1

Analysis of Design and Control of Reactive Thermally Coupled Distillation Sequences

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Abstract

This work presents a study of the production of ethyl acetate from ethanol and acetic acid through three reactive thermally coupled systems: a thermally coupled distillation sequence with a side stripper, a thermally coupled distillation sequence with a side rectifier and a Petlyuk-type column. Using the process simulators Aspen Plus™ and Aspen Dynamics™, a parametric study was carried out in order to understand the effect of the process variables on the production of ethyl acetate. In the first part of the study, we found that most of the water produced in the sterification reaction can be removed by the use of side columns coupled to a main column. This favors the production of ethyl acetate and only the ethyl acetate-water heterogeneous azeotrope is formed in the distillate product. A similar result was also found in the case of the dividing wall distillation column (Petlyuk-type column) i. e., the side stream product is mainly water. In addition, this distillation sequence required the lowest amount of energy, compared to the thermally coupled distillation with side columns. In the second part of the study, dynamic closed-loop responses were obtained for the most energy-efficient reactive distillation scheme (Petlyuk column). The results showed that with this complex scheme, one can achieve changes in the set point and also elimininate the effect of disturbances with only simple PI controllers tuned by the Ziegler and Nichols' method. From these results, one may conclude that thermally coupled distillation systems present significant advantages over the classical process used to produce ethyl acetate.

1. Introduction

Distillation is a unit operation that is still widely used to separate multicomponent mixtures, in spite of its high energy consumption and low thermodynamic efficiency [1,2,3]. Finding new distillation schemes capable of reducing total annual cost is therefore currently of significant interest in process separations research. In this context, Thermally Coupled Distillation Systems (TCDS) are proving to be excellent options because, with them, it is possible to achieve energy savings of up to 50% in comparison to conventional distillation trains [4,5,6]. Such energy savings are possible because remixing is avoided in the TCDS options. With conventional distillation sequences used for the separation of ternary mixtures, the concept of remixing can best be explained in terms of the intermediate component's composition profile. In such conventional distillation systems, 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); as such remixing by the middle component implies a low thermodynamic efficiency because more energy must now be supplied to re-purify the mixture. This latter condition can be avoided by using the TCDS options where a side column is fed with a sidestream extracted from the stage in the main distillation column where the intermediate component's composition profile reaches a maximum [5,7]. In general in a TCDS system, a liquid stream or a vapor stream can be replaced either by a reboiler or by a condenser, allowing direct heat transfer between material streams.

Implementing TCDS systems in practice was not possible approximately twenty years ago because very little quantitative information was available about the design, optimization methods and control properties; recently, however, many studies have established that these systems have good theoretical control properties compared to conventional distillation schemes [8,9,10]. According to these studies, an adequate control strategy with properly tuned controllers can result in a significant reduction in the total annual costs for these coupled schemes without introducing any control problems. The design and optimization methods currently available for TCDS options have now made their industrial implementation possible. Today, the BASF Company has attained a leadership position worldwide in the construction and operation of TCDS columns, specifically, the dividing-wall distillation columns that are thermodynamically equivalent to the Petlyuk column [11,12].

As a result of the problems that still remain unsolved, current studies of TCDS options typically focus on advanced control strategies (to improve the control properties), separation of azeotropic systems, and reactive distillation in addition to studies regarding design and optimization by using nonequilibrium

stage models. Along these lines, the objective of this study is to analyze a reaction-separation-system case, using three TCDS sequences shown in Fig. 1: two are arranged with side columns, and the third is a fully thermally coupled scheme (Petlyuk column)..
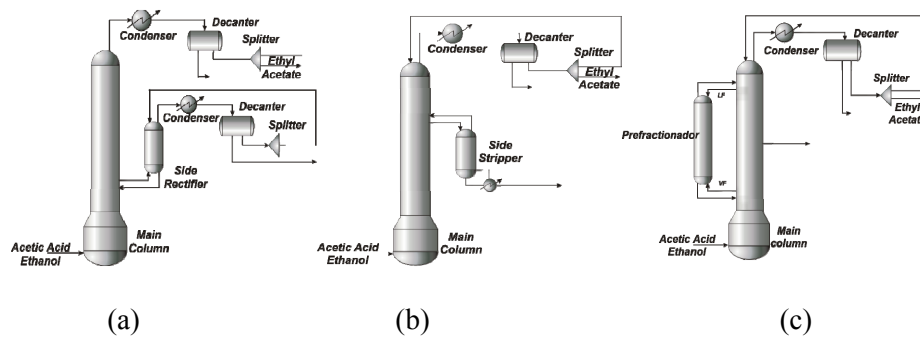

| (a) | (b) | (c) |

Figure 1 TCDS schemes: (a) TCDS with side rectifier, (b) TCDS with side stripper, (c) Petlyuk column.

