Simulation and optimization of extractive distillation sequence with pre-separator for the ethanol dehydration using n-butyl propionate

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Abstract−Extractive distillation is the most promising alternative for the ethanol-water separation than azeotropic and pressure swing distillation using suitable solvent n-Butyl propionate. We have studied, simulated, optimized and economically evaluated the separation of a mixture of 50 mole% ethanol and 50 mole% water to treat the 16 Kmol/hr (512.67 kg/hr) of the original mixture. Rigorous simulation and optimization has been carried out by means of a software CHEMCAD version 6.5 using thermodynamic model UNIQUAC with binary interaction parameters. The simulations allow us to conclude that extractive distillation is more economical and trustworthy than pressure swing distillation due to the relative pressure insensitive nature of the ethanol-water mixture after the azeotropic composition. The separation of 99.7% of ethanol from ethanol water mixture claim by Mulia-Soto, Flores-Tlacuahuac, 2011 is contradictory as the feasibility for the operating pressure of 10 atm with or without heat integration.

Key wards: Simulation, Optimization, Ethanol Dehydration, n-Butyl Propionate

INTRODUCTION

The ethanol produced from the renewable feedstocks is a promissory option to reduce environment pollution and dependence on fossil fuel. The reduction in fossil fuel is the main reason for the development and implementation of renewable alternative energy sources such as bioethanol and biodiesel. The ethanol production from biomass, sugarcane, corn is a viable option to reduce environmental pollution since the mixture of anhydrous ethanol and gasoline may be used as fuels, which reduces the environmental contamination by improving the gasoline's octane number. Furthermore, anhydrous ethanol is also widely used in the chemical industry as a raw material in chemical synthesis of esters and ethers, and as a solvent in the production of paint, cosmetics, spray, perfumery, medicine.

The most popular processes for the ethanol-water separation are heterogeneous azeotropic distillation using the known solvents such as pentane, benzene, cyclohexane and extractive distillation using the solvents, and most recently, the ionic liquids are those with alkylammonium, alkylphosophonium, N-alkylpyridinium and N,N-dialkylimidazolium cations. However, the more reliable solvent such as n-butyl propionate is untouched for the separation of ethanolwater. The pressure swing distillation process for bioethanol dehydration [1,8,12,13] was quite difficult to get the relatively desired separation due to the pressure insensitive nature of the ethanol-water mixture after the azeotropic composition.

In the previous work, we showed that the pressure swing distillation process for bioethanol dehydration was quite difficult to get the relatively desired separation due to the very minute change in vapor liquid compositions [2,5,7,19,23,24].

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Computer simulations using process simulators such as CHEMCAD are used with success as an aid for process development for a long time. Experiments in the laboratory, either for extractive distillation or the pressure swing distillation, are time consuming and very expensive because of the large number of variables involved in the processes. Hence, it would be beneficial and desirable to predict the data with the help of available simulation software. The results furthermore can be used to set up as a guideline for further industrial experiments to optimize the operating parameters governing the steady state process. The extractive distillation design involves the selection of one or more solvents, which alters the relative volatilities in the mixture through the physical and chemical changes with original components and the process design, which involves the search for the optimal process parameter values by the choice of one or more column configurations in sequences.

In this work, for the dehydration of ethanol we have studied n-butyl propionate as solvent based on guidelines like the entrainer should be highly polar and/or from the same homologous series of the key components [3,4,6,17,22] for the screening of the solvents for the rigorous extractive distillation simulation using the thermodynamic UNIQUAC, K-value model in the CHEMCAD version 6.5 and we designed the separation sequence and optimized the operating parameters for the economic evaluation. We have also investigated the feasibility of pressure swing distillation sequence for the ethanol dehydration which forms the azeotrope at various pressures. The nature of the T-xy diagram after the azeotropic composition even for high pressures shows that pressure swing distillation is quite relatively infeasible for the desired high purity separation of ethanol. Several authors use the mixture of solvents that leverage synergic behaviors and embrace the possibility to achieve balance between the capacity of the solvent and selectivity. The substances featuring high selectivity for the key components to be separated have a low capacity.

