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STEADY-STATE MODELING OF N-BUTYL ACETATE TRANSESTERIFICATION PROCESS USING ASPEN PLUS: CONVENTIONAL VERSUS INTEGRATED

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ABSTRACT

This work has been carried out to compare the performances of conventional system and integrated one using the transesterification process between n-butanol and ethyl acetate for the production of n-butyl acetate and ethanol as the case study. The transesterification process was modeled using Aspen PLUS by choosing the reaction involved as an equilibrium type and using UNIQUAC model as the base property method. The reaction was allowed to take place in a liquid phase at the atmospheric pressure and a temperature of $75^{o}C$. The conventional system consisted of a mixer, a reactor and a distillation column while the integrated one comprised a mixer and a distillation column the middle of which was used as the reactor. The results obtained from the simulation have proven that the integrated system was better than the conventional one because the integrated system was able to give higher conversion and higher product purities. The optimization of the integrated system gave an optimum value of reflux ratio to be 3.1 and the maximum value of n-butyl acetate mole fraction that was obtained at the bottom segment to be 0.9990. Therefore, for the transesterification process that was used for the production of n-butyl acetate and ethanol, the integrated system has been proved to be more efficient than the conventional one.

Keywords: n-butyl acetate, transesterification, aspen PLUS modeling, conventional system, integrated system.

1. INTRODUCTION

n-Butyl acetate is transparent liquid that is widely used as an organic solvent, an extraction solvent and a dehydrant in industries (He *et al*., 2010). It is also used in large quantities in the manufacture of coatings and other branches of chemical industry. In spite of modern trends towards elimination of volatile solvents, consumption of butyl acetate is expected to grow in near future because of its lower impact on environment, compared to some other types of solvents (Hanika *et al*., 1999). Owing to its lower impact on environment, n-butyl acetate is able to replace the toxic and teratogenic ethoxy ethyl acetate that is often used as a solvent (Steinigeweg and Gmehling, 2002).

Butyl acetate is commonly produced by esterification of acetic acid with butanol. Apart from the esterification process, n-butyl acetate can also be produced from transesterification process. The two processes are equilibrium types and they need to be catalyzed by strong acids. Sulphuric acid, p-toluenesulphonic acid or some solid acidic catalysts, e.g. ion exchangers, are usually used for this purpose (Hanika *et al*., 1999). In addition, either of the processes can be accomplished using either the conventional (reactor plus distillation) system or the integrated one (reactive distillation). It is of the opinion that the reactive distillation should be more advantageous than the conventional system in the production of n-butyl acetate.

Reactive distillation is a process that combines both separation and chemical reaction in a single unit. It is especially very attractive whenever conversion is limited by reaction equilibrium (Balasubramhanya and Doyle III, 2000) because it combines the benefits of equilibrium reaction with distillation to enhance conversion provided that the product of interest has the largest or the lowest boiling point (Taylor and Krishna, 2000). It has a lot of advantages which include reduced investment and operating costs due to increased yield of a reversible reaction by separating the product of interest from the reaction mixture (Pérez-Correa *et al*., 2008), higher conversion, improved selectivity, lower energy consumption, scope for difficult separations and avoidance of azeotropes (Jana and Adari, 2009).

The information gathered from the literature revealed that Lone and Ahmad (2012) carried out modeling and simulation of ethyl acetate reactive distillation column using Aspen Plus and concluded that reactive distillation was important from the economic point of view and hence it was preferred over the old conventional processes. Giwa and Karacan (2012) demonstrated the advantages of integrated systems over the conventional one by investigating, using the production of ethyl acetate as the case study, how to reduce global warming using process integration and they recommended to the industrial engineers to always integrate their processes, where possible, in order to contribute their quotas in reducing global warming. Dunn and Bush (2001) used process integration technology to demonstrate CLEANER (Combining Lower Emissions and Networked Energy Recovery) production and discovered that the technique did not only ensure compliance with all environmental regulations but also kept the cost of manufacturing products very low.

This work has been carried out to model, simulate and compare both the conventional and the integrated systems of the production of n-butyl acetate and ethanol from the transesterification reaction between ethyl acetate and n-butanol with the aid of Aspen PLUS. In addition, taking the n-butyl acetate bottom mole fraction as the

objective function, the better one among the two systems was optimized.

2. MODELING PROCEDURE

The Aspen PLUS (a market-leading process modeling environment for conceptual design, optimization, and performance monitoring for the chemical, polymer, specialty chemical, metals and minerals, and coal power industries (Aspen, 2012)) models used in this work are as shown in Figures 1 and 2,

