Production Technological Design for 500,000 Tonnes Per Year of Ethylene Glycol

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Abstract. Effective and reasonable chemical design of ethtlene glycol production process is of vital significance for the further improvement of our ethylene glycol production capacity. This paper carried out reasonable design of ethylene glycol water lawful production process, using reaction rectifying tower device, and optimizing calculation for each link of production, so as to obtain satisfactory products. In the comprehensive consideration of production efficiency and cost saving and other aspects of the relevant equipment is reasonable selection, and draw the PID process flow chart. It is expected to produce 500,000 tons of pharmaceutical grade glycol with mass fraction of 99.89%.

Keywords: Ethylene glycol, Chemical engineering design, Equipment selection, Plate calculation.

1. Introduction

Ethylene glycol, an important organic chemical raw material, can be used in the production of lubricants, plasticizers and so on. In the recent years, ethylene glycol production capacity of our country was at the rising tendency. With the increase of put into production facilities, ethylene glycol output increases year by year. From the production market, oil to ethylene glycol is the main production route as of February 2, the overall load of ethylene glycol in mainland China is 62.40%, among which the load of coal to ethylene glycol is 56.19%. The reasons for the low operation rate of China's coal-to-ethylene glycol plant mainly include too many projects put into production, oversupply of products, and it is also positively related to high steam consumption and the upstream industrial chain, or the project is built in the west, which leads to high transportation costs, and it is also affected by the national "two- carbon" strategy, enterprise safety issues, high cost and other factors.

The physical properties of ethylene glycol are shown in Table 1 below.

Table 1. Physical properties of ethylene glycol

Boling point	197.3℃
molecular mass	62.06
density	1.1155
melting point	-12.9℃
combustion heat	1180.26KJ/mol

Ethylene Glycol, also known as ‘Glycol’ or EG for short, is the simplest diol. Ethylene Glycol is a colourless, odourless, sweet-smelling liquid which is toxic to animals and the lethal dose for humans is about 1.6g/kg. It is an important chemical raw material, miscible with solvents such as water/ethanol/acetone/glycerol pyridinium acetate, slightly soluble in ether, soluble in inorganic substances such as calcium chloride/zinc chloride/potassium carbonate/potassium iodide/potassium hydroxide and is easily absorbed when the concentration is high.

Glycol is the main raw material for the synthesis of polyester resins, and the familiar polyester fibre is synthesised from glycol and terephthalic acid. Glycol can also be used as antifreeze. In addition to being used as an antifreeze for automobiles, it is also used for the transport of industrial cold, and is generally referred to as a refrigerant. It is also used to produce the synthetic resin PET, which is used to make mineral water bottles.

The method of ethylene oxide hydrate to produce ethylene glycol has the advantages of low hydration ratio, high selectivity of ethylene glycol, simple process and less pollution, etc. In this paper, this method is used to produce ethylene glycol, and a series of operations after that are also built on the basis of this process. The main reaction of this production process: EO+H2O→EG Secondary reaction: EG+EO→DEG; DEG+EO→TEG.

The entire flow of this production process includes a distillation section, a dehydration section, and a refining section.

This design will also use reactive distillation technology, which is a unit operation in which the chemical reaction and the separation operation can be carried out under operating conditions. In this process, the chemical reaction and distillation separation at the same time, because ethylene oxide hydration to produce ethylene glycol reaction generated compounds as well as the boiling point of the reactant components directly are a large difference, we can in the process of the reaction at the same time go to the distillation to remove the recombinant glycol, to speed up the rate of the reaction, and at the same time, because of the hydration of ethylene oxide will release a large amount of heat, we can use the reaction of the heat energy for the distillation to provide the Necessary energy for distillation, reaction to promote distillation, distillation to promote the reaction, the interaction between the two, improve the conversion rate of the reactants, speed up the reaction rate.

2. Table of Design Conditions And Main Physical Properties

2.1. Determination of Reaction Temperature

Firstly, there are several facts: an increase in the feed temperature of water and ethylene oxide decreases the selectivity of ethylene glycol and the reaction rate equations for both the main reaction EO+H2O→EG and the side reaction EG+EO→DEG can be expressed in the form of the Arrhenius equation shown in Table 2.

