10^{-12} T^4 / 4]_{150}^{110} \end{aligned}$$

$$\begin{aligned} -10825.4477 &= m [(3.7004 * 10^{-3} T + 0.041624 + 3.37364 * 10^{-3} \\ &\quad - 1.3151 * 10^{-4}) \end{aligned}$$

$$- (5.614 * 10^{-3} + 0.0774 + 8.5545 * 10^{-3} - 4.547 * 10^{-4})]$$

$$-10825.4477 = [(0.0596) - (0.0905)]$$

$$-10825.4477 = m (- 0.03453)$$

$$m = 313508.4767 \text{ mol/hr}$$

2.2.9- Energy balance on the distillation column T-101

$$Q_R = h_D - h_B - Q_C - h_{Feed}$$

$$X_{M,D} = 0.903 \quad , \quad X_{H_2O,D} = 0.0961$$

$$h_D = n_{M,D} \int_{T_{ref}}^T cp_M dt + n_{W,D} \int_{T_{ref}}^T cp_W dt \quad T_{ref} = 25 \text{ }^\circ\text{C} \quad , \quad T = 68.3 \text{ }^\circ\text{C}$$

$$= 1.25622 \text{ kmol/hr} * 1000 \text{ mol/kmol} \int_{25}^{68.3} cp_{m,L} dt + 0.13432 \text{ kmol/hr} * 1000 \text{ mol/kmol} \int_{25}^{68.3} cp_{w,L} dt$$

$$= 1256.22 \int_{25}^{68.3} (75.86 * 10^{-3} + 16.83 * 10^{-5} T) dt + 134.32 \int_{25}^{68.3} (75.4 * 10^{-3}) dt$$

$$= 1256.22 [75.86 * 10^{-3} T + 16.83 * 10^{-5} T^2/2]_{25}^{68.3} + 134.32 [75.4 * 10^{-3} T]_{25}^{68.3}$$

$$= 1256.22 [3.26482 + 0.015777] + 438.536$$

$$= 4299.528514 + 438.536$$

$$h_D = 4738.0591 \text{ KJ/hr}$$

$$X_{M,B} = 0.00017 \quad , \quad X_{F,B} = 0.0395 \quad , \quad X_{W,B} = 0.6037$$

$$h_B = n_{M,B} \int_{T_{ref}}^T cp_{M,gas} dt + n_{F,B} \int_{T_{ref}}^T cp_{F,gas} dt + n_{W,B} \int_{T_{ref}}^T cp_{W,gas} dt$$

$$T = 25 \text{ }^\circ\text{C}$$

$$T_{ref} = 110 \text{ }^\circ\text{C}$$

$$h_B = 0.00378 \text{ kmol/hr} \int_{25}^{110} cp_{M,gas} dt + 8.6526 \text{ kmol/hr} \int_{25}^{110} cp_{F,gas} dt$$

$$+ 13.2978 \text{ kmol/hr} \int_{25}^{110} cp_{W,GAS} dt$$

$$= 3.787 [42.93 * 10^{-3} T + 8.301 * 10^{-5} T^2/2 - 1.87 * 10^{-8} T^3/3 - 8.03 * 10^{-12} T^4/4]_{25}^{110}$$

$$+ 8652.6 [\{ 34.28 * 10^{-3} T + 4.268 * 10^{-5} T^2/2 \} - 8.694 * 10^{-12} T^4/4]_{25}^{110}$$

$$+ 13297.8 [33.46*10^{-3}T + 0.688*10^{-5}T^2/2 + 0.76*10^{-8}T^3/3 - 3.593*10^{-12}T^4/4]_{25}^{110}$$

$$= 14.93966 + 26544.329 + 38170.8414$$

$$= 64730.11009 \text{ kJ/hr}$$

$$Q_C = h_D - \text{heat reflux}$$

$$\text{heat reflux} = H_{M,\text{reflux}} + H_{W,\text{reflux}}$$

$$= n_{M,\text{reflux}} [\int_{T_{\text{ref}}}^{68} c_{pL} dt + \Delta H_{V,M} + \int_{68}^{102} c_{pL} dt] + n_{w,\text{reflux}} [\int_{T_{\text{ref}}}^T c_{pW,L} + \Delta H_{V,W} + \int_{100}^{102} c_{p_{\text{gas}}} dt] \dots\dots\dots(1)$$

$$V_1 = R + D$$

$$\text{ASSUM. } R / D = 1.3$$

$$R = 1.3 D$$

$$V_1 = 1.3 D + D$$

$$V_1 = 3.197 \text{ kmol/hr}$$

$$n_{M,\text{reflux}} = X_{W,D} * V_1 = 0.903 * 3.197 = 2.8868 \text{ kmol/hr} \dots\dots\dots (2)$$

$$n_{W,\text{reflux}} = X_{W,D} * V_1 = 0.0966 * 3.197 = 0.3088 \text{ kmol/hr} \dots\dots\dots(3)$$

Sub. (2) , (3) in (1)

$$\text{Heat reflux} = 2.886.8 \{ [(75.86*10^{-3}T + 16.83 *10^{-5}T^2/2)]_{25}^{68} + 35.27 + [42.93*10^{-3}T + 8.301*10^{-5}T^2/2 - 1.87*10^{-8}T^3/3 - 8.03 *10^{-12}T^4/4]_{68}^{102} \}$$

$$+ 308.8 \{ [75.4 *10^{-3} T]_{25}^{100} + 40.656 + [33.46*10^{-3}T + 0.688*10^{-5}T^2/2 + 0.7604*10^{-8} T^3/3 - 3.593 *10^{-12} T^4 / 4]_{100}^{102} \}$$

$$= 116034.4968 + 14321.5059$$

$$= 130356.0027 \text{ KJ/hr}$$

$$Q_c = h_D - \text{heat reflux}$$

$$= 4738.0591 - 130356.0027$$

$$= -125617.9436 \text{ kJ/hr}$$

$$h = n_M \int_{T_{\text{ref}}}^T C_{P_{M,\text{gas}}} + n_F \int_{T_{\text{ref}}}^T c_{p_F} + n_W \int_{T_{\text{ref}}}^T c_{p_{W,\text{gas}}}$$

$$= 1260 * 3.7048 + 8652.6 * 2.8480 + 13378.68 * 2.612$$

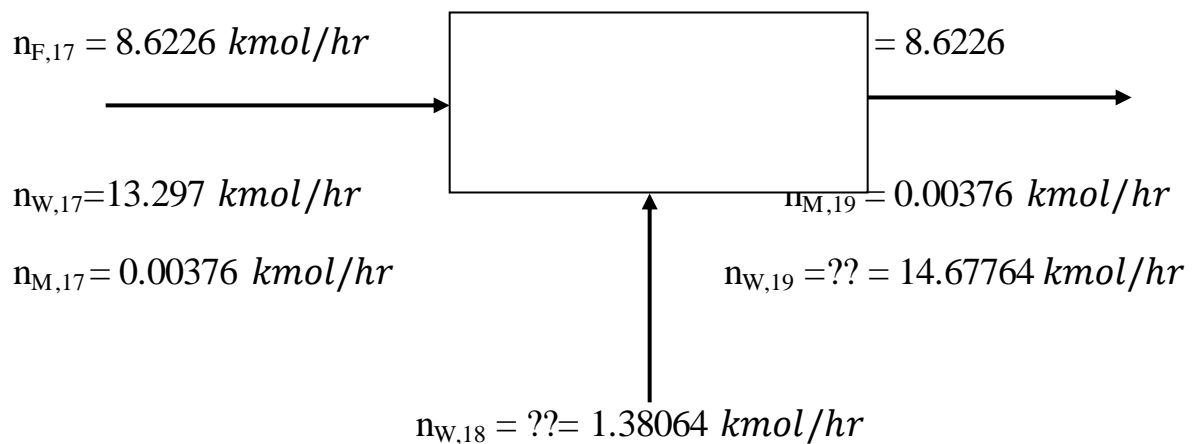
$$= 64263.79 \text{ kJ/hr}$$

$$Q_R = h_D - h_B - Q_C - h_{\text{Feed}}$$

$$= 4738.0591 + 64730.11009 - (-125617.9436) - 64263.79$$

$$= 130822.3228 \text{ kJ/hr}$$

2.2.10- Mixing point of stream 17, 18 and 19



$$0.37 = n_{F,19} / n_{19}$$

$$0.37 = 8.6226 / n_{19}$$

$$n_{19} = 23.304 \text{ kmol/hr}$$

$$n_{19} = n_{F,19} + n_{W,19} + n_{M,19}$$

$$23.304 = 8.6226 + n_{W,19} + 0.00376$$

$$n_{W,19} = 14.67764 \text{ kmol/hr}$$

$$n_{W,18} + n_{W,17} = n_{W,19}$$

$$n_{W,18} = 14.67764 - 13.297$$

$$= 1.38064 \text{ kmol/hr}$$

$$Q_{in} = Q_{out}$$

$$n_{W,17} \int_{25}^{110} cp_W dt + n_{M,17} \int_{25}^{110} CP_M dt + n_{F,17} \int_{25}^{110} CP_F$$

$$+ n_{W,18} \int_{25}^{30} CP_W dt = n_{W,19} \int_{25}^T CP_W dt + n_{M,19} \int_{25}^T CP_M dt + n_{F,19} \int_{25}^T CP_F dt$$

$$13.297 \int_{25}^{110} 75.4 * 10^{-3} dt + 0.00376 \int_{25}^{110} (75.86 * 10^{-3} + 16.83 * 10^{-5} T) dt$$

$$+ 8.6226 \int_{25}^{110} 34.28 * 10^{-3} + 4.268 * 10^{-5} T - 8.694 * 10^{-12} T^3) dt$$

$$+ 1.38064 \int_{25}^{30} 75.4 * 10^{-3} dt$$

$$= 14.67764 \int_{25}^T 75.4 * 10^{-3} dt + 0.00376 \int_{25}^T (75.4 * 10^{-3} + 16.83 * 10^{-5} T) dt$$

$$+ 8.6226 \int_{25}^T (34.28 * 10^{-3} + 4.268 * 10^{-5} T - 8.694 * 10^{-12} T^3) dt$$

