DESIGN OF A PLANT FOR THE MANUFACTURE OF FORMALDEHYDE

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Of

GAUHATI UNIVERSITY

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A

PROJECT REPORT

ON

DESIGN OF A PLANT FOR THE MANUFACTURE OF FORMALDEHYDE

SUBMITTED BY

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TABLE OF CONTENTS

CERTIFICATE

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This is to certify that Anjali Agarwala (Roll no: CHE/16/242), Modhusmita Taye (Roll no: CHE/16/291), Liza Mili (Roll no: CHE/16/292), Dorody Priya Shyam Gohain (Roll no:CHE/16/293) of B.E. 8^{th} semester have jointly carried out the project entitled "**Design a plant for the manufacture of Formaldehyde"** under our supervision and submitted the report in partial fulfilment of the requirement for the degree of Bachelor of Engineering in Chemical Engineering of Gauhati University, which may be accepted.

Date:25/06/2020

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ABSTRACT

Formaldehyde, the target product of the present work, is an organic compound representing the most elementary configuration of the aldehydes. It behaves as a synthesis baseline for many other chemical compounds, including phenol formaldehyde, urea formaldehyde, melamine resin, Paints, and Glues. It is also used in medical field i.e. as a disinfectant and preservation of cell and tissues. The aim of the present work is to reach 98% conversion of methanol using Metal Oxide. Detailed calculations were performed in this report for all equipment in the plant including Material Balance, Energy Balance, Design, taking into account the required process conditions to achieve a production capacity of 75000 TPA of formaldehyde.

TABLE OF FIGURES

LIST OF TABLE

CHAPTER-1

INTRODUCTION

This Chapter gives an insight of project. A brief discussion of the chapter is included here. It also deals with the introduction of formaldehyde and its history. This project deals with production of formaldehyde in presence of methanol and oxygen. This study will take into consideration aspects including the entire plant's process unit design, process flow diagrams, cost estimations, operation parameters, equipment sizing, construction materials and environment/safety precautions. This project requires the theoretical application of mass transfer and heat transfer.

Formaldehyde (CH_2O), the target product of the project's plant, is an organic compound representing the simplest form of the Aldehydes. It acts as a synthesis baseline for many other chemical compounds including phenol formaldehyde, urea formaldehyde and melamine resin. The most widely produced grade is formalin (37 wt. % formaldehyde in water) aqueous solution. In this project's study, formaldehyde is to be produced through metal oxide process involving methanol and oxygen according to the following reactions:

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

$HCHO + \frac{1}{2} O_2 \longrightarrow CO + H_2O$

The reactions occur over a mixed oxide catalyst containing molybdenum oxide and iron oxide in a ratio 1.5 to 3.The reaction is carried out at 250 –350 ^{0}C and essentially at atmospheric pressure. Methanol conversion is 95 – 98% per pass. The desired reaction is exothermic.

The project's target is to design a plant with a capacity of 75,000 tons formalin/year. This plant is to include major unit such as a reactor and absorber. Also it includes pumps, compressors and heat exchangers. All are to be designed and operated according to this production capacity.

1.1 HISTORY OF FORMALDEHYDE

Formaldehyde occurs in nature and it is formed from organic material by photochemical processes in the atmosphere. Formaldehyde is an important metabolic product in plants and animals (including humans), where it occurs in low but measurable concentrations. It has a pungent odour and is an irritant to the eye, nose and throat even at low concentrations.

However, Formaldehyde does not cause any chronic damage to human health. Formaldehyde is also formed when organic material is incompletely combusted. Formaldehyde is an important industrial chemical and is employed in the manufacture of many industrial products and consumer articles. Formaldehyde was first synthesized in 1859, when BUTLEROV hydrolyzed Methylene acetate and noted the characteristic odour of the resulting solution. In 1867, HOFMANN conclusively identified formaldehyde, which he prepared by passing methanol vapour and air over a heated platinum spiral. This method, but with other catalyst, still constitutes the principal method of manufacture.

Industrial production of formaldehyde became possible in 1882, when TOLLENS discovered a method of regulating the methanol vapour: air ratio and affecting the yield of the reaction. In 1886 LOEW replaced the platinum spiral catalyst by more efficient copper gauze. A German firm, Hugo Blank, patented the first use of a silver catalyst in 1910.In 1905, Badische Aniline and Soda-Fabrik started to manufacture formaldehyde by a continous process employing a crystalline catalyst.

Formaldehyde output was 30 kg/day in the form of an aqueous 30 wt% solution. The methanol required for the production of formaldehyde was initially obtained from the timber industry by carbonizing wood. 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, woodworking, cabinet-making industries, glues, adhesives, paints, explosives, disinfecting agents, tissue preservation and drug testing.

CHAPTER 2
PROPERTIES

2.1 PHYSICAL PROPERTIES OF FORMALDEHYDE

Formaldehyde is also known as Methanal, Methylene oxide or Formalin. It is the first in the series of aliphatic Aldehydes, with the structure $H_2C{=}O$. Formaldehyde is a reactive and versatile chemical intermediate. Pure formaldehyde is a colourless gas with a pungent and suffocating odour at ordinary temperatures. At ordinary temperatures formaldehyde gas is readily soluble in water, alcohols and other polar solvents.

It has following physical properties:

Boiling point at 101.3 kPa = -19.2 ^{0}C

Melting point = -118 ^{0}C

Density at –80 ^{0}C = 0.9151 g/cm^3

At –20 ^{0}C = 0 .8153 g/cm^3

Vapor density relative to air = 1.04

Critical temperature = 137.2 – 141.2 (^{0}C)

Critical pressure = 6.784 – 6.637 Mpa

Cubic expansion coefficient = 2.83 x 10–3 K $^{-1}$

2.2 THERMAL PROPERTIES

Heat of formation at 25 ^{0}C = -115.9 + 6.3 kJ/mol

Heat of combustion at 25 ^{0}C = 561.5 kJ/mol

Heat of vapourisation at –19.2 ^{0}C = 23.32 kJ/mol

Specific heat capacity at 25 ^{0}C = 35.425 J/mol K

Heat of solution at 23 ^{0}C

In water = 62 kJ/mol

In methanol= 62.8 kJ/mol

In 1-propanal = 59.5 kJ/mol

In 1-butanol = 62.4 kJ/mol

Entropy at 25 ^{0}C= 218.8 + 0.4 kJ/mol K

2.3 CHEMICAL PROPERTIES

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

Decomposition

At 150 ^{0}C formaldehyde undergoes heterogeneous decomposition to form methanol and CO_2 mainly. Above 350 ^{0}C it tends to decompose in to CO and H_2.

