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Simulations and Economic Analyses of Ethyl Acetate Productions by Conventional and Reactive Distillation Processes Using Aspen Plus

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ABSTRACT

This work has been carried out to simulate and analyze the economic advantages of the conventional and the reactive distillation process methods used for the production of ethyl acetate through the Fischer esterification reaction between acetic acid and ethanol with the aid of Aspen Plus.The conventional and the reactive distillation models of the process were developed in Aspen Plus environment by employing an equilibrium reactor and a packed RadFrac column having 23 segments including the condenser and the reboiler. For the reactive distillation process method, the main column was divided into three sections, namely the rectifying(upper), the reaction (middle) and the stripping (lower) sections, but in the conventional process method, the main column was only divided into the rectifying and the stripping sections. The esterification reaction, occurring in the reactor of the conventional method and in the reaction section of the reactive distillation method,of the process was modeled as an equilibrium type. The higher purity of ethyl acetate, the lower total capital cost, the lower operating cost, the lower total utilities cost, the lower equipment cost and the lower total installed cost obtained from the reactive distillation process method have revealed that, in the production of ethyl acetate using the Fischer esterification, the reactive distillation process method was found to be better than the conventional process method both in giving ethyl acetate in higher purity and economically.

Keywords: Ethyl acetate production, conventional method, reactive distillation, total capital cost, Aspen Plus.

1. INTRODUCTION

Ethyl acetate has been largely employed as a solvent in paints, coatings, inks and adhesives (Sakamuri, 2004; Zonetti et al., 2011).It can be used as an ideal substitute for aromatic compounds for the purpose of improving working environment (Li et al., 2012) because aromatic compounds cause serious damage to human beings and the environment (Sakamuri, 2004; Zonetti et al., 2011).

Industrial production of ethyl acetate is mainly classified into three categories (Weissermel and Arpe, 1994; Inui et al., 2001). The first one is the classical Fischer esterification process of ethanol with acetic acid (Monick, 1968; McMurry, 2000; Inui et al., 2001). This process needs acid catalysts such as sulfuric acid and p-toluene sulfonic acid (McMurry, 2000; Inui et al., 2001). The second one is Tishchenko reaction of acetaldehyde using aluminum triethoxide as a catalyst (March, 1992; Ogata and Kawasaki, 1969; Inui et al., 2001). The third one, which has just been recently commercialized, is addition of acetic acid to ethylene using clay (Gregory et al., 1983; Inui et al., 2001) and heteropoly acid (Atkins and Sharma, 1997; Sano et al., 1993; Sato et al., 1999; Inui et al., 2001)as the catalyst of the reaction.

Fischer esterification process of producing ethyl acetate is an equilibrium reaction occurring between acetic acid and ethanol. In using this process for the production of ethyl acetate, one of the key issues that should be addressed is low reaction conversion. As a result of this low conversion, heavy capital investments and high energy costs are inevitable in this process, especially, based on the experience obtained from the conventional method of the process. As such, reactive distillation has been discovered to be a very attractive way to reduce these investments and energy costs (Lai et al., 2007; Giwa and Karacan, 2012f).

Reactive distillation is a process that combines both separation and chemical reaction in a single unit. It is sometimes an excellent alternative to conventional flow sheets with separate reaction and separation sections (Al-Arfaj and Luyben, 2002; Giwa and Karacan, 2012e; Giwa, 2013; Giwa et

al., 2013). It combines the benefits of equilibrium reaction with distillation to enhance conversion provided that the product of interest has the highest or the lowest boiling point (Giwa, 2013; Giwa and Karacan, 2012b; Giwa et al., 2013). It has a lot of advantages, especially for those reactions occurring at temperatures and pressures suitable for the distillation of the resulting components (Giwa, 2013; Giwa and Karacan, 2012c; Giwa et al., 2013), which include: (a) shift of chemical equilibrium and an increase of reaction conversion by simultaneous reaction and separation of products, (b) suppression of side reactions, and (c) utilization of heat of reaction for mass transfer operation, especially if the reaction is exothermic. In addition, another important advantage ofreactive distillation is its ability to avoid azeotropes(Giwa and Karacan, 2012a).These good benefits of this process (reactive distillation) normally result in significant economic advantages of reactive distillation compared to a conventional design. These economic benefits include: (a) lower capital investment, (b) lower energy cost and, (c) higher product yields (Moritz and Hasse, 1999; Giwa and Karacan, 2012d; Giwa et al., 2013).