$$112.2204 = 14.67764 [75.4 * 10^{-3} T - 75.4 * 10^{-3} (25)]$$

$$+ 0.00376 [(75.4 * 10^{-3} T + 16.83 * 10^{-5} T^2 / 2) - (75.4 * 10^{-3} (25)$$

$$+ 16.83 * 10^{-5} (25)^2 / 2)] + 8.6226 [(34.28 * 10^{-3} T + 4.268 * 10^{-5} T^2 / 2$$

$$+ 8.694 * 10^{-12} T^4 / 4) - (34.28 * 10^{-3} (25) + 4.268 * 10^{-5} (25)^2 / 2$$

$$+ 8.694 * 10^{-12} (25)^4 / 4)]$$

$$112.2204 = 1.106694 T - 27.66735 + 2.835 * 10^{-4} T + 3.164 * 10^{-7} T^2$$

$$- 7.0876 * 10^{-3} - 3.955 * 10^{-4} + 0.29558 T + 1.84006 * 10^{-4} T^2$$

$$+ 1.8741 * 10^{-11} T^4 - 7.3895 - 0.115003 - 7.3207 * 10^{-6}$$

$$147.39974 = 2.102 T + 1.843 * 10^{-4} T^2 + 1.88741 * 10^{-11} T^4$$

$$T = 68.22 \text{ } ^\circ\text{C}$$

2.2.11- Energy balance on the heat exchanger E – 106

$$Q = \sum n \text{ cp } \Delta T$$

$$= (n \text{ cp } \Delta T)_F + (n \text{ cp } \Delta T)_{H_2O}$$

$$= 8622.6 [34.28 * 10^{-3} T + 4.268 * 10^{-5} T^2/2 - 8.694 * 10^{-12} T^4/4]_{68.22}^{30}$$

$$+ 14677.64 [75.4 * 10^{-3} T]_{68.22}^{30}$$

$$= 11565.5 + 42297.846$$

$$= -53\,863.4 \text{ KJ/hr} \quad (\text{heat that must be removed from the heat exchanger})$$

$$Q = m \text{ cp } \Delta T$$

$$53863.4 = m \int_{25}^{65} 75.4 * 10^{-3} dt$$

$$53863.4 = m [75.4 * 10^{-3} T]_{25}^{65}$$

$$53863.4 = m [(75.4 * 10^{-3} * 65)] - [(75.4 * 10^{-3} * 25)]$$

$$53863.4 = m [4.901 - 1.885]$$

$$53863.4 = m [3.016]$$

$$m = 17859.21 \text{ kmol/hr}$$

chapter 3

design

3.1 Introduction of design

The main units to be designed are the reactor, absorber, distillation column. The reactor design covered mainly the volume of the reactor, the weight of the silver catalyst with its distribution along the packed bed reactor, the temperature inlet and outlet of the reactor, the pressure drop across the reactor. The absorber design is concerned with determining the height of the packed tower, the diameter and the type of packing. The design of the distillation tray column covered the minimum reflux ratio, the minimum and actual number of stages, the diameter and height of the column, the efficiency of the trays, and the detailed layout of the sieve tray dimensions for the rectifying and stripping sections.

3.2 Reactor design

In this section, designing a Packed Bed reactor for multi reaction and non-isothermal condition has been done. This reactor is supported with a heat exchange to remove the heat generated from the exothermic reaction.

3.2.1- Reactor design equation

The reactions involved are:



More convenient representation of all reactions' equations:



Where:

A: is methanol

B: is Oxygen.

C: is formaldehyde.

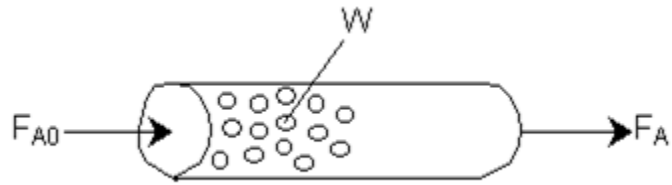
D: is Water.

E: is hydrogen

I: is Nitrogen inert gas

3.2.2 Mole balance

Packed Bed Reactor Mole Balance



$$F_{A0} - F_A + \int r'_A dW = \frac{dN_A}{dt}$$

Steady State $\frac{dN_A}{dt} = 0$

$$F_{A0} - F_A + \int r'_A dW = 0$$

Differentiate with respect to W and rearrange

$$\boxed{\frac{dF_A}{dW} = r'_A}$$

The integral form to find the catalyst weight is:

$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A}$$

The basic mole balances of all components involved in the main reaction are:

Methanol(A):

$$\frac{dF_A}{dW} = r'_A \quad \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

Oxygen (B):

$$\frac{dF_B}{dW} = r'_B \quad \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

Formaldehyde (C):

$$\frac{dFC}{dw} = \dot{r}_C \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

Water (D):

$$\frac{dFD}{dw} = \dot{r}_D \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

Hydrogen (E):

$$\frac{dFE}{dw} = \dot{r}_E \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

Where:

F_i : is the molar flow rate in (mol/s).

W: is the weight of the catalyst in (Kg)

r'_i : is the reaction rate in (mole i reacted/ (Kg cat. hr))

3.2.3 Net rate laws

$$\dot{r}_A = \dot{r}_{A1} + \dot{r}_{A2} \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

$$\dot{r}_B = \dot{r}_{B1} + \dot{r}_{B2} \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

$$\dot{r}_C = \dot{r}_{C1} + \dot{r}_{C2} \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

$$\dot{r}_D = \dot{r}_{D1} + \dot{r}_{D2} \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

$$\dot{r}_E = \dot{r}_{E1} + \dot{r}_{E2} \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

3.2.4 Rate laws

The reaction rate expressions are

$$r_{A1} = \frac{-K1 \cdot PA}{1 + K2 \cdot PA} \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

$$r_{A2} = \frac{-K3 \cdot \sqrt{PA}}{1 + K4 \cdot \sqrt{PA}} \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

The reaction rate constant (k) is given in the form:

$$\ln K1 = 12.5 - \frac{8743}{T}$$

$$\ln K2 = 17.29 - \frac{7976}{T}$$

$$\ln K3 = 16.9 - \frac{1260}{T}$$

$$\ln K4 = 25 - \frac{14803}{T}$$

Where

$$\frac{E1}{R} = 8743$$

$$\frac{E2}{R} = 7976$$

$$\frac{E3}{R} = 1260$$

$$\frac{E4}{R} = 14803$$

So, to get the value of the k_i , it has to be evaluated at each temperature:
to evaluate the partial pressure of methanol, ideal gas law is needed in which:

$$PA = CA \cdot R \cdot T \quad (\text{atm}).$$

Where:

CA - is the molar concentration of methanol in (kmol/m^3)

T - is in (K)

R - is the gas constant = $0.082 \text{ (atm.m}^3/\text{kmol.K)}$

And so the reaction rate expressions will be:

$$\dot{r}_{A1} = \frac{-0.082 CA \cdot T \cdot K1}{1 + 0.082 CA \cdot T \cdot K2} \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

$$\dot{r}_{A2} = \frac{-K3 \cdot \sqrt{0.082 CA \cdot T}}{1 + K4 \cdot \sqrt{0.082 CA \cdot T}} \left(\frac{\text{K mole A}}{\text{Kg cat. hr}} \right)$$

Based on the stoichiometric coefficients, the relative rates can be found using these relationship:

$$-\dot{r}_{A1} = 2\dot{r}_{B1} = \dot{r}_{C1} = \dot{r}_{D1}$$

$$\dot{r}_{A2} = \dot{r}_{C1} = \dot{r}_{E1}$$

3.2.5- - Stoichiometry

Calculation will be done in case there is a variation in both temperature and pressure. So for gas phase, the concentration can be found as follow:

$$C_i = C_{T0} \cdot \left(\frac{F_A}{F_T} \right) \cdot \left(\frac{T^\circ}{T} \right) \cdot \left(\frac{P}{P^\circ} \right) \frac{\text{K mole}}{\text{m}^3}$$

$$C_A = C_{T0} \cdot \left(\frac{F_A}{F_T} \right) \cdot \left(\frac{T^\circ}{T} \right) \cdot \left(\frac{P}{P^\circ} \right) \frac{\text{K mole}}{\text{m}^3}$$

$$C_B = C_{T0} \cdot \left(\frac{F_A}{F_T} \right) \cdot \left(\frac{T^\circ}{T} \right) \cdot \left(\frac{P}{P^\circ} \right) \frac{\text{K mole}}{\text{m}^3}$$

$$C_C = C_{T0} \cdot \left(\frac{F_A}{F_T} \right) \cdot \left(\frac{T^\circ}{T} \right) \cdot \left(\frac{P}{P^\circ} \right) \frac{\text{K mole}}{\text{m}^3}$$

$$C_D = C_{T0} \cdot \left(\frac{F_A}{F_T} \right) \cdot \left(\frac{T^\circ}{T} \right) \cdot \left(\frac{P}{P^\circ} \right) \frac{\text{K mole}}{\text{m}^3}$$

$$C_E = C_{T0} \cdot \left(\frac{F_A}{F_T} \right) \cdot \left(\frac{T^\circ}{T} \right) \cdot \left(\frac{P}{P^\circ} \right) \frac{\text{K mole}}{\text{m}^3}$$

$$C_I = C_{T0} \cdot \left(\frac{F_A}{F_T} \right) \cdot \left(\frac{T^\circ}{T} \right) \cdot \left(\frac{P}{P^\circ} \right) \frac{\text{K mole}}{\text{m}^3}$$

The inlet pressure “Po” to be 5.7 atm. where the following parameters mean: □

$$C_{T0} = P_0 / (R \cdot T_0) = 820.732.5 \text{ kPa} / (8.314 \text{ kPa} \cdot \text{m}^3 / (\text{kmol} \cdot \text{K}) \cdot 500 \text{ K}) = 0.1974338 \text{ (kmol/m}^3)$$

$$F_T \text{ (kmol/h)} = F_A + F_B + F_C + F_D + F_E + F_I$$

$$y_{Ao} = \frac{F_{Ao}}{F_{To}} = 97.7948/282.26 = 0.34647$$

$$C_{Ao} = y_{Ao} * C_{To} = 0.34647 * 0.1974338 = 0.0684 \text{ (kmol/m}^3\text{)}$$

So, the final reaction rate expression is

$$\dot{r}_{A1} = \frac{-0.082 \text{ CA} \cdot \text{T} \cdot \left(\exp\left(12.5 - \frac{8743}{\text{T}}\right)\right)}{1 + 0.082 \text{ CA} \cdot \text{T} \cdot \left(\exp\left(17.29 - \frac{7976}{\text{T}}\right)\right)} \quad \left(\frac{\text{K moleA}}{\text{Kg cat. hr}}\right)$$

$$\dot{r}_{A2} = \frac{-\left(\exp\left(16.9 - \frac{1260}{\text{T}}\right)\right) \cdot \sqrt{0.082 \text{ CA} \cdot \text{T}}}{1 + \exp\left(25 - \frac{14803}{\text{T}}\right) \cdot \sqrt{0.082 \text{ CA} \cdot \text{T}}} \quad \left(\frac{\text{K moleA}}{\text{Kg cat. hr}}\right)$$

