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METHYL ACETATE REACTIVE DISTILLATION PROCESS MODELING, SIMULATION AND OPTIMIZATION USING ASPEN PLUS

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ABSTRACT

The modeling, simulation, and optimization of the reactive distillation esterification process used for the production of methyl acetate have been carried out in this work with the aid of Aspen PLUS. The Aspen PLUS reactive distillation process model was developed and simulated using RadFrac packed column the rectification and the stripping sections of which were filled with Raschig Type packing of dimension 25 mm and the reaction section of which was filled with Sigma Type packing material of 10 mm dimension. In addition, Non-Random Two-Liquid property method, volumetric feed rates of both acetic acid and methanol of 0.03 L/min, feed temperature and pressure of 25 ^{o}C and 1 atm respectively were used. The optimization of the process was accomplished using the Optimization Section of Model Analysis Tools of Aspen PLUS. The good convergence obtained from the simulation of the developed Aspen PLUS model of the reactive distillation process has shown the versatility of Aspen PLUS in successfully representing the behavior of the complex reactive distillation process used for methyl acetate production. Furthermore, the achievement of the value of the objective function given by the optimization of the process when the estimated optimum values of reflux ratio and reboiler duty were used to run the developed model revealed that the optimum values obtained from Aspen PLUS were valid ones.

Keywords: reactive distillation, methyl acetate, aspen PLUS, modeling, simulation, optimization.

1. INTRODUCTION

Methyl acetate, also known as MeOAc, acetic acid methyl ester or methyl ethanoate, is a carboxylate ester with the formula CH_3COOCH_3. It is a flammable liquid with a characteristically pleasant smell reminiscent of some glues and nail polish removers. Methyl acetate is occasionally used as a solvent, being weakly polar and lipophilic, even though its close relative, ethyl acetate, is a more common solvent being less toxic and less soluble in water. Methyl acetate has a solubility of 25% in water at room temperature. At elevated temperature, its solubility in water is much higher. Methyl acetate is not stable in the presence of strong aqueous bases or aqueous acids. It is volatile organic compound (VOC) exempt (Wicks *et al*., 2007).

Methyl acetate is produced industrially via the carbonylation of methanol as a byproduct of the production of acetic acid (Cheung *et al*., 2002). It also arises from esterification of acetic acid with methanol in the presence of strong acids such as sulfuric acid. The last-mentioned methyl acetate production process is very famous because of Eastman Kodak's intensified process using a reactive distillation.

Reactive distillation is a process that combines both separation and chemical reaction in a single unit. It is sometimes an excellent alternative to conventional flowsheets with separate reaction and separation sections (Al-Arfaj and Luyben, 2002a; Giwa and Karacan, 2012b; Giwa, 2013). It has been used in a small number of industrial applications for many years, but the last decade has shown an increase in both its research and applications (Al-Arfaj and Luyben, 2002b). In applying reactive distillation, the volatilities of the components must be such that products can be removed and reactants retained inside the column. The temperature levels for both reaction and vapor-liquid equilibrium must overlap (Al-Arfaj and Luyben, 2002a). By carrying out chemical reaction and separation in one process, the operating and investment costs can be minimized. Some additional benefits offered by reactive distillation technology include (Prakash *et al*., 2011): (i) increased yield, because of overcoming chemical and thermodynamic equilibrium limitations, (ii) improved selectivity via suppression of side reactions, (iii) reduced energy consumption, due to effective utilization of reaction heat, in the case of exothermic reactions, (iv) avoidance of hot spots by simultaneous liquid evaporation, and (v) ability to separate close boiling components. Due to these advantages and with growing process understanding, the chemical process industry has developed an increasing number of processes based on reactive distillation (Bock *et al*., 1997). However, reactive distillation is not extensively used in industry since it is perceived that its operation will always be more difficult and will pose higher requirements on the quality of the design than the conventional flow sheet in which a reactor is typically followed by a train of distillation columns. This behavior is mainly attributed to the complex interactions between the underlying physical phenomena taking place in reactive columns, having a significant influence on the robust operation of the system (Giwa and Karacan, 2012b). As such, the determination of the optimum conditions required for the smooth operation of this process must be carefully carried out.

According to the information obtained from the literature concerning the optimization of reactive distillation process, it was discovered that Giwa and Karacan (2012a) used Aspen HYSYS to optimize ethyl acetate reactive packed distillation process and they were able to obtain results from the Aspen HYSYS model of the process that compared well with the experimental ones.

