

Design and simulation of Mono Ethylene Glycol recovery unit from effluent waste of Morvarid petrochemical Company-Iran

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Abstract: - Oil price and its products together with environment issues results in increasing the attention toward waste recycling of different chemical and petrochemical sectors. In this study, separating and recycling Glycols family from Salt/water impurities in Morvarid Petrochemical Sector has been investigated. The petrochemical company did not considered any special unit to recovery its wastes and it seems necessary to design a new unit for recycling valuable products from wastes. To do so, Aspen Hysis simulation software has been used to design and optimize the process of separating glycols from water/salt solutions. Sensitivity Analysis has been performed on simulation model to optimize the process. The results show that MEG, DEG, TEG, TTEG can be recycled to the system with the flow rate of 5.01, 2.039, 0.062 and 0.089 respectively.

Keywords: Glycol, Aspen, Water, Salt, Distillation

I. INTRODUCTION

Polyhydroxy compounds such as glycols and glycerol are difficult and expensive to recover from aqueous solution because of their high boiling points and affinity towards water. Propylene glycol (1,2-propanediol, PG) and ethylene glycol (1,2-ethanediol, EG) are commodity chemicals produced via hydration of their respective epoxides in aqueous solution. In order to obtain pure PG and EG from aqueous solution, water must be boiled off; the energy utilized in this process constitutes a substantial portion of the cost of recovery. Vacuum distillation is often used to lower temperatures and thus avoid formation of undesired polyglycols and decomposition products and to reduce energy cost.

Feng et al. [1] used pervaporation with chitosan membranes for separation of water from ethylene glycol by a chitosan/polysulfone composite membrane. It was shown that conditioning of the membrane in the pervaporation system at the maximum operating temperature led to a quasi-permanent change in membrane permselectivity. Huang et al.[2] studied Pervaporation separation of ethylene glycol aqueous solutions using sulfonated poly(ether ether ketone) homogeneous membranes. Membrane relaxation in separation processes was observed and alleviated by heat treatment. The heat-treated pervaporation membranes experience further relaxation in the separation process by the swelling interactions of the feed mixtures before steady-state transport is reached. Membrane performance is investigated in terms of sorption and pervaporation separation.

Dhale et al. [3] investigate the recovery of PG and EG from water via acetal formation in bench- and pilot-scale continuous RD columns using cationic exchange resins as catalysts. Hydrolysis of acetals to recover the purified glycols is also studied using the same columns. Initial studies were carried out on the bench-scale column; based on these experimental findings, scale-up studies were performed on a larger pilot-scale unit. Along with experimentation, simulation of PG acetalization was performed using the RADFRAC module of Aspen Plus 11.1 process simulation software. Simulation of commercial-scale acetal formation from PG shows that complete PG recovery from aqueous solution is possible using a reasonably sized (25 stage) RD column. Mohammadi and Akbarabadi [4] presented the feasibility of VMD for concentration of ethylene glycol (EG) from a used coolant liquid. VMD experiments were performed with water-EG mixtures using a flat-sheet polypropylene membrane at various temperatures and recirculation rates. Results show that the membrane almost completely rejects EG and the desired concentration was achieved.

Guo et al. [5] investigated dehydration of ethylene glycol (EG) aqueous solution by pervaporation by surface crosslinked poly(vinyl alcohol) membrane using glutaraldehyde as crosslinking reagent. The membrane shows desirable thermal stability, mechanical stability and pervaporation performance (for 80 wt.% EG aqueous solution at 70 °C).

KHARG MEG plant is one of Iranian large glycol production unit with annual capacity is based on 7920 on stream production hours per year. Unfortunately, the plant waste including salt/water/glycols are not recycled to the system and instead, are disposed to the environment. In this study, we will try to study the feasibility of glycols recovery from the plant waste. To do so, Aspen Simulation Software will be used.

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II. PROCESS DESCRIPTION

Three different waste streams exist in the Plant. The inlet streams for the process were: NaHCO_3 and a mixture of glycols and water. The basis for the simulation was 764 kg/h of mixture, condition that was obtained from plant waste. The specification of these streams are:

Table 1. Feed streams specification

Name	Feed 1	Feed 2	Feed 3
Temperature (C)	120/4	166/9	186/1
Pressure (bar)	1/42	1/420	1/420
Vapor Frac	0	0	0
Mole Flow (kmol/hr)	13	4	0/18
Mass Flow (kg/hr)	416	317	31
MEG (kg/h)	212/2	99/9	0
DEG (kg/h)	0	208/7	0
TEG (kg/h)	0	0	13/1
TTEG (kg/h)	0	0	18/1
H_2O (kg/h)	166/6	0/1	0
NaHCO_3 (kg/h)	37/7	8/4	0

All the work was developed using Aspen Plus Simulator, version 8.6. Activity coefficient calculations for the mixture were made with the NRTL thermodynamic model for electrolytes systems [6-7]. In Figure 1 the flowsheet of the system on which the simulation was run is shown.