The purpose of this study is to establish the operating conditions at plant level for the extractive distillation of ethanol dehydration using n-Butyl propionate as a separating agent.

CASE STUDY

The number of ideal stages, the feed stage and the initial extractant stage in the extractive distillation and pressure swing distillation sequence were set after the optimization of the structure of the conventional sequences was carried out. These parameters enabled a successful separation. The UNIQUAC model was used to describe thermodynamic properties. Different extractant/feed (E/F) ratios were investigated. The design pressure for each separation was chosen to ensure the use of cooling water in the condensers. The pressure drop for a single tray is given based on the heuristics. Purities of 99% in mole in the products were assumed.

STEADY STATE DESIGN AND SIMULATION OF EXTRACTIVE DISTILLATION COLUMN SEQUENCE

Based on the guidelines such as process heuristics and the various thermodynamic K-value models knowledge, we propose a process design of the extractive distillation column sequence so as to meet the design targets such as desired purity of ethanol and the economic viability of the process. The processes whose concentrations of ethanol is around 50 mole% are concentrated in a rectifying column or a series of them, and finally anhydrous ethanol is obtained by means of extractive distillation process. Hence, in this work
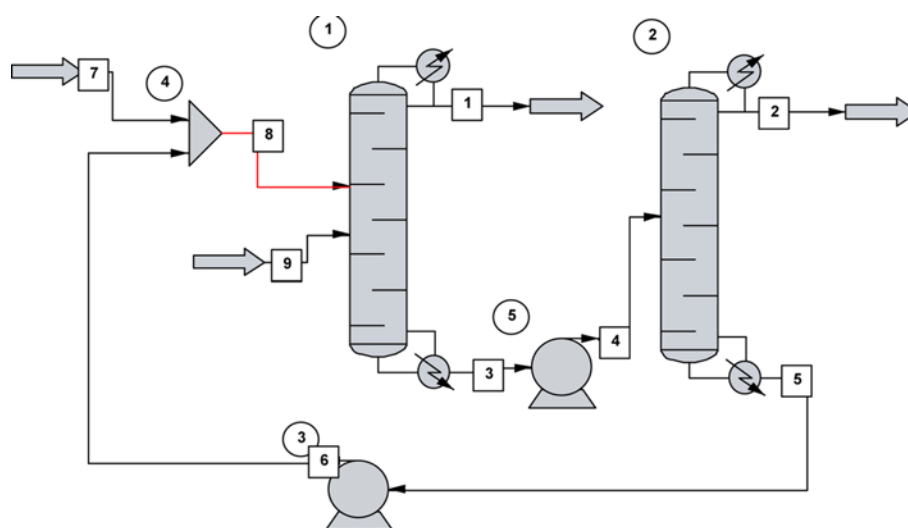