respectively for the conventional system and integrated one and the data used to develop the models are as given in Table-1. As can be seen from Figure-1, the conventional system for the transesterification process composed of a mixer, a reactor and a distillation column while the integrated system shown in Figure-2 comprised just a mixer and a reactive distillation column. The equilibrium reaction of the transesterification process occurring in the systems is as given in Equation (1).
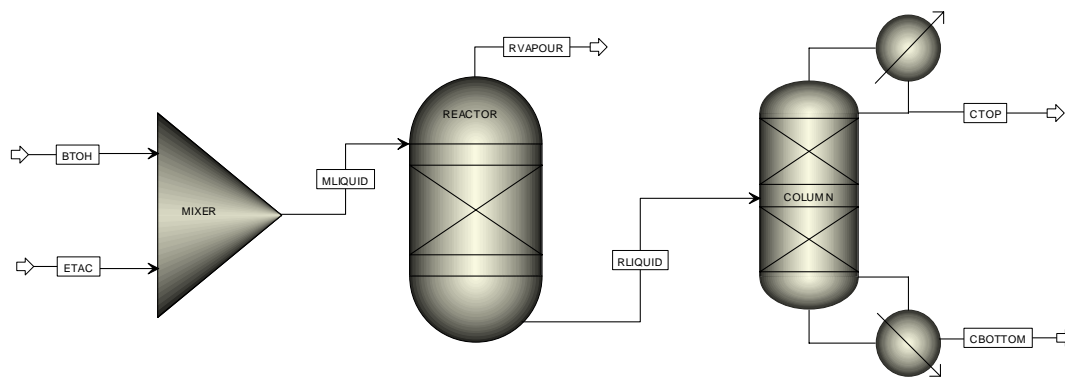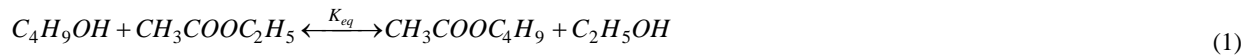
$$C_4H_9OH + CH_3COOC_2H_5 \xleftrightarrow{\;K_{eq}\;} CH_3COOC_4H_9 + C_2H_5OH \tag{1}$$

Figure-1. Conventional system for the production of n-butyl acetate by transesterification process.
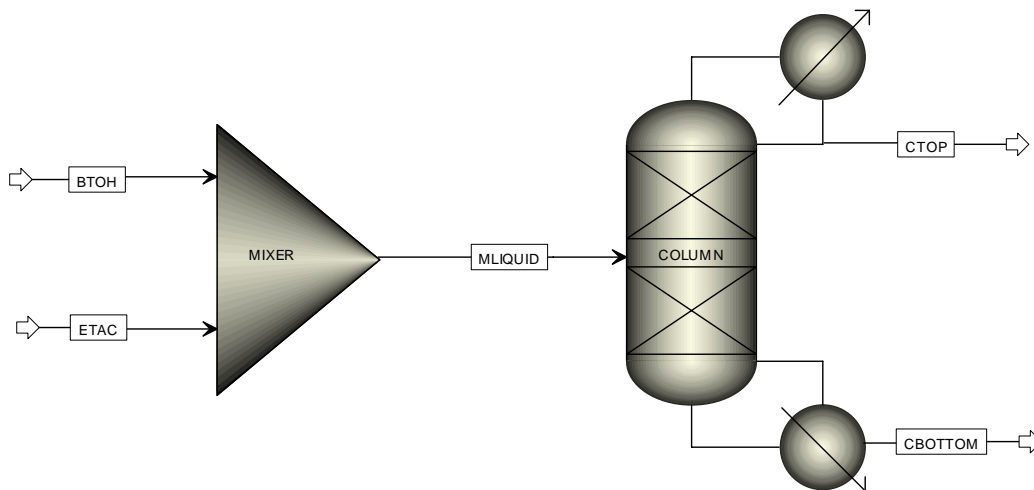

Figure-2. Integrated system for the production of n-butyl acetate by transesterification process.

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Table-1. Aspen PLUS steady-state model parameters.

	Conventional System	Integrated System
n-butanol feed		
Flow rate (L/min)	0.03	0.03
Temperature (^{o}C)	25	25
Pressure (atm)	1	1
Ethyl acetate feed		
Flow rate (L/min)	0.03	0.03
Temperature (^{o}C)	25	25
Pressure (atm)	1	1
Property system	UNIQUAC	UNIQUAC
Reaction		
Type	Equilibrium	Equilibrium
K_{eq} source	Temperature approach	Temperature approach
Valid phase	Liquid	Liquid
Temperature (^{o}C)	75	
Distillation column		
Type	RadFrac	RadFrac
No of segment	28	28
Feed segment	14	14
Reflux ratio	4	4
Reboiler duty (J/s)	1400	1400
Condenser type	Total	Total
Condenser pressure (atm)	1	1
Pressure drop (atm)	0	0

After carrying out the steady-state modeling of the transesterification process with the two systems (conventional and integrated), the better one between the two was optimized with the aid of Model Analysis Tool of Aspen PLUS using reflux ratio as the manipulated variable. The lower and upper limits used for the reflux ratio were 1 and 9, respectively. The objective function of the optimization was taken as the maximization of the n-butyl acetate liquid mole fraction present in the bottom segment of the column and Large-Scale Sequential Quadratic Programming (LSSQP) was used as the solver.

3. RESULTS AND DISCUSSIONS

The results obtained from the Aspen PLUS modeling of transesterification process for the production of n-butyl acetate using the conventional and the integrated systems (shown in Figures 2 and 3, respectively) are as shown in Figures 3-9 and the results of the optimization of the better one among the two systems are given in Figures 10-12.