The arrangement has a first separation column to which a salt/water/glycols solution is fed on one of the middle stages. As overhead product, in the separation column, water/glycols mixture is obtained, and as bottom product a mixture of water- NaHCO_3 is withdrawn. This mixture is taken to a heat exchanger for increasing its temperature to 119 °C, and then fed to water-glycols separation column in order to separate water from the glycols. Glycols have been collected from the bottom of column and sent to glycols separation columns. MEG, DEG, TEG and TTEG will be separated in turn respectively.

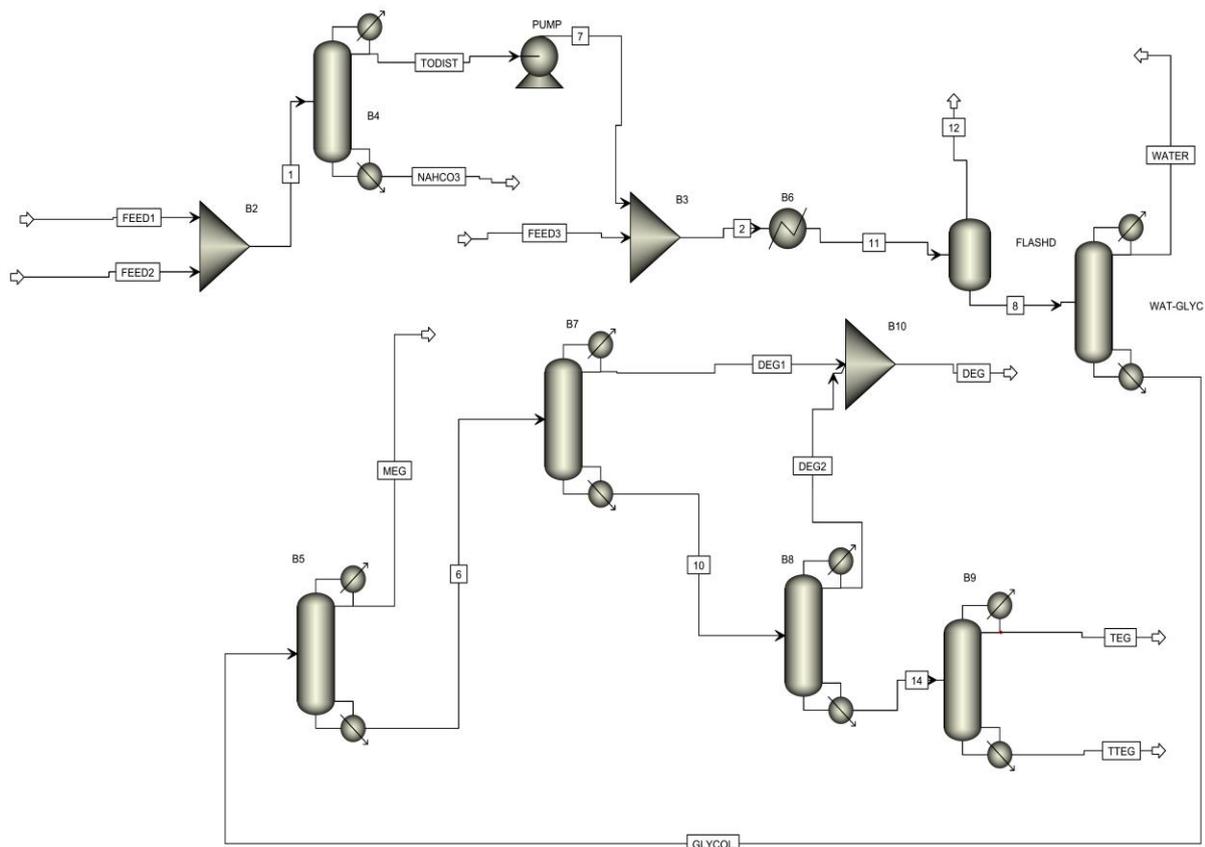


Figure 1. Process flowsheet

III. PROCESS SIMULATION

a) Thermodynamic Model

Initially, the thermodynamic model was validated calculating the vapor-liquid pseudo-binary equilibrium in the Aspen Split simulator by Aspen Tech.

For a binary mixture the following equations are used:

$$\begin{cases} \ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \\ \ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \end{cases} \quad (1)$$

With:

$$\begin{cases} \ln G_{12} = -\alpha_{12} \tau_{12} \\ \ln G_{21} = -\alpha_{21} \tau_{21} \end{cases} \quad (2)$$

In here τ_{12} and τ_{21} are the dimensionless interaction parameters, which are related to the interaction energy parameters Δg_{12} and Δg_{21} by:

$$\begin{cases} \tau_{12} = \frac{\Delta g_{12}}{RT} = \frac{U_{12} - U_{22}}{RT} \\ \tau_{21} = \frac{\Delta g_{21}}{RT} = \frac{U_{21} - U_{11}}{RT} \end{cases} \quad (3)$$

Here R is the gas constant and T the absolute temperature, and U_{ij} is the energy between molecular surface i and j. U_{ii} is the energy of evaporation. Here U_{ij} has to be equal to U_{ji} , but Δg_{ij} is not necessary equal to Δg_{ji} .

