جمهورية العراق

وزاره التعليم العالي والبحث العلمي

جامعة بابل /كلية الهندسة

قسم الهندسة الكيمياوية

Manufacture of Formic acid

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بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

(قالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا إِنَّكَ أَنتَ الْعَلِيمُ الْحَكِيم)

[سورة البقرة]

صدق الله العلي العظيم

الاهداء

إلى والدي الذي علمني كيف أفكر الفكرة الأولى .. إلى والدتي التي علمتني كيف أكتب الحرف الأول..

"إلى أولئك الاستثنائيين ، الذين علموا أن الحياة قصيرة فقرروا أن يصنعوا فيها إنجازا عظيما ، وعلموا أن عدد سكان الكرة الأرضية تجاوز السبعة مليارات شخص فقرروا أن لا يكونوا مثلهم ، وعلموا أن طريق النجاح مليء بالصعاب فقرروا أن يسلكوه لأنهم يؤمنون بأنه لو كان طريقا سهلا لسلكه الجميع وما كان هناك استثناء"

الى من قدمت لنا الدعم السخي والكبير بتواضع جميل للخروج بهذا البحث حتى النهاية ... الاستاذة مروة داوود

Table of Contents

CHAPTER 1

INTRODUCTION

• Formic acid (HCO2H), also called methanoic acid, the simplest of the carboxylic acids, used in processing textiles and leather. Formic acid was first isolated from certain ants and was named after the Latin formica, meaning “ant.” which are an organic acids with a carbonyl (i.e., C = O) and hydroxyl (i.e., -O-H) functional groups. The chemical formula of formic acid is HCOOH or HCO2H and its molecular structure is shown in Figure 1.

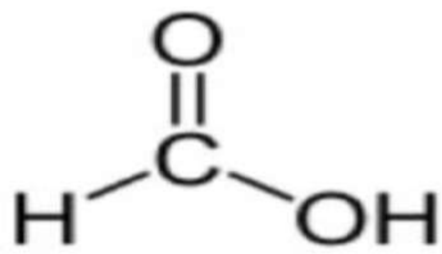


Figure 1. Molecular Structure of Formic Acid

Formic acid is found naturally in small amounts in some fruits and nectars and is a natural component of honey.

<u>Natural occurrence</u>

In nature, formic acid is found in most ants and in stingless bees of the genus Oxytrigona.Thewoodants from the genus Formica can spray formic acid on their prey or to defend the nest. Formic acid is anaturally occurring component of the atmosphere primarily due to forest emissions

<u>History</u>

Some alchemists and naturalists were aware that ant hills give off an acidic vapor as early as the 15thcentury. The first person to describe the isolation of this substance (by the distillation of large numbers of ants) was the English naturalist John Ray, in 1671.Ants secrete the formic acid for attack and defense purposes. Formic acid was first synthesized from hydrocyanic acid by the French chemist Joseph Gay Lussac. In 1855Formic acid was long considered a chemical compound of only minor interest in the chemical industry. In the late 1960s, however, significant quantities became available as a byproduct of aceticacid production. It now finds increasing use as a preservative and antibacterial in livestock feed.

Properties

Formic acid is a colorless liquid having a pungent, penetrating odor at room temperature, not unlike the related acetic acid. It is miscible with water and most polar organic solvents, and is somewhat soluble in hydrocarbons. In hydrocarbons and in the vapor phase, it consists of hydrogen-bonded dimers rather than individual molecules. Owing to its tendency to hydrogen-bond, gaseous formic acid does not obey ‹the ideal gas law. Solid formic acid, which can exist in either of two polymorphs consists of an effectively endless network of hydrogen-bonded formic acid molecules

Formic acid forms a low-boiling azeotrope with water (22.4%). Liquid formic acid tends to supercool.

Chemical properties:

●Clear, colorless liquid with a pungent odor

●Corrosive to metals and tissue

●Soluble in water with release of heatFormic acid reacts exothermically with all bases both organic and ino rganic

●Reacts with active metal to form gaseous hydrogen and metal sal.

Physical Properties

	Properties
Chemical formula	CH_2O_2
Molar mass	46.03 g·mol^{-1}
Appearance	Colourless fuming liquid
Odour	Pungent, penetrating
Density	1.220 g/Ml
Melting point	8.4 °C (47.1 °F; 281.5 K)
Boiling point	100.8 °C (213.4 °F; 373.9 K)
Solubility in water	Miscible
Solubility	Miscible with ether, acetone, ethyl, glycerol, methanol, ethanol Partially soluble in benzene, toluene, xylenes
log P	−0.54
Vapor pressure	35 mmHg (20 °C)[2]
Acidity (p*K*a)	3.77[3]
Magnetic susceptibility (χ)	-19.90·10−6 cm3/mole
Refractive index(nD)	1.3714 (20 °C)
Viscosity	1.57 cP at 268 °C

Uses

A major use of formic acid is as a preservative and antibacterial agent in livestock Feed. it also allows fermentation to occur quickly, and at a lower temperature, reducing the loss of nutritional value. Formic acid arrests certain decay processes and causes the feed to retain its nutritive value longer, and so it is widely used to preserve winter feed for cattle. Formic acid is also significantly used in the production of leather, including tanning and in dyeing and finishing textiles because of its acidic nature. Use as a coagulant in the production of rubber Formic acid is also used in place of mineral acids for various cleaning products Some formate esters are artificial flavorings and perfumes

Formic acid can be used as a fuel cell (it can be used directly in formic acid fuel cells and indirectly in hydrogen fuel cells).

The many industrial uses of formic acid include the following:

- A reducing and decalcifying agent in dyeing and finishing of textiles.
- An agent for plumping and dehairing hides in leather tanning.
- A solution for electroplating.
- A rubber coagulating agent in the creation of latex rubber and in regenerating old rubber

Historic Use:

Historically, formic acid has been used as an antibacterial agent and preservative for livestock feed. Formicacid is applied to hay in order to delay or halt decay, thereby allowing the feed a longer usable period. As a fumigant, formic acid vapors are released inside of beehives to kill invasive mite species.

CHAPTER 2

production

Production

:The installed formic acid processes can be classified in four groups

1-Acidolysis of Formate salts.

2- oxidation of hydrocarbons

3-hydrolysis of formamide.

4-methyl formate hydrolysis

●**Acidolysis of Formate salts**

Acidolysis of formate salts is the oldestindustrial process for producing formic acid. For instance, aldolization reactions carried out in the presence of strong alkali yieldformates as stoichiometric co products. The reaction between the formate salts and mineral acids such as sulphuric acid produces formic acid and a salt. The reaction is technically straightforward, but the inevitable production of the salt is a clear disadvantage of this route.

•**Oxidation of Hydrocarbons**:

For many years, a large amount of formic acid utilized is obtained as a by-product of acetic acid produced by the oxidation of hydrocarbons. This process is complex, and the amount of formic acid produced is very small compared to the effort devoted to the process.

•Hydrolysis of Formammide:

The production of formic acid by hydrolysis of Formamide played a significant role. The disadvantages of the Formamide route are the consumption of ammonia and sulphuric acid in other processes, along with the unavoidable coproduction of ammonium sulphate. Thus, the economic and environmental drawbacks of the first three processes led to the development of a process specifically dedicated to the production of formic acid, with no undesirable by-product.

Methyl Formate Hydrolysis

Huang et al. proposed a novel process by integrating a reactor and a conventional distillation column in the Methyl Formate hydrolysis based process into a single reactive distillation unit (RD).

Synthesis of formic acid by hydrolysis of methyl formate is based on a two-stage Process:

in the first stage, methanol is carbonylated with carbon monoxide; in the second

stage, methyl formate is hydrolyzed to formic acid and methanol. The methanol is

returned to the first stage:

$CH_3OH + CO \longrightarrow HCOOCH_3$

$CH_3OOCH + H_2O \longrightarrow CH_3OH + HCOOH$

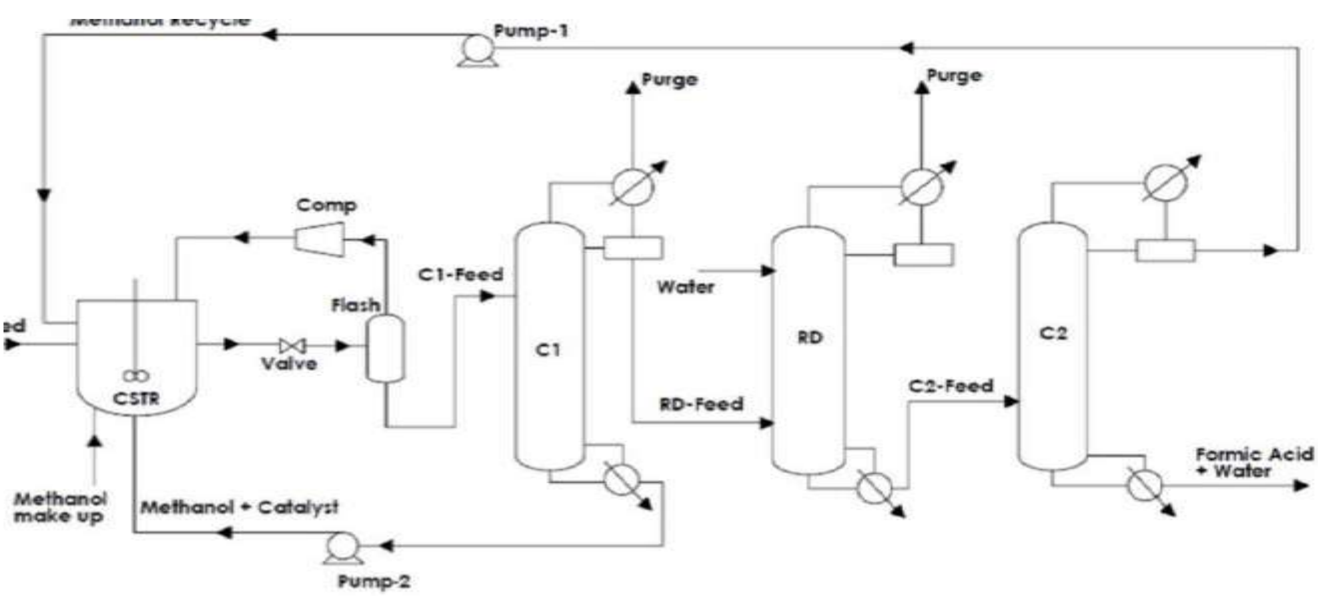
$CO + H_2O \longrightarrow HCOOH$

The main advantages of integrating the reactor and distillation are:

●The yield and selectivity are improved.

●Energy requirements decreases.

●Hot spots are avoided.



Process flow sheet for Huang’s patented process.

CHAPTER 3

MATERI BALANCE

Basis: 100 Kmol/hr. of Carbon Monoxide (CO) as fresh feed.

Assumptions: For the ease of calculations and visualization of the theoretical concepts, some assumptions need to be made. For the process studied in this report, the following assumptions were made based on the references referred and for simplification in calculations:

A-Ratio of CO: MEOH entering into the CSTR is 1:6.6

B-CO is the Limiting Reactant;

C-Conversion of CO in the reactor outlet is 95%;

D-90% of CO is flashed out;

e-90% of Methanol recovered as residue in C1 column and 75% of CO as purge;

f-Complete removal of CO in Reactive Distillation column (RD) as purge;

g-Water is an input to the RD with a flow-rate equal to the flow-rate of Methyl Formate (MF)

h-Conversion of water in RD is 58%.

Stoichiometric reactions:

(CSTR) ... $CO + CH_3OH \leftrightarrow HCOOCH_3$

(RD) … $H_2O \rightarrow CH_2O_2 + CH_3OH$ + ٣ HCOO

Steady-State Material Balance across various Unit Processes/Operations:

1-CSTR

Overall material Balance for CSTR:

$M1 + M2 + M10 + M6 + M14 = M3$

The mass flow rate of M1 is equal to 2800 kg/hr.

$M1 + M6 = 2926$ kg/hr

$M2 + M6 + M14 = (M1 + M6)*6.57 = 19223.82$ kg/hr

So, $M3 = 19223.82 + 2926 = 22149.82$ kg/hr

M3 consists of 75% of MEOH, therefore,

MEOH in S3 = 22149.82*0.75 = 16612.365 kg/hr

CO in S3 as per assumption (c) = 2800*0.05 = 140 kg/hr

MF in S3 = 22149.82 - 16612.365 – 140 = 5397.45 kg/hr.

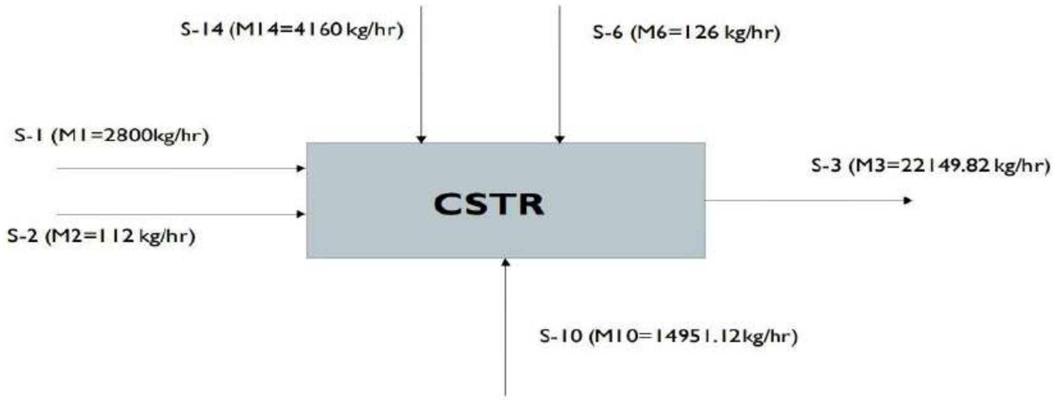


Fig. : Mass balance over CSTR

CSTR					
inlet stream			Outlet stream		
Stream no.	Flow rate(kg/hr)	Composition	Stream no.	Flow rate(kg/hr)	Composition
S-1	2800	100% CO			
S-2	112	100% MEOH			
S-6	126	100% CO	S-3	22149.82	0.6% CO 24.4% MF75% MEOH
S-10	14951.92	100% MEOH			
S-14	4160	100% MEOH			

2-Flash Column:

Material Balance for Flash:

M3 = M5 + M7

CSTR outlet has 5% of unreacted CO (140 kg/hr), 90% of which is flashed out from top. M5 = 140*0.9 = 126 kg/hr

M7 = M3 – M5 = 22023.82 kg/hr with individual compositions of CO = 14 kg/hr

MF = 5397.45 kg/hr and

MEOH = 16612 kg/hr.

