

Thermally Coupled Distillation Systems: Study of an Energy-efficient Reactive Case

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Thermally coupled distillation systems (TCSD) have become excellent means to achieve important energy savings and consequently lesser capital investment for multicomponent-mixture separations. Reports, concerning the design, the operation and the control of those systems have recently been published, therefore allowing a practical implementation for the chemical industry. In this contribution the production of the compound ethyl acetate is studied, using three distinct thermally coupled distillation systems to carry out the purported reaction-separation process. Two of the distillation systems are arranged with side columns (stripper or rectifier) and the third one is the Petlyuk column. The thermally coupled system arranged with the side stripper shows some advantages in comparison with the thermally coupled system to which a side rectifier has been considered, because the former reduces the energy demanded by utilizing the traditional process, removing additionally the water produced in the chemical reaction avoiding the known azeotrope condition for this mixture, allowing a higher ethyl acetate compound production. A similar advantageous result has been observed in the case regarding the Petlyuk distillation column. Furthermore, this latter scheme turns out to be more a conveniently proposed system than the TCDS with the arranged side stripper given a lesser demanded energy.

Key words:

Thermally coupled systems, chemical reaction, ethyl acetate, energy savings

Introduction

Distillation is a unit operation widely used to separate multicomponent mixtures, in spite of its high energy consumption and low thermodynamic efficiency.^{1,2,3} A current trend in process separation has attracted interest in finding new distillation schemes capable of reducing the total annual costs. To fulfil this objective, Thermally Coupled Distillation Systems (TCDS) might be an excellent option because it is possible to attain important energy savings up to 50 % in comparison to conventional distillation trains.^{4,5,6,7} Those energy savings are attained because remixing is avoided in the TCDS options. In the case of conventional distillation sequences for the separation of ternary mixtures, the remixing can be explained in terms of the composition profile of the intermediate component. For the conventional distillation system, the composition of the middle component reaches a maximum at a certain point in the first column and then declines before reaching the upper-part (indirect sequence) or the bottom-part of the column (direct sequence); that remixing by the middle component implies a low thermodynamic efficiency because more en-

ergy should be supplied to re-purify the mixture. The latter fact can be avoided by using the TCDS options where a side column is fed with a sidestream that is extracted from the stage where the composition profile for the intermediate component reaches a maximum in the main distillation column.^{5,8} Generally, in a TCDS system, a liquid stream or a vapour stream may be replaced either by a reboiler or by a condenser allowing direct heat transfer between material streams.

Twenty years ago approximately, the real implementation of TCDS systems was not possible because of the lack of information related to the design, the optimization methods and the control properties; however, recent studies have shown that those systems have good theoretical control properties in comparison with conventional distillation schemes.^{9,10,11} According to these studies, an adequate control strategy and tuning quantities for the controllers might result in a practical reduction in the total annual costs for those coupled schemes with introducing almost no control problems.

The design and optimization methods for TCDS options have allowed their industrial implementation, in fact, nowadays the BASF Company has attained a leading position in the world for the

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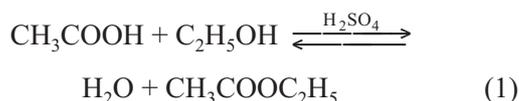
construction and operation of TCDS columns, specifically, the dividing-wall distillation columns that are thermodynamically equivalent to the Petlyuk column.^{12,13} Regarding second law efficiencies, *Agrawal* and *Fidkowski*¹⁴ have reported that it is really important to calculate the thermodynamic efficiency of the separation, because the TCDS sequences can have thermodynamic efficiencies lower than those of the conventional distillation sequences. They reported that the second law efficiency of the separation depends on the components and composition of the mixture to be separated.

Current trends in the study of TCDS options are focused on advanced control strategies attempting to improve the control properties, separation of azeotropic systems, reactive distillation and studies regarding design and optimization by using non-equilibrium stage models.

According to these research fields, the objective of this study is to analyze a reaction-separation-system case, using three TCDS sequences, two of them arranged with side columns, the third being the fully thermally coupled scheme (Petlyuk column). The three schemes are shown in Fig. 1, 2 and 3.