According to the information obtained from the literature, some researches have been carried out on the production of ethyl acetate especially using reactive distillation process, and most especially with the aid ofprocess simulators. For instance, Hu et al. (2011) carried out a research on an approach to intensify a reactive distillation process for ethyl acetate production using a mass separation agent (entrainer), and a new process flowsheet with a sidedraw to the reactive distillation column. They employed an equilibrium stage model based on the RadFrac module of Aspen Plus for the steady-state simulation of their process.Giwa and Karacan (2012f) simulated and optimized a reactive packed distillation process for the production of ethyl acetate from the esterification reaction between acetic acid and ethanol using Aspen HYSYS. They divided their column, apart from the condenser and the reboiler, into five sections: rectifying, acetic acid feed, reaction, ethanol feed and stripping sections and used Non-Random Two-Liquid model as the fluid package and the reaction occurring in the reaction section of their column was modeled as an equilibrium type. They also performed experiments in a reactive packed distillation pilot plant to validate their simulated results. Tavan and Hosseini (2013) studied the production of high-purity ethyl acetate using reactive distillation embedded in HYSYS process simulation software by proposing a new configuration of reactive distillation process through dividing a single reactive distillation column into two separate columns,namelyreactive distillation and rectifier. In their work, the impacts of three parameters, including reactant flow rate, reaction trays, and feed-inlet location on the temperature profile and the component compositions in the columns were investigated to achieve an optimum condition of the process in terms of energy demand.Lone and Ahmad (2012) modeled and simulated ethyl acetate reactive distillation column using Aspen Plus simulation software by employing RadFrac model of Aspen Plus. Gautam et al. (2013) also simulated a reactive distillation column for the production of ethyl acetate using Aspen Plus. In their work, the component compositions and temperature at each stage of the column were predicted.

From all the researches came across so farin the literature and summarized above, it has been discovered that no work has used Aspen Plus to both simulate and carry out the economic analysesof reactive distillation processfor the production of ethyl acetate through Fischer esterification. Therefore, this work is carried out to simulate and demonstrate the importances of a reactive distillation processused for the production of ethyl acetatethrough Fischer esterificationwith the aid of Aspen Plus,both in terms of product quality and economically. The results obtained from the reactive distillation process are compared with those of the conventional method of ethyl acetate production also using Fischer esterification process.

2. PROCEDURES

2.1 Azeotrope Search

Before going into the modeling and simulation of the processes (conventional and reactive distillation), the azeotrope search of the components involved were investigated with the aid of Aspen Plus(Aspen, 2012). In achieving this, the four components (acetic acid, ethanol, ethyl acetate and water) were considered in their vapor and liquid phases using UNIFAC Property Model. In addition, a pressure of 1 bar was used. The reason for carrying out the azeotrope search was to establish the significance of applying reactive distillation to this process of ethyl acetate production through Fischer esterification because if no azeotrope was present among the components involved in the

process, just a simple distillation column coupled with a reactor, instead of reactive distillation, might be sufficient to produce good yield from the Fischer esterification process.

2.2 Modeling and Simulations

The conventional and the reactive distillation process methods used for the production of ethyl acetate were modeled and simulated in this work with the aid of Aspen Plus (Aspen, 2012). The developed models are as shown in Figures 1 and 2 below respectively for the conventional and the reactive distillation ethyl acetate production processes.