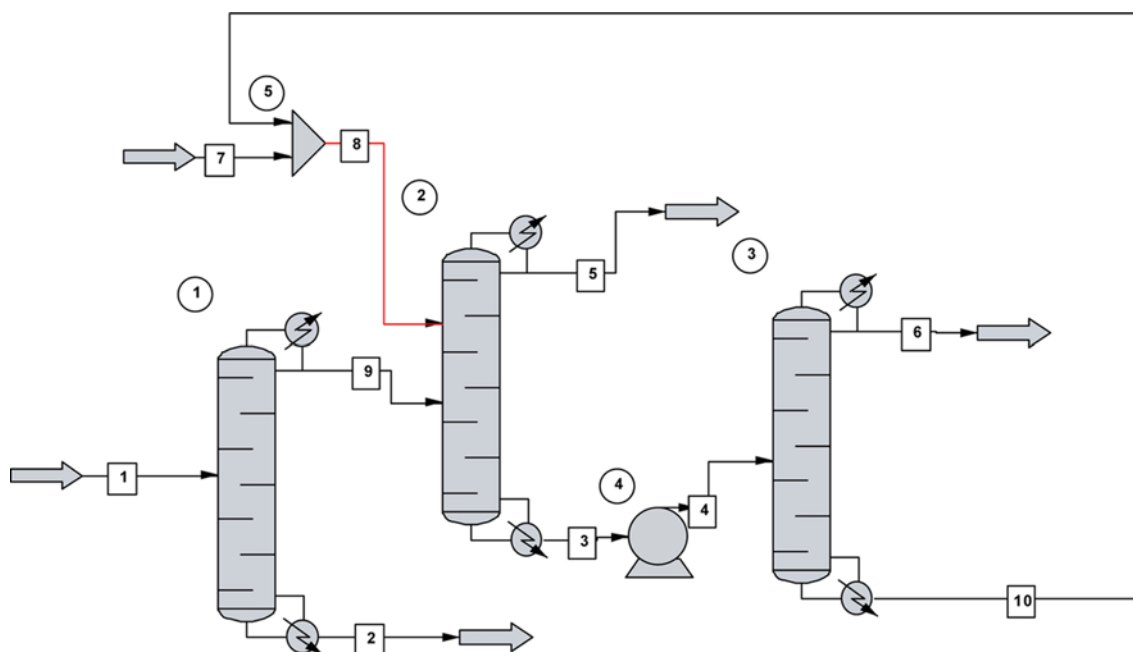**Fig. 1. Original extractive distillation sequence.**

Fig. 2. Extractive distillation sequence with preseparator.

a feed stream consists of 16 kmol/hr, 90 °C, 1 atm and 50 mole% of ethanol compositions is taken as the base case. In the design requirements the product stream should be considered as purity of ethanol requirement is greater than 99 mole% and the recovery at least 96 mole%. The design variables are the number of trays, tray locations of the feed stream, the tray locations of the recycle streams, thermal duties in the condenser and reboiler in each extractive and solvent recovery columns. After specifying the design variables, computing the values of the states like flows, compositions and temperature of each streams of liquid and vapor through the separation systems is quite easier using the thermodynamic model UNIQUAC. The T-xy diagram predicted with the help of CHEMCAD simulator and experimental data observed as shown in Fig. 3 and Fig. 4. The experimental data are taken from [14,16,17,21].

SEQUENCING AND OPTIMIZATION OF EXTRACTIVE DISTILLATION

After selecting the entrainer as n-butyl propionate for ethanol dehydration, our attention was directed towards the sequencing of the distillation columns. The process configurations are shown by Fig. 1 and Fig. 2 in which the first column is the extractive column and the second column is solvent recovery column for Scheme 1 and first two columns are the extractive columns and third column is a solvent recovery column for the enhanced capacity. The simulations show that the solvent n-butyl propionate increases the relative volatility of ethanol with respect to water and thus makes the separation easier; and due to the less volatile nature of the solvent with respect to ethanol or water, it flows down and will be obtained as the bottom product. The solvent recovery column removes water from the solvent because the solvent is much less volatile than water. Thus, causing the recovery of the solvents with high purity requires less solvent makeup in the feed.

The partial optimization specifying some variables and using the reboiler heat duties of the extractive and solvent recovery columns, we have selected the best operating conditions for the global economic optimization of the process. In this study, we specified the design variables temperatures, pressures, flow rates and compositions of the binary feed. For the first column distillate purity of ethanol and for the solvent recovery column bottom purity of solvent is specified. The solvent makeup was chosen as a pure component which is at atmospheric conditions. Once the design variables have been specified, their values should be kept constant throughout the simulations and optimization procedures. The optimization variables are those that must be an arbitrarily assigned value. The values are subject to change from the base case to optimal design. The solvent-to-feed ratio and the number of trays in each column are optimizations variables. The optimization procedure using CHEMCAD requires setting the number of trays in both columns and with short-cut design method of CHEMCAD analyze the variations of stage number and reboiler heat duty as a function of reflux ratio in order to set the number of ideal trays and feed positions of the solvent recovery column, i.e., for the set number of trays 30 the optimum feed entry stage is 9.