Methodology

According to the design and optimization methodology applied for the TCDS schemes reported by *Hernández* and *Jiménez*¹⁵, an essential part turns out to be the minimization of the heat duty supplied to the reboilers attained by finding the proper values of the interconnecting flow rates. The reaction stage of the typical production process of the ethyl acetate compound shown in Fig. 4 was studied by using reactive TCDS sequences. The classical process calls for the design of a reactor-column where ethanol and acetic acid flow rates are introduced to the reboiler, and the chemical reaction proceeds as catalyzed by sulphuric acid according to the following reaction at equilibrium:



Ethyl acetate and water are produced inside the reboiler of the reactor-column, then a separation ensues from a liquid mixture of reactants and products by operating a decanter to separate the aqueous and organic phases. The organic phase is fed into the purification column of the reactor-column system to obtain a high purity ethyl acetate compound ($w = 99.5\%$) while the separated aqueous phase is fed into a different conventional distillation column in

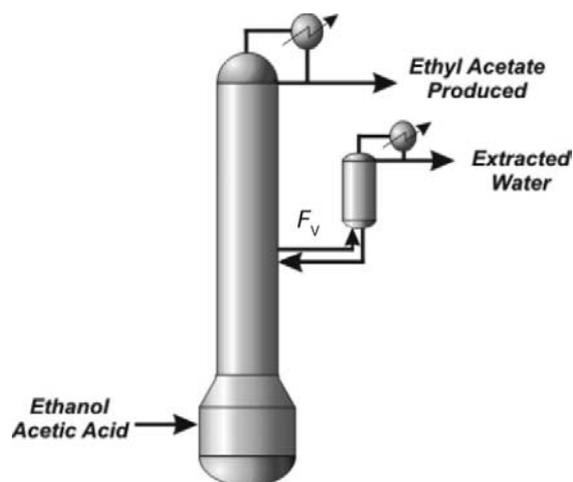


Fig. 1 – Reactive TCDS option arranged with a side rectifier

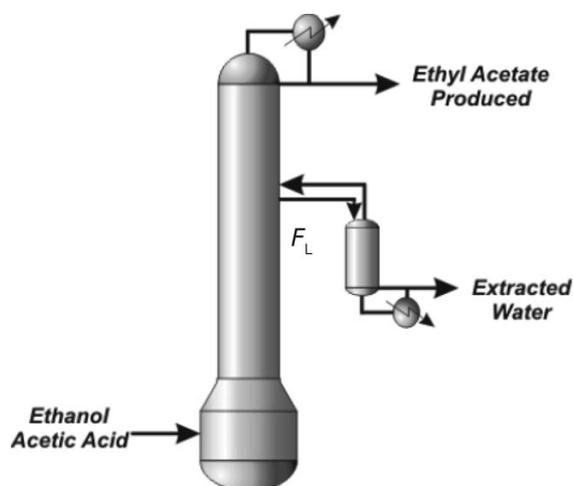


Fig. 2 – Reactive TCDS option arranged with a side stripper

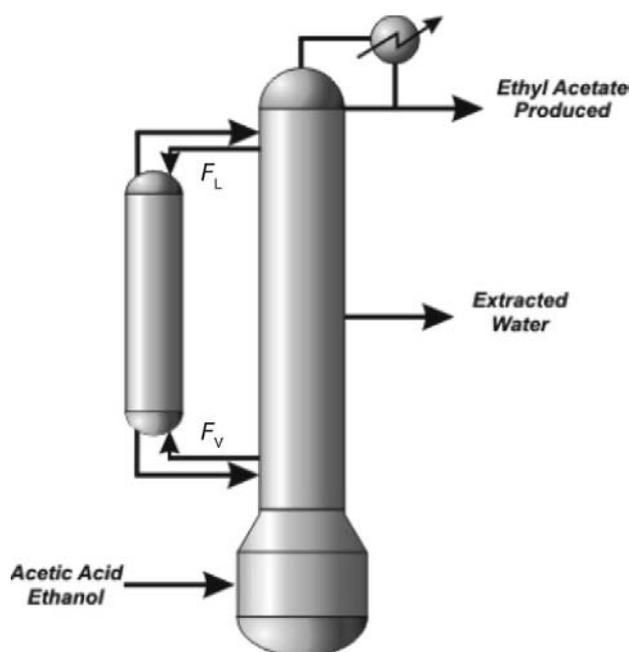


Fig. 3 – Reactive Petlyuk column

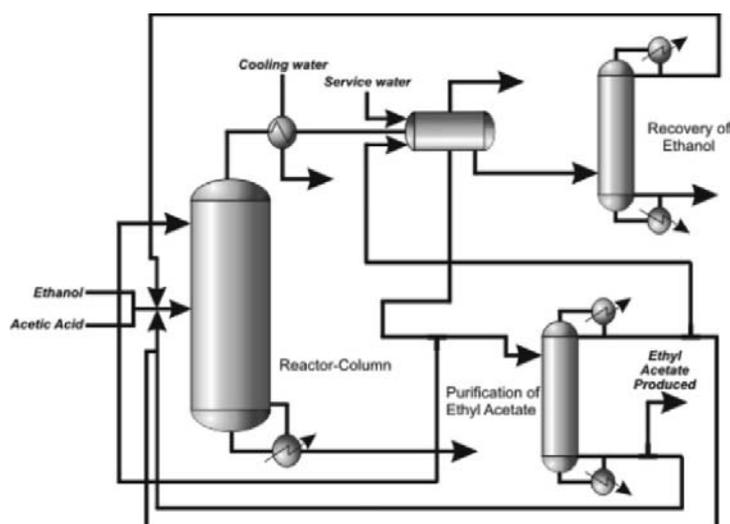


Fig. 4 – Conventional process for ethyl acetate compound production

order to recover the ethanol which is then returned to the reactor-column.