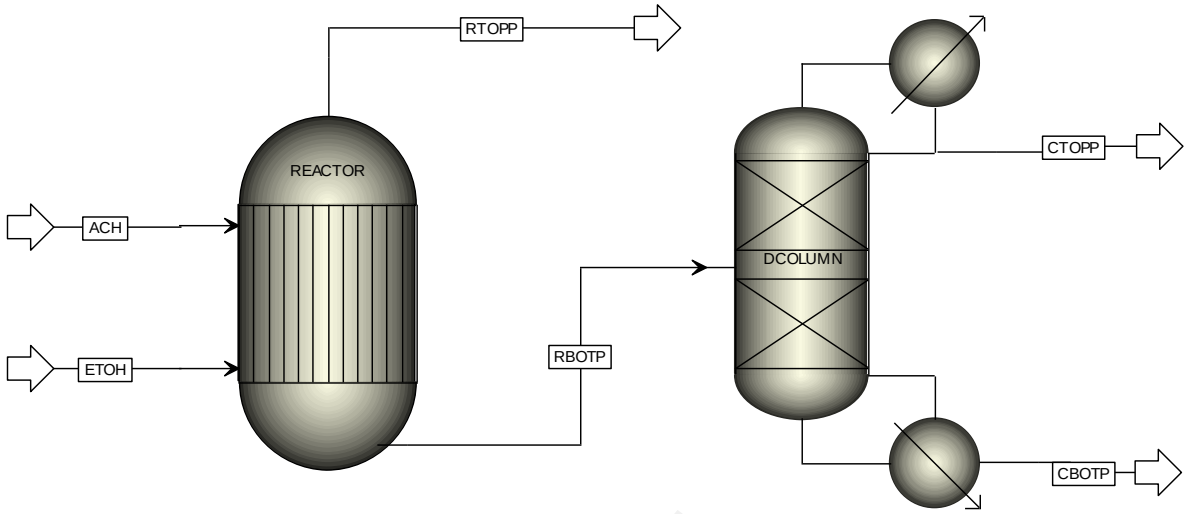

Figure 1. Aspen Plus model of conventional ethyl acetate production process

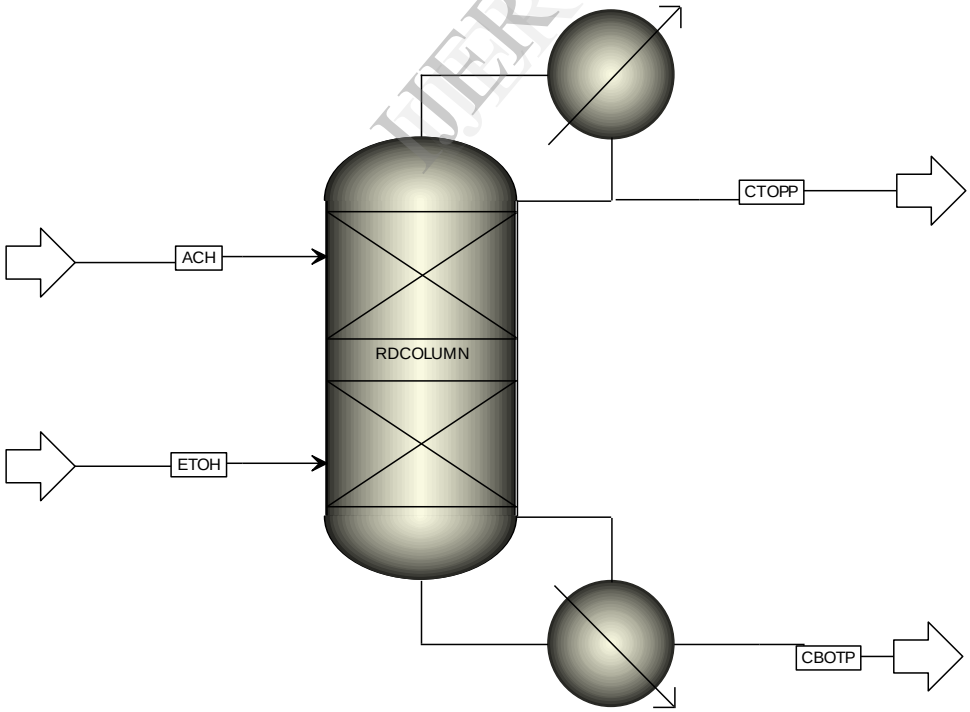

Figure 2. Aspen Plus model of reactive distillation ethyl acetate production process

The data used for the developmentsand the simulations of the Aspen Plus models of the conventional and the reactive distillation ethyl acetate production processes are given below in Table 1.

Table 1. Aspen PLUS conventional and reactive distillation modeling and simulation parameters

	Conventional Process	Reactive Distillation Process
Acetic acid feed		
Flow rate (L/min)	0.05	0.05
Temperature (^oC)	25	25
Pressure (bar)	1	1
Ethanol feed		
Flow rate (L/min)	0.05	0.05
Temperature (^oC)	25	25
Pressure (bar)	1	1
Property method	UNIFAC	UNIFAC
Reaction		
Type	Equilibrium	Equilibrium
K_{eq} source	Temperature approach	Temperature approach
Valid phase	Liquid	Liquid
Temperature (^oC)	55	-
Column		
Type	RadFrac	RadFrac
No of segment	23	23
Column feed segment	12	-
Acetic acid feed segment	-	8
Ethanol feed segment	-	14
Reaction section segments	-	8 - 14
Reflux ratio	3	3
Reboiler duty (kJ/s)	0.7	0.7
Condenser type	Total	Total
Condenser pressure (bar)	1	1

At the end of the modeling and simulations, the mole fractions of the components involved in the process especially that of ethyl acetate, which was the desired product of the process, obtained from the two process methods were compared.

2.3 Economic Analysis

After the simulations of the developed Aspen Plus models of the conventional and the reactive distillation processes for the production of ethyl acetate through Fischer esterification reaction between acetic acid and ethanol, their economic analyses were carried out also with the aid of Aspen Plus in order to determine the more economical one between the two process methods (conventional and reactive distillation). In this case, the total capital cost, the total operating cost, the total utilities cost, the equipment cost and the total installed cost of the two process methods were estimated with the aid of Aspen Plus and compared.

3. RESULTS AND DISCUSSIONS

The results obtained from the pure component analyses of this studyare as given in Table 2 below. From the table, it was discovered that acetic acid had the highest temperature while the temperature of the desired product (ethyl acetate) was the lowest one among those of the components

involved in the process. It should be recalled that one of the conditions required for the application of reactive distillation to any process is that the product of interest (desired product) of the process must have the highest or the lowest boiling temperature. As can be seen from Table 2 below, this condition has been satisfied because the desired product (ethyl acetate) has been found to have the lowest boiling temperature among the components taking part in the esterification process. Also noticed from the analyses of the pure components of this process was that the temperatures of both acetic acid and water occurred at stable nodes while those of ethanol and ethyl acetate were saddle in nature. The stable nodes of acetic and water implied that these pure componentshad high boiling temperatures and low vapor pressures in the distillation region of the process components. Also, the saddle points obtained from the pure component analyses for ethanol and ethyl acetate revealed that theirpure components hadintermediateboiling temperatures andvapor pressures in the distillation region of the process components. Looking at Table 2, it can be noticed that the boiling temperatures of ethanol and ethyl acetate were between those of water and acetic acid. The boiling temperatures of the components have, therefore, confirmed the results obtained from the analyses of the pure process components.