Figure-3 shows the temperature profiles of the two systems (conventional and integrated). It was seen from the figure that the general trends of the two profiles were the same. Also observed from the figure was that the top segment temperature of the two systems were found to be very close to each because the top segment temperature of the conventional system was found to be 78.67^{o}C while that of the integrated one was 78.24^{o}C. It can be seen from the results of the top segment temperature that, even though the methods for the two systems were different, they were able to give the top segment temperatures that were close to each other. Considering the small magnitude of the difference between the top segment temperatures of the two systems, it was noticed that the top segment temperature of the conventional system was higher than that of the integrated one. This situation was not the same in the bottom segment (reboiler) where the temperature (122.76^{o}C) of the integrated system was found to be higher than that (120.08^{o}C) of the conventional one.
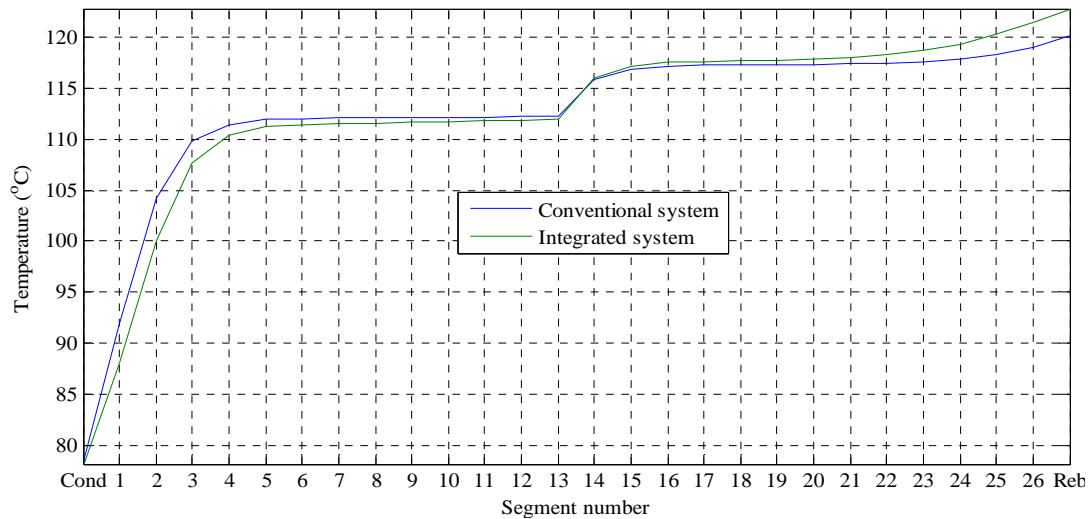
Figure-3. Temperature profiles of conventional and integrated processes for the production of n-butyl acetate.

Figure-4 shows the liquid composition profiles of the components involved in the transesterification process for the conventional system. As can be observed from the figure, the highest mole fraction (0.7190) of the desired product was found at the bottom segment of the column while that of the second product (ethanol) was discovered to be negligible at the bottom segment. However, the highest mole fraction (0.4621) of ethanol was obtained at the top segment of the column. It was also discovered from the results shown in Figure-4 that the conversion was not totally completed because some amounts of the reactants (n-butanol and ethyl acetate) were found at the top segment of the column while at the bottom segment, even though the amount of ethyl acetate present there was negligible, mole fraction of 0.2810 of the other reactant (n-butanol) was found to be present.
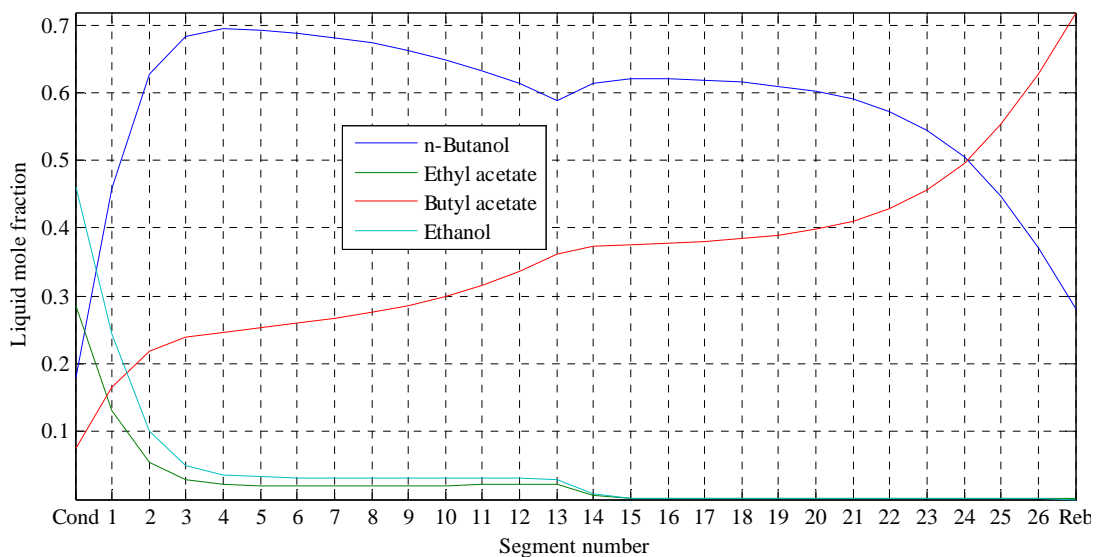

Figure-4. Composition profiles of conventional system for the production of n-butyl acetate.