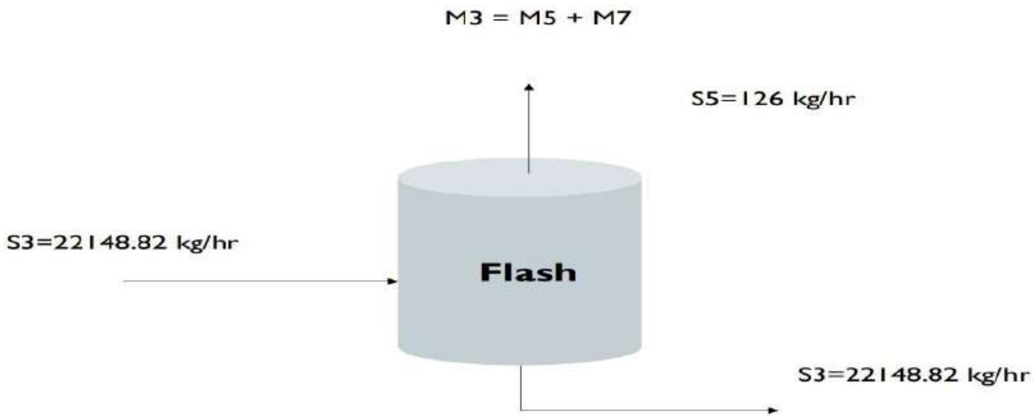


Fig. : Mass balance over Flash

Flash

inlet stream			Outlet stream		
Stream no.	Flow rate(kg /hr)	Compo sition	Stream no.	Flow rate(kg/ hr)	Compo sition
			S5	126	100% CO
S3	22149.82	0.6% CO 24.4% MF75% MEOH	S7	22023.82	0.06% CO24. 5 % MF 75.4% MEOH

3-Distillation column (C1)

CO, MF and Methanol enter C1 as feed of which CO is separated as purge, Methanol (obtained as residue from C1) is sent back to the CSTR as a recycle and the distillate (MF) is further sent to the RD column.

Material Balance for C1:

M7 = M8 + M9 + M10

M8 = 14 * 0.75 = 10.5 kg/hr

M10 = 16612.365 * 0.9 = 14951.12 kg/hr

Material Balance for C1:

M7 = M8 + M9 + M10

M8 = 14 * 0.75 = 10.5 kg/hr

M10 = 16612.365 * 0.9 = 14951.12 kg/hr

M9 = M7 -M8 -M10 = 22023.82 -10.5 –14951.12 = 7620.2 kg/hr.

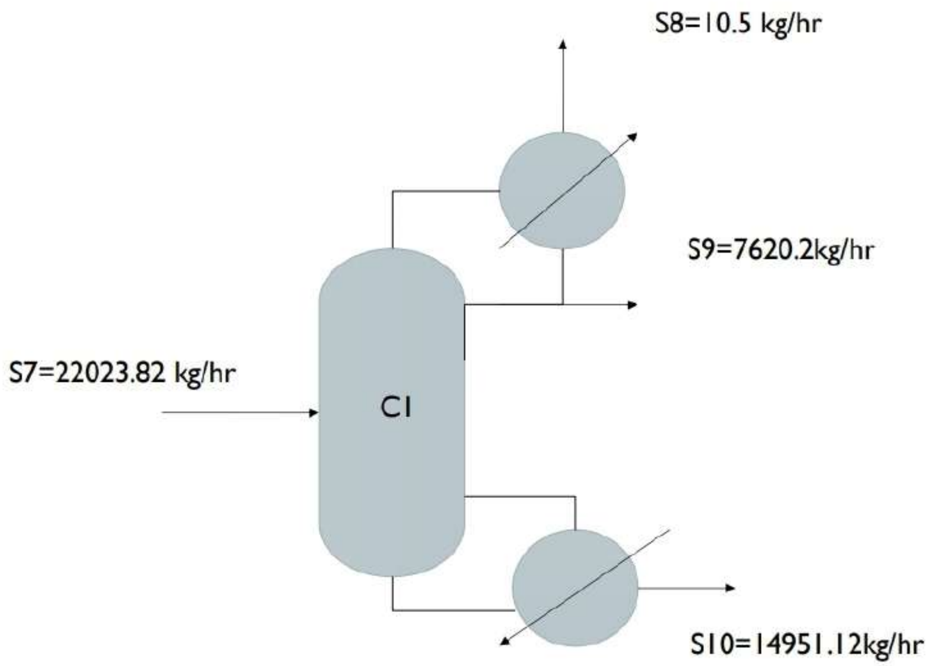


Fig. : Mass balance over C1

Distillation column (C1)					
inlet stream			Outlet stream		
Stream no.	Flow rate(kg/hr)	Composition	Stream no.	Flow rate(kg/hr)	Composition
			S8	10.5	100% CO
S7	22023.82	0.06% CO24.5 % MF 75.4% MEOH	S9	7602.2	0.046% Co 78% MF 22%MEOH
			S10	.1495112	100% MEOH

4-Reactive Distillation column (RD)

The distillate from C1 consisting MF and fresh water are the feeds to RD at stages 33 and 2 respectively as obtained from the references used. The following reaction occurs in the RD column:

$$HCOOCH_3 + H_2O \leftrightarrow CH_2O_2 + CH_3OH$$

CO (whatever amount remains) is removed out as purge and the residue which consists of FA, MF and water is fed into the C2 column.

Material Balance for RD:

M9 + M11 = M12 + M13

M12 = 3.5 kg/hr

M13 = M9 - M11 - M12 = 7062.2 - 1602 – 3.5 = 8678.7 kg/hr.

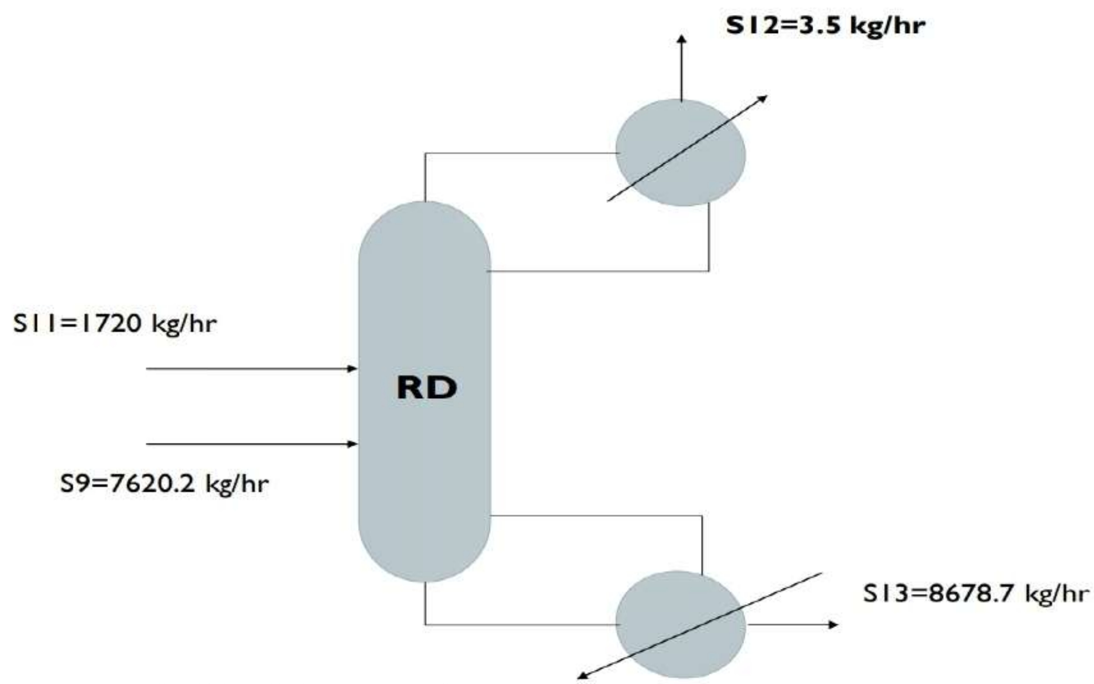


Fig. : Mass balance over RD

Reactive Distillation column (RD)					
inlet stream			Outlet stream		
Stream no.	Flow rate(kg/hr)	Composition	Stream no.	Flow rate(kg/hr)	Composition
S11	1620	100% H2O	S12	3.5	100% CO
S9	7602.2	0.046% Co 78% MF 22%MEOH	S13	8678.7	48% MEOH 44.2% FA7.8% H2O

5-Distillation column (C2):

Material Balance for C2 :
M13 = M14 + M15
(Sum of CO flow rates into the CSTR)*(6.6) = 19223.82 kg/hr
M14= 19223.82 –M10 –M2 = 4160.7 kg/hr
M14 = 4160.7 kg/hr
M15 = M13 -M14 = 8678.7 –4160.7 = 4518 kg/hr
The individual compositions of FA and water are 3840.3 kg/hr and 677.7 kg/hr respectively.
FA has 85% mass purity

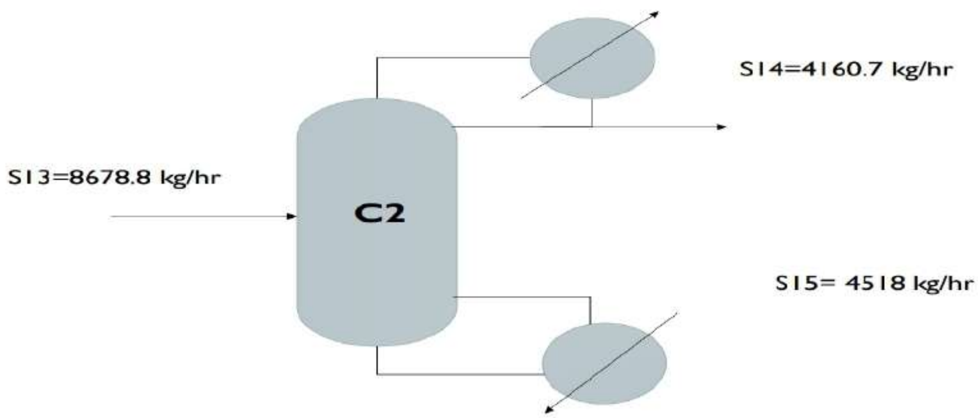


Fig. : Mass balance over C2

Distillation column (C2)					
inlet stream			Outlet stream		
Stream no.	Flow rate(kg/hr)	Composition	Stream no.	Flow rate(kg/hr)	Composition
S13	8678.7	48% MEOH 44.2% FA 7.8% H2O	S14	4160.7	100% MEOH
			S15	4518	85% FA 15 % H2O

6-Overall mass balance:

The overall mass balance equation is:

M1 + M2 + M11 = M8 + M12 + M15

M1 + M2 + M11 = 2800 + 112 + 1620 = 4532 kg/hr

M8 + M12 + M15 = 10.5 + 3.5 + 4518 = 4532 kg/hr

The overall mass balance equation is:

M1 + M2 + M11 = M8 + M12 + M15

inlet stream			Outlet stream		
Stream no.	Flow rate(kg/hr)	Composition	Stream no.	Flow rate(kg/hr)	Composition
S1	2800	100% CO	S12	3.5	100% CO
S2	112	100% MEOH	S15	4518	85% FA 15 % H_2O
S11	1620	100% H_2O	S8	10.5	100% CO

.