Table 2. Pure component analyses

#	Component	T (^oC)	T_b(^oC)	Classification
1	ACH	118.01	117.9	Stable node
2	ETOH	78.31	78.29	Saddle
3	ETAC	77.20	77.06	Saddle
4	H2O	100.02	100	Stable node

Contained in Table 3 are the results obtained from the azeotrope analyses of the mixtures of the components of the Fischer esterification process used for the production of ethyl acetate. As can be seen from the table, four azeotropes were found to exist between the components and each of the azeotropes involved two components. In other words, the azeotropes were found to be binary in nature. Apart from that, the four azeotropes formed by the component mixtures were found to be homogenous (that is, the constituents of the mixtures were completely miscible). In addition, the azeotropes involving acetic acid and water, ethanol and ethyl acetate, and ethanol and water were found to occur at saddle points; that is, the resulting azeotropeswere neither positive nor negative.The azeotrope involving ethyl acetate and water was, however, discovered to occur at an unstable node.

Table 3. Mixture azeotrope analyses

#	T (^oC)	Classification	Type	Component #	ACH	ETOH	ETAC	H2O
1	98.55	Saddle	Homogeneous	2	0.1657	0.0000	0.0000	0.8343
2	71.05	Saddle	Homogeneous	2	0.0000	0.4656	0.5344	0.0000
3	78.04	Saddle	Homogeneous	2	0.0000	0.8933	0.0000	0.1067
4	70.26	Unstable node	Homogeneous	2	0.0000	0.0000	0.6321	0.3679

Among the azeotropes found from the component mixtures, the maximum mole fraction of ethyl acetate was obtained from the azeotrope between ethyl acetate and water to be 0.6321 and it was obtained when the temperature of the azeotrope mixture was 70.26 ^oC.

It has been discovered from the azeotrope analyses of the component mixtures that the maximum mole fraction that can be obtained from ordinary distillation of these process mixtures is less than 0.6321. Therefore, now, the task is how to develop a process that can break this azeotropic point so as to obtain ethyl acetate higher than the azeotropic value (0.6321). As such, both the conventional and the reactive distillation process methods of ethyl acetate production were investigated to determine the one that could give very high ethyl acetate mole fraction value, especially a value higher than its obtained azeotropic mole fraction value of 0.6321. In order to carry out the investigations, the process models of the two methods were developed and simulated with the aid of Aspen Plus.

Shown in Figures 3 – 7 are the results obtained from the simulationsof the developed Aspen Plus models of the conventional and the reactive distillation process methods used for the production of ethyl acetate,carried out using UNIQUAC Functional-group Activity Coefficients (UNIFAC) model as the fluid package. In all the figures (Figures 3 - 7), the first segment (segment 1) was taken as the condenser segment while the last segment (segment 23) was the reboiler segment of the each of the columns (conventional process method column and reactive distillation column).

Shown in Figure 3 are the temperature profiles obtained from the simulations of the conventional and the reactive distillation Aspen Plus models of the Fischer esterification used for ethyl acetate production. As can be observed from the figure, the profiles of the two process methods were found to be entirely very different from each other especially in the rectifying and the reaction sections of the columns, even though their behaviors were similar in the stripping sections of the columns. Looking at the profile of the reactive distillation process given in Figure 3, high temperatures were observed to occur at the reaction section. This high temperature given by the reactive distillation process in the reaction section was discovered to be as a result of the exothermic reaction occurring in that section of the column. Such high temperatures were, however, not observed to occur in the case of the column profile of the conventional process method because, in this case, the column was only used for separation, but not for simultaneous reaction and separation. From the two profiles (those of the conventional and the reactive distillation process methods), the minimum temperature of the columns were found to be approximately the same and occur in the condenser segments of the columns. The observance of the minimum temperatures in the condensers was discovered to be in conformity with the expectation because light components were expected to be found in high percentages in the top (condenser) segments of the columns.