Figure-5 shows the liquid composition profiles of the components involved in the transesterification process for the integrated system. For this system (integrated), the highest mole fraction (0.8723) of the desired product (n-butyl acetate) and that (0.6687) of the other product (ethanol) were obtained at the bottom and top segments of the column respectively. The presence of the highest mole fraction of n-butyl acetate at the bottom segment and that of the ethanol at the top segment of the column was found to be in agreement with was what observed in the case of the conventional system. In addition, as it was discovered in the case of the conventional system, the total conversion obtained in the integrated system was not 100% because unconverted n-butanol was found at the bottom segment and both unconverted n-butanol and ethyl acetate were found to be present at the top segment of the column.
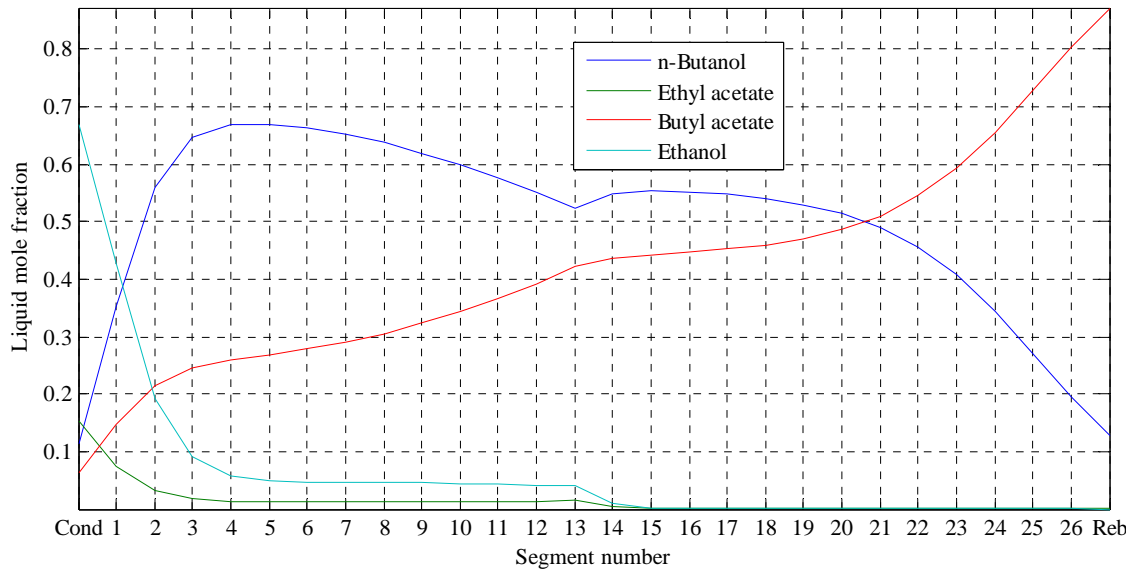
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Figure-5. Composition profiles of integrated system for the production of n-butyl acetate.

It can be observed from the results shown in Figures 4 and 5 that, for the two systems, while the mole fraction of the desired product (n-butyl acetate) was the highest at the bottom segment of the columns, that of the other product (ethanol) was found to be the highest at the top segment of the columns. This was due to the fact that the heaviest component of the process (as seen by considering the basic properties of the components given in Table-A1 in Appendix A) was n-butyl acetate and as such it was collected from the bottom of the column.

Using the liquid mole fractions of the components shown in Figures 4 and 5 separately and respectively for the conventional and integrated systems, the mole fraction profiles of each of the components for the two systems was compared as shown in Figures 6-9.

