SEPARATION OF PROPIONIC ACID BY FREEZE CRYSTALLIZATION

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ABSTRACT

Industrial effluents may contain substances which are very difficult and cost intensive to separate out. One such component is Propionic acid which forms azeotrope with water at 17.7% mass concentration. The method employed here for separating the system is Freeze Crystallization. Also, it is compared with conventional method of extractive distillation.

Keywords: *Propionic Acid, Azeotrope, Freeze Crystallization, Effluent System*

1. INTRODUCTION

The principle of the freeze crystallization process is, when a solution containing dissolved contaminants is slowly frozen, water ice crystals form on the surface, and the contaminants are concentrated in the remaining solution (the mother liquor). The ice crystals can be separated from the mother liquor, washed and melted to yield a nearly pure water stream. The mother liquor will contain a pure salt, which crystallizes at the eutectic temperature. Theoretically, a 100% yield can be obtained in a binary system, which is one of the advantages of EFC technology. The level of accumulation of impurities can be controlled by means of purge streams.

The basis of the eutectic freeze crystallization (EFC) process is the existence of the eutectic point. The eutectic point is a characteristic point in the phase diagram of a salt-water mixture. At the eutectic point equilibrium exists between ice, salt and a solution with a specific concentration. This specific concentration is called the eutectic concentration and the temperature at which this equilibrium is found is the eutectic temperature.

Propionic acid with water is found in several biotech industries along with its major source is from effluent of ethyl Propionic acid industry, where water is added in the ethanol and Propionic acid, to form ethylpropionc acid solution. Thus, water and Propionic acid mixture is obtained from the waste stream.[1,2,3]

2. SEPARATION BY FREEZE CRYSTALLIZATION

2.1 Sample Preparation
To prepare a 365 ml of 17.7 % Propionic Acid solution by mass we require 65 ml Propionic Acid and rest water.

2.2 Properties of Propionic Acid

Chemical formula	$C_3H_6O_2$
Molar mass	74.08 g/mol
Appearance	Colorless , Oily liquid
Odor	Pungent, rancid, unpleasant
Density	0.98797 g/cm^3
Melting Point	-20.5 ^{0}C
Boiling Point	141.2 ^{0}C

2.3 Procedure

1. Take Propionic Acid solution (17.7%) sample in Glass test jar up to the filling mark and start the refrigerator.
2. Set the desired temperature at temperature indicator as 0^0C. Wait till the desired temperature is reached. When the desired temperature is reached, sample is taken out.
3. Ice is crushed into fine crystals and washed by melt. Then crystals and melt are separated and analyzed.

2.4 Analysis method of Propionic Acid

After the Separation of Crystals and Melt take 10 ml sample from either crystals or melt and add 2 to 3 drops of phenolphthalein indicator and titrate it against 1.4N NaOH solution until light pink color is obtained.

Propionic Acid Solution
300 ml Water + 65 ml Propionic Acid

NaOH Solution
22.4 gm NaOH + 400 ml Water
After separation it is found that
Propionic acid solution in Crystals = 225 ml
Propionic acid solution in Melt = 140 ml

Fig. 1: Crystals of Propionic Acid Obtained after Experiment

2.5 Calculations
Calculation for crystals
Burette reading = 10.2 ml
$$N_1V_1 = N_2V_2$$
$$1.4 \times 10.2 = N_2 \times 10$$
$$N_2 = 1.43 \ N$$
Amount of Propionic acid present in crystals =
$$\frac{21.5 \times 225 \times 1.43}{2.9 \times 100} = 23.95 \ gm$$

Calculation for Melt
Burette Reading = 27.9 ml
$$N_1V_1 = N_2V_2$$
$$1.4 \times 27.9 = N_2 \times 10$$
$$N_2 = 3.9 \ N$$
Amount of Propionic Acid Present in Melt =
$$\frac{21.5 \times 140 \times 3.9}{2.9 \times 100} = \textbf{40.47 gm}$$
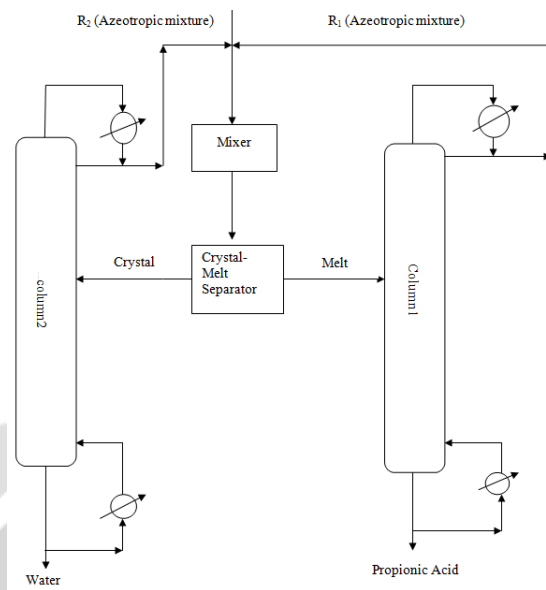
2.6 Suggested Flow Sheet