The parameters α_{12} and α_{21} are the so-called non-randomness parameter, for which usually α_{12} is set equal to α_{21} . For a liquid, in which the local distribution is random around the center molecule, the parameter $\alpha_{12} = 0$. In that case the equations reduce to the one-parameter Margules activity model:

$$\begin{cases} \ln \gamma_1 = x_2^2 [\tau_{21} + \tau_{12}] = Ax_2^2 \\ \ln \gamma_2 = x_1^2 [\tau_{12} + \tau_{21}] = Ax_1^2 \end{cases} \quad (4)$$

In practice, α_{12} is set to 0.2, 0.3 or 0.48. The latter value is frequently used for aqueous systems. The high value reflects the ordered structure caused by hydrogen bonds. However in the description of liquid-liquid equilibria the non-randomness parameter is set to 0.2 to avoid wrong liquid-liquid description. In some cases a better phase equilibria description is obtained by setting $\alpha_{12} = -1$. However this mathematical solution is impossible from a physical point of view, since no system can be more random than random ($\alpha_{12} = 0$). In general NRTL offers more flexibility in the description of phase equilibria than other activity models due to the extra non-randomness parameters. However in practice this flexibility is reduced in order to avoid wrong equilibrium description outside the range of regressed data [8-10].

b) Configuration

In this work the reflux ratio, number of theoretical stages required for the separation, feed temperature, were evaluated. Operating parameters of columns were presented in Table 2. When the model was prepared, sensitivity analyses were made and it was possible to visualize the effect of different variables on a specific design condition by observing different plots. The efficient operating criteria considered were: energy consumption of the reboilers for each column and the distillate composition in the glycols columns, which should be 99% molar of glycols. The bottom pressure should be lower than 0.01bar to avoid thermal problems of the first column.

Table 2. Operating parameters of columns

	B4	WATER-GLYCOL	B5	B7	B8	B9
Calculation type	Equilibrium	Equilibrium	Equilibrium	Equilibrium	Equilibrium	Equilibrium
Number of stage	10	17	20	20	20	20
Condenser	Total	Total	Total	Total	Total	Total
Reboiler	Kettle	Kettle	Kettle	Kettle	Kettle	Kettle
Valid phases	Vapor-Liquid	Vapor-Liquid	Vapor-Liquid	Vapor-Liquid	Vapor-Liquid	Vapor-Liquid
Convergence	Standard	Standard	Standard	Standard	Standard	Standard
Reflux ratio(Mass)	0/1	0/6	5/01	1/95	0.89	0.62
Bottoms ratio(kmole/hr)	0/55	7/2	1/5	5	5	3

IV. RESULTS AND DISCUSSION

4-1- Water-Glycol Column:

Figure 2 shows the temperature profile for water-glycol separation column at different pressure. As found from this figure, increasing column pressure will increase reboiler duty. Figure 3 shows the reboiler and condenser duty at different pressure. Base on the figure, although increasing pressure will lead to increasing boiler duty, it will decrease condenser duty. This is attributed to the fact that increasing pressure will ease liquid condensing and as a result, decreasing condenser duty.