Figure-6 shows the comparison between n-butanol liquid mole fraction profiles obtained from the two systems. As can be seen from the Figure, the profiles of the liquid mole fraction of the two systems followed the same trend. According to the profiles, the lowest n-butanol liquid mole fractions of the two systems were found at the top segment of the column. Also noticed from the figure was that the liquid mole fractions of n-butanol present in both the top segment and the bottom segment of the column for the conventional system were higher than those of the integrated system. The presence of higher liquid mole fractions of n-butanol at the top and bottom segments of the column for the conventional system implied that the conversion obtained in terms of n-butanol from the integrated system was higher than that of the conventional system.
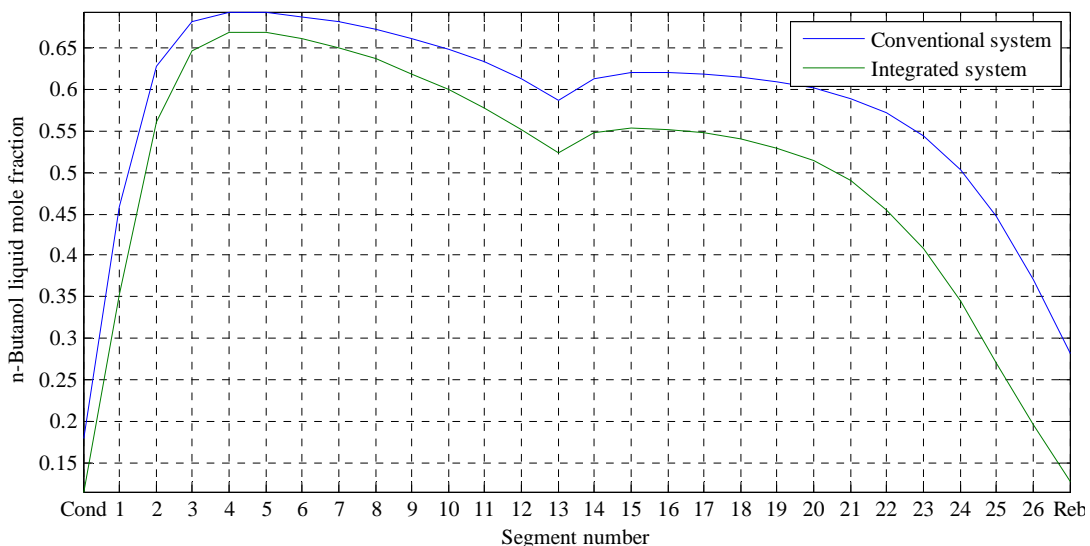

Figure-6. N-Butanol composition profiles of conventional and integrated systems for the production of n-butyl acetate.
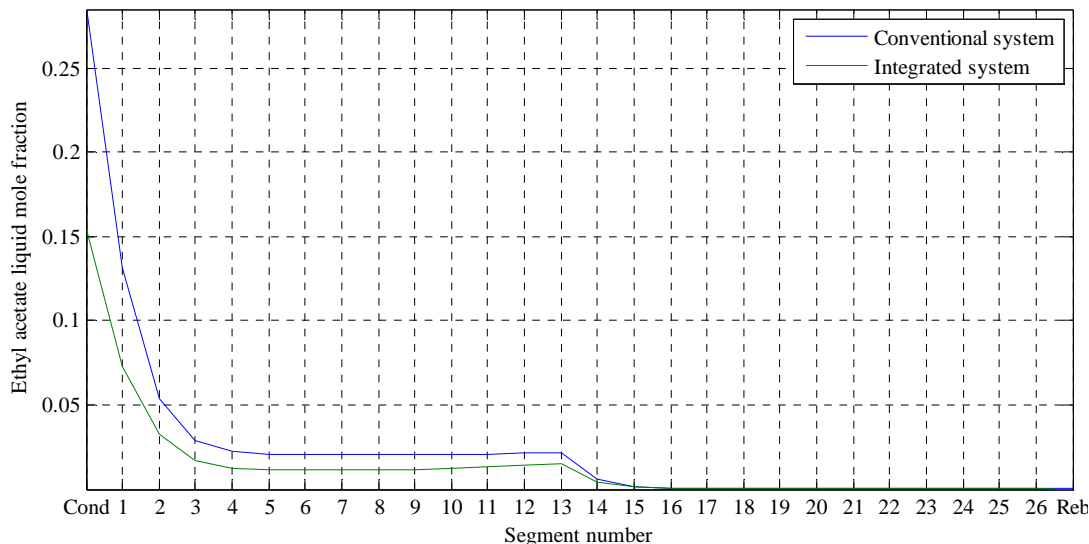
Figure-7. Ethyl acetate composition profiles of conventional and integrated systems for the production of n-butyl acetate.

The liquid mole fractions of ethyl acetate present at the segments of the column can be seen from Figure-7. It was discovered from the figure that the liquid mole fractions of ethyl acetate decreased downwards from the top segment towards the bottom segment for the two systems that were used in this work. The mole fraction of ethyl acetate present at the bottom segment were found to be very negligible for the two systems but that present at the top segment were not, for the two systems. Similar to what was observed at the top segment in the case of n-butanol (Figure-6), the amount of ethyl acetate that remained unconverted when the integrated system was used was found to be less than that of the conventional system. This is another indication of the fact that the

conversion obtained with the integrated system was higher than that of the conventional system.