We have studied different cases for the extractive column by varying the number of trays from 40 to 90 since less than 40 stages did not converge the simulation even if the solvent-to-feed ratio is very large and the higher than 100 is not economical and reasonable by selecting the best solvent entry stage and feed entry stage.

From the simulation runs, it was found that the solvent to feed ratio has a significant effect on the reflux flow rate in the extractive and solvent recovery column, therefore ultimately affecting the total reboiler heat duty. Henceforth, the partial optimization required for the variable and the solvent-to-feed ratio was then adjusted to minimize the total reboiler heat duty required for the process.

GLOBAL ECONOMIC OPTIMIZATION FOR EXTRACTIVE DISTILLATION SEQUENCE

From Table 2 of optimum solvent-to-feed ratio in the extractive column for each case, it can be said that the minimum reboiler heat duty is required for the minimum solvent-to-feed ratio but highest number of stages, which would be a very expensive column in the

Table 1. Design variables for extractive distillation sequence

	Extractive distillation sequence		Additional pre-separator column extractive distillation sequence	
	Main column (kPa)	Solvent recovery column (SRC) kPa	Main column (kPa)	Solvent recovery column (SRC) kPa
Pressure kPa	110	101	110	101
No. of stages	50	30	25 & 21	22
Feed stage	35	13	14 & 8	9
Solvent entry stage optimum	8	-	-	-

Table 2. Optimum solvent to feed ratio for the extractive distillation sequence

Sr. no.	Solvent/feed	No. of trays	Solvent entry stage	Feed entry stage	Reboiler heat duty
1	3.0	35	7	24	5646
2	2.0	40	7	30	4562
3	1.33	50	8	35	3300
4	1.00	60	9	42	3094
5	0.9	70	10	50	2823

Table 3. Optimum solvent to feed ratio for the additional pre-separator column extractive distillation sequence

Sr. no.	Solvent/feed	No. of trays	Solvent entry stage	Feed entry stage	Reboiler heat duty
1	3.0	22 & 18	11	8	4646
2	2.0	24 & 15	13	7	4232
3	1.33	25 &21	13	17	3123
4	1.00	33 & 26	19	21	3004
5	0.9	35 & 28	22	24	2823

Table 4. Results of extractive distillation sequence and pressure swing distillation sequence

Sr. no.	Type of sequences	Energy consumption	TC/Yr×10⁻³	CO₂ emission (Ton/h)
1	Extractive distillation sequence	3350	1329.95	1.93
2	Additional pre-separator column extractive distillation sequence	3123	1120.6	1.86

process design. Hence, for finding the best possible alternative to carry out the economic evaluation based on the total annual cost which includes cost of tower with trays, reboiler, condenser, reflux pump, reflux vessel for both extractive and solvent recovery column as well as cooler, recycle pump and fixed capital investment cost for the extractive distillation process.

The O.F. for the Total Cost is

Total Cost/Year=Process Variable Cost
+Fixed Cost+(Fixed capital Recovery Rate
+Minimum rate of return)

Let C_v be the process variable cost, mostly annual utility consumption (steam, cooling water and electrical power) and solvent make up cost; C_f, the annual fixed cost, i.e., maintenance cost and wages; FCI, the fixed capital investment; C_r, the fixed capital recovery rate applied to FCI (depreciation rate); and C_m, the minimum acceptable rate of return on FCI.

$$TC/Yr=C_v+C_f+FCI(C_r+C_m)$$

In the optimization C_f was assumed to be 10% of FCI and C_r and C_m was supposed to be 20% of FCI [15,19]:

$$TC/Yr=C_v+0.3\ FCI$$

Fixed capital investment was estimated by using the costs estimation program with an updated Chemical Engineering plant cost index. A 15 years project life was selected. From the results it can be seen that there is a minimum for the case having solvent-to-feed ratio of 1.4. Table list details of extractive and solvent recovery columns needed to meet the design objectives together with the total annual cost for this optimum.