In the classical process described before, two inconvenient aspects in the operation can be observed: i) the chemical reaction yield is limited by the thermodynamic chemical equilibrium (presenting a limit to the ethyl acetate produced), and ii) the known azeotrope condition observed for the mixture turns to be slightly more complicated indeed to attain a high purity ethyl acetate compound, and the efficient recovery of ethanol and acetic acid is compromised as well. A useful tool to analyze this latter system is the residual curve map shown in Fig. 5 where pure components and azeotropes can be observed. According to Fig. 5, such a system shows the formation of two binary homogeneous azeotropes, one ternary homogeneous azeotrope and one heterogeneous binary azeotrope.

It was earlier mentioned that the design and optimization methods for the TCDS systems have

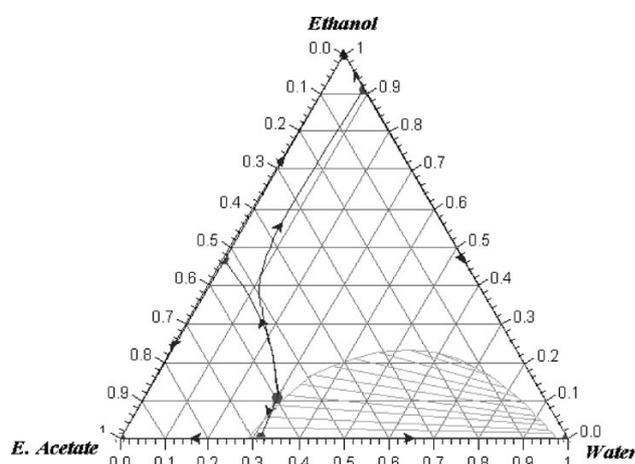


Fig. 5 – Residual curve map for the ethyl acetate system

been developed; however, there is a non-standard methodology for the design of reactive TCDS options. In previous studies regarding sterification processes in distillation columns and specifically for the ethyl acetate compound production,^{16,17} attained an optimum design, which was obtained through an optimization procedure that minimized an objective function by using as unknown variables the number of stages, feed stage, reflux ratio and also considering some constraints in the purities.

In this contribution, a parametric study was performed for each TCDS system. The structure of each system regarding the number of stages is based on columns used in an active ethyl acetate compound production process, for which real data is available. Basically, to carry out this study for each coupled reactive scheme, reactants were introduced into the reboiler that can be modelled as an equilibrium reactor.