After ascertaining the better conversion capability of the integrated system as compared to the conventional system for the transesterification process studied in this work, the purity of the desired product (n-butyl acetate) was investigated and plotted as shown in Figure-8. As can be seen from Figure-8, the mole fraction of n-butyl acetate obtained from the bottom segment of the column when the integrated system was employed was found to be higher than that of the conventional system. It was also discovered, for each of the systems used, that the amount of n-butyl acetate present at the top segment of the column was very small.
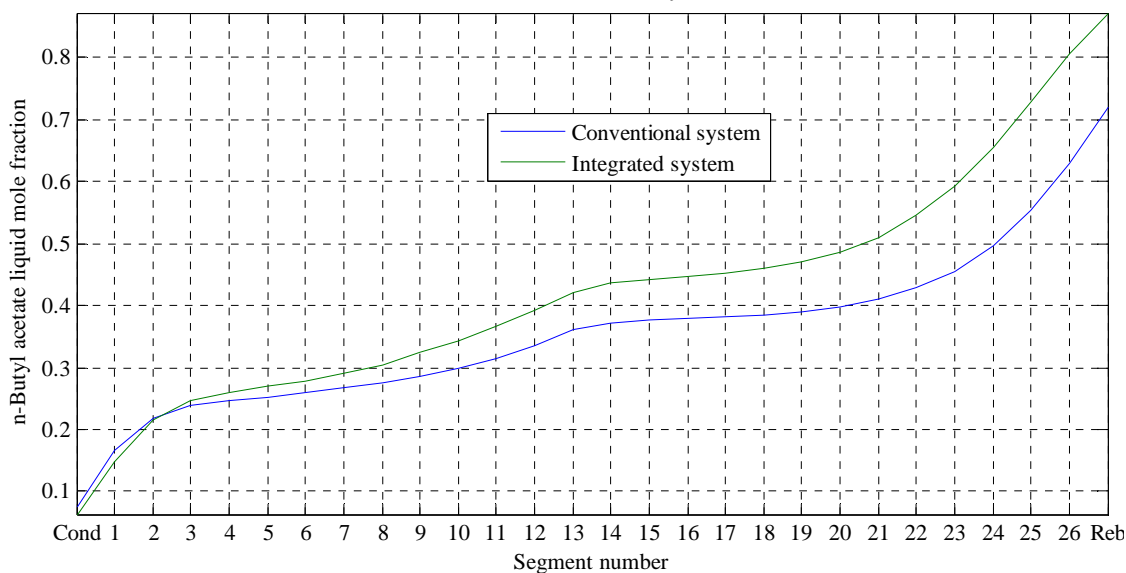

Figure-8. n-Butyl acetate composition profiles of conventional and integrated systems for the production of n-butyl acetate.
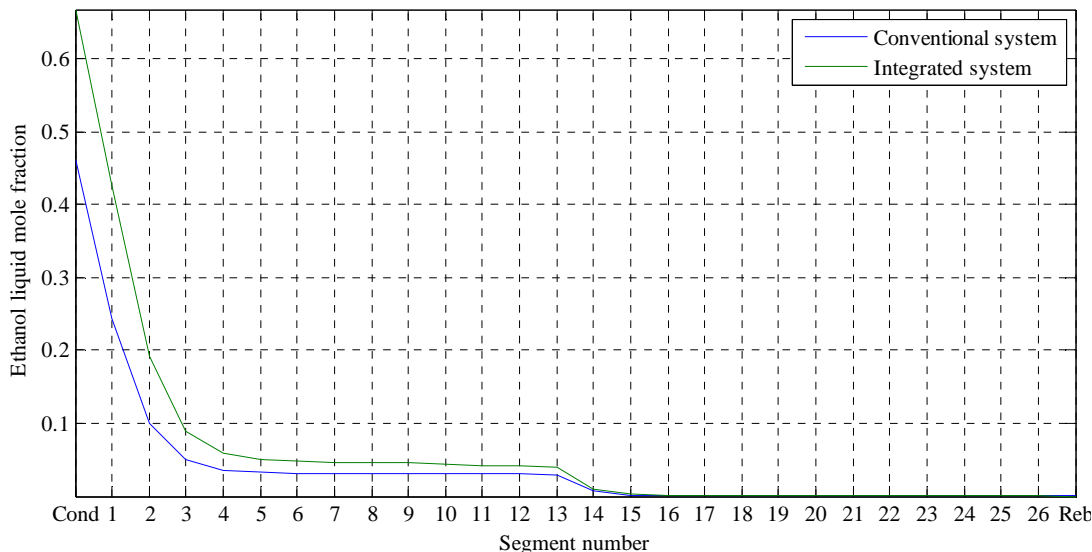
Figure-9. Ethanol composition profiles of conventional and integrated systems for the production of n-butyl acetate.

Beside the profiles of the desired product (n-butyl acetate) given above that were considered, the profiles (Figure-9) of the other product (ethanol) were also investigated and it was discovered that, in contrary to the case of the n-butyl acetate that was collected at the bottom segment of the column, ethanol was found to be present with the highest mole fraction as compared to the other components involved in the process at the top segment of the column. The reason for this has been stated before to be due to the fact that ethanol is the second lightest component among the components involved in the process (see Table-A1 in Appendix-A). Furthermore, comparing the purity of ethanol obtained from the two systems, it was discovered that that of the integrated system was better (higher) than that of the conventional system. So, at this point, it was concluded that the integrated system was better than the conventional one for the transesterification process used for the production of n-butyl acetate (desired product) and ethanol (other product) in this work. As such, the integrated system was optimized in order to improve the outputs of the process.

When the integrated system was optimized, there was a change in the reflux ratio that was the manipulated variable of the optimization because the reflux ratio used for the simulation had a value of 4 while the one given by the optimization was found to be 3.1. Based on this, a reflux ratio of 3.1 was taken as the optimum value of the

manipulated variable for the integrated system of the transesterification process. Apart from considering the reflux ratio of the optimization, the segment temperature and composition profiles were also considered in order to know whether there were improvements in the conditions of the column and the quality of the products and the other components that were involved in the process due to the optimization that was carried out.