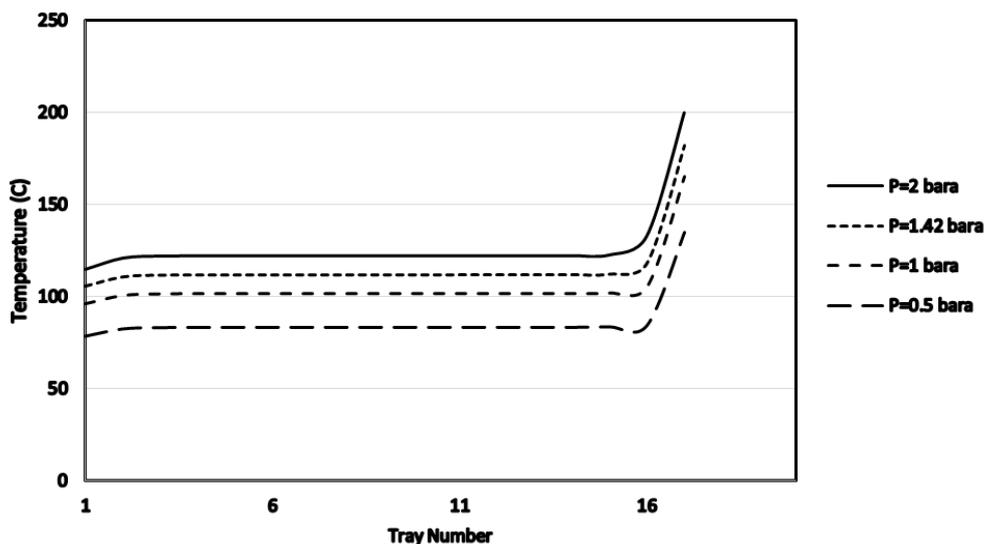


Figure 2. Temperature profile for water-glycol separation column

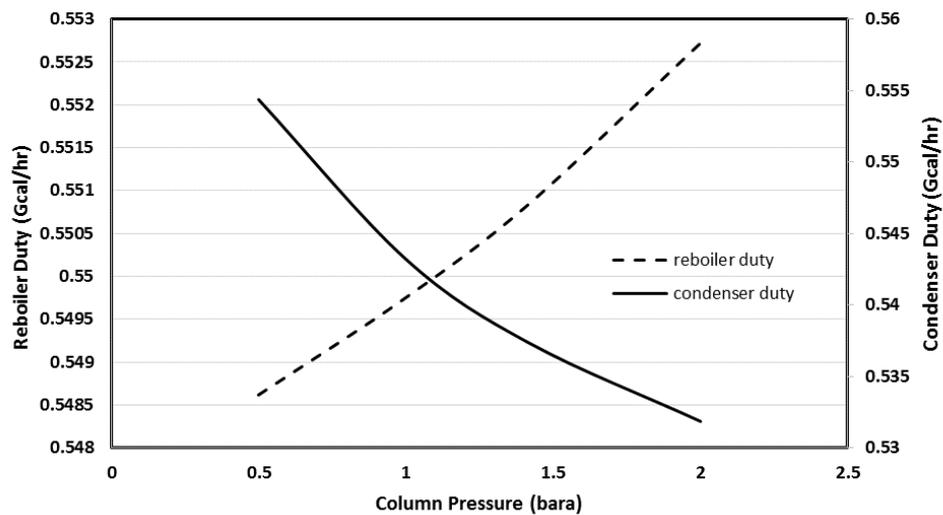


Figure 3. Reboiler and condenser duty for water-glycol separation column

Reflux ratio is another important factor which its effect on column performance must be investigated. As shown in figure 4, increasing reflux ratio improves products quality but increase reboiler and condenser duty. Since the overhead product is water and there is no need to improve its purity, increasing reflux ratio is not recommended.

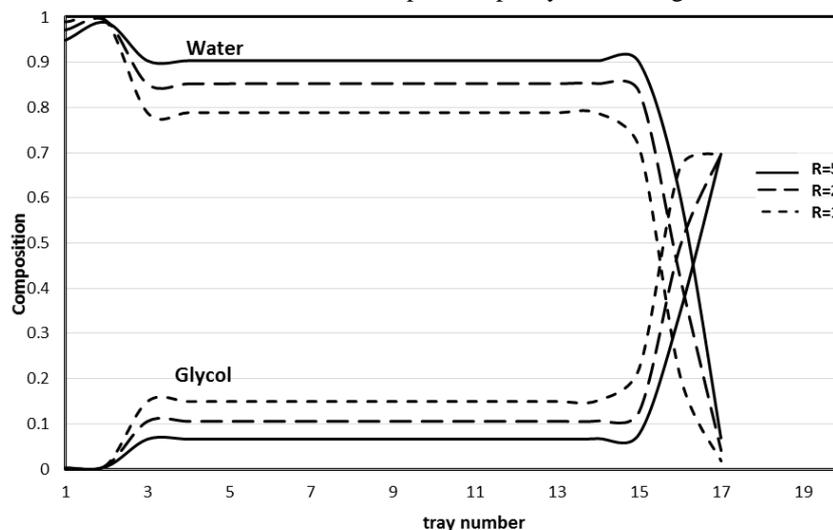


Figure 4. Products profile variation with reflux ratio on each tray in water-glycol separation column

4-2- MEG separation:

Figure 5 shows temperature profile for MEG separation column. As the same with water-glycol separation column, increasing pressure will increase column temperature and as result increases reboiler duty and decreases condenser duty (figure 6).