Fig. 2: Suggested flow sheet for Propionic Acid Water Separation Using Single Stage Freeze Crystallization

2.7 Material and Energy Balances
2.7.1 Material balance

$F + R_1 + R_2 = M = Cr + Me$
$F = P + W$
F = Feed Flow Rate = 1000 kg/h
P = Propionic acid Flow Rate = 177 kg/h
W = Water flow Rate = 823 kg/h
Me = R_1 + P = R_1 + 177
Me = Melt Flow Rate
R_1 = Azeotrope Flow Rate From Distillation Column 1
Propionic Acid Balance For column 1
$Me \times 0.289 = (R_1 \times 0.177) + 177$
$(R_1 + 177) \times 0.289 = 0.177 R_1 + 177$
R_1 = 1123.63 kg/h
Me = 1123.63 + 177 = 1300.63
Cr = R_2 + W = R_2 + 823
Cr = Crystal Flow Rate
R_2 = Azeotrope flow rate from distillation column 2
Propionic Acid Balance For column 2
$Cr \times 0.113 = (R_2 \times 0.177) + 0$
$(R_2 + 823) \times 0.113 = 0.177 R_2$
R_2 = 1453.10 kg/h
Cr = 2276.1 kg/h

2.7.2 Calculation of Heat Duty
Condenser 1
$\text{Log}_{10} p_v = A - \dfrac{B}{T+C}$

Component	Temperature (K)	A	B	C
Propionic Acid	415	4.74558	1679.869	-59.832
Water	415	3.55959	643.748	-198.043
Water	373	4.65430	1435.264	-64.848

At 142 ^{0}C
By using Antonie Equation
We get $P_{vw} = 3.9120$ bar and $P_{vp} = 1.0370$ bar
$\alpha_{top} = 1$

$$\alpha_{bottom} = \frac{p_{vw}}{p_{vp}} = \frac{3.9120}{1.030} = 3.7724$$

$$\alpha_{avg} = \sqrt{\alpha_{top} \times \alpha_{bottom}}$$
$$= \sqrt{1 \times 3.7724} = \mathbf{1.94}$$

Saturated Liquid,

$$R_m = \frac{1}{\alpha - 1}\left[\!\left[\frac{xD}{xF} - \frac{\alpha\,(1-xD)}{1-xF}\right]\!\right]$$

x_D = Mole Fraction of More Volatile Component in Distillate = 0.823
x_F = Mole Fraction of More Volatile Component in

Feed Liquid $= 0.711$

$$Q = \frac{HG - HF}{HG - HL} = 1$$
H_G = Enthalpy of Saturated Vapour, kJ/kmol
H_F = Enthalpy of feed, kJ/kmol
H_L = Enthalpy of saturated liquid, kJ/kmol

R_m = -0.032
So take R = 0.5

For reliable estimation of latent heat of vaporization Watson equation is recommended.
$$\frac{\lambda_v}{\lambda_{v1}} = \left(\frac{T_c - T}{T_c - T_1}\right)^{0.38}$$

λ_v = latent heat of vaporization at T K,
λ_{v1} = latent heat of vaporization at T_1 K,
$T_{C=}$ critical temperature, K
$$\frac{\lambda_v}{55000} = \left(\frac{598.5 - 373}{598.5 - 414}\right)^{0.38}$$

$\lambda_v = 59358.0679$ kJ/kmol
$\lambda_w = 2257.9$ kJ/kg (at 373k)
  $= 40642.2$ kJ/kmol
$\lambda_{mix} = (0.177 \times 59358.0679) + (0.823 \times 40642.2)$
   $= 43954.90$ kJ/kmol