Figure-10 shows the temperature profiles of the simulated and optimized integrated systems for the production of n-butyl acetate using transesterification process. As can be seen from the figure, there is a difference between the two profiles (simulated integrated system and optimized integrated system). For instance, the top and bottom segment temperatures obtained from the optimized integrated system were 81.30 and 126.00^{o}C respectively while those obtained from the simulated integrated system were 78.24 and 122.76^{o}C respectively. It can be observed that the temperature of, especially, the bottom segment of the column from where n-butyl acetate (desired product) was collected has changed and, as such, a corresponding change in the quality of the desired product collected from the particular segment was expected to occur. This was what necessitated the need to investigate the mole fraction profiles of the components of the process, as shown in Figures 11 and 12.
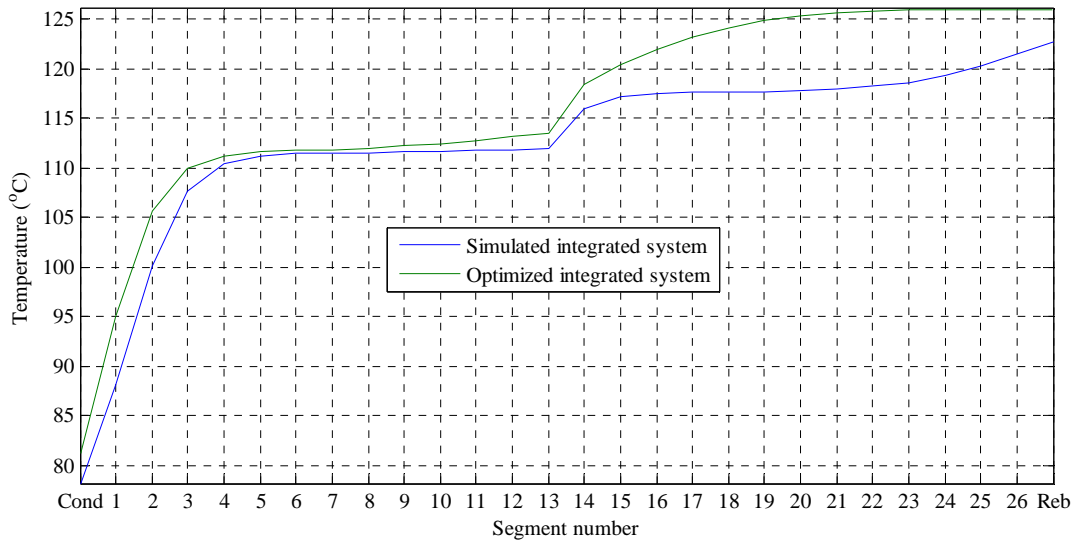
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Figure-10. Temperature profiles of the simulated and optimized integrated systems.

Figure-11 shows the liquid mole fraction profile of the components involved in the process. According to the figure, the compositions of the two reactants were approximately zero at the bottom segment of the column. For instance, the mole fraction of n-butanol (first reactant) at the bottom segment was approximately 0.0010 while that of the second reactant (ethyl acetate) was approximately 0.0000. In addition, the components with the highest mole fractions at the bottom segment and top segment of the column were found to be n-butyl acetate and ethanol respectively. This phenomenon was due to the difference in the relative volatilities of the components.

Also, the values of the desired product obtained in the case of the optimized integrated system was found to be higher than the one given by the simulated integrated system as shown in Figure-12 where the mole fraction profiles of n-butyl acetate for the simulated integrated system and the optimized integrated system are shown and compared. From the figure, it was discovered that the value of the liquid n-butyl acetate mole fraction obtained from the bottom segment of the column when the integrated system was optimized was 0.9990 while that of the simulated integrated system was 0.8723. It can be seen that the quality of the desired product has been improved as a result of the optimization that was carried out on the integrated system. This is pointing to the fact that optimization should not be neglected in chemical processes in order to achieve high qualities of products.
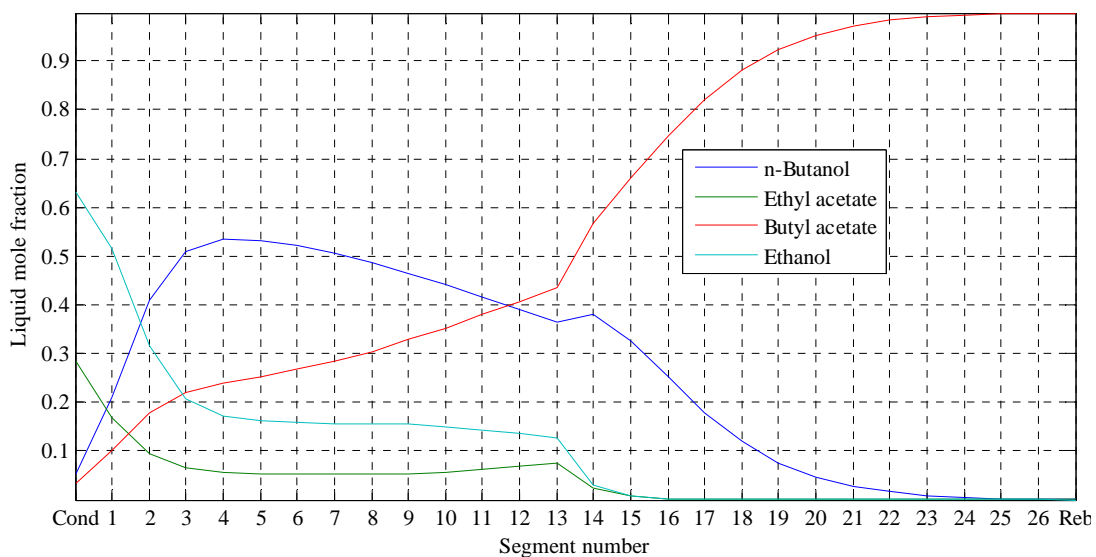