Substituting back in the mole balances:

Methanol(A):	$\frac{dF_A}{dw} = \dot{r}_{A1} + \dot{r}_{A2}$	$\left(\frac{\text{K moleA}}{\text{Kg cat.hr}}\right)$
Oxygen (B):):	$\frac{dF_B}{dw} = \dot{r}_{B1}$	$\left(\frac{\text{K moleA}}{\text{Kg cat.hr}}\right)$
Formaldehyde (C):	$\frac{dF_C}{dw} = \dot{r}_{C1} + \dot{r}_{C2}$	$\left(\frac{\text{K moleA}}{\text{Kg cat.hr}}\right)$
Water (D):	$\frac{dF_D}{dw} = \dot{r}_{D1}$	$\left(\frac{\text{K moleA}}{\text{Kg cat.hr}}\right)$
Hydrogen (E):	$\frac{dF_E}{dw} = \dot{r}_{E2}$	$\left(\frac{\text{K moleA}}{\text{Kg cat.hr}}\right)$

3.2.6- Combination

Mole balances, rate equation and stoichiometric relations are combined together to form the main design equation. Note, the temperature

Methanol(A):

$$\frac{dF_A}{dw} = \frac{-0.082 \text{ CA} \cdot \text{T} \cdot \left(\exp\left(12.5 - \frac{8743}{\text{T}}\right)\right)}{1 + 0.082 \text{ CA} \cdot \text{T} \cdot \left(\exp\left(17.29 - \frac{7976}{\text{T}}\right)\right)} + \frac{-\left(\exp\left(16.9 - \frac{1260}{\text{T}}\right)\right) \cdot \sqrt{0.082 \text{ CA} \cdot \text{T}}}{1 + \exp\left(25 - \frac{14803}{\text{T}}\right) \cdot \sqrt{0.082 \text{ CA} \cdot \text{T}}} \quad (1)$$

Oxygen (B):

$$\frac{dF_B}{dw} = \frac{-0.5 * 0.082 \text{ CA} \cdot \text{T} \cdot \left(\exp\left(12.5 - \frac{8743}{\text{T}}\right)\right)}{1 + 0.082 \text{ CA} \cdot \text{T} \cdot \left(\exp\left(17.29 - \frac{7976}{\text{T}}\right)\right)} \quad (2)$$

Formaldehyde (C):

$$\frac{dFC}{dw} = \frac{-0.082 CA \cdot T \cdot (\exp(12.5 - \frac{8743}{T}))}{1 + 0.082 CA \cdot T \cdot (\exp(17.29 - \frac{7976}{T}))} + \frac{-(\exp(16.9 - \frac{1260}{T})) \cdot \sqrt{0.082 CA \cdot T}}{1 + \exp(25 - \frac{14803}{T}) \cdot \sqrt{0.082 CA \cdot T}} \quad (3)$$

Water (D):

$$\frac{dFD}{dw} = \frac{-0.082 CA \cdot T \cdot (\exp(12.5 - \frac{8743}{T}))}{1 + 0.082 CA \cdot T \cdot (\exp(17.29 - \frac{7976}{T}))} \quad (4)$$

Hydrogen (E):

$$\frac{dFE}{dw} = \frac{-(\exp(16.9 - \frac{1260}{T})) \cdot \sqrt{0.082 CA \cdot T}}{1 + \exp(25 - \frac{14803}{T}) \cdot \sqrt{0.082 CA \cdot T}} \quad (5)$$

Conversion equation:

$$\text{Conversion} = \frac{FA^\circ - FA}{FA^\circ} \quad (6)$$

3.2.7- Pressure drop

Pressure drop can be calculated using the differential equation of Ergun

equation:
$$\frac{dy}{dW} = \frac{-\alpha T}{2 y T^\circ} \frac{FT}{FT^\circ} \quad (7)$$

Where:
$$\alpha = \frac{2\beta^\circ}{Ac(1-\phi)\rho_c \cdot P^\circ}$$

$$\beta^\circ = \frac{G(1-\phi)}{\rho_f g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right]$$

- $P_{O_1} = 820.732.5 \text{ kPa}$
- $T_o = 500 \text{ (K)}$
- $F_{T_o} = 282.26 \text{ (kmol/hr)}$
- $F_T = FA + FB + FC + FD + FE + FF + FI \text{ (kmol/hr)}$
- $F_I = F_{Bo} \cdot (0.79/0.21)$
- $G = \frac{m}{Ac} = \frac{m}{nt \cdot \pi \left(\frac{d_i}{2}\right)^2}$
- $Ac = nt \cdot A_{ci}$
- $nt = \text{number of tubes in the reactor}$

- $A_{ci} = \pi \left(\frac{d_i}{2}\right)^2$
- $m = 8439.419$ kg/hr from mass balance
- $\phi = 0.5$
- $gc = 1$ metric system
- $D_p = 0.001$ m
- $d_i =$ inside diameter
- $\rho_c = \frac{(1-\phi)}{\rho_B}$
- $\rho_B = 1500$ (Kg cat)/m³
- $\rho_f = 1.858$ Kg/m³
- $\mu = 0.00004894$ Kg/(m² s)

$$\beta^\circ = \frac{\frac{8489.41/8600}{\pi\left(\frac{d_i}{2}\right)^2}(1-0.5)}{1.858*1*0.001*0.125} \left[\frac{150(1-0.5)0.00004894}{0.001} + 1.75 \frac{8489.41/8600}{\pi\left(\frac{d_i}{2}\right)^2} \right] \quad (8)$$

$$\propto 1/\text{kg} = \frac{2\beta^\circ}{\pi\left(\frac{d_i}{2}\right)^2 (1-0.5)*300*820.732*1000} \quad (9)$$

Using the energy balance design equation of a PBR

$$\text{Reactor} \quad \frac{dT}{dw} = \frac{\frac{U_a}{\rho_B}(T_a - T) + \sum (-r_i A) * (\Delta H_{rxn_i})}{\sum F_i C_{p_i}}$$

$$\text{For two reaction} \quad \frac{dT}{dw} = \frac{\frac{U_a}{\rho_B}(T_a - T) + (-r_1 A_1) * (\Delta H_{rxn1}) + (-r_2 A_2) * (\Delta H_{rxn2})}{\sum F_i C_{p_i}} \quad (10)$$

$$T = 480 \text{ K}$$

$$\Delta H_{RX1} = \Delta H_{RX1}^\circ + \left(\int_{t_{ref}}^t \sum C_{p_i} dT - \int_{t_{ref}}^{t_{fed}} \sum C_{p_i} dT \right) \quad (11)$$

$$\Delta H_{RX2} = \Delta H_{RX2}^\circ + \left(\int_{t_{ref}}^t \sum C_{p_i} dT - \int_{t_{ref}}^{t_{fed}} \sum C_{p_i} dT \right) \quad (12)$$

by integration the C_{p_i} where t in Celsius

FOR THE FIRST REACTION

$$\sum \Delta c_{p_i} = 1000[(IC) + (ID) - (IA) - (0.5 * IB)] \text{ KJ/h}$$

FOR THE SECOND REACTION

$$\Sigma \Delta c_{pi} = 1000[(IC)+(IE) - (IA)] \text{ KJ/h}$$

$$CPIg = 29e - 3 + 0.2199e - 5 * (T - 273.15) + 0.5723e - 8 * (T - 273.15)^2 - 8.69e - 12 * (T - 273.15)^3$$

$$CPAg = 42.93e - 3 + 8.301e - 5 * (T - 273.15) - 1.87e - 8 * (T - 273.15)^2 - 8.03e - 12 * (T - 273.15)^3$$

$$CPBg = 29.1e - 3 + 1.158e - 5 * (T - 273.15) - 0.6076e - 8 * (T - 273.15)^2 + 1.311e - 12 * (T - 273.15)^3$$

$$CPCg = 34.28e - 3 + 4.268e - 5 * (T - 273.15) - 8.69e - 12 * (T - 273.15)^3$$

$$CPDg = 33.46e - 3 + 0.688e - 5 * (T - 273.15) + 0.7604e - 8 * (T - 273.15)^2 - 3.593e - 12 * (T - 273.15)^3$$

$$CPEg = 28.84e - 3 + 0.00765e - 5 * (T - 273.15) + 0.3288e - 8 * (T - 273.15)^2 - 0.8698e - 12 * (T - 273.15)^3$$

$$\text{sumFiCPi} = (FA * CPAg + FB * CPBg + FC * CPCg + FD * CPDg + FE * CPEg + FI * CPIg) * 1000$$

Evaluating the Volume of the reactor:

The size of the reactor needed is calculated from the weight of catalyst needed to achieve our reaction conversion:

$$V = \frac{\text{weight of catalyst}}{\text{bulk density}}$$

Evaluating the height of the reactor

The height of the reactor is assumed to be once and a halve of the tube height.

$$H_R = 1.25 * L$$

Evaluating the width of the reactor:

The shell size of the reactor was calculated. assuming the cover of the shell size is 10 cm.