Also, Giwa and Giwa (2012) used Design Expert and Excel Solver to optimize a reactive distillation process used for the production of n-butyl acetate, modeled with Aspen HYSYS, and they obtained results that were reliable, based on the reproducibility of the obtained objective function by the model. Furthermore, Giwa and Giwa (2013) used Aspen HYSYS model to represent a reactive distillation process used to produce isopropyl myristate, optimized the process using Response Surface Methodology and MATLAB and obtained valid optimum values of the process.

In this work, the optimum recycle ratio and reboiler duty required for the operation of methyl acetate reactive distillation process using the esterification reaction between acetic acid and methanol as the process type have been determined with the aid of Aspen PLUS.

2. PROCEDURES

2.1. Modeling

The model of the reactive distillation process used for the production of methyl acetate from the esterification reaction between acetic acid and methanol, developed with the aid of Aspen PLUS (Aspen, 2011) is as shown in Figure-1 below. In the development of the model, RadFrac packed column and Non-Random Two-Liquid (NRTL) property method were employed. The rectification and the stripping sections of the column were filled with Raschig Type packing of dimension 25 mm while the reaction section was filled with Sigma Type packing material of 10 mm in dimension.

The esterification reaction occurring in the column was modeled as an equilibrium type and it is given as shown in Equation (1) below.

$$CH_3COOH + CH_3OH \xleftrightarrow{K_{eq}} CH_3COOCH_3 + H_2O \quad (1)$$

The phase of the reaction was liquid and the basis of the equilibrium constant (K_{eq}) calculated from Gibbs free energy was taken to be molarity. The reaction was allowed to take place between segments 8 and 15 of the main column as well as in the reboiler.

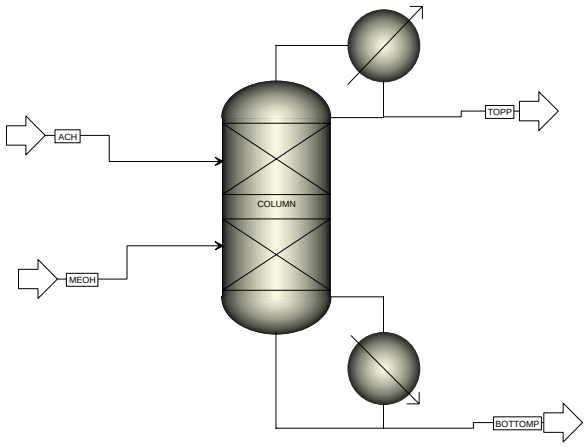

Figure-1. Methyl acetate production process Aspen PLUS model.

2.2. Simulation

After the model was developed, it was simulated in Aspen PLUS environment. The simulation of the developed Aspen PLUS model of the esterification process used for the production of methyl acetate and water (by-product) was carried using acetic acid (99% mole basis pure) feed rate of 0.03 L/min, methanol (99% mole basis pure) feed rate of 0.03 L/min, reflux ratio of 1 and reboiler duty of 700 Watt. Also, the temperature and pressure of both feeds were 25 ^oC and 1 atm, respectively.

2.3. Optimization

At the end of model development and simulation, it (the model) was thereafter optimized using the Optimization Section of Model Analysis Tools of Aspen PLUS. The manipulated variables of the optimization were the reflux ratio and the reboiler duty of the model while the objective function was the maximization of the mole fraction of methyl acetate in the top product of the column. The limits of the manipulated variables used in the optimization of the process are as given in Table-1 below.

Table-1. Limits of manipulated variables of the process.

S/N	Manipulated variable	Limit	
		Lower	Upper
1	Reflux ratio (kmol min^{-1} liquid distillate / kmol min^{-1} recycled liquid)	1	9
2	Reboiler duty (Watt)	100	700

3. RESULTS AND DISCUSSIONS

The temperature profile of the simulation carried out for the production of methyl acetate (desired product) and water (by-product) using the esterification reaction between acetic acid and methanol, with the aid of Aspen PLUS, is given in Figure-2. From the figure, it was discovered that, as expected, the temperature of the condenser was less than that of the reboiler. However, during the simulation, very high temperature of the column was observed at the reaction section of the column. The high temperature observed at the reaction section was as a result of the exothermic nature of the esterification reaction taking place there.