Table 2. List of reaction rate equations (expressed as Arrhenius equation)

Reaction	Rate/(mol/cm3s)	△H
1	3.15exp[-9547/T(K)]•EO•H_2O	-80
2	6.3exp[-9547/T(K)]•EO•EG	-13.1

K=Ae(-E_a/RT) so the preexponential factor A=3.15EO-H2O and 6.3-EO-EG (1) Then due to the van't Hoff equation: dlnk/dT=△rH_m/RT^2 when △H is a constant the left and right sides of the integration and do the difference to get: ln(K_1/K_2)=(△rH_{m1}-△rH_{m2})/RT=-66.9/RT)=(△rH_{m1}-△rH_{m2})/RT=-66.9/RT (2) Next, we assume that the two reactions for the elementary reaction, and the chemical formula to express the concentration of each chemical (3) need to let the two reactions of the rate constant difference as large as possible, all of the above formulae can be obtained by associating the reaction temperature of 34.764℃ ethylene glycol selectivity is higher, we choose 35℃ for the feed temperature.

2.2. Determination of Reaction Pressure

The reaction pressure does not have a great influence on the selectivity of ethylene glycol but it can be considered to increase the recovery of the reaction by increasing the pressure appropriately as well as preventing the reaction from stopping due to the decrease of the concentration of ethylene oxide. After simulating the reaction pressure 0.5-1MPa, 1MPa was selected [4].

2.3. Determination of Water/Ethylene Oxide Molar Ratio

Next we determined that the raw material ratios and recoveries were modelled to meet the following data.

Table 3. Ratio of raw materials in relation to the recovery rate and heat load list

Raw material ratio (water/ethylene oxide)	chemical recovery	heat load (MW)
1:1	0.928	-59.21
1:2	0.941	-101.12
1:4	0.978	-244.214
1:8	0.988	-500.02

Table 3 indicates the feedstock ratio of water to ethylene oxide in relation to recovery and heat load. It can be seen that the raw material ratio increases the selectivity of glycol will increase but the heat load will also increase, from the perspective of selectivity and cost savings and other considerations, choose the raw material ratio of 1:1.

3. Technological Design Calculations

3.1. Material Balance

It is known that 500000 tonnes of glycol products are produced annually, and the number of days of production is 300 days per year; then the glycol production per hour A is:

A=500000000/(300×24)=69444kg/hour

In the case of 69444kg of product per hour, the glycol selectivity is 0.923, so the ethylene oxide required per hour is: 53266kg.

Considering the raw material loss ratio of 0.01, then the feedstock of ethylene oxide aqueous solution: 53266×1.01/0.9=59776kg.

59776kg, feed water and ethylene oxide aqueous solution molar ratio of 1:1, so the water flow rate: 59776/44×18=24453.8kg/h, the results of material balance are shown in the Table 4 below.

Table 4. Balance sheet for distillation columns for ethylene glycol production

Project	Unit	Feedstock (temperature: 35°C)		Output (temperature: 169°C)		
distillation columns	Kg/h	ethylene oxide feedstock	Water feedstock	water output	ethylene glycol output	diethylene glycol output
mass flow		59800	48930	26090.775	69546.345	12670
mass fraction		0.9899	\	\	\	\

3.2. Energy Balance

3.2.1 Purpose of energy balance

In chemical design and production, to carry out energy balance has the following main purposes:

1) the tower equipment (reaction distillation tower, dehydration tower, distillation tower, etc.), conveying operating machinery (various pumps) need to join the power calculation, so as to facilitate the clarification of the type of each device.

2) Clearly the operating process of each unit (reaction, distillation, evaporation, cooling, heat transfer, etc.) need to add the heat or cold, and the transfer rate; calculation of the process size of the heat transfer equipment; clear heating agent or coolant consumption, such as water supply for other professions, steam supply professionals to provide the design of the conditions required.

3) Chemical reactions are often accompanied by thermal effects, this effect will lead to the temperature of the system increases or decreases, so you need to specify in order to maintain a certain range of reaction temperature needs to be added or removed from the rate of heat transfer for the reactor design and selection to provide a theoretical basis [12].

3.2.2 Energy balance results

The reboiler and condenser loads of the main equipment are mainly affected by the feed temperature, and the specific heat loads as well as the power of the reboiler and condenser of each equipment will be shown by the following Table 5.