Based on Le Chatelier Principle, the objective put forward in this study is to change dynamically the thermodynamic chemical equilibrium by removing the water content produced in the chemical reaction, by diverting a sidestream to the coupled rectifier or stripper (Fig. 1 and 2). These coupled side columns produce higher amounts of the ethyl acetate compound and consequently the azeotrope formation is overcome.

These studies were carried out by using the Aspen Plus 11.1TM process simulator. The thermodynamic properties were calculated through the use of the NRTL and Redlich-Kwong equations and the equilibrium constant was obtained from the Gibbs energy. The reaction was carried out in the liquid phase. To model these reactive TCDS systems, the MESH equations (material, energy, equilibrium and summation constraints for an equilibrium stage) were used.

Results

This study demonstrates the important role that the side columns have in increasing the ethyl acetate compound production by removing the water produced in the reaction from the system, thus increasing the reaction-separation efficiency, because the side column extracts the water produced and, consequently, the chemical equilibrium is displaced. The latter effect in turn allows a higher amount of the ethyl acetate compound produced as observed by the favourable modification of the equilibrium thermodynamic constant. The conversion for TCDS with the rectifier was 68 %, while conversions for TCDS arranged with the stripper and the Petlyuk column were 80 % for both, which

is higher in comparison to that obtained in the conventional process (56 %). It is important to note that, in the reactive TCDS options with side columns and the reactive Petlyuk column, the reaction takes place in the reboiler because of higher residence times and the produced water is removed by the side columns or sidestream. Tables 1 and 2 present the design and operating variables for the reactive TCDS options.

The case of the TCDS arranged with a side stripper, Fig. 6, shows the effect of the interconnecting liquid flow rate and the bottoms flow rate in the amount of water obtained in the lateral column.

Table 1 – Design specifications for TCDS arranged with side columns

Main Column		
feed composition	ethanol	22.7 kmol h ⁻¹
	acid acetic	22.7 kmol h ⁻¹
pressure	top	117 kPa
	bottom	144.5 kPa
number of stages		20
feed stage		20
Side column		
number of stages		10
feed stage	side stripper	1
	side rectifier	10
pressure	top	117 kPa
	bottom	144.5 kPa

Table 2 – Design specifications for the Petlyuk column

Main Column		
feed composition	ethanol	22.7 kmol h ⁻¹
	acid acetic	22.7 kmol h ⁻¹
number of stages		40
feed stage		40
pressure	top	117 kPa
	bottom	144.5 kPa
extraction stage		20
Prefractionator		
number of stages		20
pressure	top	117 kPa
	bottom	144.5 kPa

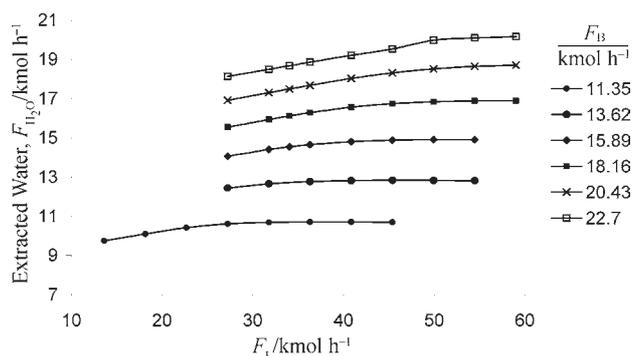


Fig. 6 – Effect of the interconnecting liquid flow rates on the amount of extracted water

According to Fig. 6, the maximum amount of water removal is obtained utilizing a bottoms flow rate of $F_B = 22.7$ kmol h⁻¹.

Fig. 7 shows the effect that the interconnecting and bottoms flow rates have on the heat duty. It can be observed that the minimum heat duty is attained through a value for the interconnecting flow rate of $F_L = 68.1$ kmol h⁻¹ and a bottoms flow rate of $F_B = 22.7$ kmol h⁻¹. The values for these variables let us obtain the maximum amount of water produced in the reaction; as a result, it is possible to conclude that those found values for the unknown variables are the convenient ones to operate this system, because a maximum amount of water can be extracted and consequently lesser heat duty needs to be supplied to the reboilers.