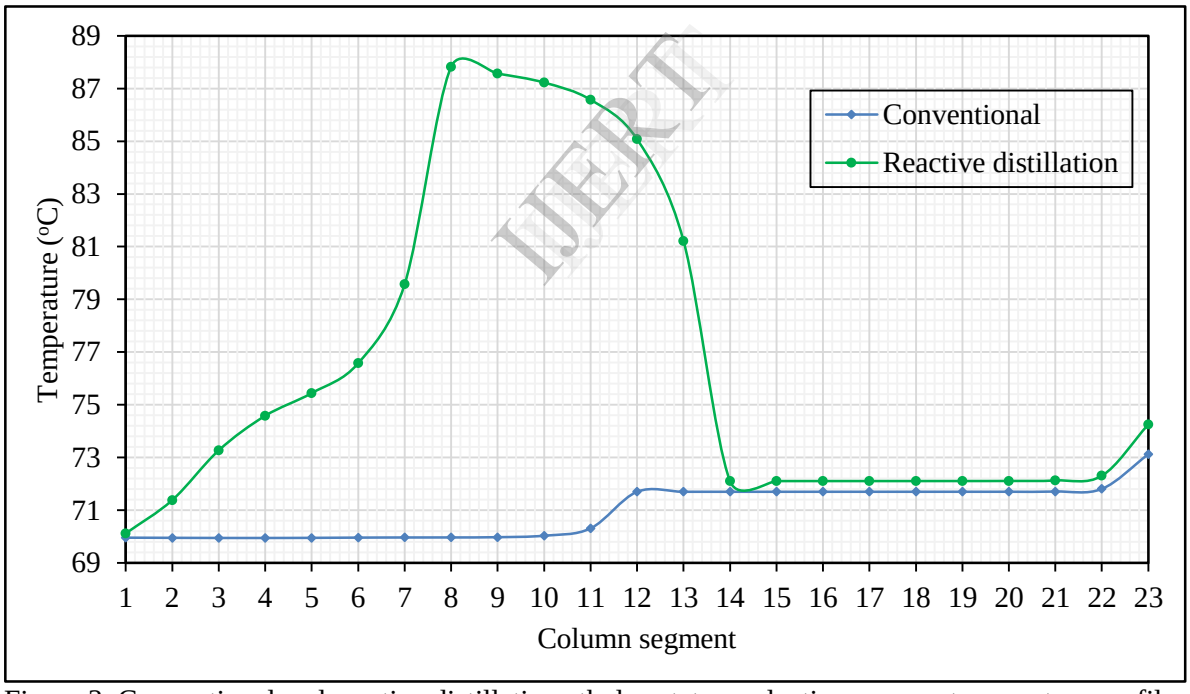

Figure 3. Conventional and reactive distillation ethyl acetate production process temperature profiles

The mole fraction profiles of acetic acid obtained from the Aspen Plus simulations of the conventional and the reactive distillation processmethods are as shown in Figure 4. The trends of the profiles were found to be similar to those of the temperature profiles of the process methods. According to the figure, the mole fractions of acetic acid obtained from the condenser segments of the columns were found to be approximately the same and very close to zero. This was an indication that good separation phenomena were achieved in the columns because, acetic acid, being the heaviest components of the process, was expected to be present in the top segments of the columns in very negligible amounts. From the profile of the reactive distillation process method, high acetic acid mole fractions were found to be available in the segments of the reaction section of the column, but this high mole fraction decreased downwards towards the stripping section. The high mole fraction of

acetic acid in the reaction was attributed to the fact that fresh acetic acid feed was continuously fed into the column during the simulation of the reactive distillation process. As can be seen from Figure 4, no such high acetic acid mole fraction was observed in the case of the conventional process method because, in this case, there was not any continuous feed of acetic acid being passed into the column.

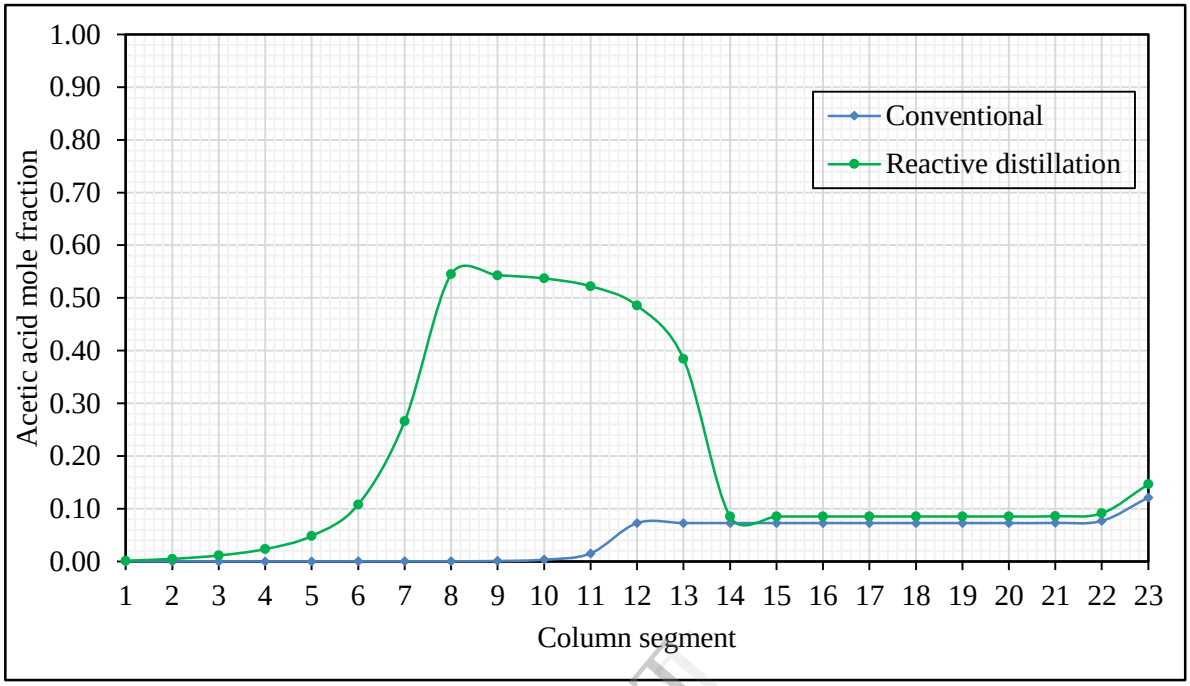

Figure 4. Conventional and reactive distillation liquid acetic acid composition profiles