So, The width of the reactor can be found using this equation

$$W_R = D_S + 0.2$$

3.2.8 - Result

POLYMATH REASULTS:

Differential equations

$$d(FA)/d(W) = rA1+rA2$$

$$d(FB)/d(W) = 0.5*rA1$$

$$d(FC)/d(W) = -rA1-rA2$$

$$d(FD)/d(W) = -rA1$$

$$d(FE)/d(W) = -rA2$$

$$d(T)/d(W) = ((306.495*4/1500/0.0092456)*(480T)+(rA1*DHRxn1)+(rA2*DHRxn2))/(\text{sumFiCPi})$$

$$\frac{d(y)}{d(W)} = (-\alpha) * (F_T / F_{T0}) * (T / T_0)^{2/y}$$

$$\frac{d(V)}{d(W)} = 1/1500$$

Explicit equations

$$T_0 = 500 \text{ K}$$

$$F_I = 144.693 \text{ kmol/hr}$$

$$k_1 = \exp(12.5 - (8774/T))$$

$$k_2 = \exp(-17.29 + (7439/T))$$

$$k_3 = \exp(16.9 - (12500/T))$$

$$k_4 = \exp(25 - (15724/T))$$

$$C_{T0} = 8.2 / (0.082 * T_0) \text{ kmole/m}^3$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_I \text{ kmole/hr}$$

$$C_A = C_{T0} * (F_A / F_T) * (T_0 / T)^y \text{ kmole/m}^3$$

$$P_a = 0.082 * C_A * T \text{ atm}$$

$$r_{A1} = -((P_a * k_1) / (1 + P_a * k_2))$$

$$r_{A2} = -((P_a^{0.5} * k_3) / (1 + P_a^{0.5} * k_4))$$

$$C_B = C_{T0} * (F_B / F_T) * (T_0 / T)^y \text{ kmole/m}^3$$

$$C_C = C_{T0} * (F_C / F_T) * (T_0 / T)^y \text{ kmole/m}^3$$

$$C_D = C_{T0} * (F_D / F_T) * (T_0 / T)^y \text{ kmole/m}^3$$

$$C_E = C_{T0} * (F_E / F_T) * (T_0 / T)^y \text{ kmole/m}^3$$

$$F_{T0} = 282.26 \text{ kmol/hr}$$

$$C_I = C_{T0} * (F_I / F_T) * (T_0 / T)^y \text{ kmole/m}^3$$

$$C_{A0} = 0.3465 * C_{T0} \text{ kmole/m}^3$$

$$\text{Conversion} = (97.79 - F_A) / 97.79$$

$$S_i = r_{A1} / r_{A2}$$

$$\alpha = 2 * (((8439.419 / (3600 * (3.14 * (1/2)^2))) * (1 - 0.5) / (1.858 * 1 * 0.001 * 0.5^3) * ((150 * (1 - 0.5) * 4.894e - 5 / 0.001) + (1.75 * (8439.419 / (3600 * (3.14 * (1/2)^2)))))) / ((3.14 * (1/2)^2) * 3000 * (1 - 0.5) * 101.325 * 8.2) / 1000$$

$$C_{PIg} = 29e-3 + 0.2199e-5 * (T - 273.15) + 0.5723e-8 * (T - 273.15)^2 - 8.69e-12 * (T - 273.15)^3$$

$$C_{PAg} = 42.93e-3 + 8.301e-5 * (T - 273.15) - 1.87e-8 * (T - 273.15)^2 - 8.03e-12 * (T - 273.15)^3$$

$$C_{PBg} = 29.1e-3 + 1.158e-5 * (T - 273.15) - 0.6076e-8 * (T - 273.15)^2 + 1.311e-12 * (T - 273.15)^3$$

$$C_{PCg} = 34.28e-3 + 4.268e-5 * (T - 273.15) - 8.69e-12 * (T - 273.15)^3$$

$$C_{PDg} = 33.46e-3 + 0.688e-5 * (T - 273.15) + 0.7604e-8 * (T - 273.15)^2 - 3.593e-12 * (T - 273.15)^3$$

$$C_{PEg} = 28.84e-3 + 0.00765e-5 * (T - 273.15) + 0.3288e-8 * (T - 273.15)^2 - 0.8698e-12 * (T - 273.15)^3$$

$$\text{sumFiCPI}=(\text{FA}*\text{CPAg}+\text{FB}*\text{CPBg}+\text{FC}*\text{CPCg}+\text{FD}*\text{CPDg}+\text{FE}*\text{CPEg}+\text{FI}*\text{CPIg})$$

*1000 kJ/h

$$\text{XA} = \text{FA}/\text{FT}$$

$$\text{XB} = \text{FB}/\text{FT}$$

$$\text{XC} = \text{FC}/\text{FT}$$

$$\text{XD} = \text{FD}/\text{FT}$$

$$\text{XE} = \text{FE}/\text{FT}$$

$$\text{XI} = \text{FI}/\text{FT}$$

$$\text{mc} = \text{Q}/(1910)$$

The result of solving these differential and explicit equations were

	Variable	Initial value	Minimal value	Maximal value	Final value
1	alpha	0.0001169	0.0001169	0.0001169	0.0001169
2	CA	0.0679586	0.0046567	0.0679586	0.0046567
3	CAo	0.0693	0.0693	0.0693	0.0693
4	CB	0.0305775	0.0020098	0.0305775	0.0020098
5	CC	0	0	0.0364541	0.0364541
6	CD	0.0009104	0.0009104	0.0335263	0.0335263
7	CE	0	0	0.0034786	0.0034786
8	CI	0.1005535	0.0598285	0.1005535	0.0608288
9	Conversion	0	0	0.8867272	0.8867272
10	CPAg	0.0607048	0.0607048	0.0701898	0.0688707
11	CPBg	0.0314296	0.0314296	0.0325628	0.0324091
12	CPCg	0.0438605	0.0438605	0.0493426	0.0485641
13	CPDg	0.0353701	0.0353701	0.0367835	0.0365682
14	CPEg	0.0290164	0.0290164	0.0292586	0.0292177
15	CPIg	0.0296919	0.0296919	0.0301356	0.0300765
16	CTo	0.2	0.2	0.2	0.2
17	DHrxn1	-1.565E+05	-1.565E+05	-1.564E+05	-1.564E+05
18	DHrxn2	8.53E+04	8.53E+04	8.669E+04	8.652E+04
19	FA	97.79	11.07695	97.79	11.07695
20	FB	44.	4.780681	44.	4.780681
21	FC	0	0	86.71305	86.71305
22	FD	1.31	1.31	79.74864	79.74864
23	FE	0	0	8.274411	8.274411
24	FI	144.693	144.693	144.693	144.693
25	FT	287.793	287.793	335.2867	335.2867
26	FTo	282.26	282.26	282.26	282.26
27	k1	0.0064222	0.0064222	0.2724181	0.1750521
28	k2	0.0896358	0.0037374	0.0896358	0.0054376
29	k3	0.0003035	0.0003035	0.0632314	0.0336744
30	k4	0.0015837	0.0015837	1.307468	0.5918646
31	mc	569.242	569.242	569.242	569.242
32	Pa	2.786301	0.2352352	2.786301	0.2352352
33	Q	1.087E+06	1.087E+06	1.087E+06	1.087E+06
34	rA1	-0.0143181	-0.1176075	-0.0143181	-0.0411258
35	rA2	-0.0005053	-0.0217943	-0.0005053	-0.0126897
36	Si	28.3337	3.240879	28.3337	3.240879
37	sumFICPi	1.166E+04	1.166E+04	1.274E+04	1.264E+04
38	T	500.	500.	635.7779	616.0361
39	To	500.	500.	500.	500.
40	V	0	0	1.198667	1.198667
41	W	0	0	1798.	1798.
42	XA	0.3397928	0.0330373	0.3397928	0.0330373
43	XB	0.1528877	0.0142585	0.1528877	0.0142585
44	XC	0	0	0.2586236	0.2586236
45	XD	0.0045519	0.0045519	0.2378521	0.2378521
46	XE	0	0	0.0246786	0.0246786
47	XI	0.5027676	0.43155	0.5027676	0.43155
48	y	1.	0.8683294	1.	0.8683294

3.3- Packed-bed absorber design

3.3.1- Introduction

The packed-bed absorbers are the most common absorbers used for gas removal. The absorbing liquid is dispersed over the packing material, which provides a large surface area for gas-liquid contact. Packed beds are classified according to the relative direction of gas-to-liquid flow into two types. The first one is co-current while the second one the counter current packed bed absorber. The most common packed-bed absorber is the countercurrent-flow tower.

3.3.2 -Packing material

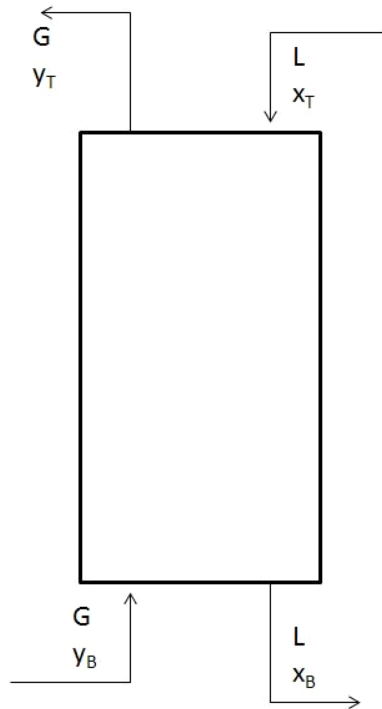
The main purpose of the packing material is to give a large surface area for mass transfer. However, the specific packing selected depends on the corrosiveness of the contaminants and scrubbing liquid, the size of the absorber, the static pressure drop, and the cost. There are three common types of packing material: Mesh, Ring, and Saddles. In our project Ceramic Berl Saddles packed was selected since it is good liquid distribution ratio, good corrosion resistance, most common with aqueous corrosive fluids and Saddles are best for redistributing liquids low cost. Also we use 2 inches diameter packing.

3.3.3- Sizing of packed tower

ASSUMPTIONS:

Some assumptions and conditions were design calculation based on:

1. G and L are representing the gas and liquid flow rates.
2. x and y are for the mole fraction of Methanol in liquid and gas respectively.
3. Assuming the column is packed



3.3.3.1- Packed tower diameter

Gas velocity is the main parameter affecting the size of a packed column. For estimating flooding velocity and a minimum column diameter is to use a generalized flooding and pressure drop correlation. One version of the flooding and pressure drop relationship for a packed tower in the Sherwood correlation .