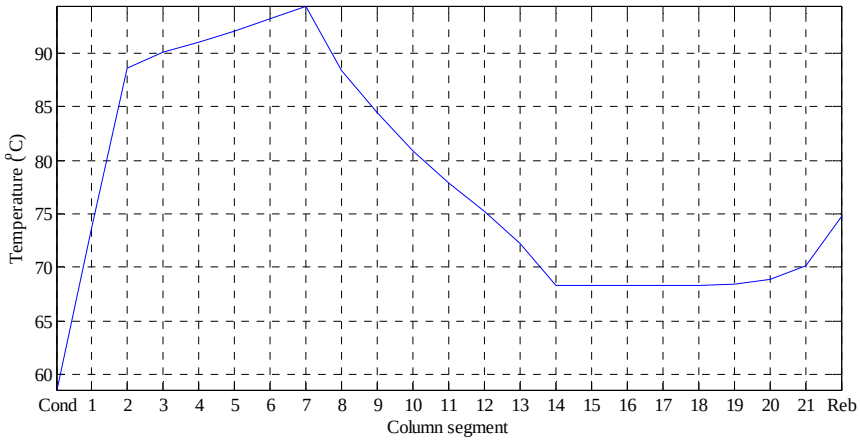

Figure-2. Temperature profile of methyl acetate reactive distillation process simulation.

Figure-3 shows the composition profiles of the components (acetic acid, methanol, methyl acetate and water) involved in the esterification process studied in this work. As can be seen from the figure, the mole fraction of acetic acid decreased from segment 7 down the column towards the bottom section. The reason for this decrease in the mole fraction of acetic acid downwards from segment 7 was due to the fact that it was one of the reactants and it was being consumed in the reaction section after it was fed into the column from the upper feed segment. The mole fraction of the other reactant (methanol) was found to decrease upward towards the top section of the column from the lower feed segment where it was fed. As can be observed, the two feeds involved in this process were fed into the reaction section of the column in a countercurrent manner to each other and their mole fractions in the reaction section also decreased countercurrently to each other. It was also discovered from the composition profiles shown in Figure-3 that the desired product, which is methyl acetate, had the highest mole fraction (0.6531) at the top segment (condenser) while the by-product of the process (water) had the highest mole fraction (0.5713) at the bottom segment (reboiler) of the column. The presence of higher percentage of methyl acetate at the top segment of the column was as a result of the difference in the physical properties of the components (see Table-A1 given in the Appendix).

It was found from the simulation carried out that the desired product (methyl acetate) and acetic acid were not present in the reboiler. The absence of acetic acid in the reboiler was an indication that, with respect to acetic acid, total conversion was occurring in the reboiler. In addition, acetic acid, as a result of its absence from some segments of the reaction section down to the reboiler, can be said to be the key reactant of the simulation of the esterification reaction studied in this work because it was totally consumed in both the reaction section and in the reboiler whereas the other reactant (methanol) was not totally consumed.

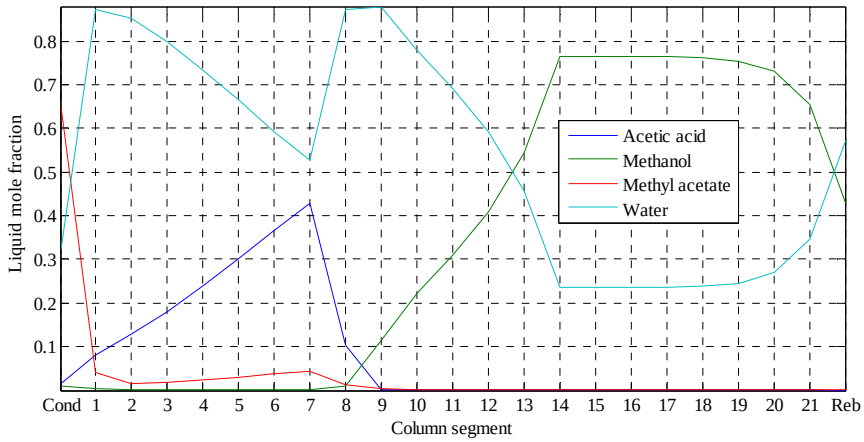

Figure-3. Composition profiles of methyl acetate reactive distillation process simulation.

Shown in Figure-4 below is the molecular weight profile of the liquid from each segment of the column. As can be seen from the Figure, the molecular weight of the liquid leaving the condenser segment of the column had

the highest value. The lowest molecular weight of the mixture involved in the reactive distillation process studied in this work was that of the liquid leaving the ninth segment of the column. This ninth segment was found to correspond to one of the segments of the reaction section of the column.