Given in Figure 5 are the liquid mole fractions of ethanol obtained from the simulations of the conventional and the reactive distillation processes. From the figure, the mole fraction profile of ethanol obtained from the conventional process method was found to be almost constant along all the segments of the column while that of the reactive distillation process method was only almost constant from the top segment of the column up to about segment 13, thereafter, there was an increase in the mole fraction a bit, which later decreased again a bit. Furthermore, as from segment 15 of the column, the liquid ethanol mole fraction found in the reactive distillation column was discovered to be almost constant again up to the bottom segment (reboiler) of the column. As can be observed from the profiles of the reactive distillation and the conventional process, used for the production of ethyl acetate through Fischer esterification, given in Figure 5, in the top segments of the columns, the mole fraction of ethanol given by the reactive distillation process method was found to be less than that of the conventional process method. However, in the bottom segments of the columns, the reverse was the case; that is, in the reboiler segments of the columns, the ethanol mole fraction obtainedfrom the conventional process method was less than that of the reactive distillation process method. For the reactive distillation process method, according to the profile given in Figure 5, the highest mole fraction of ethanol was found to occur in the segment very close to ethanol feed segment of the column which was column segment 14. Also noticed from Figure 5 was that the mole fraction of ethanol decreased upwards from the ethanol feed segment towards the acetic acid feed segment (segment 8). This was discovered to be owing to the fact that ethanol, after being fed into the column, being very volatile (the second most volatile component of the process) was moving upwards and being consumed in the reaction section of the reactive distillation column.

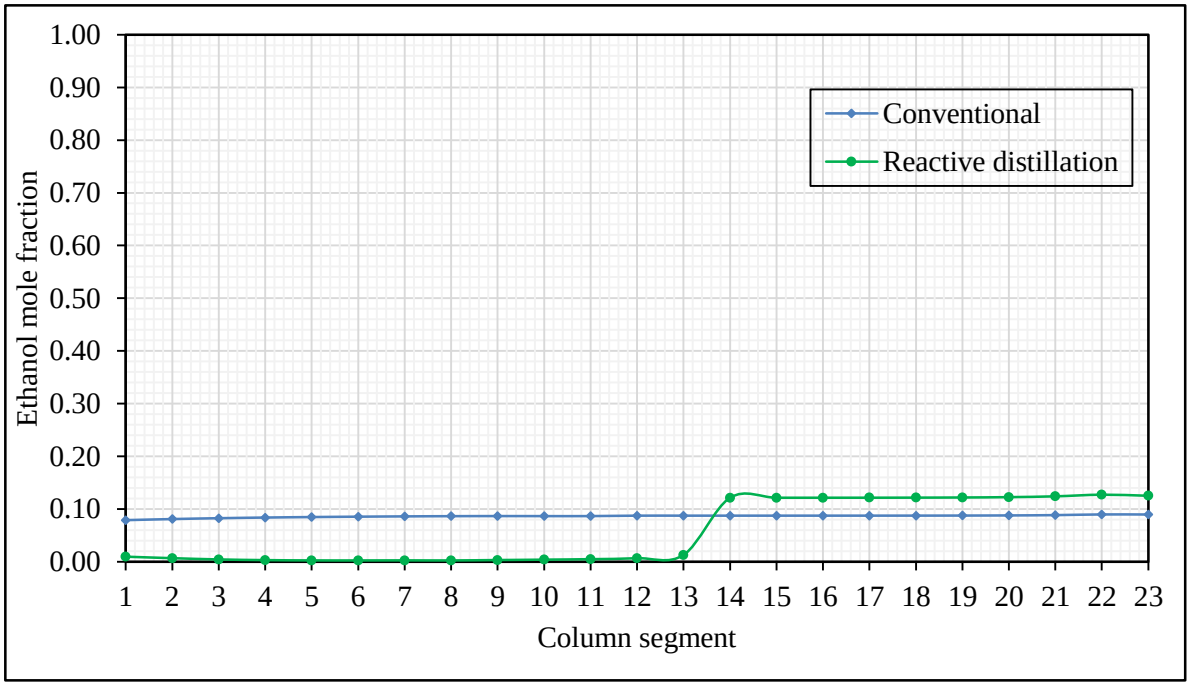

Figure 5. Conventional and reactive distillation liquid ethanol composition profiles

Now, in Figure 6, the liquid mole fraction profiles of the desired product (ethyl acetate) obtained from the simulations of the conventional and the reactive distillation process methods are given. Considering the results given in the figure (Figure 6), the ethyl acetate that was obtained from the reactive distillation process method was found to have higher mole fraction in the top segment (condenser) of the column than that given by the conventional process method. In the reboiler (bottom segment) of the column, ethyl acetate with the lower mole fraction was discovered to be the one obtained from the reactive distillation process method. That is to say, employing reactive distillation process method, higher mole fraction of the desired product (ethyl acetate)than that obtained from the conventional process methodcould be obtained.