$Q_{c1} = (R + 1)\,D\,\lambda_{mix}$
$$Q_{c1} = \frac{(0.5 + 1) \times 1123.63 \times 43954.9}{3600 \times \left((0.177 \times 74.08) \times (0.823 \times 18)\right)} \quad (D = R_1)$$
   $\mathbf{=736.9\ kW}$

Condenser 2
At 373 K,
$P_{vw} = 0.9923$ bar
$Pvp = 0.24071$ bar
$\alpha_{bottom} = \dfrac{0.9923}{0.24071} = 4.1223$
$\alpha_{top} = 1$
$\alpha avg = \sqrt{\alpha_{top} \times \alpha_{bottom}}$
$= \sqrt{1 \times 4.1223}$
= 2.030

$Rm = \dfrac{1}{\alpha - 1}\left[\left[\dfrac{xD}{xF} - \dfrac{\alpha\,(1 - xD)}{1 - xF}\right]\right]$
$= \dfrac{1}{2.030 - 1}\left[\left[\dfrac{0.823}{0.887} - \dfrac{2.030(1 - 0.823)}{1 - 0.887}\right]\right]$
= -2.18

We can take R = 0.5, $\lambda_{mix} = 43954.90$ kJ/kmol

$Q_{c2} = (R + 1)\, D\, \lambda_{mix}$
$= \dfrac{(0.5 + 1) \times 1453.10 \times 43954.9}{3600 \times \left((0.177 \times 74.08) \times (0.823 \times 18)\right)}$
= 952 kW
Reboiler Duty,
1st reboiler

Component	a	b×10³	c×10⁶	d×10⁹
Propionic Acid	31.7072	930.795	-2330.49	2457.4
Water	50.845	213.08	-631.398	648.746

Bottom Product = 99.99 % Propionic acid, so Take $x_i = 1$,

$a_i x_i$	$b_i x_i \times 10^5$	$c_i x_i \times 10^6$	$d_i x_i \times 10^9$
31.7072	930.795	-2330.49	2457.4

Enthalpy of Residue,
$H_w = \sum a_i x_i (T - T_0) + \sum b_i x_i\left(\dfrac{T^2 - T_0^2}{2}\right) + \sum c_i x_i\left(\dfrac{T^3 - T_0^3}{3}\right) + \sum d_i x_i\left(\dfrac{T^4 - T_0^4}{2}\right)$
Bubble Point Temperature of Distillate = 382K
Dew Point Temperature of Residue = 388k
T_0 = Reference Temperature $= \dfrac{TBubble + TDew}{2} = \dfrac{382 + 388}{2} = 385k$
Bubble Point Temperature of Residue T = 415K
By putting all that value in above equation we get,
H_w = 15738.72 kJ/kmol
$H_w w = \dfrac{15738.72 \times 177}{74.08 \times 3600}$
$= 10.44$ kW
Now Enthalpy of Feed,
T_{BP} = Bubble Point of Feed = 385K
$T_b - T_0 = 385 - 385 = 0$
So, $H_F F = 0$
$Q_{B1} = Q_{c1} + H_D D + H_W W - H_F F + Q_L$
$= 736.9 + 10.44 + Q_L$
$= 747.34 + 0.05 \times 747.34$
$Q_{B1} = 784.707$ kW
$m_{steam}\lambda_{156} = 787$ kW
$m_{steam} = \dfrac{787}{2094}$ (λ_{156}=2094 kJ/kg)

m_{steam}= 0.3758 kg/s
m_{steam}= 1353 kg/h

2nd Reboiler

$T - T_0 = 373 - 385 =$ Negative
T = Bubble Point Temperature of Residue
$H_W W =$ Negligible
$T_{BP} =$ Bubble Point of Feed = 382K
$T_{BP} - T_0 = 382 - 385 =$ Negative
$H_F F =$ Negligible
$H_D D = 0$
$Q_{B2} = 999.6$ kW
$m_{steam} \lambda_{110} = 999.6$ kW
$m_{steam} = \frac{999.6}{2230}$ (λ_{110}=2230 kJ/kg)
$m_{steam} = 0.4483$ kg/s
m_{steam}= 1614 kg/h

Total Steam Required = 2967 kg/h

Heat Duty of Refrigeration Cycle
M = F + R_1 + R_2
    = 1000 + 1123.63 + 1453.10
    = 3576.73 kg/h

Component	Aixi	Bixi×10^3	Cixi×10^6	Dixi× 10^9
Propionic Acid	5.612	164.75	-412.496	434.9598
Water	41.845	175.36	-519.64	533.917
Total	47.457	340.11	-932.136	968.9