CHAPTER4

ENERGY BALANCE

Steady-State Energy Balance across various Unit Processes/Operations:

The energy balance across various process equipments has been performed as follows:

1. CSTR:

Energy balance equation for CSTR:

$(M1 * C_{P1} * T_1 + M2 * C_{P2} * T_2 + M6 * C_{P6} * T_6 + M10 * C_{P10} * T_{10} + M14 * C_{P14} * T_{14} + Q) = M3 * C_{P3} * T_3$

-2160.4 – 233.33 – 232.07 - 25513 – 6540.8 – 997.850) kW =-35676 Kw

ΔH=Q

$\Delta H = M\ CP\Delta T\ , \int_{T1}^{T2} CP$

$= [A(T2-T1) + B/2\,(T2-T1)^2 + C/3\,(T2-T1)^3 + D/4\,(T2-T1)^4]$

–FROM TABLE OF LIQID GAS PHASE

$= \int_{298.15}^{303.2} \boldsymbol{CP1} = \ = [-19.312(303.2-298.15) + 2.5072/2\,(303.2-298.15)^2 - 2.8970*10^{-2}/3\,(303.2-298.15)^3 + 1.2745*10^{-4}/4\,(303.2-298.15)^4] = 0.0025443$

ΔH1=M1CP1ΔT1=2800*0.0025443*303.2=-2158KW

$\int_{298.15}^{303.2} \boldsymbol{CP2} \ = [40(303.2-298.15) + 2.5072/2\,(303.2-298.15)^2 - 1.029*10^{-4}/3\,(303.2-298.15)^3 + 1.4598*10^{-6}/4\,(303.2-298.15)^4] = 0.006802$ KJ/KG.K

ΔH2=M2CP2ΔT2=112*0.006802*303.2= -233.1KW

$\int_{298.15}^{303.2} \boldsymbol{CP3} =$ X1.CP1+ X2.CP2+ X3.CP3=0.06*0.002488+0.24*0.0024+0.75*0.006272=0.004776 KJ/KG.K

ΔH3=M3CP3ΔT3=22140.82*0.004776*349= -35676KW

Stream no.	Mass flow Kg/h	Cp(kJ/kg.k)	Q in (kW)
S1	2800	0.002544	2160.4
S2	112	0.006804	233.33
S3	22149.82	0.004776	35676
S6	126	0.003174	232.07
S10	14951.92	0.004526	25513
S14	4160	0.041052	6540.8

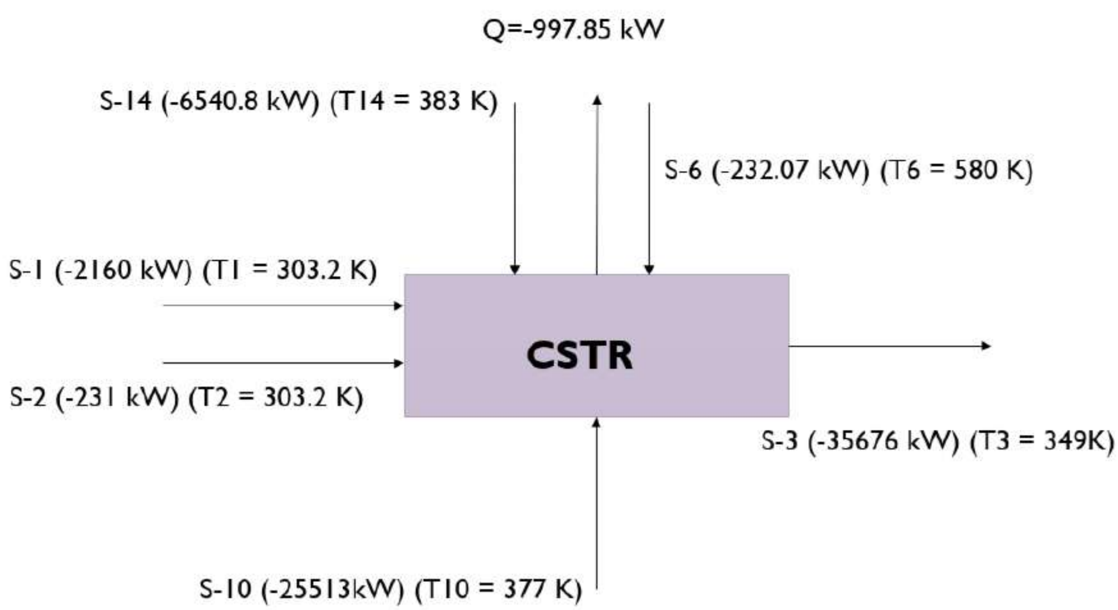


Fig. : Energy balance over CSTR

2-Flash:

Energy balance for Flash was done using the following equation:

$M3 * C_{P3} * T_3 + Nh = M5 * C_{P5} * T_5 + M7 * C_{P7} * T_7$

(-35676 + 22.739) kW= (-244.1 - 35409) kW

tream no.	Mass flow Kg/h	Cp(kJ/kg.k)	Q in (kW)
S3	22149.82	0.004615	35676
S5	126	0.005681	244.1
S7	22023.82	0.004724	35409

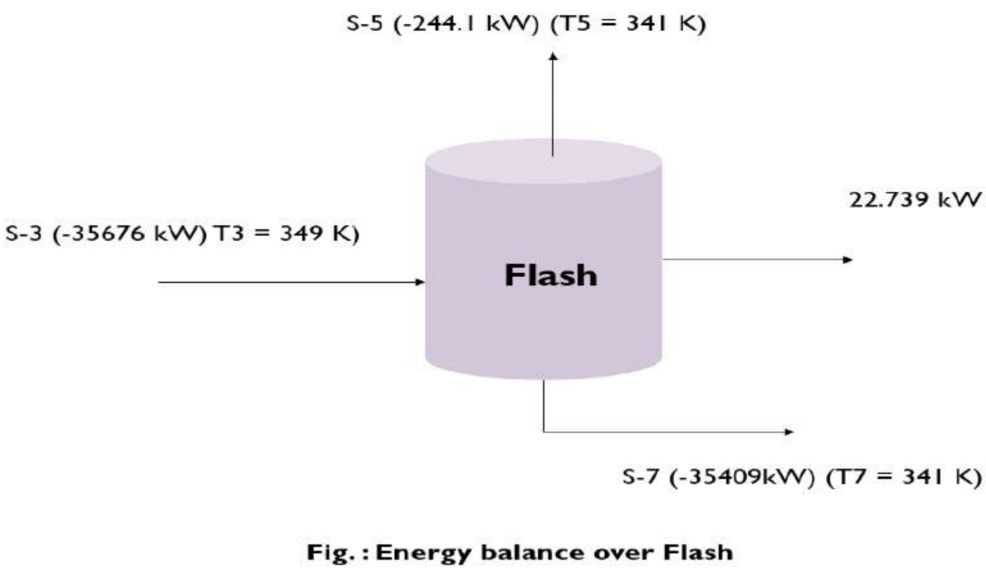


Fig. : Energy balance over Flash

3-Distillation column (C1)

For distillation columns, our primary objective is to obtain the condenser and re-boiler duties respectively. For the same, the mass flow rates, the phase change and other criteria have to be accounted.

Energy balance for C1 is given by:

$$M7 * C_{P7} * T_7 + Q_C + Q_R = M8 * C_{P8} * T_8 + M9 * C_{P9} * T_9 + M10 * C_{P10} * T_{10}$$

Condenser duty (Q_C) = $G * \Delta H_{Cond}$ = -1562.22kW

Where G = vapor flow in column = (R+1) D Kmol/hr

Re-boiler duty (Q_R) = $L * \Delta H_{Vap} + L * C_P * \Delta T$ =

1745.35kW Where L = liquid flow rate in bottom

section = (RD + F) Kmol/hr (R = Reflux ratio = 0.63,

D = Distillate rate, F = feed rate)

(- 35409 – 1562.22 + 1745.35) = (-31.168 – 9369.8– 25825.0) kW

Stream no.	Mass flow Kg/h	Cp(kJ/kg.k)	Q in (kW)
S7	22023.82	0.004618	35409
S8	10.5	0.009732	31.168
S9	7620.2	0.00389	9369.8
S10	14951.12	0.004458	25825.0

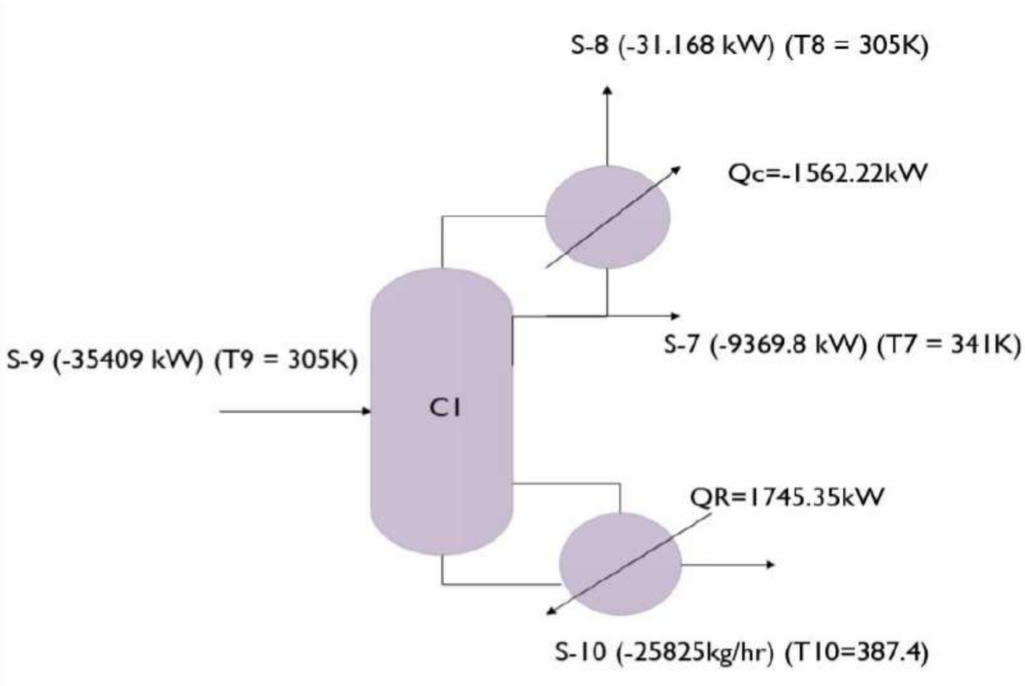


Fig. 10: Energy balance over

4-Reactive Distillation column (RD):

Energy balance for RD:

$$M9 * C_{P9} * T_9 + M11 * C_{P11} * T_{11} + Q_C + Q_R = M12 * C_{P12} * T_{12} + M13 * C_{P13} * T_{13}$$

Condenser duty (Q_C) = −7183.53 kW

Re-boiler duty (Q_R) = 7603.01 kW

(-9369.8 -7889.5-7183.83+7603.01) kW = (-272.5-16567)kW

Stream no.	Mass flow Kg/h	Cp(kJ/kg.k)	Q in (kW)
S9	7620.2	0.00389	9369.8
S11	1602	0.00524	7889.5
S12	3.5	0.002479	272.5
S13	8678.7	0.004894	16567

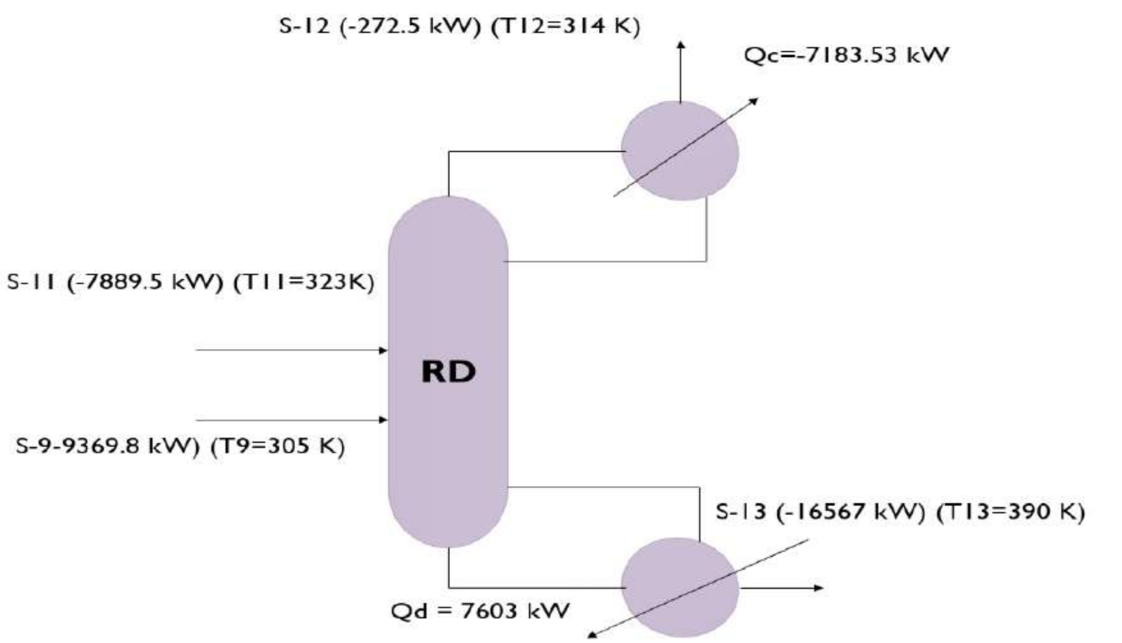


Fig. Energy balance over RD

5-Distillation column (C2):

Energy balance for C2:

$M7 * C_{P7} * T_7 + Q_C + Q_R = M8 * C_{P8} * T_8 + M9 * C_{P9} * T_9 + M10 * C_{P10} * T_{10}$

Condenser duty (Q_C) = -1545.62 kW

Re-boiler duty (Q_R) = 1569.31 kW

(-16567-1545.62+1569.31) kW = (-6556.2-9977) kW

Stream no.	Mass flow Kg/h	Cp(kJ/kg.k)	Q in (kW)
S13	8678.7	0.004894	16567
S14	4160.7	0.00419	6556.2
S15	4518	0.005264	9989