## STEADY STATE DESIGN AND SIMULATION OF PRESSURE SWING DISTILLATION

The basis of pressure swing distillation is the pressure sensitive nature of the mixture which affects the vapor-liquid equilibrium. This effect can be explored to separate the mixture containing the minimum boiling azeotrope rather than maximum boiling azeotrope, provided this mixture significantly affects changes of compositions over a small or moderate change in pressure. Herein for the mixture ethanol-water we will find hardly any change after reaching the azeo-tropic composition, even for various pressures as shown by Fig. 3(b). So we can conclude that pressure swing distillation is quite uneconomical since the number of stages required and the total reboiler heat duty required for the separation is very large. Furthermore, we have carried out simulations to find the maximum separation using a very large number of stages and found that the maximum separation possible is not economical using pressure swing distillation [article in press with Computers and Chemical Engg]. The separation of 99.7% of ethanol (claim by [13]) is contradictory as the feasibility above 86% for the operating pressure of 10 atm with or without heat integration. The flowsheet of pressure swing distillation sequence is as shown in Fig. 3(a).

CALCULATION OF GREEN HOUSE GAS EMISSIONS

The major contributor to green house gas emissions is carbon dioxide due to its highest global warming potential as compared to other contributors. So carbon dioxide is the main focus of our calculations for the green house gas effects.

In distillation systems, carbon dioxide is generated mainly from the reboiler. These utility devices are the fuel consumers and are used to provide heat, stream and power to the process by burning a fuel. Therefore, these units are key drivers in energy savings oriented projects and for reducing environmental impact of emissions. Fuel is combusted when mixed with air, producing CO_2 according to the following stoichiometric equation:

$$C_xH_y+\left(x+\frac{y}{4}\right)O_2\rightarrow xCO_2+\frac{y}{2}H_2O \qquad (1)$$
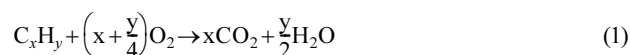
where x and y denote the number of carbon and hydrogen atoms, respectively, present in the fuel compositions and where complete oxidation of carbon is assumed.

In the combustion of fuels, air is assumed to be in excess to ensure complete combustion, so that no carbon monoxide is formed. CO_2 emission (kg/s) is related to the amount of fuel burnt, Q_{fuel} (kw), in a heating device as follows:

$$[CO_2]_{Emiss}=\left(\frac{Q_{Fuel}}{NHV}\right)\left(\frac{C\%}{100}\right)\alpha \qquad (2)$$