$Cp = a + bt + ct^2 + dt^3$
$C_{P,323} = 47.457 + (340.11 \times 323 \times 10^{-3}) + ((-932.136) \times (323)^2 \times 10^{-6}) + (968.9 \times (323)^3 \times 10^{-9})$
$C_{P,323} = 92.7085$ kJ/kmol × K
$C_{P,273} = 47.547 + (340.11 \times 273 \times 10^{-3}) + ((-932.136) \times (273)^2 \times 10^{-6}) + (968.9 \times (273)^3 \times 10^{-9})$
$C_{P,273} = 90.547$ kJ/kmol × K
$C_{P,avg} = 91.63$ kJ/kmol × K

$\lambda_{mix} = (0.177 \times 11728) + (0.823 \times 6012)$
$= 7023.732$ kJ/kmol

$Q_t = M C_{P,avg} (T_{50} - T_0) + M \lambda_{mix}$
$= \left[\left[\frac{(3576.73 \times 91.63 \times 50) + (3576.73 \times 7023.732)}{((0.177 \times 74.08) + (0.823 \times 18)) \times 3600}\right]\right]$
$= 412.88$ kW
Take COP = 4,

$Q_t = 412.88/4$
    = 103.22 kW

Refrigeration duty = 103.22 kW

Total heat duty of condenser = Q_{C1} + Q_{C2} = 736.9 + 952 **= 1688.9 kW**
$M_{water} = \frac{1688.9}{4.186 \times 8}$ = 50.43 kg/s = 181548 kg/h **= 181.5 m^3/h**

Amount of makeup water required on basis of 2% loss = 3.63 m^3/h

3. SEPARATION BY EXTRACTIVE DISTILLATION

Conventionally, Propionic Acid is separated from effluent via extractive distillation.

Extractive Distillation is defined as distillation in presence of a miscible high boiling relatively non-volatile component called solvent that forms no azeotrope with other components of the mixture. Solvent is continuously added near the top of the column so that an appreciable amount is present in the liquid phase throughout the column. The component having the greater volatility (not necessarily the lowest boiling point component) is taken overhead as relatively pure distillate. The other component leaves with the solvent via the column bottoms. The solvent is then separated from the bottoms in second distillation column.[6]

Here, for separation of 17.7% Propionic Acid - Water System, 98% (by wt.) Sulfuric Acid is taken as solvent, and the distillation column is followed by evaporator for regeneration of sulfuric acid.

3.1 Column 1
$F + S = B + D$
Propionic acid balance

$Fx_F = Dx_D$ (Solvent is free from Propionic acid & all the Propionic acid is recovered in distillate)

$x_F = \dfrac{\frac{17.7}{74}}{\frac{17.7}{74} + \frac{82.3}{18}} = 0.0497$

$1 - x_F = 0.9503$

$F = \dfrac{1000}{(0.0497 \times 74) + (0.9503 \times 18)} = 48.12$ kmol/h

Component	Mass%	Molecular Weight	x_F	$F \times x_F$
Propionic Acid	17.7	74	0.0497	2.39
Water	82.3	18	0.9503	45.73
Total	100		1.00	48.12

Distillate
For Propionic Acid

$$\log_{10} P = A - \frac{B}{T + C}$$

Where T is in K and P is in bar.

For Propionic Acid Antonie's Constant are A=4.745, B=1679.869, C = -59.832

Vapor pressure of water is taken from steam table.

After trial & error it is found that dew point temperature of the top product = 94.22[0]C

Component	p_{vi} (torr)	x_D	Dx_D (kmol/h)
Propionic Acid	143.83	0.189	2.39
Water	617.00	0.811	10.255
Total	**760.83**	**1.00**	**12.645**

$$\frac{\lambda_v}{\lambda_{v1}} = \left(\frac{T_c - T}{T_c - T_1}\right)^{0.38}$$

λ_v = latent heat of vaporization at T K,
λ_{v1} = latent heat of vaporization at T_1 K,
T_C = critical temperature, K

$$\frac{\lambda_v}{55000} = \left(\frac{598.5 - 367.37}{598.5 - 414}\right)^{0.38}$$