Polymerization

Gaseous formaldehyde polymerizes slowly at temperatures below 100 ^{0}C, polymerization accelerated by traces of polar impurities such as acids, alkalis or water. In water solution formaldehyde hydrates to methylene glycol

$$H_2C{=}O + H2O \longrightarrow HO - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - OH$$

Which in turn polymerizes to polymethylene glycols, $HO(CH_2O)_nH$, 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 CO_2 and H_2O.

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)

$$2HCHO \longrightarrow HCOOCH_3$$

Addition reactions

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

$$HCHO + HCN \longrightarrow HOCH_2 - C \equiv N$$

Formaldehyde undergoes acid catalyzed Prins reaction in which it forms α-Hydroxy-methylated adducts with olefins. Acetylene undergoes a Reppe addition reaction with formaldehyde to form 2- butyne-1, 4-diol.

$2\ HCHO + HC \equiv CH \longrightarrow HOCH_2{\equiv}CCH_2OH$

Strong alkalis or calcium hydroxide convert formaldehyde to a mixture of sugars in particular hexoses, by a multiple aldol condensation, which probably involves a glycolaldehyde intermediate. Acetaldehyde, for example reacts with formaldehyde to give pentaerythritol, C $(CH_2OH)_4$

Condensation reactions

Important condensation reactions are the reaction of formaldehyde with amino groups to give schiff's bases, as well as the Mannich reaction.

$CH_3COCH_3 + (CH_3) \longrightarrow NH.HCl + HCHO$

$CH_3COCH_2\ CH_2 \longrightarrow N(CH_3)_2HCl + H_2O$

Formaldehyde reacts with ammonia to give hexamethylene teteramine and with ammonium chloride to give monomethylamine, dimethylamine, or trimethylamine and formic acid, depending upon reaction conditions.

Aromatic compounds such as benzene, aniline, and toluidine combine with formaldehyde to produce the corresponding diphenyl methanes. In the presence of hydrochloric acid and formaldehyde, benzene is chloromethylated to form benzyl chloride. Formaldehyde reacts with hydroxylamine, hydrazines, or semicardazide to produce formaldehyde oxime, the corresponding hydrazones, and semicarbazone, respectively.

Resin formation

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

2.4. ANALYSIS AND SPECIFICATIONS

Qualitative Methods:

Qualitative detection of formaldehyde is primarily by colorimetric methods. Schiff's fuchsin-bisulfite reagent is the general reagent used for detecting aldehydes. In the presence of strong acids, it reacts with formaldehyde to form a specific bluish violet dye.

Quantitative Methods:

Physical Methods: Quantitative determination of pure aqueous solutions of formaldehyde can be carried out rapidly by measuring their specific gravity. Gas chromatography and high-pressure liquid chromatography can also be used for direct determination.

Chemical Methods:

The most important chemical method for determining formaldehyde is the sodium sulfite method. It is based on the quantitative liberation of sodium hydroxide when formaldehyde reacts with excess sodium sulfite.

$$CH_2O + Na_2SO_3 + H_2O \longrightarrow HOCH_2SO_3Na + NaOH$$

The stoichiometrically formed sodium hydroxide is determined by titration with an acid.

Formaldehyde in air can be determined with the aid of gas sampling apparatus. In this procedure formaldehyde is absorbed from a definite volume of air by a wash liquid and is determined quantitatively by a suitable method like pararosanline method.

Formaldehyde is sold in aqueous solutions with concentrations ranging from

25 – 56 wt% HCHO. Formaldehyde is sold as low methanol (uninhibited) and high methanol (inhibited) grades. Formaldehyde solutions contain 0.5-12 wt% methanol or other added stabilizers. They have a pH of 2.5–3.5, the acid reaction being due to the presence of formic acid.

2.5. COMMERCIAL USES OF FORMALDEHYDE

Formaldehyde resins are one of the major applications of formaldehyde. Some of the derivatives are given below.

Manufacturing Of Glues and Resin

Due to the higher binding properties of formaldehyde, it is used widely in the production of glues and resins used in cabinetry, shelving, stair systems, and in other items of home furnishing. Not only are these glues widely effective, they are also reasonable due to the fact that formaldehyde is easily accessible. The greatest common products produced from formaldehyde include urea formaldehyde resin, melamine resin, and phenol formaldehyde resin. These are manufacturing by the reaction of formaldehyde with urea, melamine, and phenol, respectively. These are strong glues, and are used in carpentering as adhesives for particleboard, fiberboard and plywood. They are also used for compression molded plastic parts, as wet-strength additives for paper treating, and as bonders for glass fiber roofing materials. Phenol formaldehyde is use as an adhesive in waterproof plywood. These resins are also used for binding glass fiber insulation.

Acetylenic chemical uses of formaldehyde involve the reaction with acetylene to form butynediol, which in turn can be converted to butanediol, butyrolactone and

pyrolidones. Their major applications are as specialty solvent and extractive distillation agents. Urea-formaldehyde concentrates are used as controlled release nitrogen fertilizers. Melamines resins are thermosetting resins produced from melamine and formaldehyde and are primarily used for surface coatings.

As a Disinfectant

Formaldehyde is a extremely effective disinfectant. It fully negates the actions of bacteria, fungi, yeast and molds. Aqueous solution of formaldehyde can kill bacteria, and it is used in the treatment of skin infections. It is also used to deactivate toxic bacterial products for the manufacturing of vaccinations for certain infections. Methylamine, a derived of formaldehyde, is used to treat urinary tract infections. Hexamethylene tetramine is formed by the reaction between formaldehyde and ammonia. It is used as a partial replacement for phosphates as a detergent builder and as a chelating agent.

Textile Industry

Formaldehyde also discovers usage in the textile industry where it is added to dyes and pigments. This helps the pigments to bound better with the fabric, thus avoiding the colors from fading. Formaldehyde-based resins are used to increase a fabric's resistance to folds and wrinkles.

Automobile Industry

Key constituents of automobiles are produced using formaldehyde-based products. Since phenol formaldehyde resins are resistant to fire and high temperatures, they are used to production automobile parts, such as brake linings.

Preserving Cells and Tissues

Formaldehyde solution is used in laboratories for the safety of human and animal. A 4% solution is used for the same.