where α=3.67 is the ratio of molar masses of CO_2 and C, while NHV (kJ/kg) represents the net heating value of the fuel with carbon
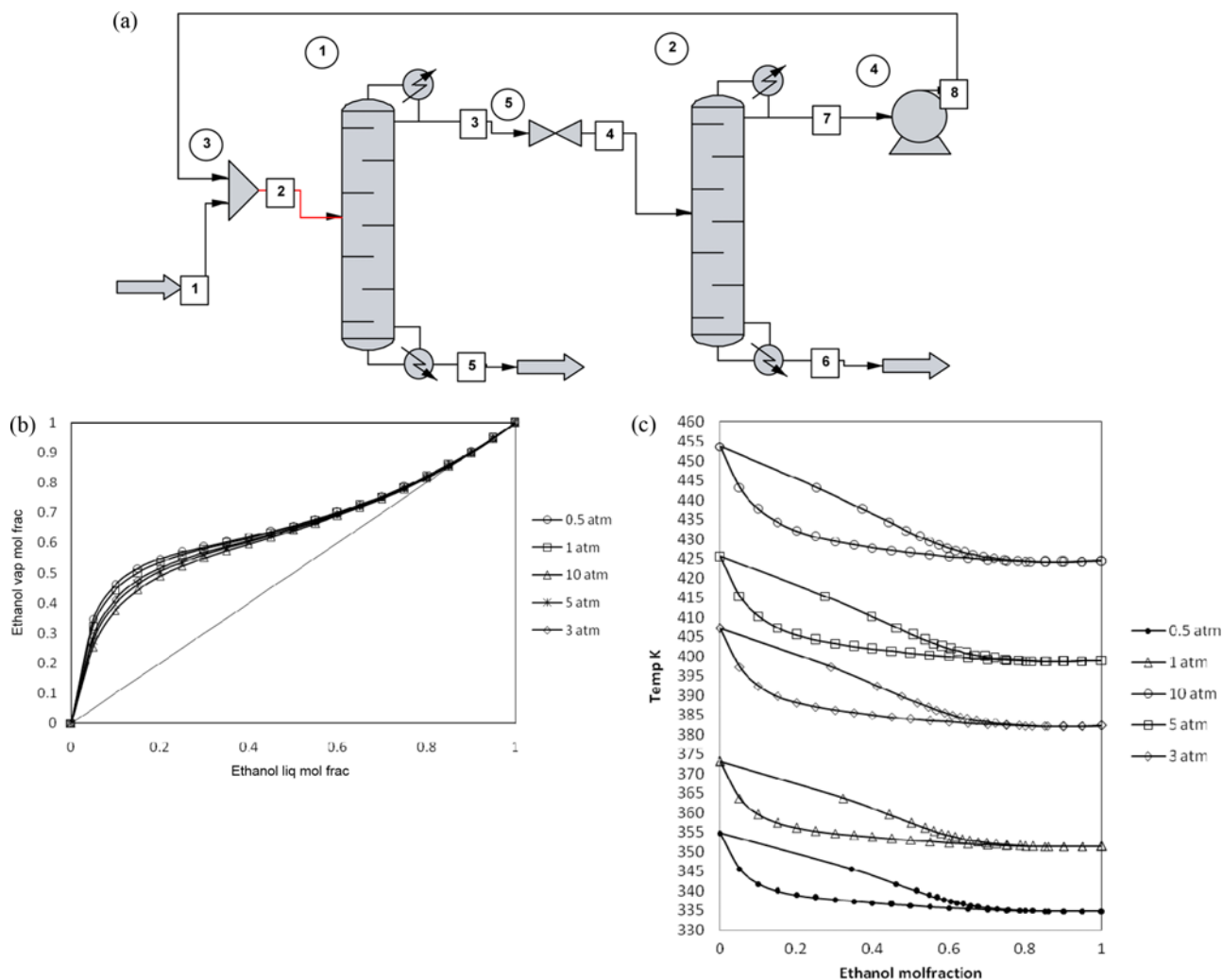
Fig. 3. (a) Pressure swing distillation sequence, (b) VLE for ethanol+water at various pressures, (c) T-xy for ethanol+water at various pressures.
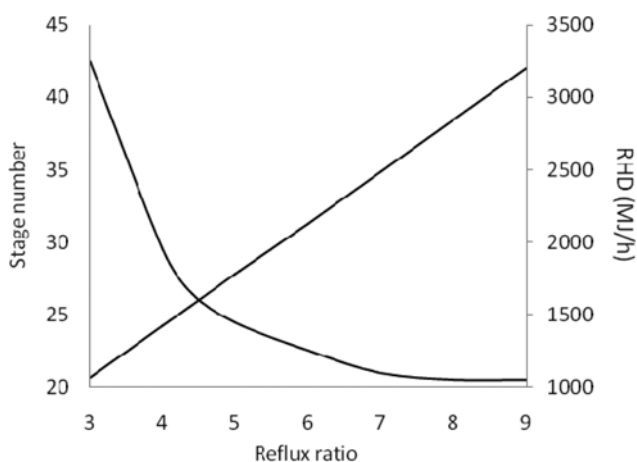

Fig. 4. Effect of reflux ratio on reboiler heat duty in extractive distillation sequence with preseparator.

content of C %.