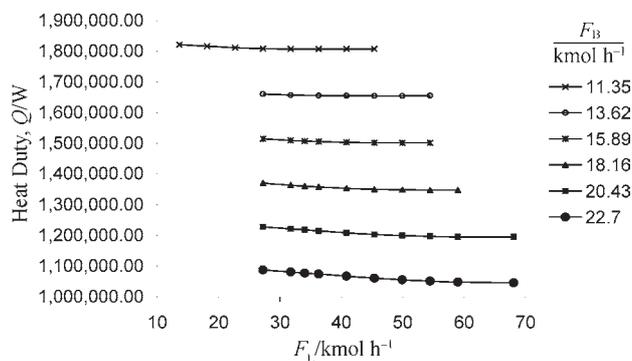


Fig. 7 – Effect of the interconnecting liquid flow rates on the heat duty

When the TCDS with the rectifier was studied, the results obtained are showed in the Figs. 8 and 9, where the maximum amount of extracted water is $F_{H_2O} = 15.9$ kmol h⁻¹ with an interconnecting vapour flow rate of $F_V = 27.24$ kmol h⁻¹ and a distillate flow rate of $F_D = 22.7$ kmol h⁻¹.

In order to complete this study for the three thermally coupled distillation systems mostly reported elsewhere, the Petlyuk column was then analyzed. Fig. 10 shows the effect that the liquid and

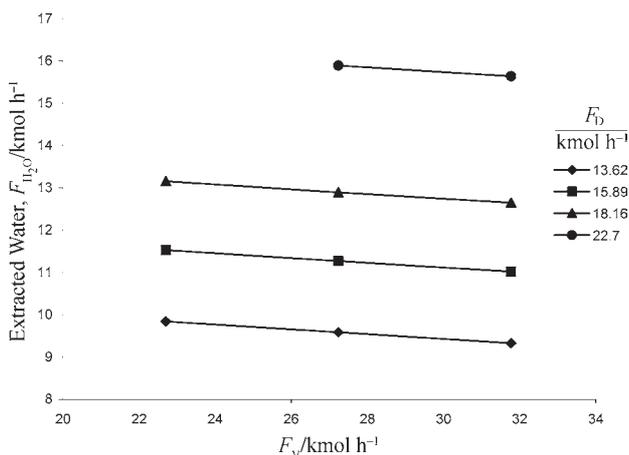


Fig. 8 – Effect of the interconnecting vapour flow rates on the amount of extracted water

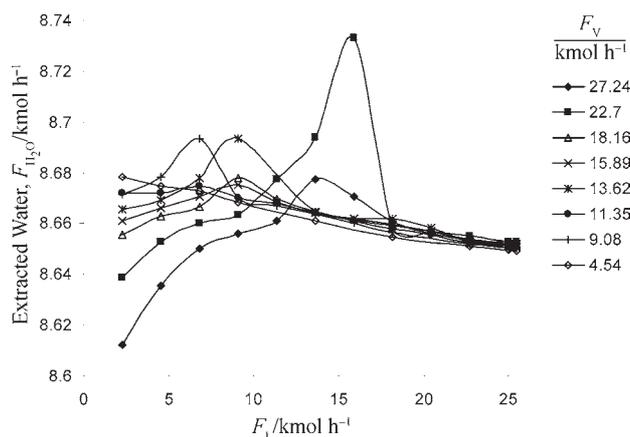


Fig. 11 – Effect of the interconnecting liquid flow rates on the amount of extracted water