Packing diameter calculation:

$$\text{The gas flow rate } G = 33.543 \frac{\text{kmol}}{\text{h}} = 896.9398 \frac{\text{kg}}{\text{h}}$$

$$\text{The liquid flow rate } L = 18.675 \frac{\text{kmol}}{\text{h}} = 336.15 \frac{\text{kg}}{\text{h}}$$

Calculate the value of the abscissa ϵ :

$$\frac{L}{G} \sqrt{\frac{\rho_G}{\rho_L}} = \epsilon$$

Where: L and G = mass flow rates $(\frac{\text{kg}}{\text{h}})$

ρ_G = density of the gas stream $(\frac{\text{kg}}{\text{m}^3})$

ρ_L = density of the absorbing liquid $(\frac{\text{kg}}{\text{m}^3})$

$$\rho_G = 1.620 \text{ (} kg/m^3 \text{)} \quad \rho_L = 1000 \text{ (} \frac{kg}{m^3} \text{)}$$

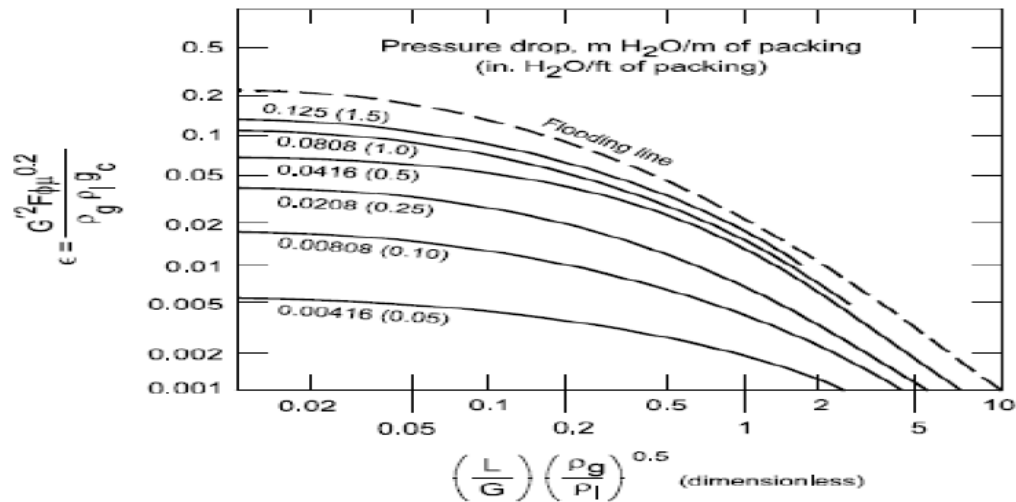
$$\psi = \frac{\rho_{\text{water}}}{\rho_L} = 1$$

$$\mu = 0.797 \cdot 10^{-3} \text{ P} \quad g_c = 9.8 \frac{\text{m}}{\text{s}^2}$$

$$\frac{L}{G} \sqrt{\frac{\rho G}{\rho_L}} = \frac{336.15}{896.9398} \sqrt{\frac{1.620}{1000}} = 0.015$$

$F_p = 130 \text{ m}^{-1}$ from the table for ceramic saddles 2 in size

	Size		Bulk density (kg/m ³)	Surface area <i>a</i> (m ² /m ³)	Packing factor <i>F_p</i> , m ⁻¹
	in.	mm			
Raschig rings ceramic	0.50	13	881	368	2100
	1.0	25	673	190	525
	1.5	38	689	128	310
	2.0	51	651	95	210
	3.0	76	561	69	120
Metal (density for carbon steel)	0.5	13	1201	417	980
	1.0	25	625	207	375
	1.5	38	785	141	270
	2.0	51	593	102	190
	3.0	76	400	72	105
Pall rings metal (density for carbon steel)	0.625	16	593	341	230
	1.0	25	481	210	160
	1.25	32	385	128	92
	2.0	51	353	102	66
	3.5	76	273	66	52
Plastics (density for polypropylene)	0.625	16	112	341	320
	1.0	25	88	207	170
	1.5	38	76	128	130
	2.0	51	68	102	82
	3.5	89	64	85	52
Intalox saddles ceramic	0.5	13	737	480	660
	1.0	25	673	253	300
	1.5	38	625	194	170
	2.0	51	609	108	130
	3.0	76	577	72	72



From the figure, and using the flooding line: $\epsilon = 0.20$

$$G' \text{ flooding} = \sqrt{\left(\frac{\rho_G \rho_L g_c \epsilon}{\mu^{0.2} F_p \psi}\right)}$$

Where:

G' = mass flow rate of gas per unit cross-sectional area of column, $\text{g/s}\cdot\text{m}^2$

F = packing factor given

ψ = ratio of specific gravity of the scrubbing liquid to that of water

μ = viscosity of liquid

$$G' \text{ flooding} = \sqrt{\left(\frac{1.62 * 1000 * 9.8 * 0.2}{(0.797 * (0.001))^{0.2} * 130 * 1}\right)} = 11.045$$

$$G' \text{ operating} = 0.55 (G' \text{ flooding}) = 0.55 * 11.045 = 6.075 \frac{\text{Kg}}{\text{m}^2 \text{ s}}$$

$$\text{Area of packing} = \frac{G}{G' \text{ operating}} = \frac{8969.398 \frac{\text{kg}}{\text{h}}}{6.075 \frac{\text{Kg}}{\text{m}^2 \text{ s}} \frac{3600 \text{ s}}{1 \text{ h}}} = 0.41 \text{ m}^2$$

$$\text{Area} = \frac{\pi D^2}{4} = 0.41 \text{ m}^2 \quad D \text{ packing} = 0.722 \text{ m}$$

$$D_{\text{TOWER}} = D \text{ packing} * 1.25 = 0.722 * 1.25 = 0.903 \text{ m}$$

3.3.3.2 - Packing height (Z packing)

$$Z = H_{OG} * N_{OG}$$

N_{OG} = number of transfer units based on an overall gas-film coefficient.

H_{OG} = height of a transfer unit based on an overall gas-film coefficient, m

H_{OG} was obtained from table 15-4 in "Separation Process Engineering". For ceramic packing with size 2 in, $H_{OG} = 3 \text{ ft} = 0.9 \text{ m}$

For N_{OG} calculation we need G_m and L_m and m

where

G_m = molar gas flow-rate per unit cross-sectional area

L_m = molar liquid flow-rate per unit cross-sectional area

m = is the slope of the equilibrium line

$$G_m = \frac{N_{10}}{A} = \frac{33.543}{0.41} = 81.81$$

$$L_m = \frac{N_{11}}{A} = \frac{18.675}{0.41} = 45.54$$

$$(y_1 - y_2) = m(x_1 - x_2)$$

$$(0.2605 - 0.00302) = m(0.3715 - 0)$$

$$m = 0.693$$

$$\frac{mG_m}{L_m} = \frac{0.693 * 81.81}{45.54} = 1.245$$

$$\frac{y_1}{y_2} = \frac{0.2605}{0.00302} = 86.25$$

y_1 is mole fraction of formaldehyde in stream 10

y_2 is mole fraction of formaldehyde in stream 10

x_1 is mole fraction of formaldehyde in stream 13

x_2 is mole fraction of formaldehyde in stream 11

$$NOG = \frac{1}{1 - \frac{mG_m}{L_m}} \ln \left[\left(1 - \frac{mG_m}{L_m} \right) \frac{y_1}{y_2} + \frac{mG_m}{L_m} \right]$$

$$NOG = \frac{1}{1 - 1.245} \ln [(1 - 1.245)86.25 + 1.245]$$

$$NOG = 12.2$$

$$Z = H_{OG} * N_{OG}$$

$$Z = 0.9 * 12.2$$

$$Z_{Packing} = 10.98 \text{ m}$$

$$Z_{column} = Z_{Packing} * (D_{tower} + 0.25)$$

$$Z_{column} = 10.98 * (0.903 + 0.25)$$

$$Z_{column} = 12.62$$

Absorber summary table	
Diameter (m)	0.903
Height (m)	12.62
Orientation	Vertical
Internals	Ceramic, saddles

3.4 - Distillation column design

3.4.1 – introduction

These calculations include a mass balance of the distillation unit, average physical properties of the components and relative volatilities. The minimum reflux ratio of the column is obtained through Underwood's equations. The diameter of the column is sized in the rectifying section and the stripping section. The minimum tray number is obtained through Fenske's relation along with their correlated efficiencies (top & bot).

Assumptions

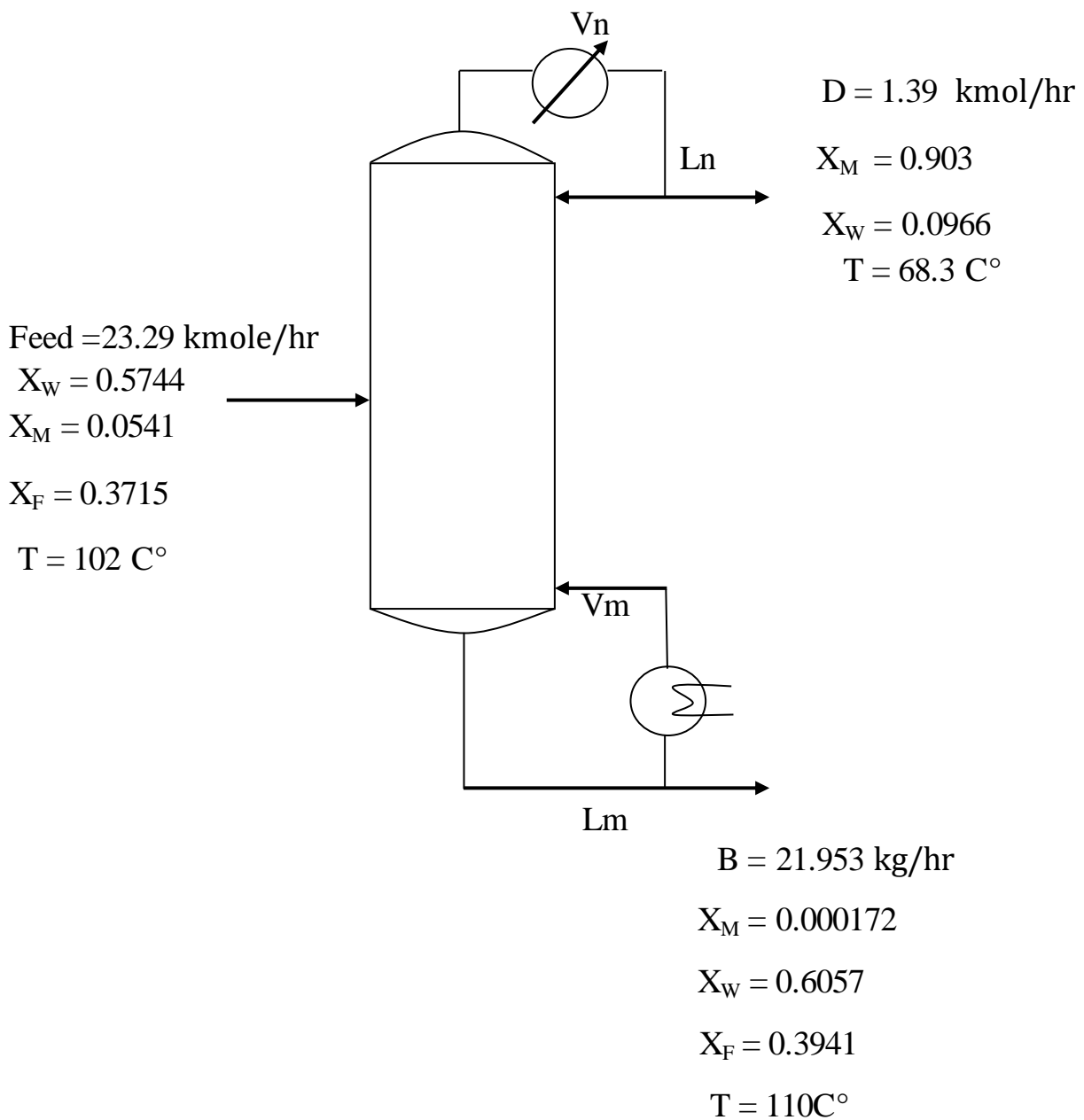
Light Key : methanol

Heavy key: H₂O

$$n_{14} = D + B$$

3.4.2 – From material balance

MATERIAL	MOLE FRACTION	n_i	M.wt	Mass = $n_i * M.wt$	Mass fraction
Methanol	0.00017	0.00378	32.042	0.1211	0.000243
Formaldehyde	0.395	8.6526	30.02	259.751	0.5212
Water	0.6047	13.2448	18	238.4064	0.4784
Σ				498.2785	