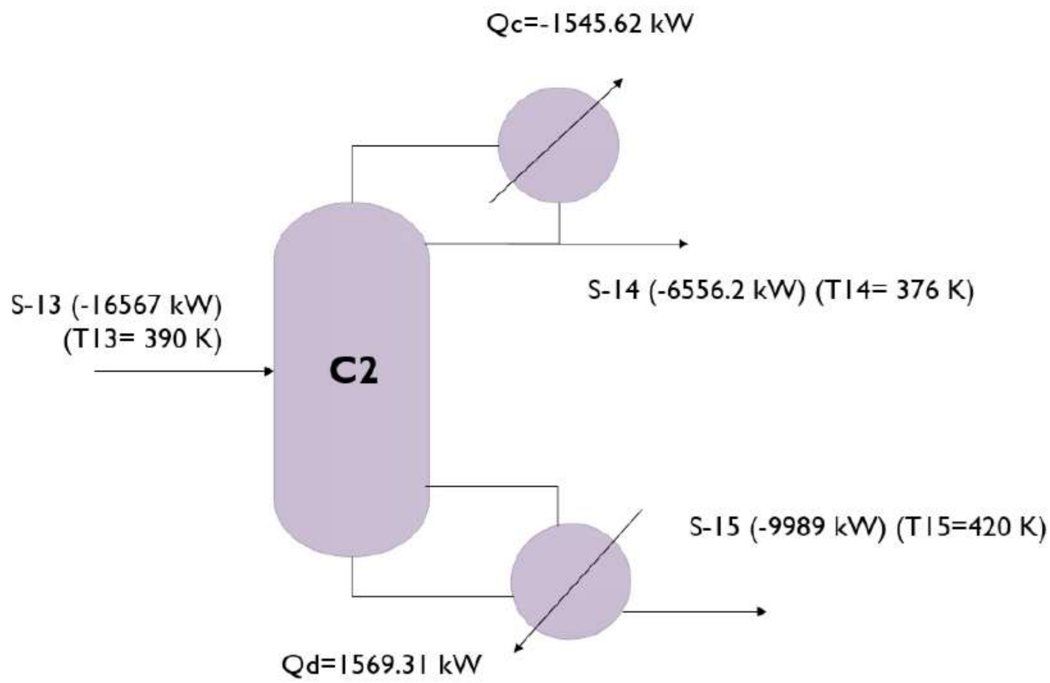


Fig. Energy balance over C2

6-Overall energy balance:

Energy balance equation is:

$M1 * C_{P1} * T_1 + M2 * C_{P2} * T_{11} + M11 * C_{P11} * T_{11} = M12 * C_{P12} * T_{12} + M8 * C_{P8} * T_8 + M15 * C_{P15} * T15$

(-2160-230.33-7889.5) kW = 10280 kW

(-31.16-272.5-9977) kW=10280 kW

CHAPTER 5
DESIGN CALCULATIONS

For distillation column (C2) the above mentioned procedure can be followed to obtain design parameters

1-Flow rates and stages

Molecular weight of feed = (0.517*32) + (0.332*46) + (0.15*18) = 34.516 moles Feed = 8678.8/34.516 = 251.4 Kmol/h

Top product D = 130.02 Kmol/h

Vapour rate V = D (1+R) = 217.7Kmol/h

As mass balance, give bottom product is 121.2 Kmol/hr

L' = Liquid rate below feed = RD+F = 381.82 Kmol/h

V' = Vapour rate below feed = L' -B = 260.6 Kmol/hr

Column specifications are:

Number of stages = 12 Feed entry stage = 8 Reflux ratio = 0.67

Top compositions – 97% methanol and 3% water Bottom compositions – 85% Formic acid and 15% water

2-PHYSICAL PROPERTIES Top:

97% methanol and 3% water

Temperature – 378K, pressure – 4 atm,

Average mol.wt = 0.97(32) + 0.03(18) = 31.58 kg/mole.

ρ_V=4.07kg/m^{3}and ρ_l=816kg/m^3

Surface tension a = $1.56 * 10^{-2}$ N/m

Bottom:

85% Formic acid and 15% water

Temperature – 432K, pressure – 4 atm,

Average mol.wt = 0.85(46) + 0.15(18) = 41.8 kg/mole

ρv=4.07kg/m3and ρl=816kg/m3

Surface tension a = 3.52 ∗ 10–2 N/m

3-Column diameter

V = Vapour rate = D (1+R) = 217.7 Kmol/hr

L = Top section liquid flow rate = 87.1 Kmol/hr

V' = Vapour rate below feed = 260.6 Kmol/hr

L' = Liquid rate below feed = 381.82 Kmol/hr

$$F_{lv}(top) = \frac{L}{V}(\frac{\rho_v}{\rho_l})^{0.5} = \frac{87.1}{217.7}(\frac{4.07}{816})^{0.5} = 0.0282$$

$$F_{lv}(bottom) = \frac{L}{V}(\frac{\rho_v}{\rho_l})^{0.5} = \frac{381.82}{260.6}(\frac{4.72}{887.8})^{0.5} = 0.106$$

Assuming plate spacing of 0.5 m from the figure 13 we have

$K_1(top) = 9 * 10^{-2}$ and $K_1(bottom) = 8 * 10^{-2}$

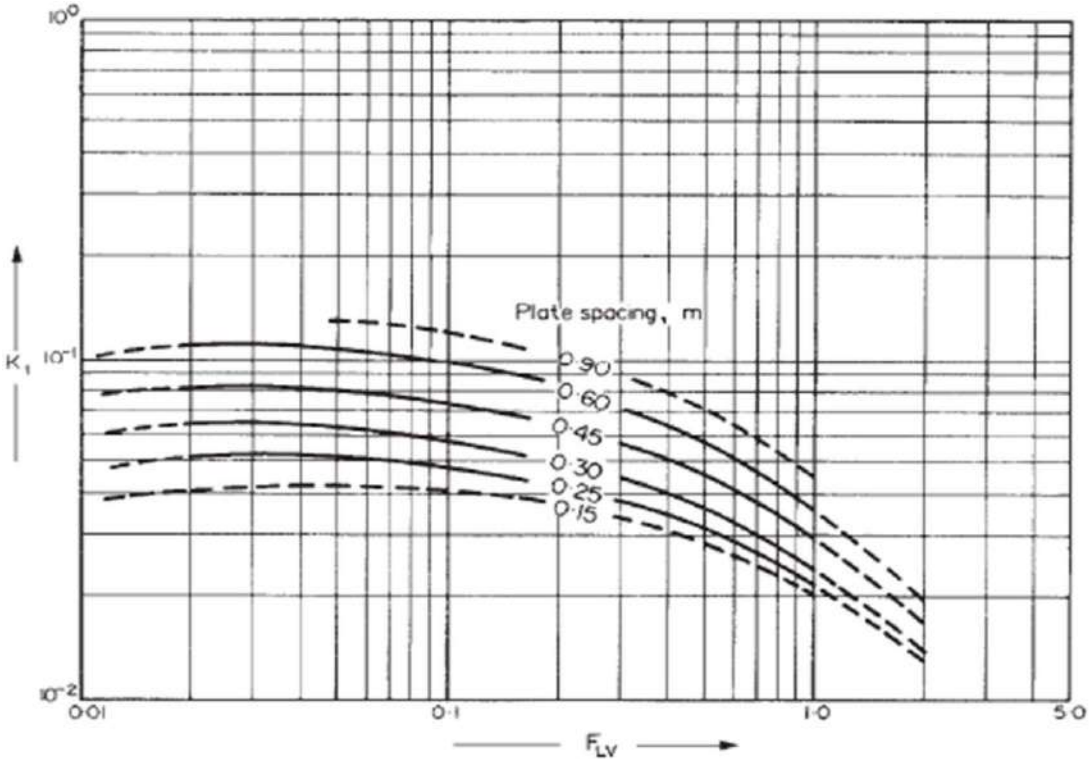


Fig.13 flooding velocity sieve plates

flooding velocity

Uf(top)=k1*(Ϭ/20)*(ρI – ρv/ ρv) $^{0.5}$ = 9 *10^{-2} *(15.6/20)$^{0.5}$*(816-4.07/4.07)$^{0.5}$=1.209 M/S

Uf(BOT)=k1*(Ϭ/20)*(ρI – ρv/ ρv) $^{0.5}$ = 8 *10^{-2} *(35.2/20)$^{0.5}$*(887.8-4.7/4.07)$^{0.5}$=1.209 M/S

By considering 85% flooding

$U_n(top) = 0.85 * 1.209 = 1.027$ N/s

$U_n(bottoN) = 0.85 * 1.217 = 1.034$ N/s

Max volumetric flow rate

$Q_{max}(top)$ = V*M/ ρv=217*31.58/4.07*3600 = 0.46 m/s

Qmax(BOT) = V*M/ ρv=260.6*41. 8/4. 72*3600 = 0.64m/s

Net area

Area (top) =Qmax/Un=0.46/1.027=0.447m^2

Area (bot) =Qmax/Un=0.64/1.034=0.618m^2

As first trial, take down comer area as 12 per cent of total.
Area (top)= 0.447/0.88=0.51m^2
Area (bot)= 0.618/0.88=0.70m^2

Column diameter

DC(TOP)= √4*area/ π)= √4*0.51/ π=0.806 m

DC(bot)= √4*area/ π)= √4*0.70/ π=0.94 m

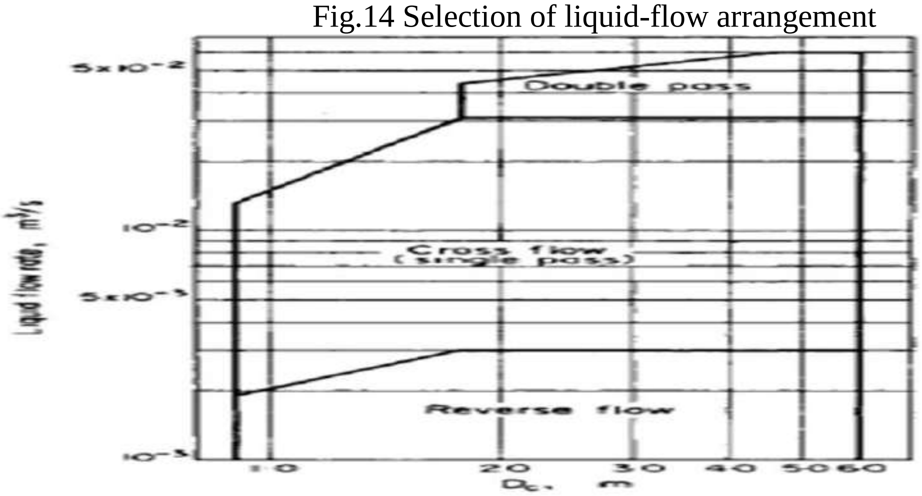
We are using the higher value of the tower diameter for the uniformity between sections, if the difference is not greater than 20%. In this case, the bottom diameter is used both in top and bottom sections. Area higher than the design area (here top section) can be taken care by reducing the perforated area. Hence, bottom diameter is used for further calculations.

4-Liquid flow rate

Max volumetric flow rate =L′*M/ ρi =381.2*41.8=887.8*3600=4.99*$10^{-3}$$m^3$/s

from Fig.14 single pass can be used

Fig.14 Selection of liquid-flow arrangement



5-Provisional plate design

Column diameter = D_c = 0.94m

Area of column = Ac$= \pi \underline{r}^2 = 0.785 * 0.94 = 0.7379N^2$

Down comer area = $A_d = 0.12 * 0.7379 = 0.0885N^2$

Net area = $A_n = A_c - A_d = 0.6493N^2$ Active area = $A_a = A_c - 2 * A_d = 0.5609N^2$

Hole area A_h can be taken as 10% of active area, so $A_h = 0.05609N^2$

From Fig.15 weir length to column diameter ratio is Lw/Dc= 0.75

So Weir length = 0.75*0.94 = 0.71m

Take weir height h_w= 50 mm

Hole diameter = 5 mm Plate

thickness = 5 mm

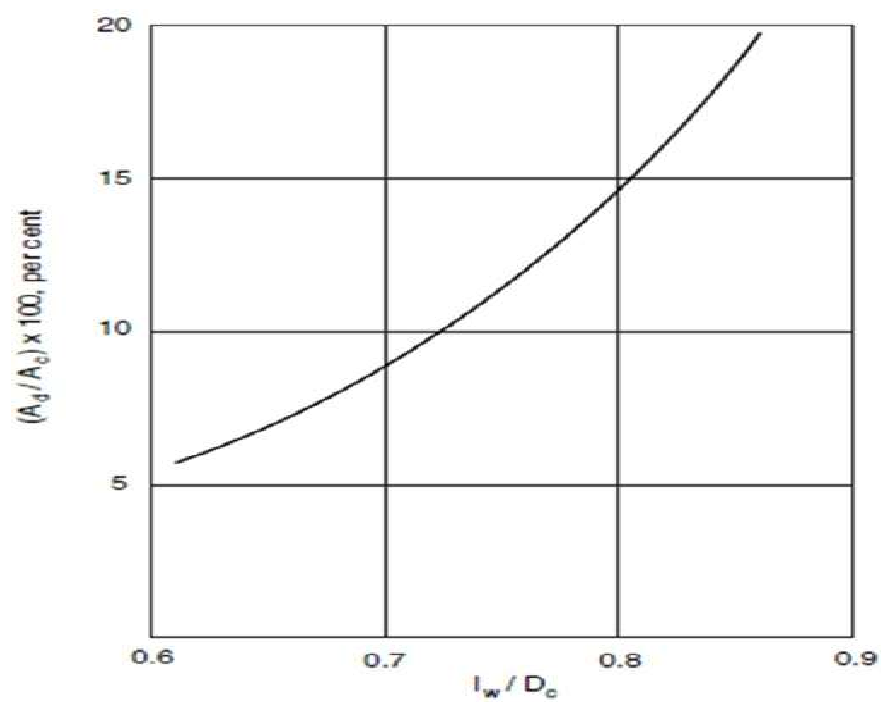


Fig.15 Relation between down comer area and weir length

6-Weeping

Max liquid rate= 381.2*41.8/3600= 4.43 kg/s

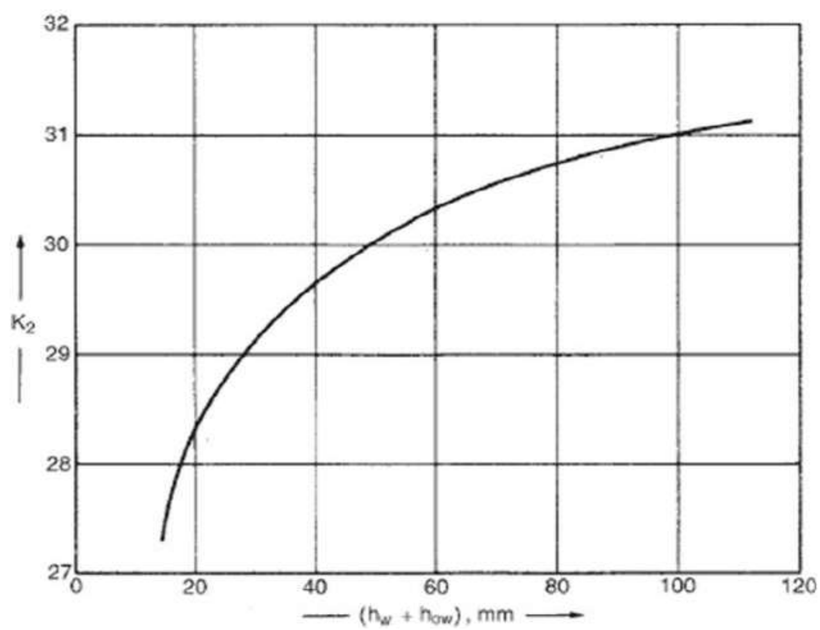
Max liquid rate at 70% turn down = 0.7*4.43 = 3.101kg/s _