As an Embalming Agent: Embalming is a process which briefly stalls the decay of human remains. Formaldehyde is one of the embalming agents. It also repairs those tissues that are accountable for the firmness of the muscles in an embalmed body. A normal use of formaldehyde is in the production of ink. Formaldehyde-based resins are used in the natural gas and petroleum industries to get improved the yield of these fuels. Hexamine, a derived of formaldehyde, is used as a component in the manufacture of the quick-tempered RDX. Formaldehyde is added to paints as a stabilizer. Pentaerythritol is formed by the reaction of formaldehyde, acetaldehyde and sodium hydroxide. Its largest use is in the manufacture of alkyd resins for paints and other protective coatings It is also used as a chemical adding in cosmetics. It is also used in the manufacturing of polyacetal which are thermoplastics used in electrical and electronic application and it is produced from the anionic polymerization of formaldehyde. These resins are used in plumbing materials and automobile components.

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CHAPTER 3
LITERATURE SURVEY

This chapter deals with the various production processes for the production of formaldehyde, resulting in the selection of most feasible and economical process.
Most of the world's commercial formaldehyde is manufactured from methanol and air either by a process using a silver catalyst or one using a metal oxide catalyst.

SILVER CATALYST PROCESS

The silver catalyst processes for converting methanol to formaldehyde are generally carried out at an atmospheric pressure and at 600 – 720 °C .The reaction temperature depends on the excess of methanol in the methanol-air mixture. The composition of mixture must lie outside the explosive limits. The amount of air used is also determined by the catalytic quality of the silver surface. The following reactions take place

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

$$CH_3OH \longrightarrow HCHO + H_2$$

Methanol conversion is 65 – 75% per pass.

METAL OXIDE PROCESS

In this process formaldehyde is formed by oxidation process only. The reactions are:

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

$$HCHO + \frac{1}{2}O_2 \longrightarrow CO + H_2O$$

The oxide process for formaldehyde production uses a metal oxide (modified iron molybdenum-vanadium oxide) catalyst. The feed mixture of steam, air and methanol is lean in methanol (to avoid the explosive range) and almost complete conversion of methanol is obtained (98-99%) per pass. The reaction is carried out at 250 –350 ^{0}C and essentially at atmospheric pressure. All of the formaldehyde is made via reaction (the exothermic oxydehydrogenation of methanol). By-products are carbon monoxide, dimethyl ether, carbon dioxide and formic acid. Overall yields are in the range of 88 - 92 %.

Table 3.a. LITERATURE REVIEW IN TABULAR FORM

Year	Author’s Name	Works and Finding	Final Results
2017	Graeme J. Millar and Mary Collins	Industrial Production of Formaldehyde Using Polycrystalline	This paper aims at improving the overall performance of formaldehyde synthesis and Catalyst physical properties.
2012	Mohammed Ahmad Sanhoob Abdullah Al-Sulami Fawaz , Sabil Al-Rasheedi	Production of Formaldehyde from Methanol through catalytic vapour phase oxidation reaction.	Here the target is to design a plant with a capacity of 60,000 tons formalin/year
2005	S. Gayathri G.Muthamilarasi	Manufacture of formaldehyde from methanol by oxidation of metal oxide process Silver Catalyst.	This paper aims at designing plant that produce 37wt% formalin and checks for feasibility of production

2018	Attique Ahmed Baber, Zain Ali, Md Zeeshan, Waqas Anjum	Production of 66000 TPY of formaldehyde from methanol using Silver Catalyst.	The product has 40-55 wt.% formaldehyde, 1.3 wt% methanol and 0.01 wt% formic acid. The yield ranges between 89.5 and 90.5%. The largest well-known reactor for this process has a diameter of 3.2 m and an annual production of 72000 tons, calculated as 100% formaldehyde.
1978	Wachs, I.E. and Madix, R.J.	The oxidation of methanol on a silver Catalyst	. The properties of silver in the oxidative dehydrogenation of methanol were studied in a flow reactor under near industrial conditions and found different oxygen species on the silver surface play different roles in the reactions to CO, CO_2 and H_2CO. Gas phase reactions only contribute to the conversion to CO
2010	G. Leota J.Ma H.Park S.Park G.Voloshenk	Formaldehyde Production from Methanol	The product is a mixture of formaldehyde and methanol in water that is run through an absorber to remove inert gases and distillation column to recycle residual methanol

2019	Paschal Onuorah, Tekena Osaki Lawson	Design of a 60000 TPA formaldehyde production plant via the vapour-phase dehydrogenation of methanol using Silver Catalyst.	Fully integrated and detailed report on the design of a 60,000 TPA Formaldehyde production plant. The design equations developed for the reactor, absorber, distillation column and Pipelines were solved using a POLYMATH 7.1 program and an excel spreadsheet
1998	Nagy, A., Mestl, G., Ruhle, T., Weinberg, G. and Schlogl	The Dynamic Restructuring of Electrolytic Silver during the Formaldehyde Synthesis Reaction	The partial oxidation of methanol to formaldehyde is studied over an industrial electrolytic silver catalyst. This incorporation of oxygen into the silver lattice results in an increased conversion of methanol with a higher conversion to formaldehyde

CHAPTER 4
SELECTION OF PROCESS

This chapter includes a brief comparison between the two processes, resulting in the selection of most feasible and economical process.

Table.4.a.

SPECIFICATION	**SILVER CATALYST PROCESS**	**METAL OXIDE CATSLYST PROCESS**
PRESSURE	Atmospheric pressure	Atmospheric pressure
TEMPERATURE	600-700 ^0C	250-350 ^0C
NATURE OF REACTION	Exothermic	Exothermic
BY PRODUCT	CO,HCOOH, $C_2H_4O_2$	CO, C_2H_6O
REACTION	$CH_3OH + \frac{1}{2}O_2 \rightarrow HCHO + H_2O$ $CH_3OH \longrightarrow HCHO + H_2$	$CH_3OH + \frac{1}{2}O_2 \rightarrow HCHO + H_2O$ $HCHO + \frac{1}{2}O_2 \longrightarrow CO + H_2O$
METHANOL CONVERSION	65-75% per pass	95-98% per pass
PRODUCT CONCENTRATION	37%(aqueous)	57%(aqueous)

It is because of the following reasons we selected metal oxide catalyst process over silver catalyst process:

a) Metal oxide catalyst process has a very low reaction temperature, which permits high catalyst selectivity, and has the very simple method of steam generation. The conversion is around 95-98% per pass, which is greater than silver oxide process.
b) The higher concentration can reduce transport and storage costs and can be later diluted to the desired concentration.
c) In production of formaldehyde using metal oxide, conversion of methanol to formaldehyde is comparatively high than the silver catalyst process, so less methanol is required to achieve better results to those in the silver catalyst process.
d) Even when recycled gas is used (to decrease the oxygen concentration of the feed and therefore the quantity of air needed to prevent the flammable range), the total volume of gas passing over the oxide process is 3-3.5 times that of the silver process. This means that the equipment used for the oxide process must have a greater capacity. The absorption column in particular is much higher.
e) As the vast majority is converted to formaldehyde, the resulting solution remains relatively pure, with only minimal amounts of carbon monoxide, Dimethyl ether, carbon dioxide, and formic acid byproducts.