Component	X_F Mol%	X_D Mol%	X_B Mol%
Methanol	5.41	90.3	0.0172
H_2O	57.44	9.7	60.57

3.4.3 – Calculation number of plates

Calculation of equilibrium data:

$$\ln p^0 = A - \frac{B}{T+C}$$

Where:

p^0 = vapor pressure (mmHg)

A, B, C = constants

T = Temperature (K^0)

Table (4-5) A,B and C constants

Components	A	B	C
Methanol	16.5785	3638.27	239.5
H_2O	16.3872	3885.70	230.170

At top $T=68.3 C^0 = 341.3 K^0$

$$\ln p^0_w = 16.3872 - \frac{3885.70}{341.3 + 230.170} \Rightarrow p^0_w = 14584.54 \text{ mmHg}$$

$$\ln p^0_M = 16.5785 - \frac{3638.27}{341.3 + 239.5} \Rightarrow p^0_M = 30159.67 \text{ mmHg}$$

$$\alpha_{top} = \frac{p_M^0}{p_W^0} = \frac{30159.67}{14584.54} = 2.06$$

At Bottom $T=110\text{ C}^\circ = 383\text{ K}^\circ$

$$\ln p_W^0 = 16.3872 - \frac{3885.70}{383 + 230.170} \Rightarrow p_W^0 = 23158.84\text{ mmHg}$$

$$\ln p_M^0 = 16.5785 - \frac{3638.27}{383 + 239.5} \Rightarrow p_M^0 = 45884.81\text{ mmHg}$$

$$\alpha_{bot} = \frac{p_M^0}{p_W^0} = \frac{45884.81}{23158.84} = 1.98$$

$$\alpha_{av} = (\alpha_{top} * \alpha_{bot})^{0.5}$$

$$\alpha_{av} = (2.06 * 1.98)^{0.5} = 2.02$$

$$Y = \frac{\alpha_{av} * X}{1 + (\alpha_{av} - 1) * X}$$

$$Y = \frac{2.02 * X}{1 + 2.02 * X - X}$$

equilibrium curve

At $X=0.10$

$$Y = \frac{2.02 * 0.1}{1 + 2.02 * 0.1 - 0.1} = 0.183$$

X	Y
0.000	0.000
0.100	0.168
0.200	0.335
0.300	0.464
0.400	0.573
0.500	0.668
0.600	0.751
0.700	0.824
0.800	0.889
0.900	0.947
1.000	1.000

Calculation of q-line

$$q = \frac{\text{heat required to vaporized 1K mol of feed}}{\text{molar latent heat of feed}}$$

$$Q = \frac{C_{p\text{mix}} * T \text{ feed} + \lambda \text{mix}}{\lambda \text{mix}}$$

where:

$C_{p\text{mix}}$ = average molar heat capacity of feed KJ/Kmol. °C

λmix = Average molar latent heat of feed KJ/Kmol

ΔT = feed bubble point – feed temperature °C

Table (5-1) specific heat and latent heat for components

Component	CP KJ/Kmol.C°	λ KJ/Kmol	Xf mol%
Methanol	87.354	35246.2	5.41
H ₂ O	75.4	40626	57.44
Formaldehyde	37.19	12187.31	37.15

$$C_{p\text{mix}} = C_{p1} * X_{f1} + C_{p2} * X_{f2} + C_{p3} * X_{f3}$$

$$C_{p\text{mix}} = (87.354 * 0.0541) + (75.4 * 0.5744) + (37.19 * 0.3715)$$

$$C_{p\text{mix}} = 61.85 \text{ KJ/Kmol.C}^\circ$$

$$\lambda \text{mix} = \lambda_1 * X_{f1} + \lambda_2 * X_{f2} + \lambda_3 * X_{f3}$$

$$= (35246.2 * 0.0541) + (40626 * 0.5744) + (12187.31 * 0.3715)$$

$$= 29769.9 \text{ KJ/Kmol}$$

\therefore Feed bubble point = 102°C

$$q = \frac{61.85 \cdot 102 + 29769.9}{29769.9} = 1.21$$

$$\text{Slop of } q\text{-line} = \frac{q}{q-1} = \frac{1.21}{0.21} = 5.76$$

$$V_1 = R + D$$

$$\text{ASSUM } R / D = 1.3$$

$$R = 1.3 D$$

$$V_1 = 1.3 D + D \qquad D = 1.39 \text{ kmol/hr}$$

$$V_1 = 3.197 \text{ kmol/hr}$$

$$R = 1.807 \text{ kmol/hr}$$

Calculation number of plates step

- Draw the equilibrium data X vs Y.
- Draw the q-line with slope = $\frac{q}{q-1} = \frac{1.21}{0.21} = 5.76$
- Draw the top of operating line from X_D on the diagonal
- $Q = \frac{X_d}{R+1} = \frac{0.903}{1.807 + 1} = 0.32$
- Draw the bottom operating line from X_B on the diagonal to the point of intersection of the operating line and the q-line.

- Starting at X_D step off the number of stages.

From plot No. of stage = 21

$$\begin{aligned} \text{No. of plate} &= \text{No. of stages} - 1 \\ &= 21 - 1 = 20 \end{aligned}$$

E_0 = plate efficiency

Viscosity (μ) = 0.1329

Relative volatility = 0.0709

$$\begin{aligned} E_0 &= 0.52782 - 0.27511 * \log(\alpha \mu) + 0.044923 * [\log(\alpha \mu)]^2 \\ &= 0.52782 - 0.27511 * \log(0.09432) + 0.044923 * [\log(0.09432)]^2 \\ &= 0.8573 = 85.7\% \end{aligned}$$

$$\text{Actual Number of stages} = \frac{21}{0.8573} = 25 \text{ stages}$$

3.4.4 – Column height

The column height is heavily dependent upon the spacing between the sieve trays. In our design, 18 inches were chosen for spacing to provide a reasonable space to ease the accessibility for manual workers to crawl between the plates for maintenance. According to Turton's Distillation Column Design Heuristics (1955), a safety factor of 10% is to be added to the final design height. The column height is determined as follows.

Total Actual number of stages = 25 stage

Safety Factor = $25 * (0.1) = 2.5$ stage

Total Construction stages = $2.5 + 25 + 1 \approx 29$ STAGE including reboiler

Column Height = Tray Spacing * (Num. of stages + safety factor)

$$\begin{aligned} &= 18 \text{ inch} \frac{0.0254 \text{ m}}{1 \text{ inch}} * (25 + 2.5) \\ &= 12.57 \text{ m} \end{aligned}$$

3.4.5 Column diameter

Rectifying (TOP) Section Diameter

The first step is the determination of the flow parameter as follows

$$F_p = \frac{Ln}{vn} * \left(\frac{\rho v}{\rho L}\right)^{0.5}$$

$$F_p = 0.9958 * \left(\frac{0.08259}{51.35}\right)^{0.5}$$

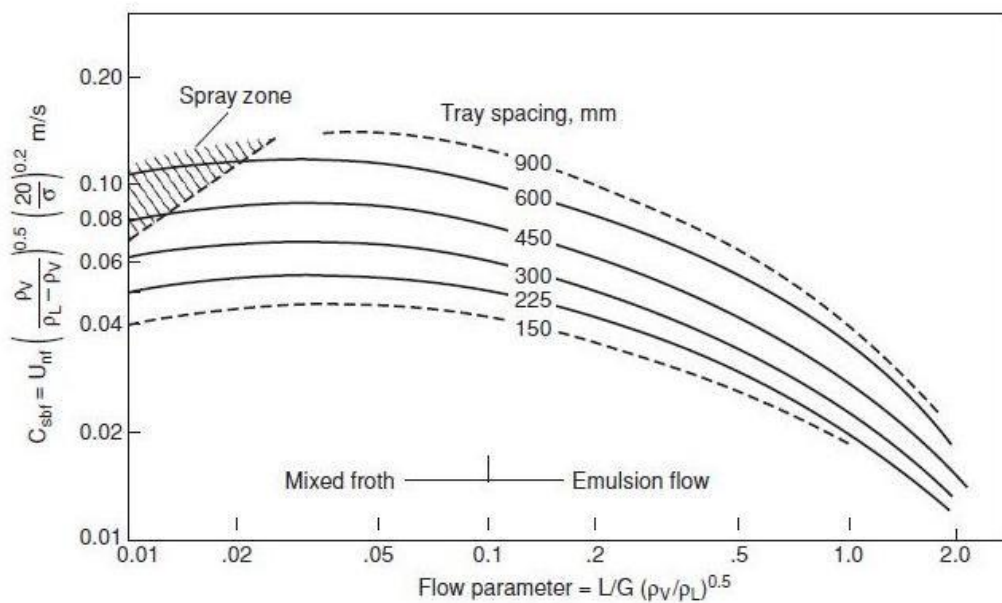
$$F_p = 0.03993$$

18 inch tray spacing is to be used as moderate average of the capacity factor of flooding. Utilizing a nonlinear regression of the capacity factor chart by Kessler and Wankat (1987) as follows

$$\text{Log } C_{sb,f} = -1.0262 - 0.63153 * \log F_p - 0.20097(\log F_p)^2$$

$$\text{Log } C_{sb,f} = -1.0262 - 0.63153 * 0.03993 - 0.20097(0.03993)^2$$

$C_{sb,f} = 0.2994 \text{ ft/s}$ This is correlated by the following chart



Then, the operation velocity is calculated as follows

$$U_{flood} = C_{sb,f} \left(\frac{\sigma}{20}\right)^{0.2} \sqrt{\frac{\rho_L - \rho_v}{\rho_v}}$$

$$U_{flood} = 0.2994 \left(\frac{25}{20}\right)^{0.2} \sqrt{\frac{51.35 - 0.08259}{0.08259}}$$

$$U_{flood} = 7.6705 \text{ ft/s}$$

From mass balance

$$v = 3.197 \frac{\text{kmole}}{\text{hr}} = 2519.9 \text{ lbmole/hr}$$

According to *Wankat* (1987), the fraction of flooding that is utilized by the operational velocity is ranging between 0.65 and 0.9. *Jones and Mellbom* (1982) suggested an average fraction of 0.75.