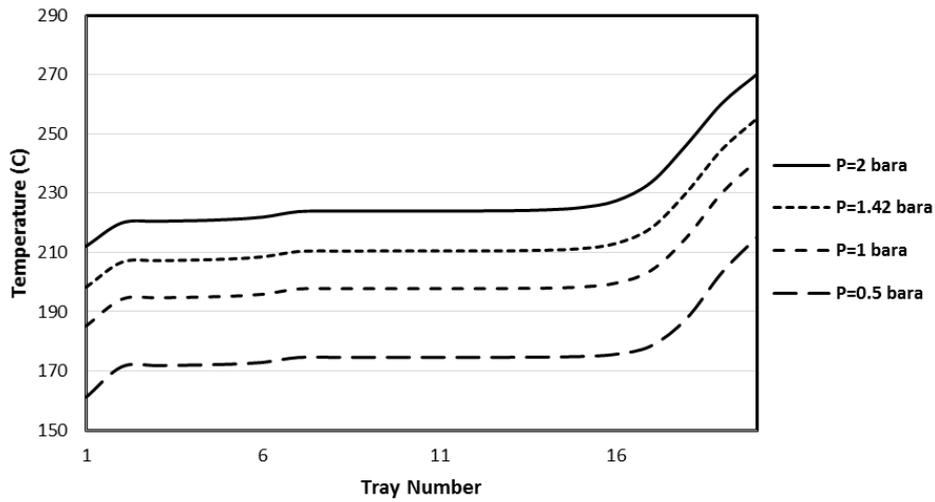


Figure 5. Temperature profile for MEG separation column

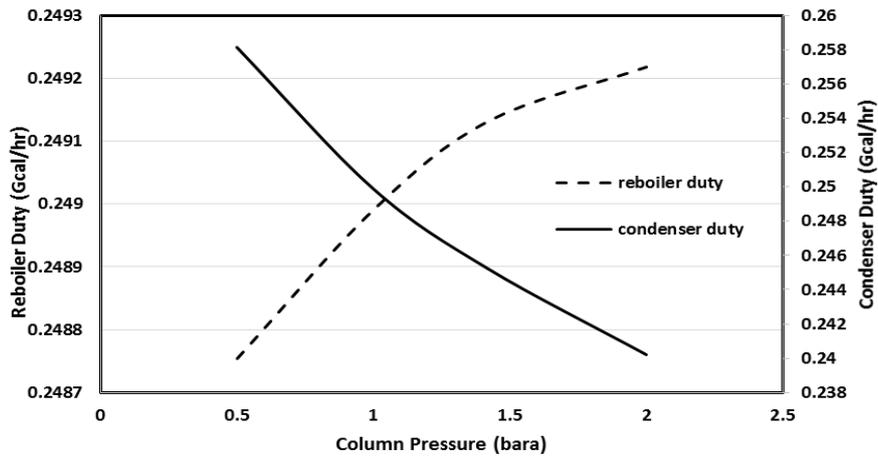


Figure 6. Reboiler and condenser duty for MEG separation column

Figure 7 shows that increasing reflux ratio will result in product with higher purity. At the same time, the required energy and operational cost due to the reboiler and condenser duty. Optimum value of 1.5 was selected for MEG column separation.

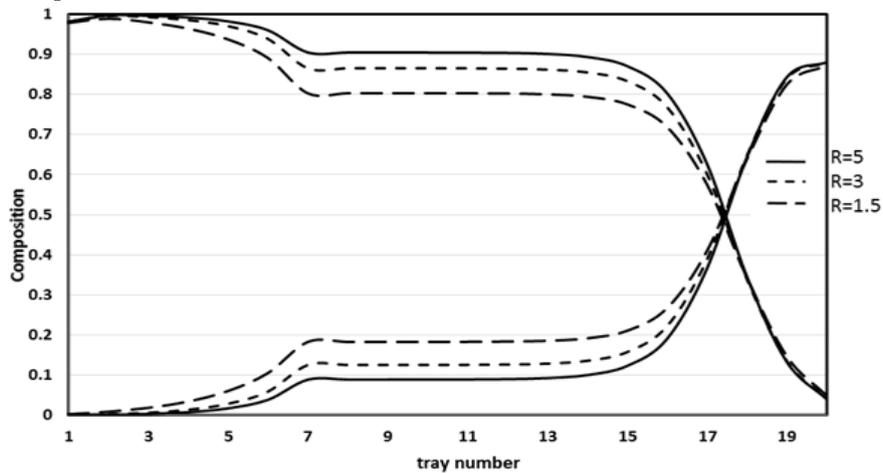


Figure 7. Products profile variation with reflux ratio on each tray in MEG separation column

4-3- DEG separation columns:

To distillation column were considered for DEG separation since it was not possible to separate DEG from other remaining glycols completely. Figure 8 shows temperature profile for columns at different pressures. As found from the figure, the same trend can be observed for the columns with previous columns in which increasing pressure results in higher temperature at each tray. The only difference condition at these columns is that increasing pressure results in decreasing reboiler duty. As the figures 9 show, the columns work under 1 bara pressure. Although higher pressure leads to lower reboiler duty but higher tray temperature compared to lower pressure, it must be considered that higher temperature degrades glycols and decrease process efficiency. Therefore it is logical to set column pressure at lower value.