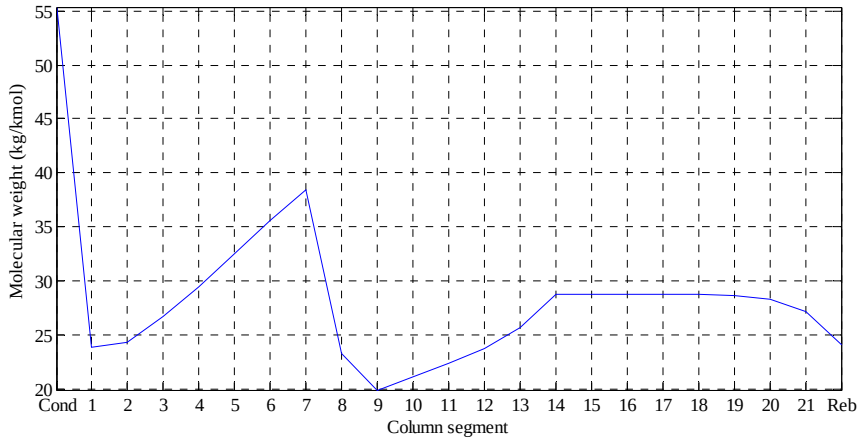

Figure-4. Molecular weight profile of methyl acetate reactive distillation process simulation.

Apart from considering the molecular weight of the liquid leaving each segment of the column (molecular weight profile shown in Figure-4), the density profile of the liquid mixture of the process was also investigated by plotting the density of the liquid leaving each of the column segment against the column segment number, as shown in Figure-5. As can be seen from Figure-5, the liquid leaving the segment below the condenser of the column (segment 1 of the main column) had the highest density value. The densities of the liquid leaving the different segments of the rectification section were not too different from one another, but a drastic decrease in the density profile was observed from the liquid present in the reaction section. The drastic change in the density of the process liquid mixture in the reaction section was as a result of the consumption of the components owing to the reaction occurring there (in the reaction section). Looking at the figure very well, it was discovered that the lowest-density liquid mixture of this process was found in the stripping section of the column.

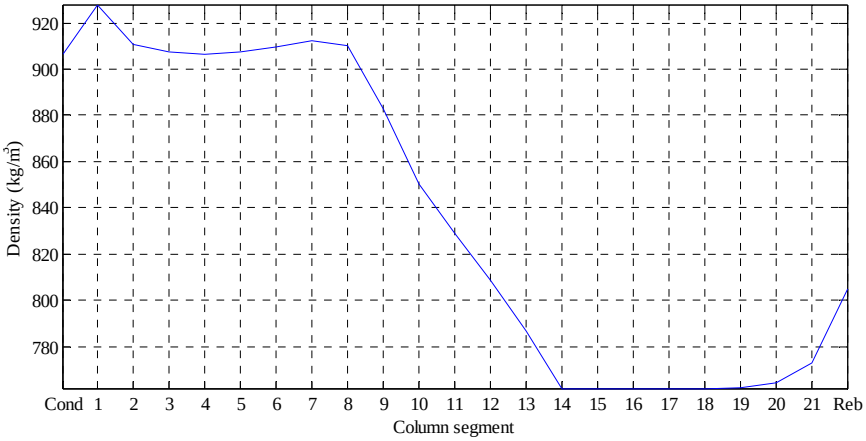

Figure-5. Density of methyl acetate reactive distillation process simulation.

From the results of the simulation of the esterification process used for the production of methyl acetate, the maximum mole fraction of methyl acetate (desired product) obtained at the top segment was found to be 0.6531. Actually, that was a good value, but it was the desired to obtain a better purity of the desired product, probably greater than the one obtained from the simulation. As such, the Optimization Section contained in the Model Analysis Tools of Aspen PLUS was used to optimize the mole fraction of methyl acetate found at the top segment (condenser) of the column.

The results obtained from the optimization revealed that a mole fraction value of 0.9873 of methyl acetate could be obtained from the process by using the optimum reflux ratio of approximately 13 and the optimum reboiler duty of 100 Watt. The obtained value

(0.9873) of mole fraction of methyl acetate was actually very encouraging and, thus, the obtained optimum values of reflux ratio and reboiler duty were used to simulate the process in order to ascertain the validity of the optimization carried out. The results obtain from the simulation carried out in Aspen PLUS environment using the obtained optimum values are given and discussed thus.