As for the fraction of cross-sectional area that is available for vapor flow η , *Wankat* (1987) presented a range of 0.85 and 0.95. An average of $\eta=0.9$ is to be used in our design

Diameter sizing of the top section

$$\text{Dia} = \sqrt{\frac{4 * V * R * T}{\pi * \eta * 3600 * P * \text{Ffraction} * U_{\text{flood}}}}$$

$$\text{Dia} = \sqrt{\frac{4 * 2519.9 * 1.314 * 349.4}{\pi * 0.9 * 3600 * 1 * 0.75 * 7.6705}}$$

$$\text{Dia} = 8.115 \text{ ft} = 2.474 \text{ m}$$

Stripping (BOTTOM) Section Diameter

$$F_p = \frac{L_n}{V_n} * \left(\frac{\rho_v}{\rho_L}\right)^{0.5}$$

$$F_p = 7.9039 * \left(\frac{0.04571}{46.77}\right)^{0.5}$$

$$F_p = 0.24709$$

$$\text{Log } C_{\text{sb,f}} = -1.0262 - 0.63153 * \log F_p - 0.20097(\log F_p)^2$$

$$\text{Log } C_{\text{sb,f}} = -1.0262 - 0.63153 * 0.24709 - 0.20097(0.24709)^2$$

$$C_{\text{sb,f}} = 0.1929 \text{ ft/s}$$

Molecular Weight

$$\text{Rectifying Section: } MW_T = X_M * MW_M + X_F * MW_F + X_W * MW_W$$

$$MW_T = 0.00017 * 32.042 + 0.395 * 30.02 + 0.6047 * 18$$

$$MW_T = 22.7479 \text{ g/mole}$$

$$\text{Stripping Section: } MW_B = X_m * MW_m + X_W * MW_W$$

$$MW_B = 0.903 * 32.042 + 0.0961 * 18$$

$$MW_B = 30.66 \text{ g/mole}$$

$$\begin{aligned} \frac{(Dia \text{ top})}{(Dia \text{ bot})} &= \left(\frac{V_{top}}{V_{bot}}\right)^{0.5} * \left(\frac{MW_{top}}{MW_{bot}}\right)^{0.25} * \left(\frac{T_{top}}{T_{bot}}\right)^{0.25} * \left(\frac{\sigma_{top}}{\sigma_{bot}}\right)^{0.1} \\ &\quad * \left(\frac{C_{sb, top}}{C_{sb, bot}}\right)^{0.5} * \left(\frac{\rho l \text{ top}}{\rho l \text{ bot}}\right)^{0.25} \\ \frac{(Dia \text{ top})}{(Dia \text{ bot})} &= (0.99)^{0.5} * \left(\frac{30.66}{22.7479}\right)^{0.25} * \left(\frac{341.3}{383}\right)^{0.25} * \left(\frac{37.23}{25}\right)^{0.1} \\ &\quad * \left(\frac{0.1929}{0.2944}\right)^{0.5} * \left(\frac{46.77}{51.35}\right)^{0.25} \end{aligned}$$

$$\frac{(Dia \text{ top})}{(Dia \text{ bot})} = 0.87789$$

$$\text{Diameter of bottom} = \frac{Dia \text{ top}}{0.87789} = \frac{2.474}{0.87789} = 2.81 \text{ m}$$

$$A_{bot} = \frac{\pi * (Dia_{bot})^2}{4} = \frac{\pi * (2.81)^2}{4} = 6.19 \text{ m}^2$$

Column cross-sectional area

$$A_c = \frac{\pi * (Dia \text{ top})^2}{4} = \frac{\pi * (2.474)^2}{4} = 4.8 \text{ m}^2$$

Down comer area

$$A_d = (1-\eta) A_c$$

$$A_d = (1-0.9) 4.8$$

$$A_d = 1.5764 \text{ m}^2$$

Value of η is chosen 0.1 according to Wankat (1987) as a common standard of the relation between the weir length and diameter.

The $\frac{\text{WEIR LENGTH}}{Dia \text{ top}}$ ratio is provided by Wankat (1987) as 0.726

$$I_{\text{weir}} = Dia \text{ top} * 0.726 = 2.474 * 0.726$$

$$I_{\text{weir}} = 1.796 \text{ m}$$

Active area

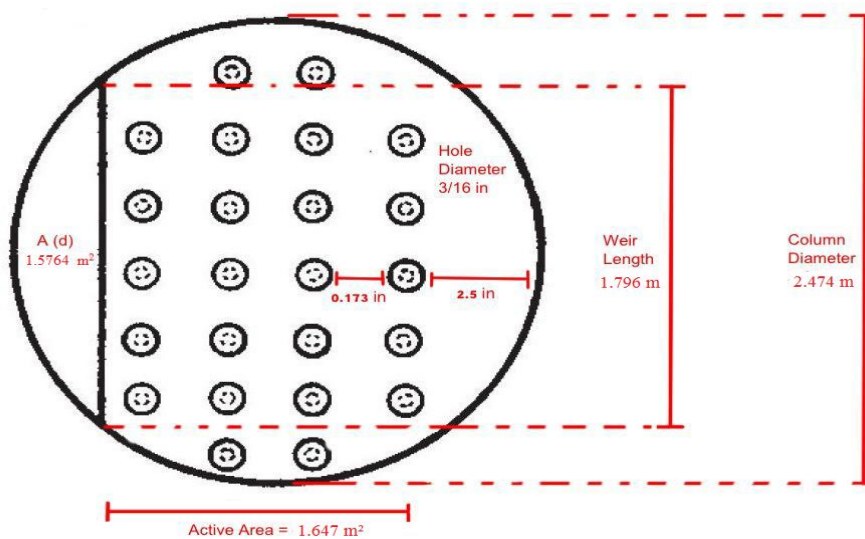
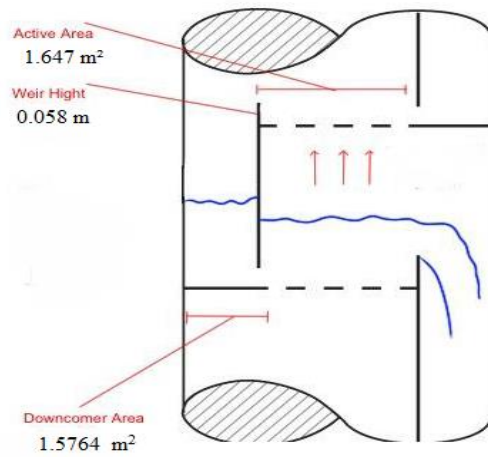
$$A_a = A_c - 2A_d = 4.8 - 2 * 1.5764 = 1.647 \text{ m}^2$$

Hol area

$A_h = 10\% A_a$ as first trial

$$A_h = 0.1 * 1.647 = 0.1647 \text{ m}^2$$

Chosen tray is a std. 25gauge tray with thickness (T tray) = 0.078 in with a common hole diameter $d_o = 3/16$ inch for normal operation and clean service. Pitch Std. spacing between the holes of $3.8d_o = 0.1725$ inches. A 2.5 in space between the edge holes and the column wall is chosen, and a space of 4 in between the edge hole and the tray weir



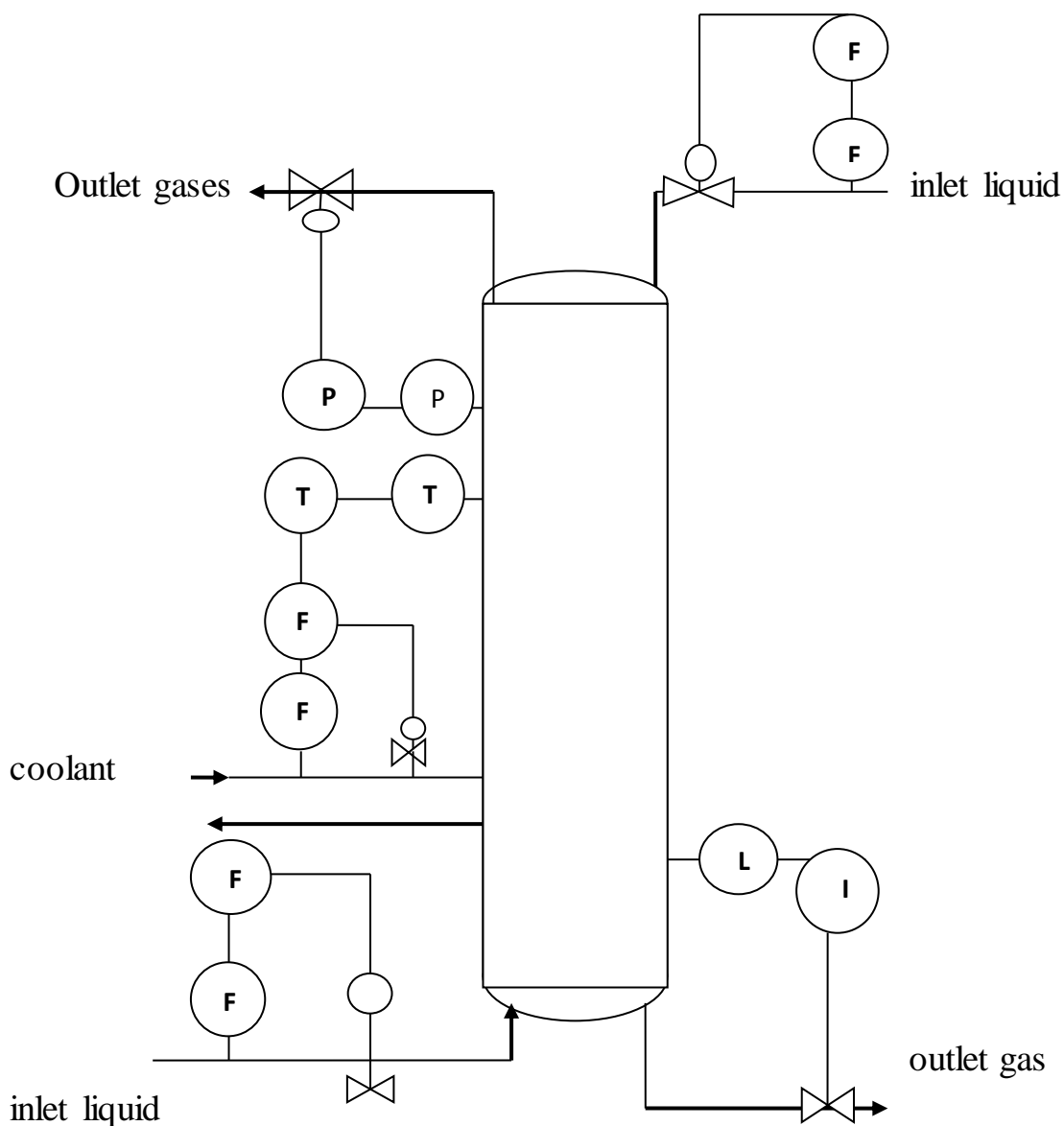
DESIGN ITEM	SPECIFICATION
Material of Construction	Stainless Steel
Tray Type	SS Sieve Trays
Flow Type	Gas-liquid Counter-flow
Number of Trays	25 plus a Reboiler
Reflux Ratio	1.807
Feed Tray	13 from top
Number of Tray Passes	Single
Down comer Type	Vertical Straight Segment
Down comer Area	1.5764 m ²
Tray Efficiency	85%
Tray Spacing	18 inch
Tray Thickness	0.078 in
Top Weir Height	2 inch
Bottom Weir Height	0.5 inch
Weir Length	1.796 m
cross-sectional area	4.8 m ²
Active area	1.647 m ²
Hole Diameter	3/16 in
Hole – Hole Spacing	0.1725 in
Hole – Wall Spacing	2.5 in
Hole – Weir Spacing	4 in
Top Column Diameter	2.474 m
Column Height	12.57 m