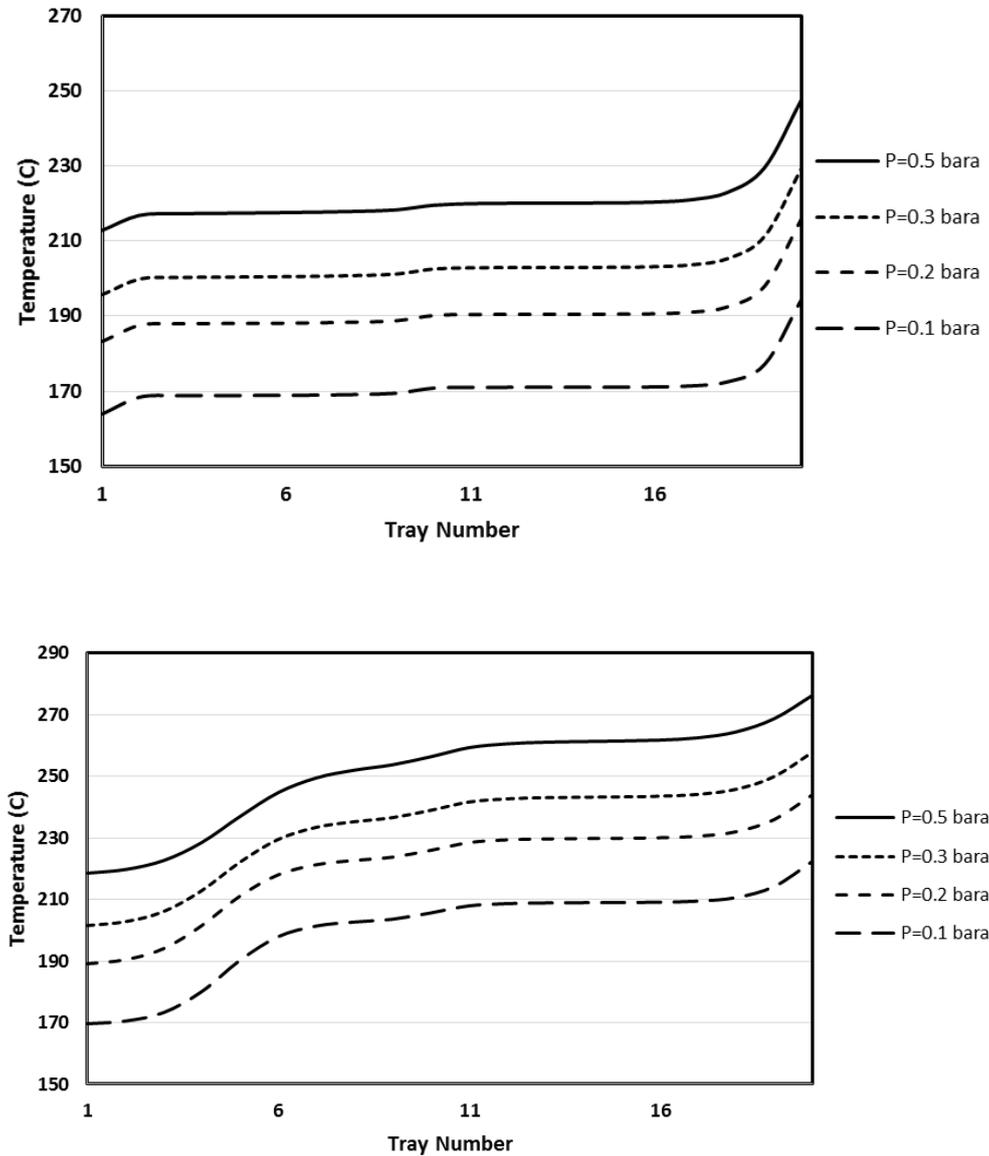


Figure 8. Temperature profile for DEG-1 and DEG-2 separation columns

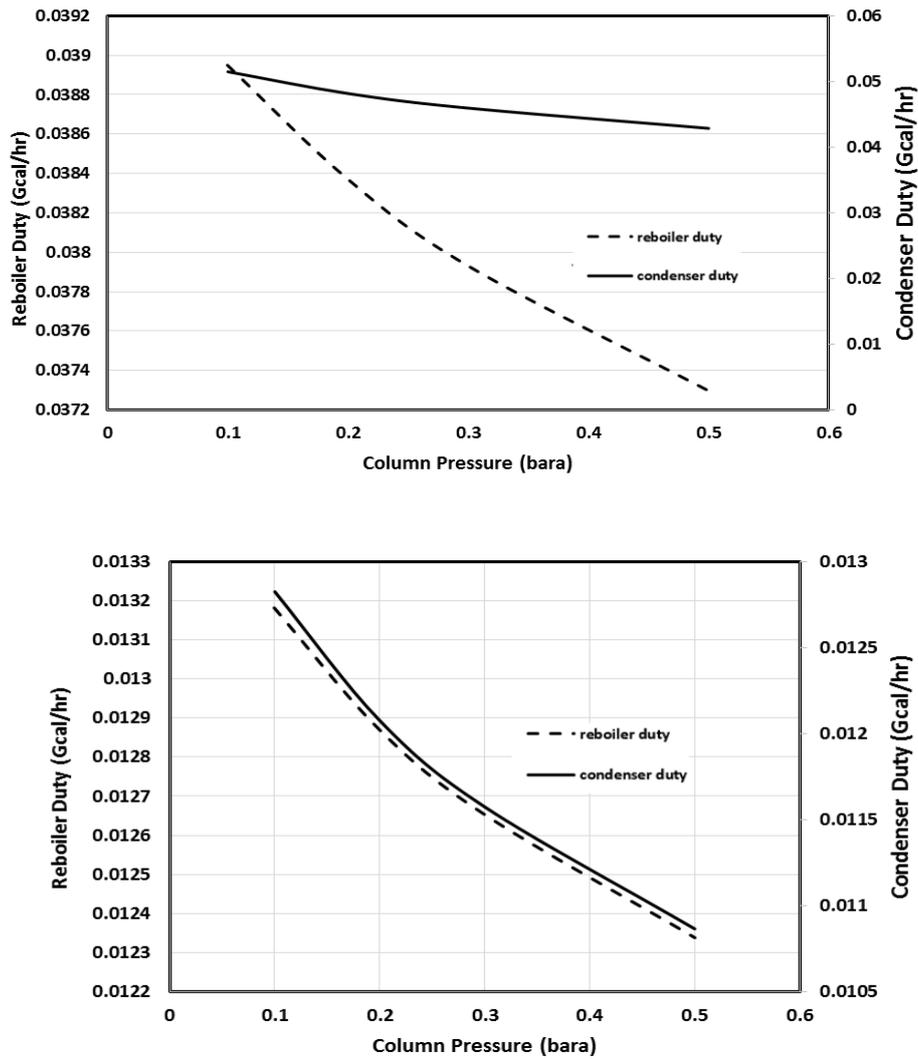
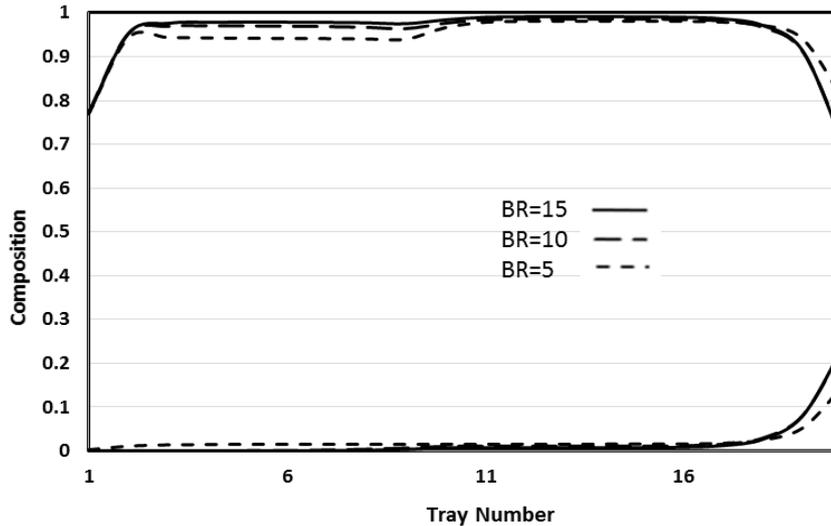


Figure 9. Reboiler and condenser duty for DEG-1 and DEG-2 separation columns

Comparing different boilup ratios shows that it has no effect on products quality. Optimum boilup ratio was set to 5 for this column.



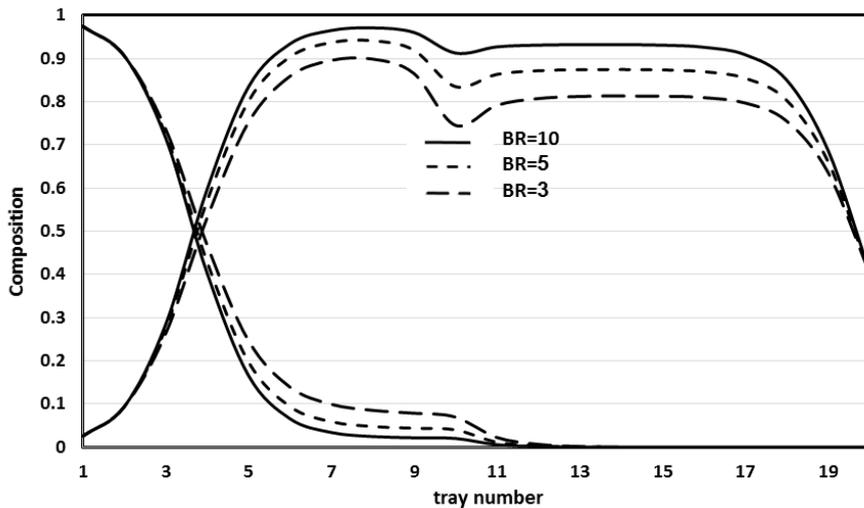


Figure 10. Products profile variation with boilup ratio on each tray in water-glycol separation column

4-4- TEG and TTEG column:

Overhead product of the last column is TEG and the bottom product will be TTEG. Figure 11 shows temperature profile for this column. As seen in this figure, increasing pressure will increase temperature in each tray but increase reboiler duty (Figure 12). The increased temperature will degrade glycols which is not an appropriate step in column modification.