Shown in Figure-6 is the temperature profile obtained from the simulation carried out using the optimum reflux ratio and reboiler duty. As can be seen from the figure, as was obtained from the former temperature profile (Figure-2) of the simulation of the process, the temperature of the reboiler was found to be higher than that of the condenser. However, comparing Figures 2 and 6, the trends of the temperature profiles obtained from the optimized simulation (Figure-6) and that of the ordinary simulation (Figure-2) were found not to be similar. Also, close to what was discovered from the temperature profile obtained from the ordinary simulation of the process (see Figure-2), very high temperature (in fact, in this case, the maximum temperature) of the column was found to occur in the reaction section of the column (see Figure-6).

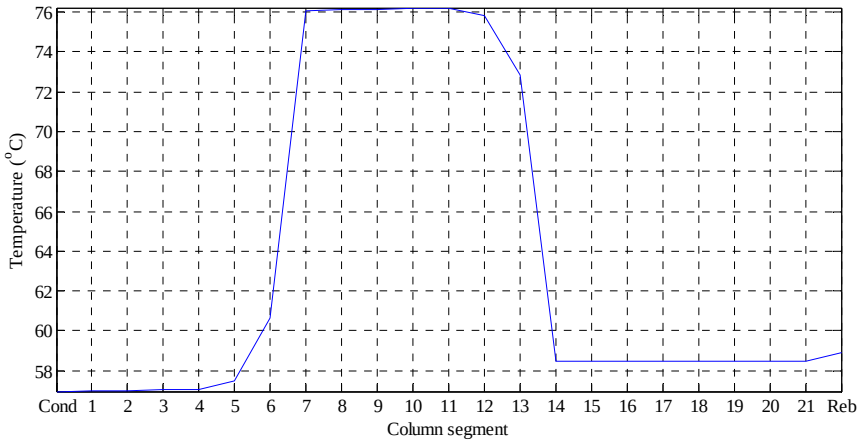

Figure-6. Temperature profile of methyl acetate reactive distillation process optimization.

Considering the composition profiles shown in Figure-7, it was found that the trend of each of the profiles obtained for each of the components from the optimized simulation was different from each of the ones (see Figure-3) obtained, before, from the ordinary simulation of the process. Among the important thing that can be seen from Figure-7 is that the mole fraction of the desired product (methyl acetate) has now changed from the steady state simulation value of 0.6531 to the optimized simulation value of 0.9874. Also, the mole fractions of the reactants as well as those of the other components were not zero in the reboiler, in this case, contrary to the observation made before from the ordinary simulation of the process. This was an indication that, in the optimized simulation, with respect to acetic acid, there was no total reaction conversion. In fact, according to Figure-7, in the optimized simulation case, the reaction conversion was found to be better with respect to methanol, especially in the reaction section, because the mole fraction of methanol present in the middle of the reaction section of the column was approximately zero.

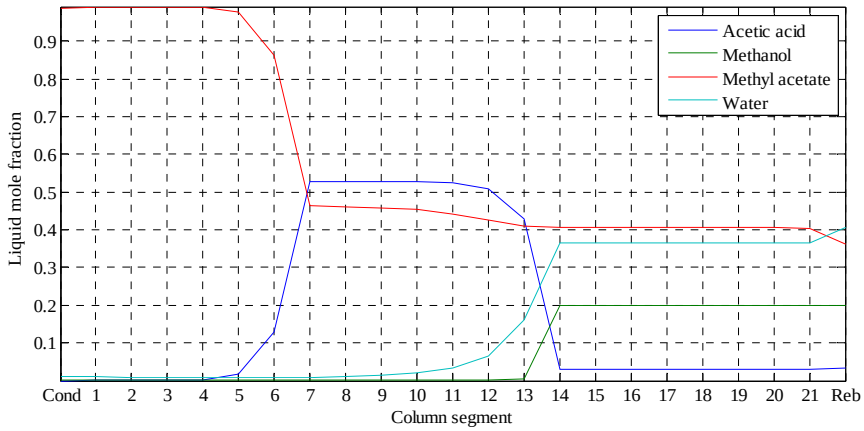

Figure-7. Composition profiles of methyl acetate reactive distillation process optimization.

In Figure-8, the profile of the molecular weight of the liquid mixture leaving each segment of the column during the optimized simulation of the process is shown. As can be seen from the figure, the liquid mixture at the upper part of the column had the highest molecular weight while the molecular weight of the liquid in the reboiler was the lowest. This observation was also found to be contrary to what was observed from the results of the ordinary simulation of the process. Thus, the general trends of the two Figures (Figure-4 and Figure-8) were found to be entirely different. It was also noticed from Figure-8 that the molecular weight of the liquid at the very upper part as well as at the stripping section of the column was approximately constant.