It is estimated that nearly 70% of commercial formaldehyde is produced by metal oxide process. Also by comparing and contrasting the methods we have noted that the iron oxide formaldehyde production process is the more efficient method for producing formaldehyde from methanol.

CHAPTER 5

PROCESS DESCRIPTION

The following shows a simplified flow diagram of metal oxide process considered in this study.

Metal oxide process: Vaporized methanol is mixed with air and optionally recycled tail gas is passed through catalyst filled tubes in a heat exchanger reactor. The following reactions take place

$$CH_3OH + \frac{1}{2} O_2 \longrightarrow HCHO + H_2O + 37 \text{ Kcal/g-mol}$$

$$HCHO + \frac{1}{2} O_2 \longrightarrow CO + H_2O + 51 \text{ Kcal/g-mol}$$

The temperature inside the reactor is maintained at 250 – 350 °C. The heat released by the exothermic reaction is removed by vaporization of a high boiling heat transfer fluid on outside of the tubes. Steam is normally produced by condensing the heat transfer fluid. The catalyst is granular or spherical supported Fe/Mo and has an effective life of 12 –18 months. A typical reactor has short tubes of 1-1.5 m and a large shell diameter of 2.5 m or more. The exit gases from the reactor pass through a heat exchanger where the temperature is reduced to 110 ^{0}C and then to the absorption column where water is used as the scrubbing medium. The absorber can be either of packed or tray type. It is necessary to remove the heat of solution plus the residual sensible heat of the feed gases, and this is done by circulating down flow liquid through external heat exchangers and in some cases by the use of cooling coils. The bottom stream from the absorber represents the final product. Formaldehyde concentration in the product is adjusted by controlling the amount of water added to the top of the absorber. Formic acid is removed by ion exchange. A large portion of the absorber overhead gas is recycled back to the feed system.

An almost methanol-free product can be achieved on this process design. The methanol conversion ranges from 95-99 mol% and depends on the selectivity, activity and spot temperature of the catalyst, the later being influenced by the heat transfer rate. The overall plant yield of formaldehyde is 88-95 mol%. The final product contains up to 55wt% formaldehyde and 0.5-1.5 wt% methanol. The tail gas from the oxide process did not burn by itself as the flammable content (dimethyl ether, carbon monoxide, methanol and formaldehyde) is only a few percent. It can be combust in a catalytic furnace or by adding fuel.

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 sliver catalyst. However, the disadvantage of this 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.

CHAPTER 6

PROCESS FLOW DIAGRAM

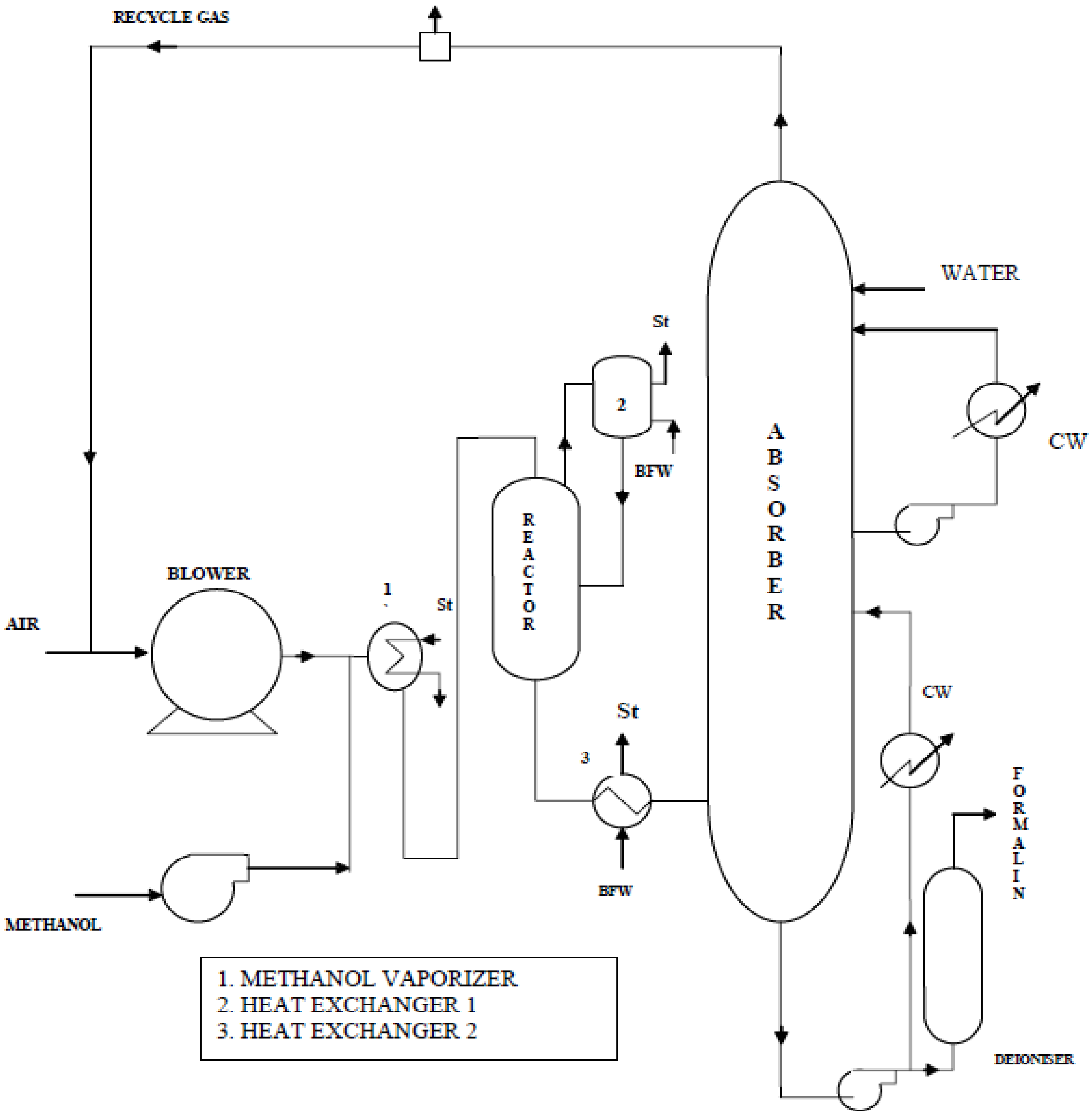


Fig.6.a. Process Flow Diagram

CHAPTER 7
MATERIAL BALANCE

7.a<u>MATERIAL BALANCE IN REACTOR</u>**:**

Basis: 100 kmoles of methanol in fresh feed per hour

Assumptions:

- Methanol Conversion is 97%
- Methanol reacts to form formic acid is 1%
- Air supply(in excess) is 250%
- $\frac{\text{Recycle stream}}{\text{Fresh feed stream}} = \frac{57}{43}$
- Percentage composition of recycle stream is

  O_2=7.78%, N_2 =88.3%, H_2O=3.89%

Molecular weight of methanol = 32 kg/kmole

Weight of methanol in feed = 3200 kg

Main Chemical Reaction:

$CH_3OH + \frac{1}{2}O_2 \longrightarrow HCHO + H_2O$ + 37 Kcal/g-mol

$HCHO + \frac{1}{2}O_2 \longrightarrow CO + H2O$ + 51 Kcal/g-mol

Hence methanol reacted = 97 kmoles = 3104 kg

Methanol reacted to form formic acid = 1 kmol

Actual O_2 required = 52kmoles = 1664 kg

Actual O_2 supplied (250% excess) = 52+52 x 2.5= 182 kmoles = 5824 kg

Excess O_2 = 182 – 52 = 130 kmoles = 4160 kg

Assume that 57% of oxygen requirement comes from recycle stream and 43% comes from fresh feed.

O_2 from fresh feed = 182 x 0.43= 78.26 kmoles = 2504.32 kg

Corresponding N_2 = 78.26 x (79/21)= 294.40 kmoles = 8243.2 kg

Hence, percentage composition in the recycle stream is

O_2= 182 x 0.57=103.74 kmoles=3319.68 kg

N_2= (103.74/7.78) x 88.3 = 1177.40 kmoles= 32967.45 kg

H_2O= (103.74/7.78) x 3.89 = 51.87 kmoles= 933.66 kg

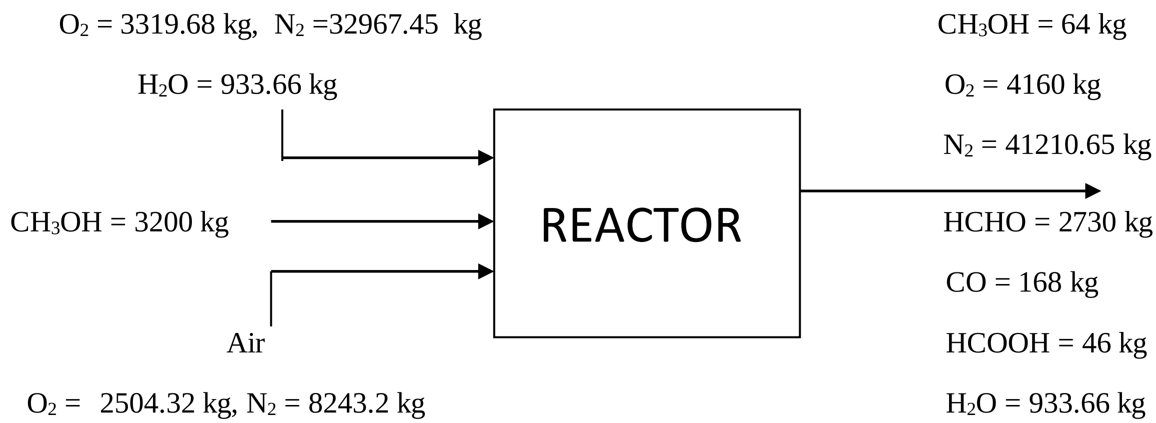


TABLE 7.a.: MATERIAL BALANCE IN REACTOR

INPUT STREAMS			OUTPUT STREAMS		
	Kmol/hr	Kg/hr		Kmol/hr	Kg/hr
Methanol	100	3200	Methanol Unreacted	2	64
Oxygen gas(R+F)	130	4160	Oxygen gas(R+F)	130	4160
Nitrogen gas(R+F)	1471.8	41210.65	Nitrogen gas(R+F)	1471.8	41210.65
Water in	51.87	933.66	Water Out	51.87	933.66
			Formaldehyde	91	2730
			Carbon monoxide	6	168
			Formic acid	1	46
Total	1753.67	51168.31	Total	1753.67	51168.31