Another interesting thing that was noticed in the case of the reactive distillation process method, as shown in its profile given in Figure 6, was that the maximum mole fraction of ethyl acetate present in the column was 0.9283. However, this product was not the one being collected as the product of the process from the condenser. It was, therefore, discovered that very high purity of ethyl acetate, higher than the one obtained from the condenser of the reactive distillation column, as pure as a mole fraction of 0.9283, could be obtained from the reactive distillation column if there were a sidedraw attached that could allow the withdrawn of the product from within the rectifying section of the reactive distillation column. This situation was not the same in the case of the conventional process method because the mole fraction of ethyl acetate obtained from the condenser of the column of the conventional method had approximately the same mole fraction with that of the one present in each segment of itsrectifying column.

So far, reactive distillation process method has been seen to give higher mole fraction of the desired product (ethyl acetate) of this esterification process than the conventional process method. As such, reactive distillation process method has been proved to be better than conventional process method in the production of ethyl acetate from the equilibrium esterification reaction between acetic acid and ethanol.

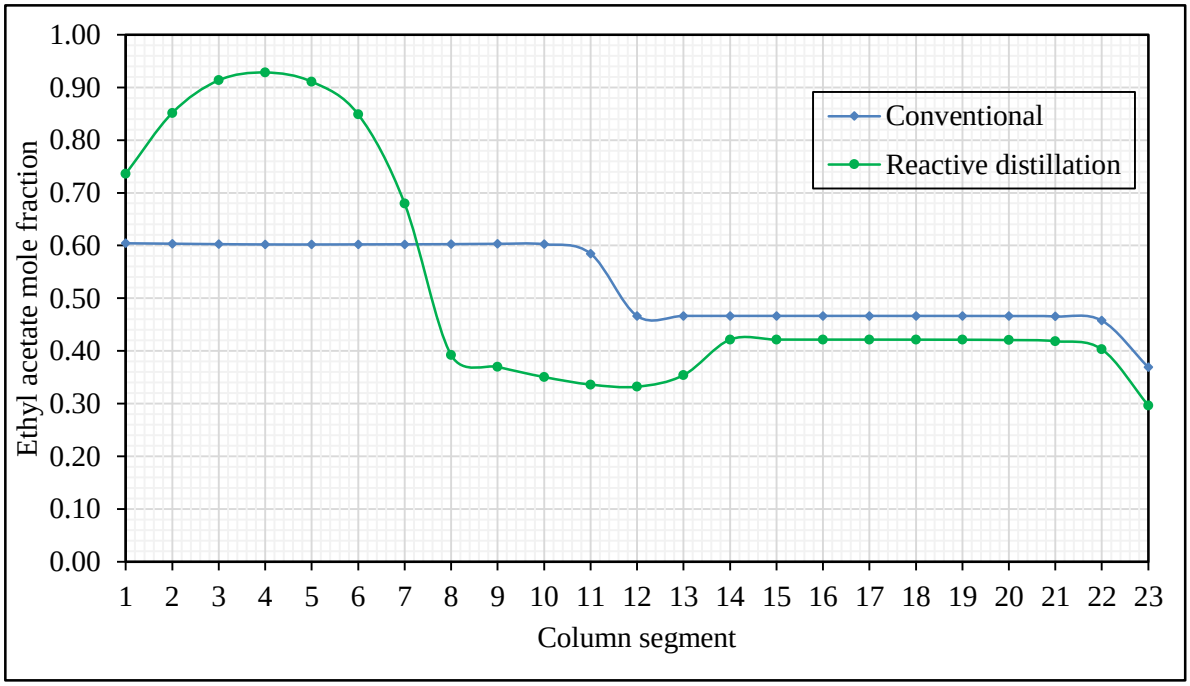

Figure 6. Conventional and reactive distillation liquid ethyl acetate composition profiles