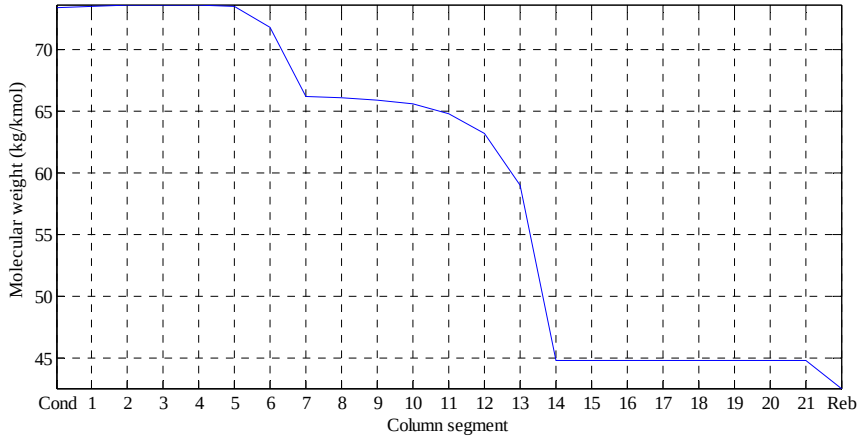

Figure-8. Molecular weight profile of methyl acetate reactive distillation process optimization.

The density profile, shown in Figure-9, obtained from the optimized simulation of the reactive distillation process used for the production of methyl acetate revealed that the density of the liquid mixture present at the top segment of the column was lower than that of the one present at the reboiler. In addition, the liquid density of the optimized simulation was found to be approximately constant at the very upper part of the column and, also, at the stripping section down to the reboiler section of the column.

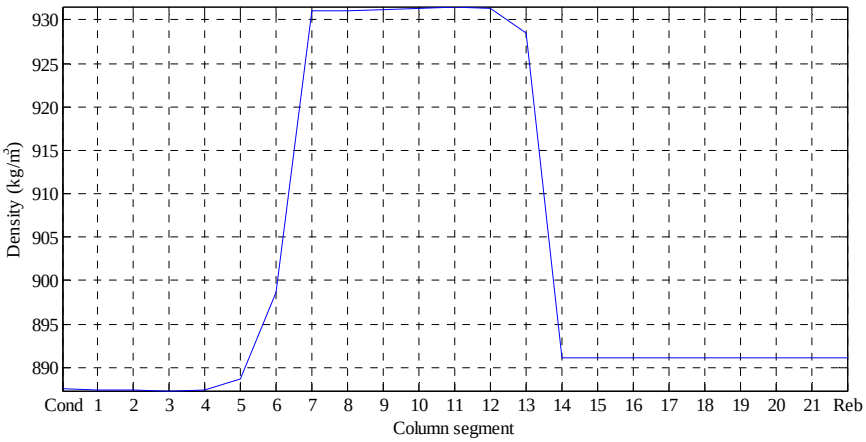

Figure-9. Density of methyl acetate reactive distillation process optimization.

The approximate constant nature of the density profile observed at the very upper part and at the stripping sections of the column down to the reboiler was attributed to the fact that, in almost those parts of the column, the temperature, the mole fractions of the components, and the molecular weight of the liquid mixture in the column were constant. This, of course, meant that little or no operation/process occurred at that part of the column during the simulation of the reactive distillation process investigated in this work.

4. CONCLUSIONS

The good convergence obtained from the simulation of the Aspen PLUS model developed for the reactive distillation esterification process used for the production of methyl acetate has shown the versatility of Aspen PLUS in successfully representing the behavior of

the complex reactive distillation process. The attainment of the objective function given by the optimization when the estimated optimum values of reflux ratio and reboiler duty were used to run the model revealed that the optimum values obtained from Aspen PLUS were valid ones.

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Nomenclatures

ACH	Acetic acid
BOTTOMP	Bottom product
Cond	Condenser
K_{eq}	Equilibrium constant
MEOH	Methanol
NRTL	Non-Random Two-Liquid
Reb	Reboiler
TOPP	Top product

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APPENDIX

Table-A1. Some physical properties of the components of the process (Aspen, 2011).

Component	**Molecular weight** (kg/kmol)	**Boiling point** (^oC)	**Density** (kg/m^3)
Acetic acid	60.0526	117.9000	1055.3000
Methanol	32.0422	64.7000	796.2000
Methyl acetate	74.0794	56.9400	930.3770
Water	18.0153	100.0000	1000.0000