$\lambda_{vPA} = 59916$ kJ/kmol

$\lambda_{vPA} \times x_{DPA} = 11324$ kJ/kmol

$\lambda_{vW} = 40896$ kJ/kmol

$\lambda_{vW} \times x_{DW} = 33167$ kJ/kmol

$\lambda_{vmix} = 44490$ kJ/kmol

R = 2

$\phi_{C1} = \lambda_{mix}D(R+1)$

$= 44490 \times 12.645 \times 3$

$= 1687728$ kJ/h

$\boldsymbol{\phi_{C1} = 468.82}$ **kW**

$M_{water} = \frac{468.82}{4.186 \times 8}$

$= 13.99$ kg/s

$= 50398.7$ kg/h

$\boldsymbol{= 50.4}$ **m³/h**

Amount of makeup water required on basis of 2% loss = 1 m³/h

Feed

$x_{FPA} = \frac{p_{vPA}}{760}$

$p_{vPA} = \frac{760 \times 0.497}{750} = 0.0503$ bar

$$\log_{10} 0.0503 = 4.745 - \frac{1679.869}{T - 59.832}$$

T = 337.81 K

   = 64.67 °C

Component	a	b × 10³	c × 10⁶	d × 10⁹
Propionic Acid	-137.5366	2838.124	-6235.805	-6253.25
H₂O	50.845	213.08	-631.398	648.746

$FH_F = -78055.4$ kJ/h= -21.682 kW

Solvent

$x_S = \frac{\frac{98}{98}}{\frac{98}{98} + \frac{2}{18}} = 0.9$

F + S = B + D

1000 + S = 361.45 + B

Sulfuric Acid balance

S × 0.98 = B × 0.8

S × 0.98 = (638.55 + S) × 0.8

S = 2838 kg/h

B = 3476.55 kg/h

$S = \frac{2838}{(0.9 \times 98) + (0.1 \times 18)} = 31.54$ kmol/h

48.12 + 31.54 = 12.656 + B

B = 67.01 kmol/h

Component	Mass%	Molecular weight	x_S	$S \times x_S$
H₂SO₄	98	98	0.9	28.386
H₂O	2	18	0.1	3.154
Total	100		1.00	31.54

$T_S = 50^0C = 298.15$ K

Reference temperature = Dew point temperature (Top temperature)

$SH_S = m \times Cp \times \Delta T$

m = mass flow rate of solvent

Cp = Specific heat of solvent

$SH_S = 2838 \times 1.43 \times (-44.22)$

$= -179459.79$ kJ/h

$= -49.85$ kW

After trial & error it is found that bubble point temperature of the bottom product = 175.7^0C

Component	Mass%	Molecular weight	X_W	$W \times x_W$
H_2SO_4	80	98	0.4235	28.386
H_2O	20	18	0.5765	38.63
Total	100		1.00	67.01

$$x_{WS} = \frac{\frac{80}{98}}{\frac{80}{98}+\frac{20}{18}} = 0.4235$$

$W \times x_W = 3476.55 \times 2.1 \times 81.48 = 594865.5$ kJ/h = 165.24 kW

$$\phi_{B1} = ((\phi_{C1}+BH_B)-(FH_F+SH_S)) \times 1.05$$
$$= ((468.82+165.24)-(-21.682-49.85)) \times 1.05$$
$$= 740.87 \text{ kW} = 2667137.76 \text{ kJ/h}$$

$m_{steam}\lambda_{200} = 740.87$ kW

$m_{steam} = \frac{740.87}{1939.2}$ (λ_{200}=1939.2 kJ/kg)

$m_{steam} = 1376$ kg/h

3.2 Evaporator

Feed to evaporator is bottom product of column 1.

$F_2 = B_1 = 67.01$ kmol/h

$F_2 = D_2 + R_s$ (Overall Balance)

Sulfuric Acid Balance

$x_{F2} \times F_2 = x_{D2} \times D_2 + x_{RS} \times Rs$

$Rs = 31.53$ kmol/h and $D_2 = 35.478$ kmol/h

Feed temperature = 175.7^0C

Component	Mass%	Molecular weight	X_F	$F \times x_F$
H_2SO_4	80	98	0.4235	28.386
H_2O	20	18	0.5765	38.63
Total	100		1.00	67.01

$F \times H_F = 165.24$ kW

Consider steam at 200 ^0C, $\lambda_V = 1936$ kJ/mol = 34902 kJ/kg

Heat Input = Δsteam + Δfeed

$= S_t(h_{St} + 34902) + 165.24$

Heat Output = Δdistillate + Δbottom + Δcondensate

For 90% Sulfuric Acid at 120 ^0C partial pressure = 0.00571bar = 4.28 mmHg = pressure of evaporator