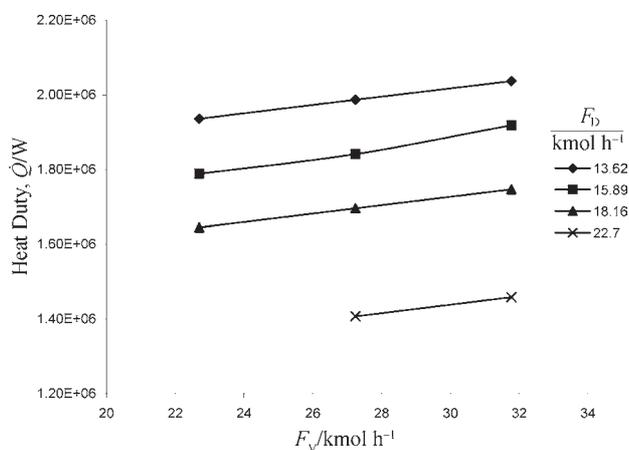


Fig. 9 – Effect of the interconnecting vapour flow rate on the heat duty

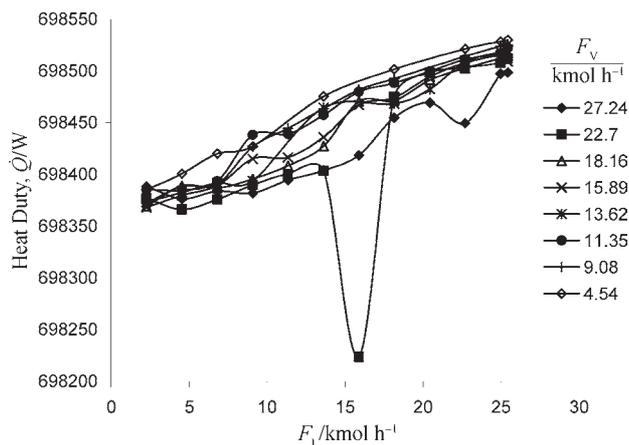


Fig. 10 – Effect of interconnecting liquid flow rates on the heat duty

vapour flow rates have on the heat duty demanded by the reboiler, the values for the interconnecting flow rates required for the minimum heat duty, were $F_V = 22.7 \text{ kmol h}^{-1}$ and $F_L = 15.89 \text{ kmol h}^{-1}$ for the vapour and liquid flow rates respectively.

However, it can be observed that the effect of the recycle streams on the energy consumption is very small. Fig. 11 shows that the maximum extracted water was 8.65 kmol h^{-1} for those latter interconnecting flow rates.

It is important to highlight that the Petlyuk system requires the lowest heat duty contrasting to both TCDS schemes with side columns; however, the amount of extracted water is lesser. With respect to the amount of the ethyl acetate compound produced, the TCDS option involving a side stripper and the Petlyuk systems gave similar results.

Finally, the Petlyuk column seems to be the best scheme to carry out this reaction-separation because the heat duty for this system turned out to be less than with that obtained by the TCDS arranged with a stripper or a rectifier.

It is essential to mention that the water extraction has a very important role in attaining the hereby reported efficiencies for the reaction-separation systems, because it avoids the formation of the azeotrope conditions. As a result, the energy required to achieve the reaction-separation task is reduced by using the TCDS options. In general, energy savings are expected between 30 and 50 % by using the fully thermally coupled distillation sequence in comparison to the classical process of production of ethyl acetate.

Conclusions

Two thermally coupled distillation sequences arranged with side columns (stripper or rectifier) and one fully thermally coupled distillation column (Petlyuk) were utilized to carry out the production of the ethyl acetate compound. The parametric studies showed that the Petlyuk column requires a lesser amount of energy in contrast to the integrated distil-

lation sequences coupled with side columns. The highest amount of the ethyl acetate compound was obtained by using the Petlyuk column or the thermally coupled distillation sequence using a side stripper. The results obtained show that it is possible to displace the thermodynamic chemical equilibrium dynamically to produce a higher amount of ethyl acetate by removal of the reaction by-products mostly of the water produced. According to these results, it can be concluded that TCDS options present significant advantages over the classical process used to produce the ethyl acetate compound. In particular, the Petlyuk column turned out to be the most convenient system because of the lesser demand of energy and a production yield of the ethyl acetate compound similar to that obtained in the thermally coupled distillation sequence with a side stripper.

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Nomenclature

F_B – bottoms flow rate, kmol h⁻¹
 F_D – distillate flow rate, kmol h⁻¹
 F_L – interconnecting liquid flow rate, kmol h⁻¹
 F_V – interconnecting vapor flow rate, kmol h⁻¹
 TCDS – thermally coupled distillation sequence
 w – mass fraction

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