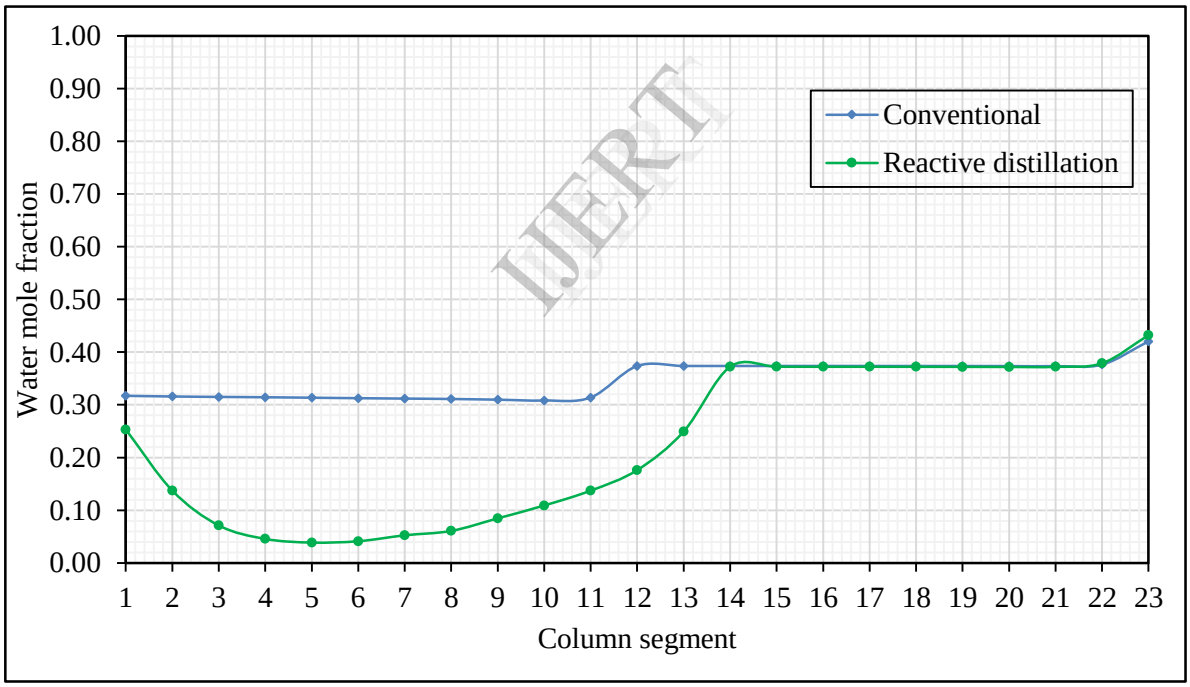

Figure 7. Conventional and reactive distillation liquid water composition profiles

The mole fraction profiles of the other product of the Fischer esterification reaction, which was water, obtained from the conventional and the reactive distillation process methods were also considered and plotted as shown in Figure 7. From the figure, it was discovered that the mole fractions of water obtained at the bottom segments of the columns when the two process methods (conventional and reactive distillation) were simulated with the aid of Aspen Plus were almost the same, but such was not the case at the top segments of the columns because, according to the mole fraction of the water obtained from the condenser segments of the columns, that obtained from the simulations of the reactive distillation process method was found to be less than the one obtained from the conventional process method.

Another thing observed from the results shown in Figure 7 was that the trends of the profiles of liquid water mole fraction contained in the stripping sections of the columnsof the conventional and the reactive distillation process methods were very almost the same.

Also investigated and considered in this work were the economic performances of the two process methods. The economic comparison of the two process methods was carried out by calculating and comparing the total capital cost, the total operating cost, the total utilities cost, the equipment cost and the total installed cost of the two process methods. The results obtained from the economic analysis calculations of the two process methods are as given in Table 4. From the table, it was observed that all the costs of the reactive distillation process method were less than those of the conventional process method. This is a very good indication of the economic advantage of the reactive distillation process method used for the production of ethyl acetate over the conventional one.

Table 4. Economic analyses of the process methods

Description	Amount	
	Conventional	Reactive Distillation
Total Capital Cost [USD]	3405340.00	2961170.00
Total Operating Cost [USD/Year]	1308080.00	971921.00
Total Utilities Cost [USD/Year]	36319.80	35818.30
Equipment Cost [USD]	148200.00	126200.00
Total Installed Cost [USD]	552900.00	401400.00

It has thus been discovered that the performances, both in terms of product purity(estimated by considering the mole fractions of the desired product - ethyl acetate) and economics (determined by comparing the costs involved in the processes) of reactive distillation process method were better than those of the conventional process method used for the production of ethyl acetate through Fischer esterification reaction between acetic acid and ethanol.

4. CONCLUSIONS

The results obtained from the simulations of the conventional and the reactive distillation process methods used for the production of ethyl acetate from the Fischer esterification reaction between acetic acid and ethanol have revealed that the reactive distillation process method was better than the conventional process method in producing ethyl acetate because higher purity of ethyl acetate, lower total capital cost, lower operating cost, lower total utilities cost, lower equipment cost and lower total installed cost were obtained from the reactive distillation process method considered.

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NOMENCLATURES

#	Number
ACH	Acetic acid feed
CBOTP	Column bottom product
CTOPP	Column top product
DCOLUMN	Distillation column
ETAC	Ethyl acetate
ETOH	Ethanol feed
H2O	Water
K_{eq}	Equilibrium reaction constant
RBOTP	Reactor bottom product
RDCOLUMN	Reactive distillation column
RTOPP	Reactor top product

T	Temperature (^oC)
T_b	Boiling temperature (^oC)
UNIFAC	UNIQUAC Functional-group Activity Coefficients model

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