Total input = 51168.31 kg/hr

Total output = 51168.31 kg/hr

7.b <u>MATERIAL BALANCE IN ABSORBER</u>**:**

$G_{ms}(Y_a - Y_b) = L_{ms}(X_a - X_b)$

Where,

G_{ms}= molar flow rate of gas on solute free basis

L_{ms} = molar flow rate of liquid on solute free basis

X_a = % of solute in liquid at inlet

X_b= % of solute in liquid at outlet

Y_a = fraction of solute in gas at inlet

Y_b = fraction of solute in gas at outlet

Hence, G_{ms} = Unreacted O_2 + N_2(in outlet) =130+ 1471.8 =1601.80 kmol/hr

From VLE data of Formaldehyde

Slope(M) = 0.0678

Hence, M = $\frac{Yb-Ya}{Xa-Xb} = \frac{0.0526-0.000314}{0.77-0}$ = 0.0678

Here, Y_a= 0.000314, Y_b= 0.0526, X_a= 0, X_b= 0.77

We know that,

Slope of VLE data = $\frac{(Lms)min}{Gms}$

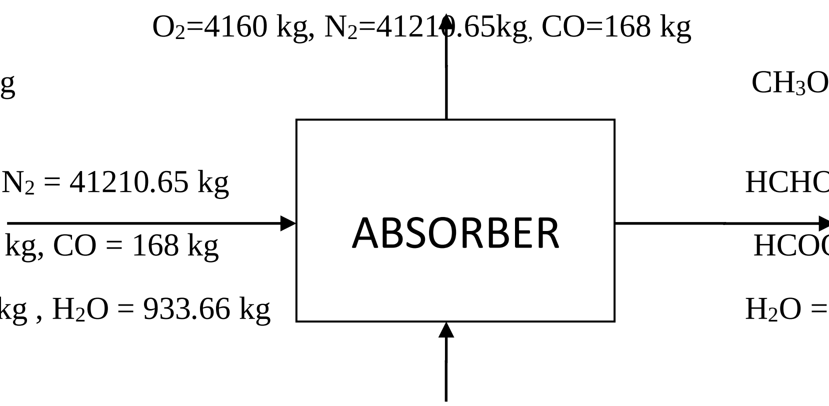
Here we get L_{ms}= 108.6 kmol

Assume, L_{ms}= 1.4(L_{ms})=152.04 kmol

O_2=4160 kg, N_2=41210.65kg, CO=168 kg

CH$_3$OH = 64 kg

CH$_3$OH = 64 kg



O_2 = 4160 kg , N_2 = 41210.65 kg

HCHO = 2730 kg, CO = 168 kg

HCOOH = 46 kg , H_2O = 933.66 kg

HCHO = 2730 kg

HCOOH = 46 kg

H_2O = 933.66 kg

Solvent H_2O = 3706.38kg

TABLE 7.b.: MATERIAL BALANCE IN ABSORBER

INPUT STREAMS			OUTPUT STREAMS		
	Kmol/hr	Kg/hr		Kmol/hr	Kg/hr
Methanol	2	64	Methanol Unreacted	2	64
Oxygen gas(R+F)	130	4160	Oxygen gas(Recycle Stream)	130	4160
Nitrogen gas(R+F)	1471.8	41210.65	Nitrogen gas(Recycle stream)	1471.8	41210.65
Water in	205.91	3706.38	Water Out	51.87	933.66
			Formaldehyde	91	2730
			Carbon monoxide(Purge)	6	168
			Formic acid	1	46
Total	1753.67	51168.31	Total	1753.67	51168.31

Total input = 51168.31 kg

Total output = 51168.31 kg

CHAPTER 8
MODIFIED MATERIAL BALANCE

MULTIPLY FACTOR**:**

Number of days in 1 year = 365 days

Number of Shutdown days = 35 days

Number of working days = 330 days

A Company named **Kanoria Chemicals &Industries,Gujarat**has a capacity of formaldehyde production as 75000 TPA.

Plant Capacity = 75000 TPA

Hence, Multiply Factor = $\frac{(75000 \text{ x } 1000)}{(330 \text{ x } 24 \text{ x } 2730)}$ = 3.46

b) After using the multiplying factor , the material balance in reactor:

For Example: CH_3OH= 3200*3.46 = 11072 kg and so on……

TABLE 8.a.: MODIFIED MATERIAL BALANCE IN REACTOR

INPUT STREAMS			OUTPUT STREAMS		
	Kmol/hr	Kg/hr		Kmol/hr	Kg/hr
Methanol	346	11072	Methanol Unreacted	6.92	221.44
Oxygen gas(R+F)	629.72	20151.03	Oxygen gas(R+F)	449.8	14393.6
Nitrogen gas(R+F)	5092.45	142588.85	Nitrogen gas(R+F)	5092.45	142588.84
Water in	179.47	3230.46	Water Out	538.86	9699.48
			Formaldehyde	314.86	9445.8
			Carbon monoxide	20.76	581.28

			Formic acid	3.46	159.16
Total	6247.64	177042.35	Total	6247.64	177042.35

TABLE 8.b.: MODIFIED MATERIAL BALANCE IN ABSORBER

INPUT STREAMS			OUTPUT STREAMS		
	Kmol/hr	Kg/hr		Kmol/hr	Kg/hr
Methanol	346	11072	Methanol Unreacted	6.92	221.44
Oxygen gas(R+F)	629.72	20151.03	Oxygen gas(R+F)	449.8	14393.6
Nitrogen gas(R+F)	5092.45	142588.85	Nitrogen gas(R+F)	5092.45	142588.84
Water in	712.44	12824.07	Water Out	712.44	12824.07
			Formaldehyde	314.86	9445.8
			Carbon monoxide	20.76	581.28
			Formic acid	3.46	159.16
Total	6780.61	186635.96	Total	6780.61	186635.96

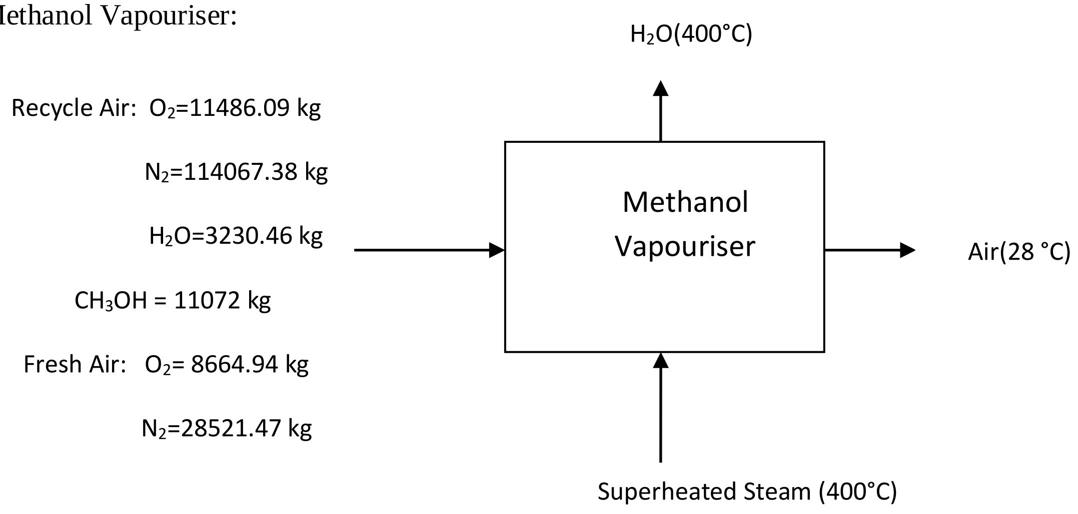
CHAPTER 9

ENERGY BALANCE

Table 9.a: Data Table

	Latent heat of vaporization, λ (kJ/kg)	Specific heat capacity, C_P (kJ/kg ^{0}C)
Methanol	1099.90 (at 64.7 ^{0}C)	2.513
Oxygen	2255 (at 100 ^{0}C)	0.928
Nitrogen	3278.20 (at 400 ^{0}C)	1.04
Water	2228.69 (at 110 ^{0}C)	1.88
CO		1.13
HCOOH		0.6
HCHO		0.5
Oil		1.75

1) Methanol Vapouriser:



$[(mC_p)_{recycle} + (mC_p)_{fresh} + (mC_p)_{methanol\ gas} + (mC_p)_{methanol\ liquid}]\ \Delta T = m\lambda_{steam}$