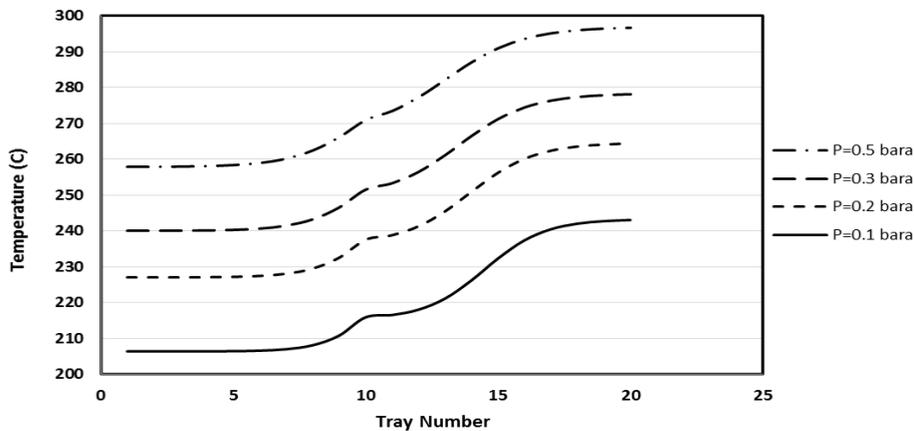


Figure 11. Temperature profile for TEG-TTEG separation column

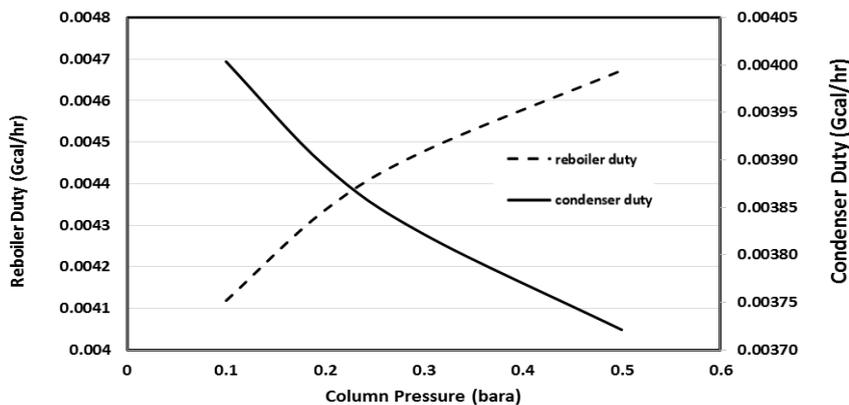


Figure 12. Reboiler and condenser duty for TEG-TTEG separation column

Figure 13 shows reflux ratio variation effect on column performance. As figure shows increasing reflux ratio increases products purity but will increase thermal duty. The optimum reflux ratio was selected 3 for this column.

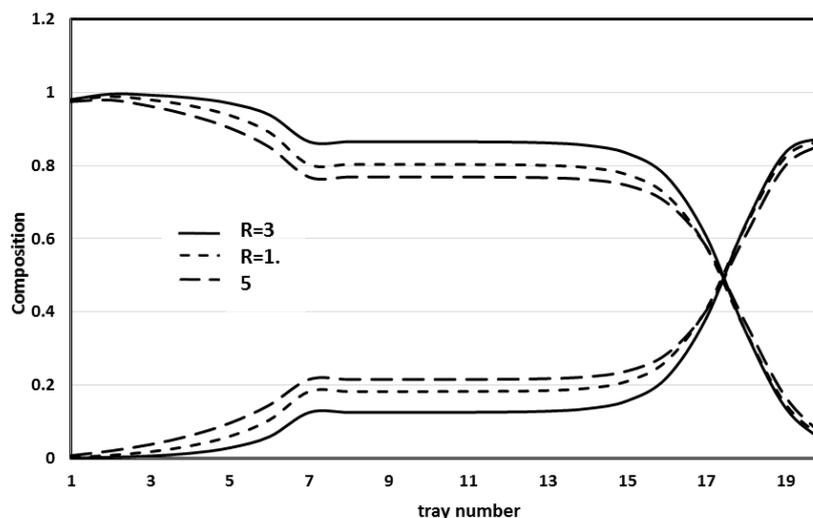


Figure 13. Products profile variation with reflux ratio on each tray in TEG-TTEG separation column After optimizing all columns performance, the results show that MEG, DEG, TEG, TTEG can be recycled to the system with the flow rate of 5.01, 2.039, 0.062 and 0.089 respectively.

V. CONCLUSION

In this study, we investigate a process system for the separation of water/salt/glycols mixture. Aspen Plus simulator was used to model the process. After optimizing all columns performance, the results show that MEG, DEG, TEG, TTEG can be recycled to the system with the flow rate of 5.01, 2.039, 0.062 and 0.089 respectively.

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