Max weir crest = h_{ow} = 750 (_lw/ ρl* lw)$^{2/3}$= 27.068mm

Min weir crest = h_{ow} = 750 (_lw/ ρl* lw)$^{2/3}$= 21.305mm

Where L_w = liquid flow rate

At minimum rate $h_w + h_{ow}$ = 50 + 21.305 = 71.305 mm



So from Fig.16 K_2 = 30.8 so

Uh(min)=k2-0.9*(25.4-dh)/ $\rho_V^{0.5}$=30.8-0.9*(25.4-5)/4.72$^{0.5}$=5.72m/s

Actual minimum vapour velocity = minimun vapour rate/Ah=0.7*0.64/0.05609=7.98m/s

So minimum operating rate is above weep point

7-Downcomer liquid back up

Take $h_{ap} = h_w - 10 = 40$ mm

Area under apron = $A_{ap} = h_{ap} * l_w = 0.04 * 0.71 = 0.0284 м^2$

So A_{ap} is less than ($A_d = 0.0886$) so h_{dc} can be calculated

$h_{dc} = 166(lw/\rho l\ Am)^2 = 166(4.43/887.8 * 0.0284)$=5.12mm

Where L_{wd} = liquid flow in down comer

A_M= smaller value of A_{ap} and A_d

Back up in down comer $h_b = h_w + h_{ow} + h_{dc} + h_t$

= 50 + 27 + 141.07 + 5.12= 223.227 mm = 0.223 m

Where 0.22 is less than average of plate spacing and weir height (0.275 m) Therefore, it is acceptable.

Residence time tr= $A_d * h_{bc} * \rho_l / L_{wd} = 0.0885 * 887.8 * 0.22 / 4.43$=3.9s

Which is greater than 3s so it is acceptable

8-Check entrainment

U_V= QMAX/An=0.64/0.6493=0.98M/S

% Flooding=$U_V/U_F = 0.98/1.217 * 100 = 80.52$ %

As $F_{Lv} = 0.106$ From Fig.17 we can have ¥= 0.012

As ¥ = 0.012 satisfied as it to be below 0.1

As the percent flooding is well below the design figure of 85%, the column diameter can be reduced, but this would increase the pressure drop.

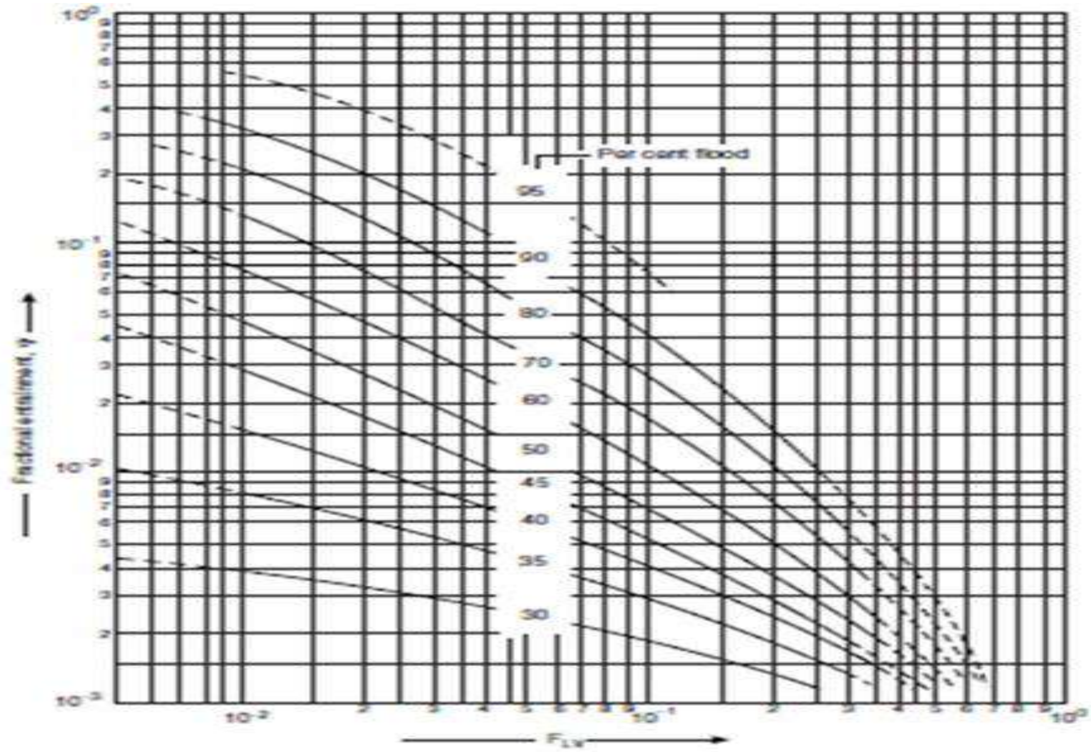


Fig.17 Entrainment correlation for sieve plates

9-Trail layout

Use cartridge-type construction. Allow 50 mm imperforated strip around plate edge; 50 mm wide calming zone

Perforated area

As lw/dc=0.71/0.94=0.755 from fig.18

We have θc=100 °C

Angle subtended by the edge of the plate = 180-100 =80^0

Mean length of the imperforated edge strip = (0.94-0.05)*3.14*80/180=1.24m

Area of imperforated edge strip = 1.24*0.05 = 0.062ɴ^2

Max length of calming zone is = weir length + width of imperforated strip

= 0.71 + 0.05 = 0.76 m

Area of calming zones = 2*(0.76*0.05) = 0.076 ɴ^2

Total area of perforation=A_p = (actual area – area of unperforated edge area of calɴing zones)

A_p = 0.5609 Ap=0.5609− 0.062 – 0.076 = 0.4229ɴ^2

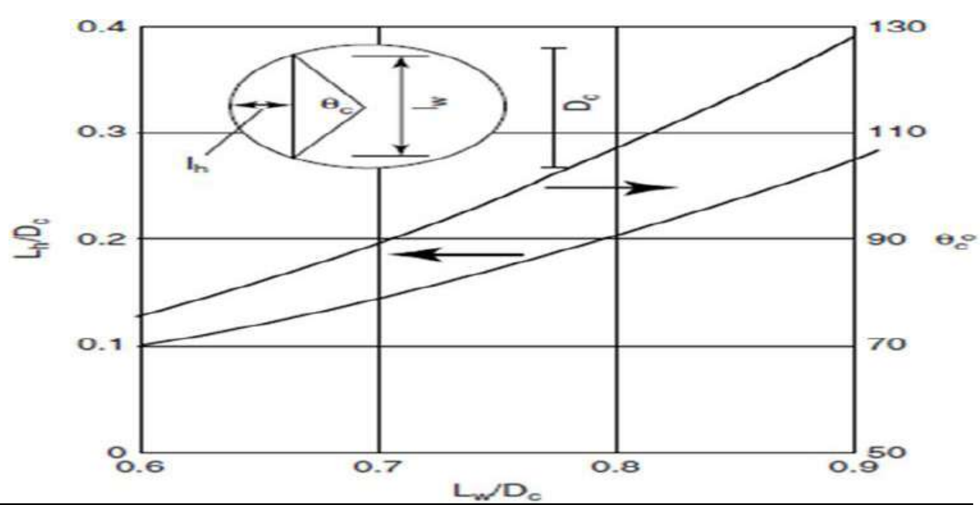
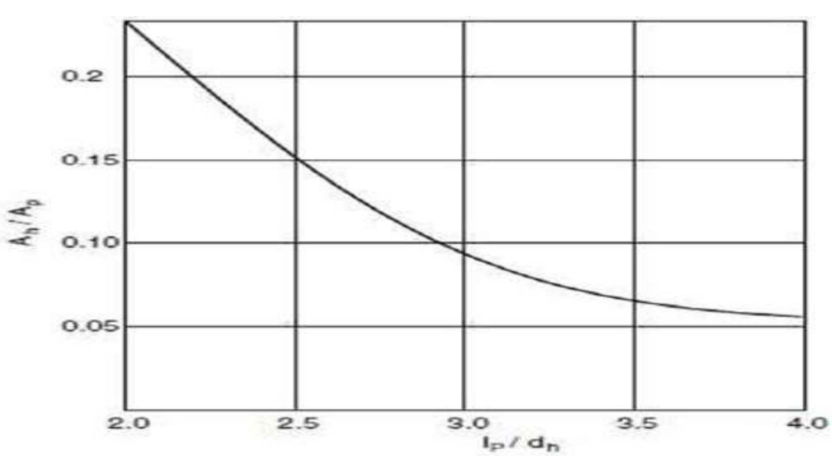


Fig.18 Relation between angle subtended by chord, chord height and c chord length



Considering L/D ratio is 10 we can have L = 0.94*10 = 9.4 m

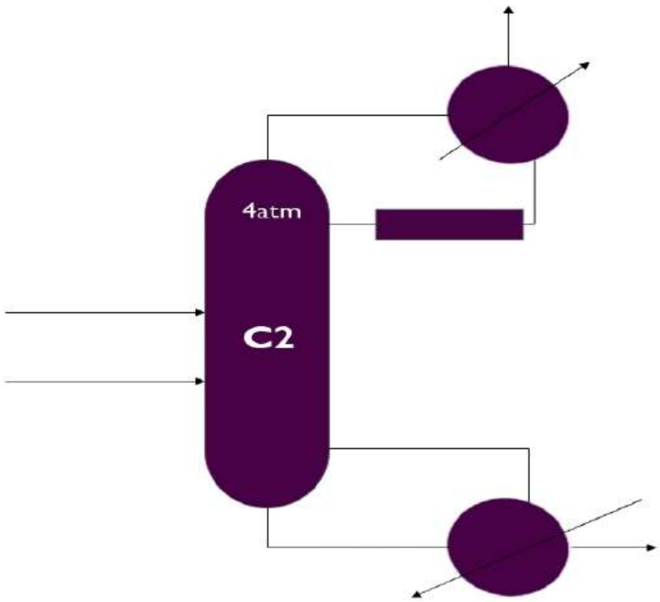


Fig .Distillation column design

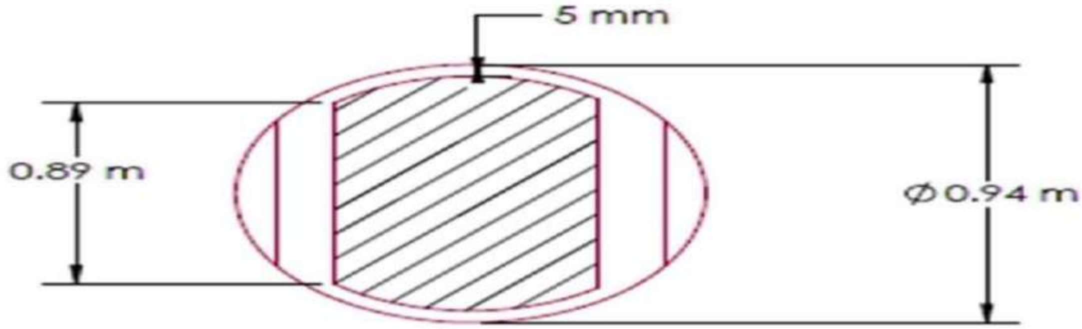


Fig : Plate design

Outer diameter – 0.94 m Inner diameter – 0.89m Thickness – 5 mm

Result of calculations

Column parameters

Parameter	**Size**
Column diameter	0.94 m
Column Height	9.4 m
Condenser duty	-2485.25 kW
Re-boiler duty	2540.36 kW
No of actual trays	12
Feed location	8
% flooding	80.52%

Tray parameters

Parameter	**Size**
Material of construction	Stainless Steel
Column area	$0.7379\mathrm{N}^2$
Down comer area	$0.0885\mathrm{N}^2$
Active area	$0.5609\mathrm{N}^2$
Total hole area	$0.05609\mathrm{N}^2$
Hole diameter	5 mm
Area under apron	$0.0284\mathrm{N}^2$
Unperforated strip around plate edge	50 mm
Hole pitch	2.5
Plate spacing	0.5 m
Plate thickness	5 mm

CHAPTER 6

COST ESTIMATION

Installed Cost of distillation column

For distillation column, purchase price is given by

$C = 1.218[f_1C_b + Nf_2f_3f_4C_t + C_{PS}]$

Where $C_b = 1.218\exp(7.123 + 0.1478(\ln W) + 0.02488(\ln W)^2 + 0.0158\left(\frac{L}{D}\right)\ln\left(\frac{T_b}{T_p}\right)$

Is base cost of material of construction.