Table 5. Main equipment load list

Equipment		Load	
T1	reboiler /MW		70.21
	condenser /MW		-69.42
T2	reboiler /MW		0.92
	condenser /MW		-0.43
T3	reboiler /MW		15.4
	condenser /MW		-1.92
H1			48.23
H2			66.24
H3			0
H4			-3121
H5			43
H6			2432
H7	heat load	333.21	
H8		-32.42	
H9		-21.23	
H10		-1.23	
	volumetric flow rate /$m^3 \cdot h^{-1}$	electric power /KW	
P1	5.847	4.953	
P2	18.21	10.75	
P3	20.34	11.99	
P4	11.42	6.98	
P5	9.97	1.11	

The temperature of the feedstock to the reactive distillation column is 35°C and the gas flow rate of the feedstock is 0. The specific energy calculations are shown in the Table 6 below.

Table 6. Energy balance for reactive distillation columns

	input1	input2	output3	output4
Temperature/°C	35	35	180	290
Pressure/Mpa	1.00	1360.00	1.00	1.00
Vapor Frac	0.00	0.00	0.00	0.00
Mass Flow kg/hr	12743.2100	6000.0000	6261.7643	16811.7433
Enthalpy Gcal/hr	-64.86		-65.32	
ΣH Gcal/hr	-121.21		-100.32	

3.3. Design of Distillation Columns

Fig.1 shows the activity coefficients of ethylene glycol and water as a function of glycol content.

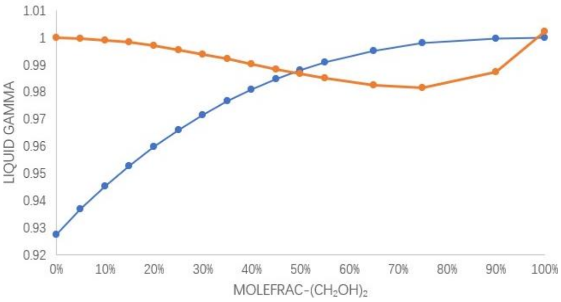

Figure 1. Plot of activity coefficients of ethylene glycol and water versus glycol content

The blue line shows the activity coefficient for glycol and the orange line shows the activity coefficient for water.

It can be seen that as the content of glycol changes glycol and water phase equilibrium relationship with the activity coefficient has been changing, so the relative volatility has also been changing a value we need to set up more levels to obtain a higher precision of the relative volatility to 1, 2 layer tower plate, for example, so that the X_m to meet the $(X_1-X_m)/(Xm-Xn)=(X_1-X_2)/(X_{n-1}-X_n)$ to get the new X_m determined by α_m is considered to be the relative volatility of the geometry of the point to meet the $\alpha=(\alpha_1\alpha_m\alpha_n)^{1/3}$, and so on can be obtained to obtain a high degree of accuracy of the relative volatility [7].

After simulation, the reflux ratio is determined to be 18, and $X_d>0.96$ is required, and the minimum 0.96 is used for the calculation here.

Ethylene oxide and water feedstock molar ratio of 1:1 so there is $X_F=0.5$ and the relative volatility through a new algorithm to find the geometric mean of 1.7, and $X_w=0.11$, so there is $y=1.7x/(1+0.7x)$ Substituting the phase equilibrium equations to get y=0.629 to determine the point of e (0.5, 0.629) Choose the bubble point of the feed: q=1 so there is a rectifying section of the operating line: $Y_{n+1}=R/(R+1)X_n+X_d/(R+1)$ i.e.: $Y_{n+1}=0.94736842X_n+0.05052632$, and the refining section of the operation line: $Y_{n+1}=R/(R+1)\ X_n+X_d/(R+1)$ that is: $Y_{n+1}=0.94736842X_n+0.05052632$, and the stripping section of the operating line after e (0.5, 0.629) and (0.11, 0.11) to obtain the stripping section of the operating line: $Y=1.43X-0.086$ The top of the tower using a total condenser so that there are: $Y_1=X_d=0.96$, the full tower calculation. The whole tower calculation is shown in Table 7 below.