⇨ (135362.43 + 37703.37 + 40080.64 + 28012.16)(285-25) = m x 3278.2

⇨ m = 19126.72

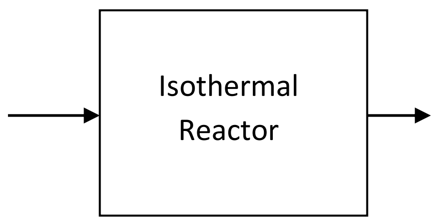
2) Isothermal Reactor:

(At 280°C)

O_2=11486.09 kg

N_2=114067.38 kg

H_2O= 3230.46 kg



CH_3OH= 221.44 kg

O_2= 14393.6 kg

N_2= 142588.84 kg

H_2O= 9699.48 kg

CO= 81.28 kg

HCOOH= 9445.8 kg

HCHO= 159.16 kg

$CH_3OH + 1/2O_2 \longrightarrow HCHO + H_2O$, ΔH_O= -4839 KJ/kg

$HCHO + 1/2O_2 \longrightarrow CO + H_2O$, ΔH_O= -7115.35 KJ/kg

$\therefore \Sigma\Delta H_{products}$ = 21263261.536

$\Sigma\Delta H_{reactants}$ = 47163.691

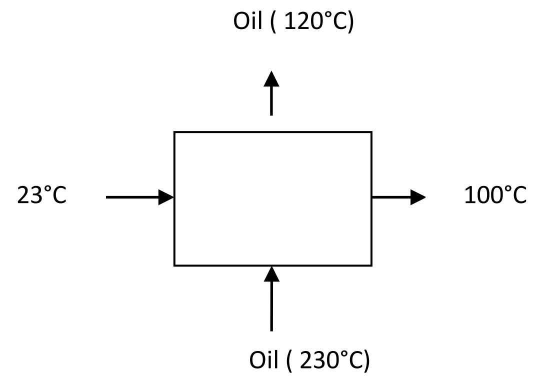
$\therefore \Delta H = \Sigma\Delta H_{products} - \Sigma\Delta H_{reactants} + \Delta H_O = 20.47 \times 10^6$

$\therefore (mC_p\Delta T)_{oil} = 20.47 \times 10^6$

⇨ m x 1.75 x (230-120) = 20.47 x 10^6

⇨ m = 106337.66 kg

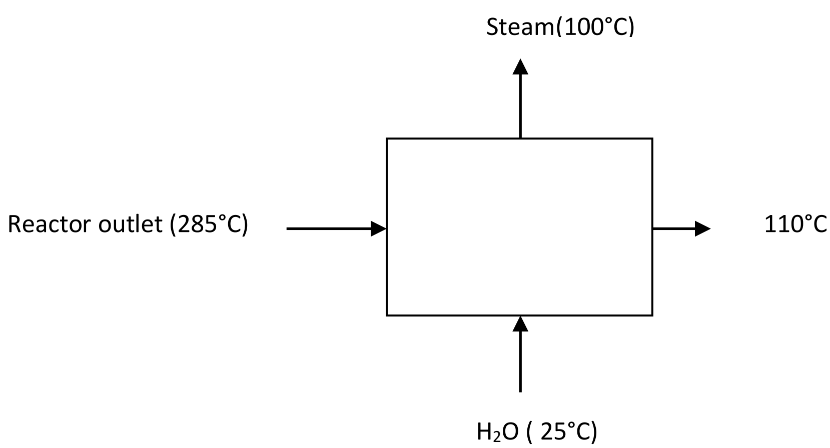
3) Heat Exchanger 1:



$\therefore (mC_p\Delta T)_{cooling\ oil} = (mC_p\Delta T)_{water} + m\lambda$

- ⇨ $20.47 \times 10^6 = m(1.88x75) + m(2255)$
- ⇨ $m = 8543.40$ kg

4) Heat Exchanger 2:



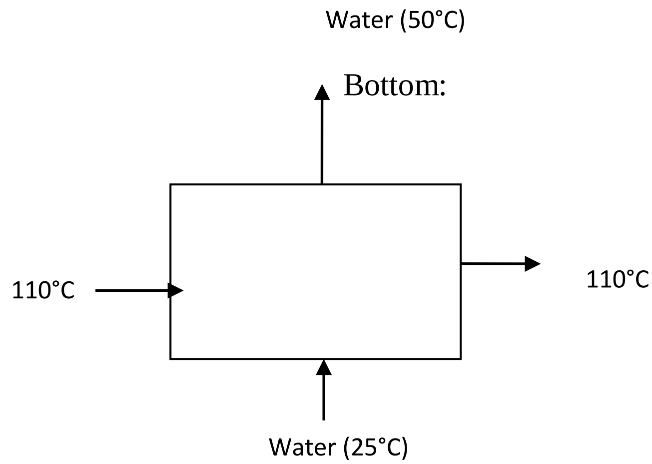
$\therefore (mC_p\Delta T)_{products} = (mC_p\Delta T)_{water} + m\lambda_{steam}$

⇨ $21263261.53 = (m \times 1.88 \times 75) + (m \times 2255)$

⇨ $m = 8896.76$ kg

5) Absorber

Bottom:

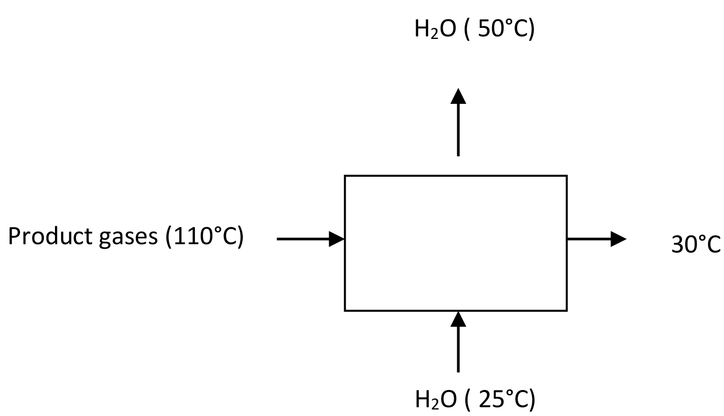


$\therefore (mC_p\Delta T)_{\text{cooling water}} = m\lambda_{\text{condensing}}$

⇨ $m \times 1.88 \times 25 = 9699.48 \times 2255$

⇨ $m = 134499.71$ kg

Top:



$\therefore (mC_p\Delta T)_{\text{cooling water}} = (mC_p\Delta T)_{\text{product gases}}$

⇨ $m \times 1.88 \times 25 = 47163.61 \times (110-30)$

⇨ $m = 79521.49$ kg

CHAPTER 10

DESIGN

10.1 Design of storage tank

Assumptions:

For large tank, $\frac{D}{H} = \frac{4C_1}{C_2+C_3+C_4+C_5}$

For small tank, $\frac{D}{H} = \frac{2C_1}{C_2+C_3+C_4+C_5}$

Where, $C_1 = 2C_2$, $C_3 = 1.8C_2$, $C_4 + C_5 = 0.4C_2$

t = Minimum thickness of shell plate in mm

H = Height of the tank in m

D = Diameter of the tank in m

G = Specific gravity of liquid to be stored

S = Allowable stress in kgf/cm^2

E = Joint efficiency factor

W = Width of each plate in m

n = Number of thickness section

Capacity of tank = (2730 x 30 x 24) kg = 1965600 kg

∴ density = $\frac{\text{Mass}}{\text{Volume}}$

$815 = \frac{1965600}{\text{Volume}}$ (density of formaldehyde = 815 kg/m^3)

Volume = 2411.779 m^3

Let us assume the tank is small,

We assume, D= 1.25H

$\therefore$ $V = \frac{\pi}{4}D^2H = 2411.779\ m^3$

$= 0.785x\ (1.25H)^2 \ x\ H = 2411.779$

H = 12.528 m = 41.10 ft

D = 1.25H = 1.25 x 41.10 = 51.378 ft

D(H – 1) = 51.378 x (41.10 – 1) = 2060.2578 > 1720

Here our assumption is wrong

Let us assume the tank is large

We assume, D = 2.5H

$\therefore$ $V = \frac{\pi}{4}D^2H = 2411.779\ m^3$

$= 0.785\ x\ (2.5H)^2\ x\ H = 2411.779$

H = 7.89 m = 25.88 ft

D = 2.5 x 25.88 = 64.71 ft

= 19.723 m

D (H – 1) = 64.71 x (25.88 – 1) = 1609.9848 > 1515 (lap joint)

$\therefore$ the tank is large

<u>Determination of thickness</u>:

πD = 3.14 x 19.723 = 61.93 m

$L = \frac{\pi D - 2n\ x\ 10^{-3}}{n}$

Assumption, n = 8, $L = \frac{61.93 - (2\ x\ 8\ x\ 10^{-3})}{8}$ = 7.74 m

n = 7, $L = \frac{61.93 - (2\ x\ 7\ x\ 10^{-3})}{7}$ = 8.84 m (Which is available in appendix B)

Therefore, width (w) = $\frac{H}{n} = \frac{7.89}{7}$ = 1.12 m

= 1250 mm

From Appendix B standard width is 1250 mm

We know thickness (t) = $\frac{50\ (H-0.3)DG}{SE}$

(Ref: IS: 2825 – 1969, page no 115, S = 14.2 kgf/mm^2 for stainless steel)

E = Joint Efficiency Factor for large tank butt joint = 0.85

t_{final} = t + t_c,

t_c = Corrosion allowance = 0.3 mm

t = Calculated thickness

t_s = Standard thickness (Reference: B.C Bhattacharya, Appendix B)

(Comparing with Clause 6.3.3.2 of IS: 803 – 1976 for D= 19.723 m, minimum thickness is 6 mm)

$t_1 = \frac{50\ (7.89-0.3) x 19.723\ x\ 1}{14.2\ x\ 0.7\ x\ 10^2}$ = 7.33 mm

t_{1f} = 7.53 + 0.3 =7.83

t_{1s} = 8 mm

$t_2 = \frac{50\ (7.89-1.25-0.3) x 19.723\ x\ 1}{14.2\ x\ 0.7 x\ 10^2}$ = 6.28 mm

t_{2s} = 6.28 + 0.3 = 6.58

t_{2f} = 7 mm

$t_3 = \frac{50\ (7.89-2x1.25-0.3) x\ 19.723\ x\ 1}{14.2\ x\ 0.7\ x\ 10^2}$ = 5.04 mm

t_{3f} = 5.04 + 0.3 = 5.34

t_{3s} = 6 mm

$t_4 = \frac{50\ (7.89-3x1.25-0.3) x\ 19.723\ x\ 1}{14.2\ x\ 0.7\ x\ 10^2}$ = 3.80 mm

t_{4f} = 3.80 + 0.3 = 4.1

t_{4s} = 6 mm

$$t_5 = \frac{50\ (7.89-4\ x1.25-0.3)x\ 19.723\ x\ 1}{14.2\ x\ 0.7\ x\ 10^2} = 2.56\ mm$$

t_{5f} = 2.56 + 0.3 = 2.86

t_{5s} = 6 mm

$$t_6 = \frac{50\ (7.89-5x1.25-0.3)x\ 19.723\ x\ 1}{14.2\ x\ 0.7\ x\ 10^2} = 1.32\ mm$$

t_{6f} = 1.32 + 0.3 = 1.62

t_{6s} = 6 mm

$$t_7 = \frac{50\ (7.89-6x1.25-0.3)x\ 19.723\ x\ 1}{14.2\ x\ 0.7\ x\ 10^2} = 0.089\ mm$$

t_{7f} = 0.089 + 0.3 = 0.389

t_{7s} = 6 mm

Table 10.a: Minimum nominal thickness of storage tank

n	t (Calculated) (mm)	t(Standard) (mm)
1	7.33	8
2	6.28	7
3	5.04	6
4	3.80	6
5	2.56	6
6	1.32	6
7	0.089	6

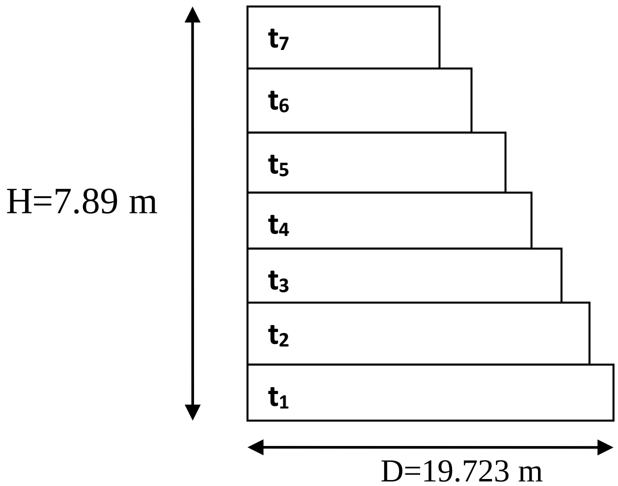


Fig 10 .a : Schematic diagram of a storage tank

CHAPTER 11

CONCLUSION

Design of the selected process for a given production output of formaldehyde and calculation of material balance and Energy balance. Design of the storage tank is done. The designing of Heat Exchanger, Absorber are yet to be done.

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