$C_t = 457.7\exp^{(0.1739*D)}$, cost of tray.

$C_{PS} = 249.6D^{0.6332}L^{0.8016}$, Cost of platform and ladders.

Calculation of C_b

We require weight of vessel (W), diameter of column, length of the column, thickness of the shell at bottom (T_b) and thickness required for operating pressure (T_p) for calculation of C_b.We will also need values of factorsf_1, f_2, f_3, and f_4.

Values of $f_1$and f_2 depends on type of material. Since, the material used in construction is stainless steel, f_1 and f_2 are 1.7 and (1.189 +0.0577D), respectively.

Material	f_1	f_2
Stainless steel, 304	1.7	$1.189 + 0.0577D$
Stainless steel, 316	2.1	$1.401 + 0.0724D$
Carpenter 20CB-3	3.2	$1.525 + 0.0788D$
Nickel-200	5.4	
Monel-400	3.6	$2.306 + 0.1120D$
Inconel-600	3.9	
Incoloy-825	3.7	
Titanium	7.7	

Value of f_3 depends on type of tray in the column. Since, we are using sieve (with down comer) in the column, the values of f_3 is 0.95 as obtained from given table.

Tray Types	f_3
Valve	1.00
Grid	0.80
Bubble cap	1.59
Sieve (with downcorner)	0.95

Value of f_4 can be calculated by using $f4 = 2.25/1.0414^N$ where N is number of trays,So, For12 trays f_4 is 1.38.

$W = D^4 H * \rho * t = 4852.31$ lb = 2200.87 Kg

Where, thickness (t)= 0.68 ft , Diameter (D)= 3.11 ft , height (H)= 30.83ft and density (ρ) = 501.

Values of all the factors are obtained for tray tower of length (L) 30.83 ft, diameter 3.11ft, thickness T_b 0.43 ft and t_D 0.68 ft, respectively. The value of C_b is,

$C_b = 1.218 \exp(7.123 + 0.1478(\ln 4852.31) + 0.02488(\ln 4852.31)^2 + 0.0158(L/D) \ \ln (Tb/TP))$

$C_b = 34939.89$

Calculation of C_t

C_t is the cost of tray. It can be calculated as follows,

$C_T = 457.7 \exp(0.1739\ D)$, For $2 < D < 16$ft , where D is diameter of tray. So,

$C_t = 786.06$, as per calculation.

Calculation of C_{Pl}

C_{PS} is the cost of platform and ladders and is calculated using the formula,

$C_{PS} = 249.6 D^{0.6332} L^{0.8016}$, for 2<D<24ft and 57<L<170 ft. So, C_{PS} = 7994.13

Therefore, by substituting all the values in the above given formula of purchase cost, we obtain the purchase cost of distillation column as $100,553.37.

So, the installing cost of distillation column is given by,

$C_{inctaSSed}$=installatio factor * purchase cost = $143791.31Where, installation factor is 1.43[2]

Formic Acid

Free on board (FOB) price of formic acid is US $700/ ton [3] Therefore,

Annual Gross Sales = FOB Price* Operation days*Efficiency*Capacity

= ($700/ton)*355*0.95*100=$23,607,500

Turnover ratio is given by,

$$TOR = \frac{\text{ANNUAL GROSS SALES}}{\text{FIXED CAPITAL INVESTEMENT}}$$

Since, the turnover ratio of formic acid is 6.4[4], from this we can calculate fixed capital investment (FCI), i.e., FCI= (23,607,500/6.4) = US $ 3688671.88

Working Capital (WC)=15% of FCI= US $ 553,300

Therefore,

Total Capital Investment (TCI) = FCI + WC

= 3688671.88+553300= US $ 4241972.661.

Estimation of Labour Cost

N_{OL} = NUMb of Opertor per shif

$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5} = 3.00832$

Where, N_{np} = nuNber of non particulate processing steps(Compressors, towers, etc) = 12

We have three shifts. Thus, the number of operators = 3*3=9

According to the bureau of labour and statistics, hourly wages of workers is US$ 34.42. Therefore, total operating labour cost= (34.42 *8*3)*3

= US $ 2478.24/ day

= US $ 879,775/ year

Direct Cost

●Purchase cost is 20% of the fixed capital investment , Purchase cost= 0.2*3,688,671.88 = US $ 737732.4

●Purchased equipment installation is 8% of the fixed capital investment, i.e., Purchased equipment installation= 0.08* 3,688,671.88 = US$ 295,093.7

●Instrumentation and control= 0.04* FCI= US $147,546.87

●Piping (installed) = 15% of FCI= US $553300.782

●Electrical (installed) = 0.06*FCI= US $221320.3

●Building (including services) = 0.08*FCI= US $ 295,093.7

●Service facilities (installed) = 0.1* FCI= US $ 368867.18

●Land = 0.01 * FCI= US $ 36886.718

Indirect Cost

●Engineering and supervision is 13% of FCI, i.e., Engineering and supervision = 0.13 * 3688671.8= US $ 479527.3

●Construction expenses is 8% of FCI, i.e., Construction expenses = 0.08 * 3688671.8= US $ 295,093.7

●Contractor fee is 2% of FCI, i.e., Contractor fee = 0.02 * 3688671.8= US $ 73,773.436

●Contingency is 12% of FCI, i.e., Contingency = 0.12 * 3688671.8= US $ 442,640. 6

The mentioned factors are been taken from reference [5]

Utilities

Utilities include electricity, cooling water and steam. Therefore, total utility cost is sum of all the utility costs, i.e.

Total utility cost= electricity cost+ cooling water cost+ steam cost

Therefore, the cost of all utilities are as follows:

- Electricity used is 204.513 kW that costs US $ 15.85/hr.
- Cooling water required is 0.2757 mm gal/ hr, which costs US $ 33.08/hr.
- Steam used is 100psi i.e. 54.82 klb/hr, which costs US $446.29/hr.

Therefore, total utility cost calculated is 495.17 USD/hr i.e. 4,218,848.4 USD/year.

Expenses

As calculated earlier, annual gross sales are US $ 23,607,500 for formic acid. Thus, by using the annual gross sales and fixed capital investment (FCI) we can calculate all the expenses of the system, which are as follows:

- Total indirect expenses, which include packing, loading, shifting, is 7% of Annual gross sales, i.e., US $ 1652525.
- Plant Indirect expense is 4% of FCI, i.e., US $ 147546.87.
- General overhead expenses are 10% of sales, i.e., US $ 2360750.00.

Depreciation

MACRS depreciation with half year convention is used to determine depreciation for 6 year period.

Depreciation= 10% of FCI + 2% of building value

= 328867.1 + 5901.874 = US $ 334766.97

Raw Material

Raw material used is carbon monoxide and methanol, which costs 600 US$/ ton [6] and 430 US$/ton[7] , respectively.

For one year, amount of CO required is = 23856 ton per year

Total CO cost = 23856 * 600 = $14313600

For one year, amount of Methanol required= 954.24 ton per year

Total methanol cost= 954.240 * 430 = $ 410323.2 Thus, total raw material cost= Rs. 14723923.3

From literature, we obtained that cost of raw materials can be approximated to be 70% of the total operating cost. As we obtained the raw material cost, we can therefore estimate the total operating expense.

Total operating expense= 14723923.3 / 0.7 = $ 21034176.14

And we know plant capacity is 100 ton/day and Formic acid price is 700$/ton so

Revenue = 700 *36500 = $25550000

Estimation of Total Product Cost

Total product cost (TPC) is estimated from total fixed charge, which includes depreciation, local taxes and insurance. We have calculated depreciation earlier as US $ 334766.97. The local taxes and insurance are calculated from FCI, i.e., local taxes is 1-4% of FCI where as insurance is 0.4- 1% of FCI. The total fixed charge is,

Total fixed charge= depreciation+ local taxes + insurance

= 334766.97+ 147546.87+ 25820.7= US $ 508136.5

Therefore, total product cost is given by,

Total product cost (TPC) = Total fixed charge/0.15= US $ 3387576.9

Direct product cost

Direct product cost includes the following:

● Raw material, i.e. 20% of TPC, which costs US $ 677515.2.

- Operation lab, i.e. 15% of TPC, which costs US $ 508136.53.

●Direct supervisory and clerical labor, i.e. 10-15% of operating labor, which costs US $76220.47.

●Utilities, i.e. as calculated earlier are US $ 4218848.4 / year.

●Maintenance and repair cost, which is 5% of FCI, i.e. US $ 169433.59.

●Operating supplies, which is 10-20% of maintenance and repair cost and in this process it is 15% of maintenance and repair cost, i.e. US $ 25415.039.

●Laboratory charges, which is 10-20% of operating labor cost and in this process, it is 15% of operating labor cost, i.e. US $ 76220.4.

●Patent and royalties, which is 3% of total product cost, i.e. US $101627.28. Therefore, total direct production cost = US $ 5843416.379.

Manufacturing cost

Total manufacturing cost is the sum of total direct production cost and plant overhead cost. Since, total direct production cost is US $ 5843416.379, as calculated earlier and plant overhead cost is 7% of total product cost i.e. US $ 237130.383; the total manufacturing cost is US $ 6080546.75.

Profitability Analysis

To carry out profitability analysis, we prepared a cumulative cash position plot, using the data estimated above. The plant life was assumed to be 10 years. We assumed that operating expenses increased 3% per year, and since we have determined the operating costs in terms of raw material costs thus we assumed that selling price of Formic acid too increase at 2% per year. MACRS method with half-year convention was used to determine the depreciation factors for a 5 year period. We assumed 20% interest factors for our calculations. Income Tax rate of 35% was assumed and a cumulative cash flow plot was obtained. At the end of 10th year land and working capital is recovered. It is shown in the figure given below

YEAR	Investment	revenue($)	Total op.expenses($)	Depreciation	Cash operating expenses($)
-2	-36886.718				
-1	-3688671.88				
0	-5,53,300				
1		2,55,50,000	21034176.14	328867.1	20705309.04
2		26061000	21665201.42	657734.2	21007467.22
3		26582220	22315157.47	657734.2	21657423.27
4		27113864.4	22984612.19	657734.2	22326877.99
5		27656141.69	23674150.56	657734.2	23016416.36
6		28209264.52	24384375.07	328867.1	24055507.97
7		28773449.81	25115906.33	0	25115906.33
8		29348918.81	25869383.52	0	25869383.52
9		29935897.18	26645465.02	0	26645465.02
10 end 11	5,90,187	30534615.13	27444828.97	0	27444828.97

operating income($)	Gross income ($)	TAX($)	Net income after tax($)	Cash flow($)	Cumulative cash flow($)
					-36886.718
					-3725558.598
					-4278858.598
48,44,691	45,15,824	1580538.351	29,35,286	32,64,153	-10,14,706
50,53,533	43,95,799	1538529.502	28,57,269	35,15,003	25,00,297
49,24,797	42,67,063	1493471.887	27,73,591	34,31,325	59,31,622
47,86,986	41,29,252	1445238.273	26,84,014	33,41,748	92,73,370
46,39,725	39,81,991	1393696.896	25,88,294	32,46,028	1,25,19,399
41,53,757	38,24,889	1338711.307	24,86,178	28,15,045	1,53,34,444
36,57,543	36,57,543	1280140.22	23,77,403	23,77,403	1,77,11,847
34,79,535	34,79,535	1217837.353	22,61,698	22,61,698	1,99,73,545
32,90,432	32,90,432	1151651.257	21,38,781	21,38,781	2,21,12,326
30,89,786	30,89,786	1081425.155	20,08,361	20,08,361	2,41,20,687
					2,47,10,874

YEAR	Cumulative cash Flow	20% interest factors	NPW	Cumulative cash flow (20%)
-2	-36886.718	1.492	-55034.98326	-55034.98326
-1	-3725558.58	1.23	-4582437.053	-4637472.037
0	-4278858.598	1	-4278858.598	-8916330.635
1	-10,14,706	0.906	-919323.636	-9835654.271
2	25,00,297	0.742	1855220.374	-7980433.897
3	59,31,622	0.608	3606426.176	-4374007.721
4	92,73,370	0.497	4608864.89	234857.1693
5	1,25,19,399	0.407	5095395.393	5330252.562
6	1,53,34,444	0.333	5106369.852	10436622.41
7	1,77,11,847	0.273	4835334.231	15271956.65
8	1,99,73,545	0.224	4474074.08	19746030.73
9	2,21,12,326	0.183	4046555.658	23792586.38
10	2,41,20,687	0.15	3618103.05	27410689.43
END 11	2,47,10,854	0.135	3335965.29	30746654.72

Now to estimate profitability following parameters were obtained:

a-Pay-out Period: It is used to calculate the amount of time that will be required to recover the depreciable fixed capital investment from the accrued cash flow of a project. It can be estimated using the formula given below:

= (Fixed-capital investment/ average annual after-tax cash flow)