Table 7. Molar distribution of liquid phase in the whole tower

Plate number	Water	Ethylene glycol	Diethylene glycol	Triethylene glycol	Ethylene oxide
1	0.99999997	1.2415E-7	2.4527E-9	5.4253E-16	5.4233E-30
2	0.99999965	5.2224E-6	4.3266E-7	5.5555E-14	0
3	0.99999907	5.4213E-4	6.4234E-6	5.5611E-13	4.4244E-28
4	0.99824213	0.00175787	2.2231E-6	3.5245E-12	5.4421E-14
5	0.99721311	0.00278623	9.6532E-5	3.4443E-12	6.5333E-8
6	0.98932155	0.01067845	4.55432E-5	3.2213E-11	4.3342E-9
7	0.97321113	0.02678887	2.66543E-5	5.4431E-10	5.4321E-10
8	0.96553221	0.03446779	4.2211E-4	4.3321E-10	6.4321E-11
9	0.9012125	0.09846637	3.2113E-4	2.2214E-9	3.3321E-12
10	0.8732134	0.12647337	3.1323E-4	2.2211E-9	4.4442E-13
11	0.54332134	0.45637656	3.021E-4	1.2213E-9	6.5532E-14
12	0.29775421	0.70011445	0.00213134	5.443E-8	5.4442E-17
13	0.08221299	0.85246513	0.06532188	3.4243E-8	4.2211E-20

From the intersection of feedstock point X_F, it can be seen that ethylene oxide is fed from the 6th layer, and the theoretical tower plate is: (14-1)=13 Layer. The content of light component water gradually decreases from the top to the bottom of the tower, the content of heavy component diethylene glycol gradually increases, and the content of ethylene oxide is very small. The liquid phase flow trend is in line with the law of distillation tower, the whole tower operation is relatively stable, and the separation effect of each plate is relatively obvious, with 92.5 per cent ethylene glycol selectivity.

3.4. Design of Dehydration Tower

3.4.1 Dehydration tower simple calculation

Reaction distillation tower discharge: glycol: 46364.115kg/h Water: 335.05kg/h Diethylene glycol: 8446.874kg/h, Tower top pressure: 0.015Mpa, Tower bottom pressure: 0.0313Mpa, that is, reduced-pressure operation, requiring light key components of water in the tower top of the recovery rate of not less than 99.9%, and heavy key components of ethylene glycol recovery rate of not more than 0.001%.

3.4.2 Dehydration tower plate calculation

Selection of reflux ratio: After simulation, the correlation between reflux ratio and product sensitivity is shown in Fig.2 below.

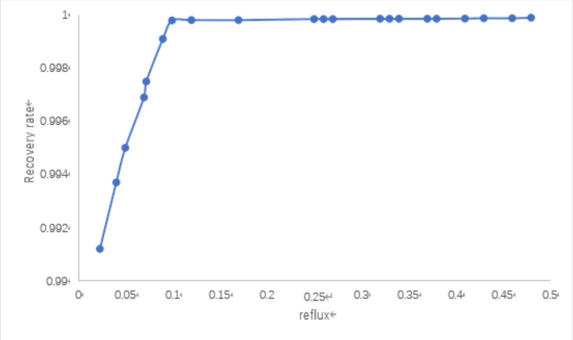

Figure 2. Plot of reflux ratio versus product sensitivity

It can be seen that when the reflux ratio is greater than 0.9 the recovery rate of ethylene glycol has not changed significantly [6] Selected reflux ratio R=0.923.

Feed stock temperature selection: when the feedstock temperature is too large, the product recovery rate decreases and the condenser heat load at the top of the tower will rise, energy consumption is large, so the selection of the feedstock temperature should not be more than 49℃, we choose: 48.8℃.

The whole tower is calculated and shown in Table 8 below:

Table 8. Calculation list of the whole tower of dehydration tower

Plate number	Water	Ethylene glycol	Diethylene glycol
1	0.9901	0.0097	1.7826E-16
2	0.5924	0.4075	3.1132E-14
3	0.3359	0.6640	1.0243E-12
4	0.2619	0.7380	4.1118E-11
5	0.1911	0.8088	7.3524E-10
6	0.1789	0.8210	2.5849E-8
7	0.1778	0.8221	1.2653E-6
8	0.1735	0.8216	0.0047
9	0.1730	0.8185	0.0083
10	0.1718	0.7306	0.0954
11	0.1729	0.7316	0.0954
12	0.1728	0.7316	0.0954
13	0.1728	0.7317	0.0954
14	0.1727	0.7317	0.0954
15	0.1697	0.7347	0.0954
16	0.1692	0.7320	0.0987

Judging the point of intersection with X_F, we can see that the feedstock layer is in the 10th layer, the theoretical number of plates is set at 19, and the liquid phase concentration distribution is shown in Fig.3 below.