Water's boiling point at this pressure is 30 ^{0}C
λ_V = 2430.5 kJ/kg

ΔDistillate = 35.478×18×2430.5
=1552157.022 kJ\h = 431kW

Rs = 31.53×((0.9×98)+(0.1×18)) = 2837.7 kg/h
Cp = 1.6 kJ/kg.K
BH_B = 2837.7 × 1.6 × (120-30)
        = 408628.8 kJ/h = 113.5 kW

ΔCondensate = $S_t \times h_{St}$
Heat Output = 431+113.5+ $S_t \times h_{St}$
Since Heat Input = Heat Output
S_t = 0.0108 kg/s = 39.18 kg/h

Therefore,
Heat Duty for evaporator = 574.66 kW
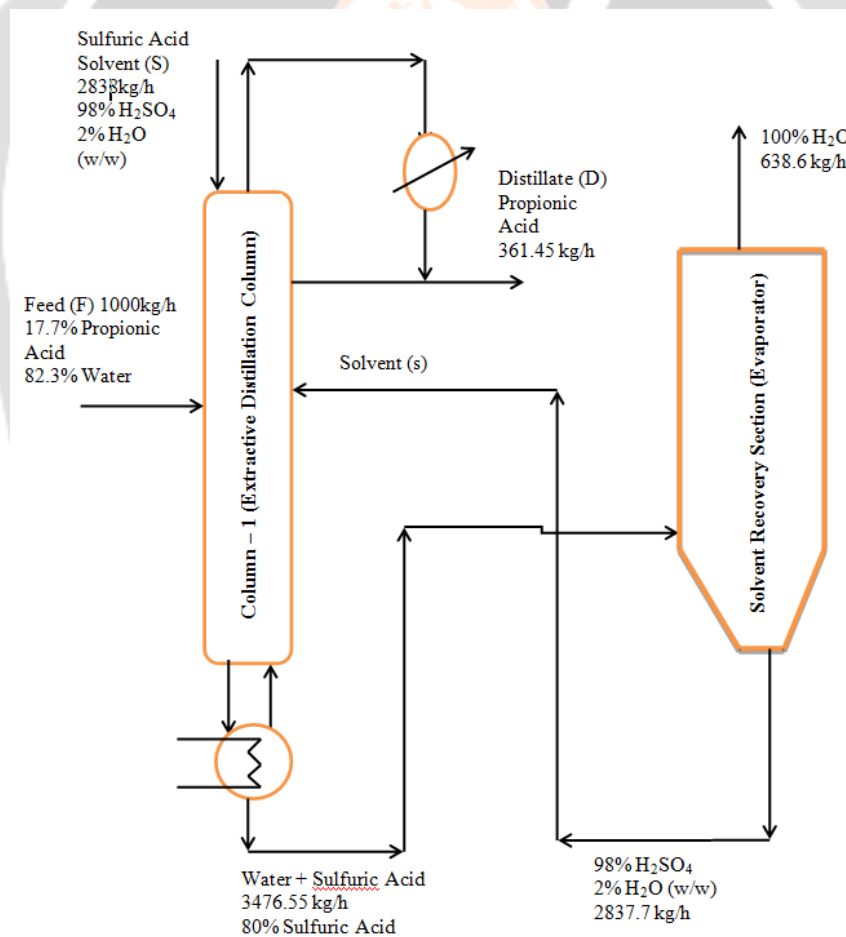
3.3 Process Flow Sheet

Fig. 3: Conventional Process Flow Diagram For Propionic Water Sepaartion

4. CONCLUSION

From the experiment and the heat duty calculations it is evident that we can break Propionic acid water azeotrope using freeze crystallization. The calculations also show that amount of heat required for 1st column is less in proposed model as compared to conventional one.

Furthermore, the use of solvent is eliminated in Freeze Crystallization thus eliminating the risk of contamination of products.

Also, handling Sulfuric Acid and vacuum operation of evaporator is difficult and involves risks which are thus nullified in the eutectic freeze crystallization.

It should also be noted that here only one stage of EFC is considered, if we go for further stages, the heat duty required will reduce gradually and thus there will be need for optimization of stages compared with energy and cost.

Lastly, complete separation of Propionic acid from effluent stream is possible by multistage freeze crystallization system as Propionic Acid Water is a eutectic system.

Hence, use of freeze crystallization for separation of Propionic acid water separation seems to have good technical feasibility.

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