= 3688671.88 / (28399546/10) = 1.30 years

b-Return on investment: It can be used to compare a company's profitability or to compare the efficiency of different **investments**. It can be estimated using the formula given below:

= (average annual net profit after taxes / total capital investment)
= (25110875/10) / 4241972.661 = 0.59 = 59%

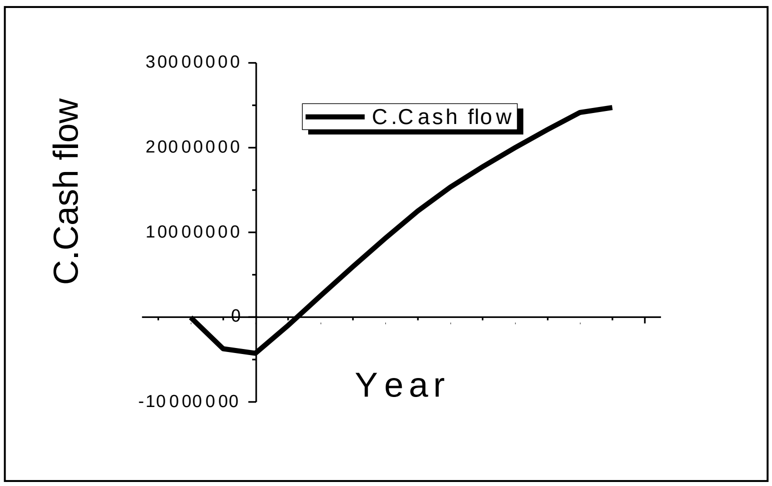


Fig 22 Cumulative cash flow plot for 0% interest

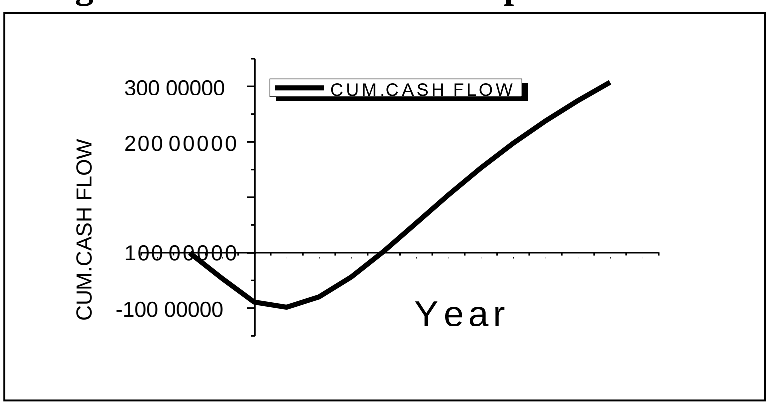


Fig 23 Cumulative cash flow plot for 20% interest

CHAPTER 7

SAFETY

Formic acid has low toxicity (hence its use as a food additive), with an LD50 of 1.8 g/kg (oral, mice). The concentrated acid is corrosive to the skin.

Formic acid is readily metabolized and eliminated by the body. Nonetheless, it has specific toxic effects; the formic acid and formaldehyde produced as metabolites of methanol are responsible for the optic nerve damage, causing blindness seen in methanol poisoning. Some chronic effects of formic acid exposure have been documented. Some experiments on bacterial species have demonstrated it to be a mutagen. Chronic exposure in humans may cause kidney damage. Another possible effect of chronic exposure is development of a skin allergy that manifests upon re-exposure to the chemical. Concentrated formic acid slowly decomposes to carbon monoxide and water, leading to pressure buildup in the containing vessel. For this reason, 98% formic acid is shipped in plastic bottles with self-venting caps. The hazards of solutions of formic acid depend on the concentration. The following table lists the EU classification of formic acid solutions:

Concentration (weight percent)	**Classification**	**R-Phrases**
2%–10%	Irritant (**Xi**)	R36/38
10%–90%	Corrosive (**C**)	R34
>90%	Corrosive (**C**)	R35

Formic acid in 85% concentration is not flammable, and diluted formic acid is on the U.S. Food and Drug Administration list of food additives. The principal danger from formic acid is from skin or eye contact with the concentrated liquid or vapors. The U.S. OSHA Permissible Exposure Level (PEL) of formic acid vapor in the work environment is 5 parts per million parts of air.

CONCLUSION

From the above study we conclude that Formic acid is an important organic acid with a variety of uses like antibacterial agent and find its extensive use in oil and gas industries. By carrying out a market survey, we found that there is a huge potential for Formic acid production as there are large numbers of consumers from Asia-pacific region that accounts for 47% of the current market share. The chosen method for Formic acid production by hydrolysis of methyl- formate does not produces by-products thereby reducing environmental concerns.

From the material balance, we need 2800kg/hr of CO and 112kg/hr Methanol makeup which produces 4518 kg/hr (100 ton/day) of Formic acid.

From the energy balance, we conclude that the Fractionation column consumes a big fraction of the total energy required by the plant. This can be attributed to the high purity of formic acid that we require of 85%.

After designing the Distillation column, we conclude that the Sieve tray one pass plate is suitable for the fractionation column.

From cost estimation:

Fixed capital investment: $ 3688671.88

Total manufacturing cost: $ 6080546.75

Pay out period: 1.30 years

Return on investment : 59%

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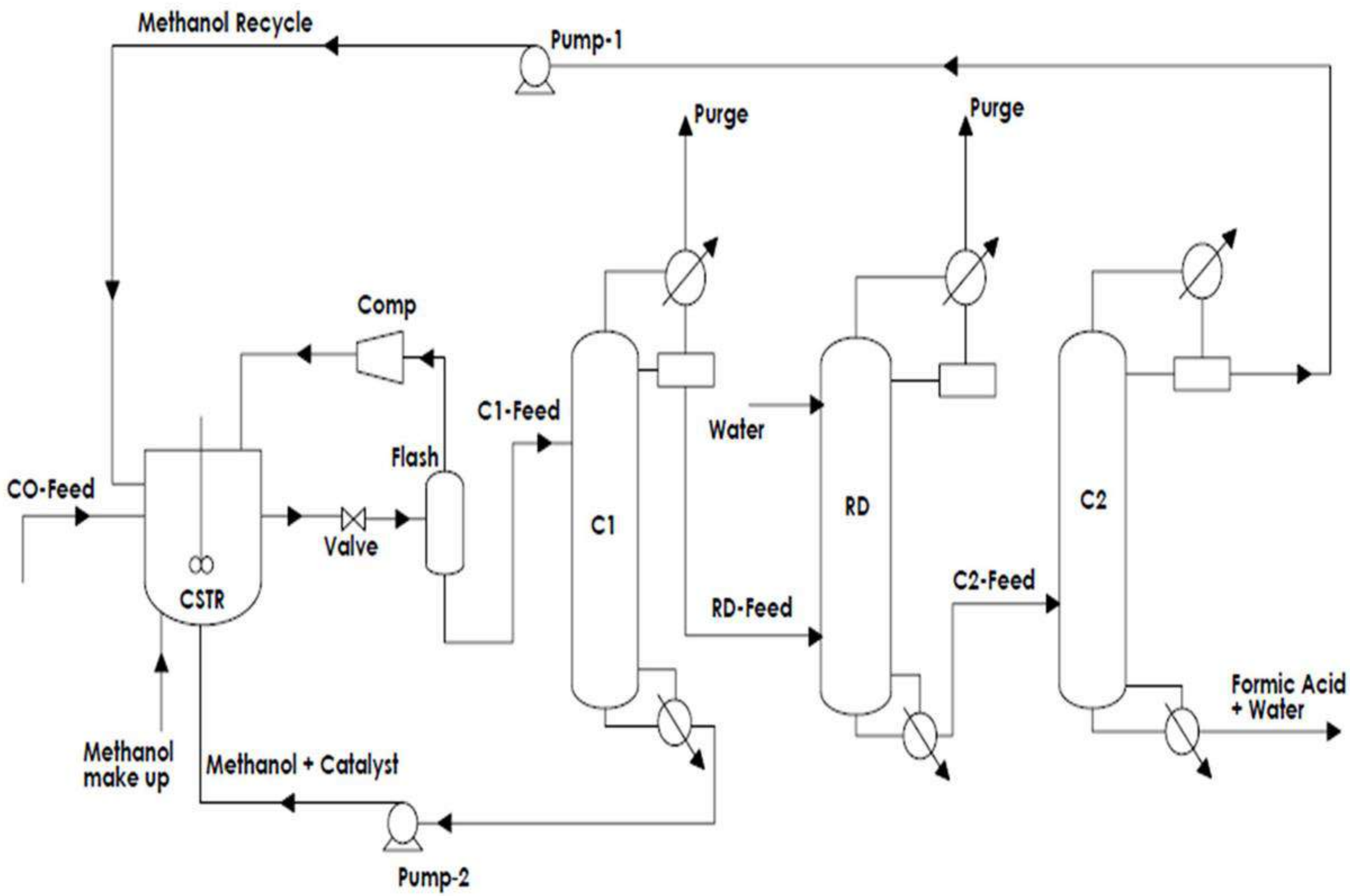

Methanol Recycle
Pump-1
Purge
Purge
Comp
C1-Feed
Water
Flash
CO-Feed
C1
RD
C2
Valve
CSTR
C2-Feed
RD-Feed
Formic Acid
+ Water
Methanol
make up
Methanol + Catalyst
Pump-2

Table B.4 Antoine Equation Constants[a]

$$\log_{10} p^* = A - \frac{B}{T + C} \qquad p^* \text{ in mm Hg}, \quad T \text{ in °C}$$

Example: The vapor pressure of acetaldehyde at 25°C is determined as follows:

$$\log_{10} p^*_{C_2H_4O}(25°C) = 8.00552 - \frac{1600.017}{25 + 291.809} = 2.9551$$

$$\Longrightarrow p^*_{C_2H_4O}(25°C) = 10^{2.9551} = 902 \text{ mm Hg}$$

Compound	Formula	Range (°C)	A	B	C
Acetaldehyde	C_2H_4O	−0.2 to 34.4	8.00552	1600.017	291.809
Acetic acid	$C_2H_4O_2$	29.8 to 126.5	7.38782	1533.313	222.309
Acetic acid*	$C_2H_4O_2$	0 to 36	7.18807	1416.7	225
Acetic anhydride	$C_4H_6O_3$	62.8 to 139.4	7.14948	1444.718	199.817
Acetone	C_3H_6O	−12.9 to 55.3	7.11714	1210.595	229.664
Acrylic acid	$C_3H_4O_2$	20.0 to 70.0	5.65204	648.629	154.683
Ammonia*	NH_3	−83 to 60	7.55466	1002.711	247.885
Aniline	C_6H_7N	102.6 to 185.2	7.32010	1731.515	206.049
Benzene	C_6H_6	14.5 to 80.9	6.89272	1203.531	219.888
n-Butane	n-C_4H_{10}	−78.0 to −0.3	6.82485	943.453	239.711
i-Butane	i-C_4H_{10}	−85.1 to −11.6	6.78866	899.617	241.942
1-Butanol	$C_4H_{10}O$	89.2 to 125.7	7.36366	1305.198	173.427
2-Butanol	$C_4H_{10}O$	72.4 to 107.1	7.20131	1157.000	168.279
1-Butene	C_4H_8	−77.5 to −3.7	6.53101	810.261	228.066
Butyric acid	$C_4H_8O_2$	20.0 to 150.0	8.71019	2433.014	255.189
Carbon disulfide	CS_2	3.6 to 79.9	6.94279	1169.110	241.593
Carbon tetrachloride	CCl_4	14.1 to 76.0	6.87926	1212.021	226.409
Chlorobenzene	C_6H_5Cl	62.0 to 131.7	6.97808	1431.053	217.550
Chlorobenzene*	C_6H_5Cl	0 to 42	7.10690	1500.0	224.0
Chlorobenzene*	C_6H_5Cl	42 to 230	6.94504	1413.12	216.0
Chloroform	$CHCl_3$	−10.4 to 60.3	6.95465	1170.966	226.232
Chloroform*	$CHCl_3$	−30 to 150	6.90328	1163.03	227.4
Cyclohexane	C_6H_{12}	19.9 to 81.6	6.84941	1206.001	223.148
Cyclohexanol	$C_6H_{12}O$	93.7 to 160.7	6.25530	912.866	109.126
n-Decane	n-$C_{10}H_{22}$	94.5 to 175.1	6.95707	1503.568	194.738
1-Decene	$C_{10}H_{20}$	86.8 to 171.6	6.95433	1497.527	197.056
1,1-Dichloroethane	$C_2H_4Cl_2$	−38.8 to 17.6	6.97702	1174.022	229.060
1,2-Dichloroethane	C_2H_4Cl	−30.8 to 99.4	7.02530	1271.254	222.927
Dichloromethane	CH_2Cl_2	−40.0 to 40	7.40916	1325.938	252.616
Diethyl ether	$C_4H_{10}O$	−60.8 to 19.9	6.92032	1064.066	228.799
Diethyl ketone	$C_5H_{10}O$	56.5 to 111.3	7.02529	1310.281	214.192
Diethylene glycol	$C_4H_{10}O_2$	130.0 to 243.0	7.63666	1939.359	162.714
Dimethyl ether	C_2H_6O	−78.2 to −24.9	6.97603	889.264	241.957
Dimethylamine	C_2H_7N	−71.8 to 6.9	7.08212	960.242	221.667
N,N-Dimethylformamide	C_3H_7NO	30.0 to 90.0	6.92796	1400.869	196.434
1,4-Dioxane	$C_4H_8O_2$	20.0 to 105.0	7.43155	1554.679	240.337
Ethanol	C_2H_6O	19.6 to 93.4	8.11220	1592.864	226.184
Ethanolamine	C_2H_7NO	65.4 to 170.9	7.45680	1577.670	173.368
Ethyl acetate	$C_4H_8O_2$	15.6 to 75.8	7.10179	1244.951	217.881
Ethyl acetate*	$C_4H_8O_2$	−20 to 150	7.09808	1238.710	217.0
Ethyl chloride	C_2H_5Cl	−55.9 to 12.5	6.98647	1030.007	238.612
Ethylbenzene	C_8H_{10}	56.5 to 137.1	6.95650	1423.543	213.091

[a]Adapted from T. Boublik, V. Fried, and E. Hala, *The Vapour Pressures of Pure Substances*, Elsevier, Amsterdam, 1973. If marked with an asterisk (*), constants are from *Lange's Handbook of Chemistry*, 9th Edition, Handbook Publishers, Inc., Sandusky, OH, 1956.