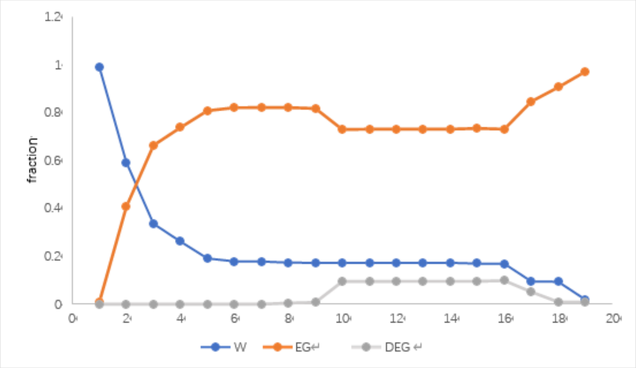

Figure 3. Liquid phase distribution of the whole tower of the dehydration tower calculation

It can be seen that the content of light component water is very high at the top of the tower, and the content gradually decreases from the top to the bottom of the tower, while the content of heavy component ethylene glycol gradually increases from the top to the bottom of the tower. Finally, the molar content of water at the bottom of the tower is not higher than 0.001%, and the separation effect is good.

In summary, the relevant parameters of the dehydration tower will be shown in the Table 9:

Table 9. Dehydration tower related parameters list

Projects	Theoretical number of plates/block	Feed stock plate/block	Feedstock temperature/℃	Reflux ratio	Recovery rate
Numbers	19	10	48.8	0.923	0.2381

4. Other Design Calculations And Equipment Selection

4.1. Reactive Distillation Column Design

4.1.1 Distillation column size

Inner pot size: 589.2mm Outer diameter size: 258.2mm

Head selection oval head: D_N=1900mm curved edge height h_1=450mm straight edge height h_2=60mm. h_3=450+60=510mm inner surface area A=3,587m^2.

H_3=450+60=510mm Inner surface area A=3.587m^2.

4.1.2 Selection of mixing device

To avoid swirl phenomenon, a six-blade turbine is used. Wheel diameter D/T=1/4 and blade width W=1/10T; Blade length L=1/4D Fluid depth H/t 2.39/2.4=0.99m Number of baffles=5 [11].

4.2. Enriching Section Piping Calculations And Sizing

Feedstock volume flow rate: 4.55m^3/h, selected flow rate: 0.2m/s then feedstock pipe diameter d=0.09m.

Output volume flow rate: 3.857m^3/h then output pipe diameter d=0.08m.

According to GB 17395-2008 seamless steel pipe, the material is Q345, select the outer diameter of 114mm, wall thickness of 5mm seamless steel pipe, i.e., Φ114×5mm, nominal diameter D_i=1400mm, so the jacket diameter $D_j=D_i+100=1400+100=1500$mm, nominal pressure P_N=6Mpa. [12]

Calculate the height of the jacket:

$Hj>(\varphi Va-V_{head})/V_{lm}=(0.8\times1.35-0.4795)/1.502=0.4m$

So the height of jacket cylinder is: 0.4+0.45=0.85m

Va-volume given by process calculation, m^3
V_{head}-volume of lower head of tank, m^3
V_{1m}-1m high cylinder volume, m^3
φ-charging coefficient, take 0.8 here.

5. Conclusion

Calculations were carried out to obtain the plate parameters for each tower to obtain a better production efficiency. Theoretical number of plates for reactive distillation columns, dehydration columns, and refining columns are 13, 19, and 20, respectively. The relevant plate parameters for each tower are shown in Table 10 below.

Table 10. List of tower layer parameters

Reactive distillation columns

Theoretical plate count	feedstock plate	Feedstock temperature
13	Ethylene oxide: 6 Water: 2	35℃

dewatering tower

Theoretical plate count	feedstock plate	Feedstock temperature
19	10	48.8℃

distillation tower

Theoretical plate count	feedstock plate
20	5

According to the above Table 10, the appropriate feed point feed as well as the appropriate feed temperature and plate pressure are selected for the production of ethylene glycol with high production efficiency and without the use of catalyst.

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