Boilers produce steam from the combustion of fuel. This steam is delivered to the process at the temperature required by the process or obtained at a higher temperature and then throttled. In distillation systems, steam is used either for heating purposes, indirectly in reboilers, or as a direct stripping agent in so-called steam distillations. The flame temperature is lower than in a furnace because the heat of combustion is removed immediately to the steam. However, the same theoretical flame temperature of 1,800 °C may still be used. The stack temperature of 160 °C is also used in the calculations. The amount of fuel burnt can be calculated as

$$Q_{Fuel} = \frac{Q_{Proc}}{\lambda_{Proc}}(h_{Proc-419})\frac{T_{FTB}-T_0}{T_{FTB}-T_{stack}} \tag{3}$$

where λ_{Proc} and h_{Proc}

(kJ/Kg) are the latent heat and enthalpy of steam delivered to the process, while T_{FTB} is the flame temperature of the boiler flue gases.

RESULTS

The resulting designs and their performance with respect to energy consumption, CO_2 emissions and thermodynamic efficiency are discussed in the following sections.
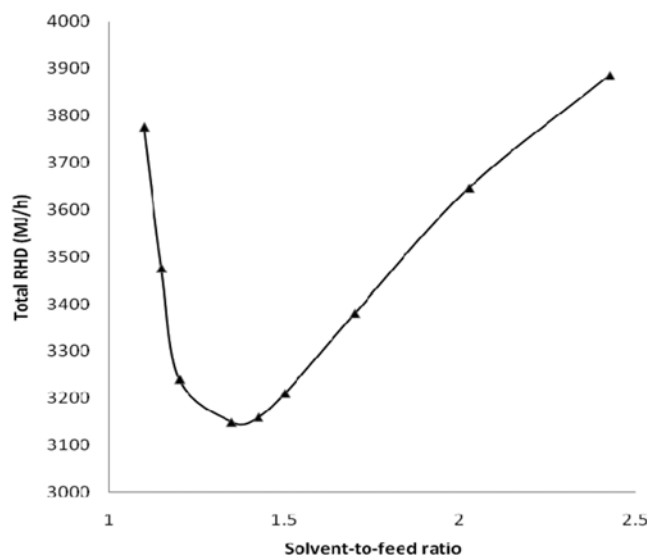
Fig. 5. Effect of solvent to feed ratio on total reboiler heat duty in extractive distillation sequence.
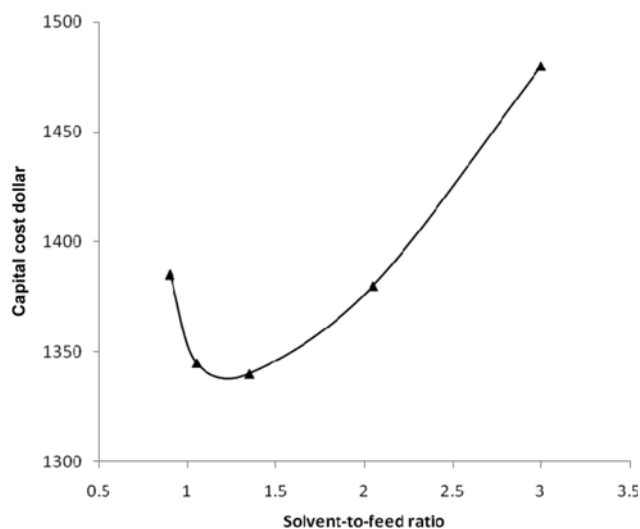

Fig. 6. Effect of solvent to feed ratio on total cost/year in extractive distillation sequence.