(*continued*)

Table B.4 (Continued)

Compound	Formula	Range (°C)	*A*	*B*	*C*
Ethylene glycol	$C_2H_6O_2$	50.0 to 200.0	8.09083	2088.936	203.454
Ethylene oxide	C_2H_4O	0.3 to 31.8	8.69016	2005.779	334.765
1,2-Ethylenediamine	$C_2H_8N_2$	26.5 to 117.4	7.16871	1336.235	194.366
Formaldehyde	HCHO	−109.4 to −22.3	7.19578	970.595	244.124
Formic acid	CH_2O_2	37.4 to 100.7	7.58178	1699.173	260.714
Glycerol	$C_3H_8O_3$	183.3 to 260.4	6.16501	1036.056	28.097
n-Heptane	n-C_7H_{16}	25.9 to 99.3	6.90253	1267.828	216.823
i-Heptane	i-C_7H_{16}	18.5 to 90.9	6.87689	1238.122	219.783
1-Heptene	C_7H_{14}	21.6 to 94.5	6.91381	1265.120	220.051
n-Hexane	n-C_6H_{14}	13.0 to 69.5	6.88555	1175.817	224.867
i-Hexane	i-C_6H_{14}	12.8 to 61.1	6.86839	1151.401	228.477
1-Hexene	C_6H_{12}	15.9 to 64.3	6.86880	1154.646	226.046
Hydrogen Cyanide	HCN	−16.4 to 46.2	7.52823	1329.49	260.418
Methanol	CH_3OH	14.9 to 83.7	8.08097	1582.271	239.726
Methanol*	CH_3OH	−20 to 140	7.87863	1473.11	230.0
Methyl acetate	$C_3H_6O_2$	1.8 to 55.8	7.06524	1157.630	219.726
Methyl bromide	CH_3Br	−70.0 to 3.6	7.09084	1046.066	244.914
Methyl chloride	CH_3Cl	−75.0 to 5.0	7.09349	948.582	249.336
Methyl ethyl ketone	C_4H_8O	42.8 to 88.4	7.06356	1261.339	221.969
Methyl isobutyl ketone	$C_6H_{12}O$	21.7 to 116.2	6.67272	1168.408	191.944
Methyl methacrylate	$C_5H_8O_2$	39.2 to 89.2	8.40919	2050.467	274.369
Methylamine	CH_5N	−83.1 to −6.2	7.33690	1011.532	233.286
Methylcyclohexane	C_7H_{14}	25.6 to 101.8	6.82827	1273.673	221.723
Naphthalene	$C_{10}H_8$	80.3 to 179.5	7.03358	1756.328	204.842
Nitrobenzene	$C_6H_5NO_2$	134.1 to 210.6	7.11562	1746.586	201.783
Nitromethane	CH_3NO_2	55.7 to 136.4	7.28166	1446.937	227.600
n-Nonane	n-C_9H_{20}	70.3 to 151.8	6.93764	1430.459	201.808
1-Nonene	C_9H_{18}	66.6 to 147.9	6.95777	1437.862	205.814
n-Octane	n-C_8H_{18}	52.9 to 126.6	6.91874	1351.756	209.100
i-Octane	i-C_8H_{18}	41.7 to 118.5	6.88814	1319.529	211.625
1-Octene	C_8H_{16}	44.9 to 122.2	6.93637	1355.779	213.022
n-Pentane	n-C_5H_{12}	13.3 to 36.8	6.84471	1060.793	231.541
i-Pentane	i-C_5H_{12}	16.3 to 28.6	6.73457	992.019	229.564
1-Pentanol	$C_5H_{12}O$	74.7 to 156.0	7.18246	1287.625	161.330
1-Pentene	C_5H_{10}	12.8 to 30.7	6.84268	1043.206	233.344
Phenol	C_6H_6O	107.2 to 181.8	7.13301	1516.790	174.954
1-Propanol	C_3H_8O	60.2 to 104.6	7.74416	1437.686	198.463
2-Propanol	C_3H_8O	52.3 to 89.3	7.74021	1359.517	197.527
Propionic acid	$C_3H_6O_2$	72.4 to 128.3	7.71423	1733.418	217.724
Propylene oxide	C_3H_6O	−24.2 to 34.8	7.01443	1086.369	228.594
Pyridine	C_5H_5N	67.3 to 152.9	7.04115	1373.799	214.979
Styrene	C_8H_8	29.9 to 144.8	7.06623	1507.434	214.985
Toluene	C_7H_8	35.3 to 111.5	6.95805	1346.773	219.693
1,1,1-Trichloroethane	$C_2H_3Cl_3$	−5.4 to 16.9	8.64344	2136.621	302.769
1,1,2-Trichloroethane	$C_2H_3Cl_3$	50.0 to 113.7	6.95185	1314.410	209.197
Trichloroethylene	C_2HCl_3	17.8 to 86.5	6.51827	1018.603	192.731
Vinyl acetate	$C_4H_6O_2$	21.8 to 72.0	7.21010	1296.130	226.655
Water*	H_2O	0 to 60	8.10765	1750.286	235.000
Water*	H_2O	60 to 150	7.96681	1668.210	228.000
m-Xylene	m-C_8H_{10}	59.2 to 140.0	7.00646	1460.183	214.827
o-Xylene	o-C_8H_{10}	63.5 to 145.4	7.00154	1476.393	213.872
p-Xylene	p-C_8H_{10}	58.3 to 139.3	6.98820	1451.792	215.111

TABLE C-5 Heat Capacity of Liquids

$C_p = A + BT + CT^2 + DT^3$										
No.	**Formula**	**Substance**	***A***	***B***	***C***	***D***	T_{min}	T_{max}	C_p **at 25° C**
1	$C_2H_3Cl_3$	1,1,1-Trichloroethane	11.142	1.0501E+00	–3.0826E–03	3.5983E–06	244	491	145.56
2	$C_2H_3Cl_3$	1,1,2-Trichloroethane	34.934	8.5054E–01	–2.3306E–03	2.6455E–06	238	542	151.46
3	$C_2H_4Cl_2$	1,1-Dichloroethane	57.325	5.6014E–01	–1.8136E–03	2.5617E–06	177	471	131.00
4	$C_2H_4Cl_2$	1,2-Dichloroethane	26.310	7.7555E–01	–2.2271E–03	2.6107E–06	238	505	128.77
5	C_4H_6	1,3-Butadiene	34.680	7.3205E–01	–2.8426E–03	4.6035E–06	165	383	122.26
6	$C_4H_8O_2$	1,4-Dioxane	–20.729	1.2913E+00	–3.5408E–03	3.5408E–06	286	528	153.23
7	$C_4H_{10}O$	1-Butanol (*n*-Butanol)	83.877	5.6628E–01	–1.7208E–03	2.2780E–06	185	507	160.12
8	C_4H_8	1-Butene	74.597	3.3434E–04	–1.3914E–03	3.0241E–06	89	378	130.74
9	$C_{10}H_{20}$	1-Decene	137.962	1.1934E+00	–3.2863E–03	3.9390E–06	208	555	306.05
10	C_9H_{20}	1-Nonane (*n*-Nonane)	98.040	1.3538E+00	–3.8058E–03	4.4991E–06	221	536	282.60
11	C_8H_{16}	1-Octene	119.984	8.3332E–01	–2.5321E–03	3.4745E–06	172	510	235.43
12	C_3H_8O	1-Propanol (*n*-Propanol)	88.080	4.0224E–01	–1.3032E–03	1.9677E–06	148	483	144.32
13	C_2H_4O	Acetaldehyde	45.056	4.4853E–01	–1.6607E–03	2.7000E–06	151	415	102.72
14	$C_2H_4O_2$	Acetic acid	–18.944	1.0971E+00	2.8921E–03	2.9275E–06	291	533	128.66
15	$C_4H_6O_3$	Acetic anhydride	71.831	8.8879E–01	–2.6534E–03	3.3501E–06	201	512	189.75
16	C_3H_6O	Acetone	46.878	6.2652E–01	–2.0761E–03	2.9583E–06	179	457	127.53
17	$C_3H_4O_2$	Acrylic acid	–18.242	1.2106E+00	–3.1160E–03	3.1409E–06	241	617	123.05
18	NH_3	Ammonia	–182.157	3.3618E+00	–1.4398E–02	2.0371E–05	195	385	80.16
19	C_6H_7N	Aniline	63.288	9.8960E–01	–2.3583E–03	2.3296E–06	268	629	210.44
20	C_6H_6	Benzene	–31.663	1.3043E+00	–3.6078E–03	3.8243E–06	280	506	137.87
21	$C_4H_8O_2$	Butyric acid	28.210	1.1040E+00	–2.8523E–03	2.9528E–06	269	565	182.09
22	CS_2	Carbon disulfide	39.938	2.3565E–01	–7.2098E–04	1.0443E–06	163	497	73.79
23	CO_2	Carbon dioxide	–338.956	5.2796E+00	–2.3279E–02	3.5980E–05	218	274	–
24	CO	Carbon monoxide	–19.312	2.5072E+00	–2.8970E–02	1.2745E–04	69	120	–
25	CCl_4	Carbon tetrachloride	9.671	9.3363E–01	–2.6768E–03	3.0425E–06	251	501	130.72
26	Cl_2	Chlorine	127.601	–6.0215E–01	1.5776E–03	–5.3099E–07	172	396	74.23
27	$CHCl_3$	Chloroform	28.296	6.5897E–01	–2.0353E–03	2.5901E–06	211	483	112.49
28	C_6H_{12}	Cyclohexane	–44.417	1.6016E+00	–4.4676E–03	4.7582E–06	281	498	162.07
29	$C_6H_{12}O$	Cyclohexanol	–47.321	1.9131E+00	–4.8388E–03	4.7281E–06	298	563	218.25
30	C_3H_6	Cyclopropane	30.543	5.0198E–01	–2.1040E–03	3.7444E–06	147	358	92.42
31	CH_2Cl_2	Dichloromethane	38.941	4.9008E–01	–1.6224E–03	2.3069E–06	179	459	101.98
32	$C_4H_{10}O$	Diethyl ether	75.939	7.7335E–01	–2.7936E–03	4.4383E–06	158	420	175.81
33	$C_5H_{10}O$	Diethyl ketone	26.231	1.2822E+00	–3.7449E–03	4.3816E–06	235	505	191.76
34	C_2H_7N	Dimethylamine	36.962	9.5817E–01	–3.5846E–03	5.3990E–06	182	394	147.08
35	C_2H_6	Ethane	38.332	4.1006E–01	–2.3024E–03	5.9347E–06	91	275	–
36	C_2H_6O	Ethanol	59.342	3.6358E–01	–1.2164E–03	1.8030E–06	160	465	107.40
37	$C_4H_8O_2$	Ethyl acetate	62.832	8.4097E–01	–2.6998E–03	3.6631E–06	191	471	170.66
38	C_2H_5Cl	Ethyl chloride	60.180	3.4553E–01	–1.2983E–03	2.1963E–06	138	414	106.00
39	C_8H_{10}	Ethylbenzene	102.11	5.5959E–01	–1.5609E–03	2.0149E–06	179	555	183.60
40	C_2H_4	Ethylene	25.597	5.7078E–01	–3.3620E–03	8.4120E–06	105	254	–
41	$C_2H_6O_2$	Ethylene glycol	75.878	6.4182E–01	–1.6493E–03	1.6937E–06	261	581	165.52
42	C_2H_4O	Ethylene oxide	35.720	4.2908E–01	–1.5473E–03	2.4070E–06	162	422	89.90
43	F_2	Fluorine	83.829	–7.8518E–01	5.2305E–03	4.6617E–06	53	137	–
44	$C_3H_8O_3$	Glycerol	132.145	8.6007E–01	–1.9745E–03	1.8068E–06	292	651	260.94
45	H_2	Hydrogen	50.607	–6.1136E+00	3.0930E–01	–4.1480E–03	14	32	–
46	HCl	Hydrogen chloride	73.993	–1.2946E–01	–7.8980E–05	2.6409E–06	165	308	98.37
47	CHN	Hydrogen cyanide	–123.155	1.7769E+00	–5.8083E–03	6.9129E–06	261	411	73.52
48	H_2O_2	Hydrogen peroxide	–15.248	6.7693E–01	–1.4948E–03	1.2018E–06	273	694	85.55
49	C_4H_{10}	*i*-Butane (*iso*-Butane)	71.791	4.8472E–01	–2.0519E–03	4.0634E–06	115	367	141.61
50	CH_4	Methane	–0.018	1.1982E+00	–9.8722E–03	3.1670E–05	92	172	–
51	CH_3OH	Methanol	40.152	3.1046E–01	–1.0291E–03	1.4598E–06	176	461	79.93