Figure-11. Composition profiles of optimized integrated system for the production of n-butyl acetate.
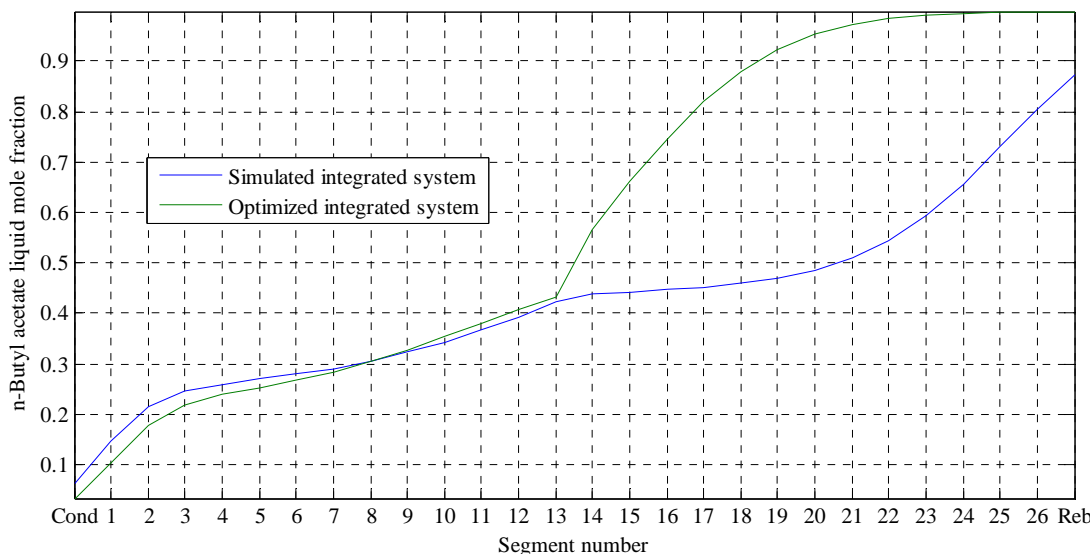
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Figure-12. n-Butyl acetate profiles of the simulated and optimized integrated systems.

Another thing that was discovered from this work was that there was a dependency of mole fraction of the product on the column segment temperatures because the change in the temperature profile of the column has actually brought about the change in the values of the mole fractions of the components involved in the process occurring in the column. That is to say that, in a distillation column, mole fraction is a function of column temperature and vice versa. In other words, the optimization of the quality of a particular product in a distillation column is more or less like the optimization of the temperature of the column under which that particular product is obtained in the column.

4. CONCLUSIONS

The results obtained from the Aspen PLUS modeling and simulation of transesterification process using the conventional system and the integrated system have proven that the integrated system of the process was better than the conventional one because higher conversion and higher purities of the products were obtained from the integrated system. Furthermore, the optimization of the integrated system gave an optimum value of the manipulated variable (reflux ratio) to be 3.1 and the value of the objective function (n-butyl acetate mole fraction at the bottom segment) that was achieved with the given optimum reflux ratio was found to be 0.9990. So, for the transesterification process between n-butanol and ethyl acetate that was used for the production of n-butyl acetate and ethanol, the integrated system has been proved to be more efficient.

ACKNOWLEDGEMENT

NOMENCLATURE

BTAC	n-Butyl acetate
BTOH	n-Butanol
CBOTTOM	Column bottom outlet
CLEANER	Combining lower emissions and networked energy recovery
CTOP	Column top outlet
ETAC	Ethyl acetate
ETOH	Ethanol
LIQUID	Reactor liquid outlet
LSSQP	Large-Scale Sequential Quadratic Programming
MLIQUID	Mixer outlet
RVAPOUR	Reactor vapour outlet

APPENDIX

Table-A1. Basic properties of the components (Hyprotech, 2003).

Components	Molecular weight (kg/kmol)	Boiling point (°C)
n-Butanol	74.12	117.75
Ethyl acetate	88.11	77.15
n-Butyl acetate	116.16	126.15
Ethanol	46.07	78.25

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