Design and energy optimization of the conventional sequences for the feed mixtures were carried out using the procedure previously described. Typical optimization curves for the extractive and pressure swing distillation sequences are shown in Fig. 5 and Fig. 6, respectively, where the optimal value for the separation can be determined in order to guarantee the minimum energy consumptions.

The optimization curves show an interesting effect of the search variables on energy consumption. The design is sensitive, in terms of its energy consumption. An implication of this observation has to do with operational considerations: tray arrangements and some important design variables for that sequence after the optimization.

The results of the rigorous optimization are collected for the extractive and pressure swing distillation configurations, indicating the effect of solvent-to-feed ratio (E/F) on energy consumption, economic evaluation, CO_2 emissions of the studied configurations. Some trends were observed like increasing solvent-to-feed ratio of the com-

plex extractive distillation systems causes a reduction of energy savings in comparison with the conventional distillation sequence. Consequently, the total annual cost will be increased, the energy savings achieved are in the considerable range in contrast to the conventional arrangement, and the reduction in global CO_2 emission, in distillation sequence is considerable.

The inefficiency of the conventional distillation sequences (associated with CO_2 emissions) has been reported as a consequence of remixing. Therefore, proper optimization should avoid such a remixing problem.

CONCLUSION

This study allows for the definite operation conditions for the extractive distillation process that uses n-Butyl Propionate as a separating agent. The selected UNIQUAC thermodynamic K-value model shows the identical nature with the experimental data on vapor-liquid equilibrium data in the ternary mixtures. The design and optimization of the additional column pre-separator extractive distillation sequence and pressure swing distillation sequence were studied and compared to those of a conventional extractive distillation sequence. A general energy efficient design procedure has been used that accounts for CO_2 emissions of the distillation sequences. The approach optimizes all process conditions in order to achieve energy savings and reductions in CO_2 emissions. Example of ethanol-water have shown that the design procedure can provide all of the operating parameters needed.

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APPENDIX A

The equations used for capital and operating cost calculations are the following.

The installed cost of column shell is calculated using Eqs. (A.1):

Installed cost of column shell,

$$\$=\left(\frac{\textbf{M\&S}}{\textbf{280}}\right)\textbf{101.9D}_{col}^{1.066}\textbf{H}_{C}^{0.802}(\textbf{2.18+F}_{C}) \qquad (A.1)$$

where the value of correction factor F_c depends on the pressure and shell material of the column and it ranges between 3-10. The chosen shell material is carbon steel.

M&S stands for the Marshall and Swift cost index published in Chemical Engineering. The M & S updates the equipment costs of process industry to the present time. This index is used to give a general estimate, but cannot take into account all factors that affect the equipment prices.

Installed cost of tower internals is calculated using column diameter and the tray stack height (H_t, [m]). The tray type is bubble cap.

$$\text{Installed cost of tower internals, } \$=\left(\frac{\textbf{M\&S}}{\textbf{280}}\right)\textbf{4.7 D}_{col}^{1.55}\textbf{H}_t\,\textbf{F}_c \qquad (A.2)$$

Where the correction factor's (f_c) value varies depending on tray spacing, type and material.

Installed cost of reboiler or condenser is estimated with installed cost of heat exchanger.

Installed cost of reboiler, condenser,

$$\$=\left(\frac{\textbf{M\&S}}{\textbf{280}}\right)\textbf{101.1 A}_{HT}^{0.65}\,(\textbf{2.29+F}_C) \qquad (A.3)$$

Where A_{HT}[m^2] is the heat transfer area. The value of correction factor (F_c) depends on the type of heat exchanger and the chosen value is 5.

Cooling water cost is calculated per year and it is the product of water price [$/t] and the mass flowrate of cooling water [t/h]. The required water mass flowrate is calculated with Eq. (A.4):

$$\text{Mass flowrate of cooling water, } [\text{kg/s}]=\textbf{Q}_{Cond}/\Delta\textbf{T}_{med}\times\textbf{c} \qquad (A.4)$$

Where c_p [kg/kgk] is specific heat capacity of cooling water.