Chapter 4

control

Control Loop System on absorber

For the control ability of the absorber four different loops will be added to the process. The first one will be added to the inlet of the liquid and gas to control the flow rate. The second one will be added to the gas outlet to control the pressure of the absorber. The third one will be added to the liquid outlet to control the level. The fourth one will be added to the liquid outlet to control the level as in Figure.



Chapter Five
SAFETY , LOCATION AND ECONOMIC
CONSEDRATION

5.1-Safety & environment precaution

The main concern is mainly with precautions and protocols that are to be followed while handling materials in the plant. Safety equipment includes: splash goggles, protective coats, gloves and safety shoes are all required in dealing with these materials regardless of the their reactivity and stability. These documentations will include the two target materials and compounds encountered and utilized in the plant as follows

5.1.1-Methanol

Flash point	11–12 °C
Auto ignition temperature	385 °C
Explosive limits	36%
Lower Explosion Limit	6% (NFPA, 1978)
Upper Explosion Limit	36% (NFPA, 1978)
Products of Combustion	Carbon monoxide (CO) and Carbon Dioxide (CO₂)

It's a light, volatile, colorless, clear and flammable liquid. It has a distinctive sweetish smell and close to alcohol in odor and colorlessness. Methanol is very toxic to humans if ingested. Permanent blindness is caused if as little as 10 mL of methanol is received and 30 mL could cause death. Even slight contact with the skin causes irritation

5.1.1.1- Exposure

Exposure to methanol can be treated fast and efficiently. If the contact was to the eyes or skin, flushing with water for 15 minutes would be the first course of action. Contaminated clothing or shoes are to be removed immediately. If the contact is much more series, use disinfectant soap, then the contaminated skin is covered in anti-bacteria cream. Inhalation of methanol is much more hazardous than mere contact. If breathing is difficult, oxygen is given, if not breathing at all artificial respiration.

5.1.1.2- Reactivity

Methanol has an explosive nature in its vapor form when in contact with heat of fires. In the case of a fire, small ones are put out with chemical powder only. Large fires are extinguished with alcohol foam. Due to its low flash point, it forms an explosive mixture with air. Reaction of methanol and Chloroform + sodium methoxide and diethyl zinc creates an explosive mixture. It boils violently and explodes.

5.1.1.3- Storage

The material should be stored in cooled well-ventilated isolated areas. All sources of ignition are to be avoided in storage areas.

5.1.2- Formaldehyde

Flash point	64 °C
Autoignition temperature	430 °C
Explosive limits	36%
Lower Explosion Limit	6%
Upper Explosion Limit	36%
Products of Combustion	Carbon monoxide (CO) and Carbon

This material is a highly toxic material that the ingestion of 30 ml is reported to cause fatal accidents to adult victims. Formaldehyde ranges from being toxic, allergenic, and carcinogenic. The occupational exposure to formaldehyde has side effects that are dependent upon the composition and the phase of the material. These side effects range from headaches, watery eyes, sore throat, difficulty in breathing, poisoning and in some extreme cases cancerous. According to the International Agency for Research on Cancer (IARC) and the US National Toxicology Program: “known to be a human carcinogen”, in the case of pure formaldehyde

5.1.2.1- Fire hazards

Formaldehyde is flammable in the presence of sparks or open flames.

5.1.2.2-Exposure

Exposure to methanol can be treated fast and efficiently. If the contact was to the eyes or skin, flushing with water for 15 minutes would be the first course of action. If the contact is much more serious, use disinfectant soap, then the contaminated skin is covered in anti-bacteria cream. Inhalation of methanol is much more hazardous than mere contact. The inhalator should be taken to a fresh air.

5.1.2.3-Storage

Pure Formaldehyde is not stable, and concentrations of other materials increase over time including formic acid and para formaldehyde solids. The formic acid builds in the pure compound at a rate of 15.5 – 3 ppm/d at 30 °C, and at rate of 10 – 20 ppm/d at 65 °C. Formaldehyde is best stored at lower temperatures to decrease the contamination levels that could affect the product's quality. Stabilizers for formaldehyde product include hydroxyl propyl methyl cellulose, Methyl cellulose, ethyl cellulose, and poly (vinyl alcohols).

5.2 Plant location

5.2.1- Introduction

Considerable care must be exercised in selecting the plant site, and many different factors must be considered. Primarily, the plant should be located where the minimum cost of production and distribution can be obtained, but other factors, such as room for expansion and safe living

conditions for plant operation as well as the surrounding community, are also important. The following factors should be considered in selecting a plant site:

1. Raw materials availability
2. Markets
3. Energy availability

4. Climate
5. Transportation facilities
6. Water supply
7. Waste disposal
8. Labor supply
9. Taxation and legal restrictions
10. Site characteristics
11. Flood and fire protection
12. Community factors.

5.2.2 - CH₂O plant location

Based on these previous factors which are required in CH₂O manufacturing plant, we select Al-Basra city as methanol can be obtained from methanol manufacturing plant which is in Basra .

CHAPTER SIX

COST

COSTS

6.1 – Introduction

This last part of the design project is done to determine a detailed yet approximate analysis for the economic feasibility of the project in relation to the Cost of Manufacturing (COM) for the formaldehyde project. This analysis covers the three major costs for the plant; Direct Manufacturing Cost (DMC), Fixed Manufacturing Costs (FMC) and General Expenses (GE). The determination of these items requires the analysis of several costs including the Fixed Capital Investment (FCI), the cost of operating labor (COL), Cost of utilities (CUT), cost of waste Treatment (CWT) and the cost of raw materials (CRM) .

6.2 – Raw material

This table gives an approximate cost (in 2015) for the major plant materials that are utilized frequently including . All costs are based upon prices provided by alibaba.com

Material	PELEMINIARY COST
Methanol	250 – 500 US \$ / Metric Ton
Formalin	380 – 838 US \$ / Metric Ton
Silver	1000 - 3,000 US \$ / Kilogram
Hydrogen	30 - 100 US \$ / 40L cylinder
DI Water	10 cents / gallon

Raw Materials Costs 6,722,144 \$

6.3 - Operating Labor Cost

Assumptions

- 1-Average total working period of single operator is 49 weeks/year
- 2- three weeks of vacation are off and sick leave.

Cost of Labor

- 1-shifts/week 5 for single operator and 245 shifts/year.
- 2-Since the plant is operating all year, (3 eight hours shift X 365 days) = 1095 shifts are required per year.
- 3- The number of operators needed to fill 1095 shifts is (1095 shifts/245 shift) = 4.5 operators

The number of non-particulate steps in the formaldehyde plant

$$N_{OL} = 1 \text{ reactor} + 2 \text{ tower} + 1 \text{ compressor} + 6 \text{ exchangers} = 10$$

The number of operators per shift (NOL) is as follows

$$N_{OL} = (6.29 + 31.7 p^2 + 0.23 N_{NP})^{0.5}$$

$$N_{OL} = (6.29 + 31.7 (0)^2 + 0.23(10))^{0.5}$$

$$N_{OL} = 2.9308$$

$$\text{Operating labor} = (4.5) * (2.9308) = 13.19 \cong 14 \text{ operators}$$

Assume for single operator 12.8\$/hr

Yearly Payment for single operator

$$12.8 \frac{\text{USD}}{\text{hr}} * 8 \frac{\text{hr}}{\text{shifts}} * 245 \frac{\text{shifts}}{\text{year}} = 25088 \frac{\text{USD}}{\text{year}}$$

$$\text{Total Operating Labor Cost} = 14 * 25088 = 351232 \text{ \$ /year}$$

6.4- Equipment cost

EQUIPMENT	Cost
Compressors C-101	517,000\$
Drives D-101	106,000\$
Exchangers E-101	64,400\$
Exchangers E-102	68,700\$
Exchangers E-103	63,500\$
Exchangers E-104	66,300\$
Exchangers E-105	63,500\$
Exchangers E-106	71,800\$
Exchangers E-107	124,000\$
Pump P-101	24,600\$
Pump P-102	32,200\$
Pump P-103	30,700\$
Tower T-101	67,500\$
Tower T-102	292,000\$
Vessels V-101	25,400\$
Total Cost	1,617,600\$

Conclusion

Our Chemical Engineering senior project design was aimed to bring forth an integrated detailed design for the PRODUCTION OF FORMALDEHYDE FROM METHANOL. This project covered several aspects of the plant's design including firstly a literature background on the production of formaldehyde through different routes. Rigorous comprehensive mass and energy balances were done throughout the plant including the reaction area. The third task was set to simulate the process to obtain an optimized view of the plant's operations. The fourth task was the detailed design and sizing of the plant's equipment including the three major units in the plant; the reactor, the absorber and the distillation column. The final task was to estimate the economical feasibility of the formaldehyde manufacturing process. The guidance and support from our mentor prof. .

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