2. Ethyl acetate process

The classical process calls for the design of a reactor-column where ethanol and acetic acid streams are introduced to the reboiler, and the chemical reaction proceeds as catalyzed by sulfuric acid, according the following equilibrium reaction:

$$CH_3COOH + C_2H_5OH \underset{}{\overset{H_2SO_4}{\rightleftarrows}} H_2O + CH_3COOC_2H_5 \qquad (1)$$
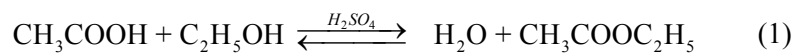
Ethyl acetate and water are produced inside the reboiler of the reactor-column, and the decanter is used to separate the liquid mixture of reactants and products into aqueous and organic phases. The organic phase is fed into the purification column of the reactor-column system to obtain a high purity ethyl acetate compound (99.5% weight) while the aqueous phase is fed into a separate conventional distillation column in order to recover the ethanol which is then returned to the reactor-column.

It is now important to note the following two inconvenient aspects of this process: i) the chemical reaction yield is limited by the thermodynamic chemical equilibrium (imposing a limit on the amount of ethyl acetate produced); and ii) the known azeotrope formed by the mixture (See Table 1)

makes attaining a high purity ethyl acetate compound a bit more complicated, and also compromises the efficient recovery of ethanol and acetic acid. This is an important issue because the azeotrope ethyl acetate-water is heterogeneous and forms two liquid phases. The organic liquid phase is used for the reflux of the reactive distillation column and the remaining is sent to a distillation column to purify the ethyl acetate to a value greater than 99.5 mass percent. The design variables for the three reactive thermally coupled distillation sequences were obtained from a previous work [13]. It is important to mention that that work did not include decanters for the separation of the two liquid phases. This is a key factor that must be taken into account, because it is important to diminish the amount of water refluxed to the reactive distillation column.

Table 1 Azeotropes for the system at the pressure of 1 atm.

Azeotrope	Mole fractions	Temperature (°C)
Ethanol-Ethyl Acetate	(0.462, 0.538)	71.81
Ethanol-Water	(0.9037, 0.0963)	78.17
Ethyl Acetate-Water	(0.6885, 0.3115)	70.38
Ethanol-Ethyl Acetate-Water	(0.1126, 0.5789, 0.3085)	70.23

2.1. Methodology

According to the design and optimization methodology applied for the TCDS schemes reported by Hernández and Jiménez [4], 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. This task was conducted in Aspen Plus. Table 2 contains the energy consumption required by each distillation sequence and the reactive Petlyuk configuration demanded the lowest amount of energy. For that reason, in this preliminary study, we explored the control of the reactive Petlyuk column. Also, this column can be implemented more easily in practice by a dividing wall distillation column.

Table 2 Energy consumptions (kW) for the reactive systems.

Reactive distillation scheme	Energy (kW)
TCDS with a side rectifier	810.0
TCDS with a side stripper	871.5
Petlyuk column	545.5

2.2. Case study

The steady state study of the reactive thermally coupled distillation systems was carried out by using an equilibrium model for the reaction, but for the dynamic

analysis, the kinetic model for the reaction was taken from Tang et al. [14]. A control loop for the mole fraction of ethyl acetate in the organic liquid phase was implemented. The mole fraction of ethyl acetate was controlled by manipulating the flowrate of the organic liquid phase returned to the reactive Petlyuk column. A simple PI controller was implemented and tuned by the Ziegler and Nichol's method.

2.3. Results & discussions

From Figure 2 we can obtain values of 5 and 14.25 min for the ultimate gain and period respectively. Then, a PI controller with Kc=2.25 and τ_i =11.875 min was used for the dynamic tests.

Figure 3 shows the dynamic responses of the control and manipulated variables for a positive set point change of magnitude 0.01 in the mole fraction of the ethyl acetate. It can be observed that the system can achieve the set point change. The dynamic response of the mole fraction of the ethyl acetate presents oscillations and reaches the new steady state in approximately 2.5 h. A similar tendency is observed in the manipulated variable. When a negative set point change of the same magnitude was implemented, the reactive Petlyuk column reached the new steady state in approximately 1 h. In general, the dynamic responses for positive set point changes presented oscillations.
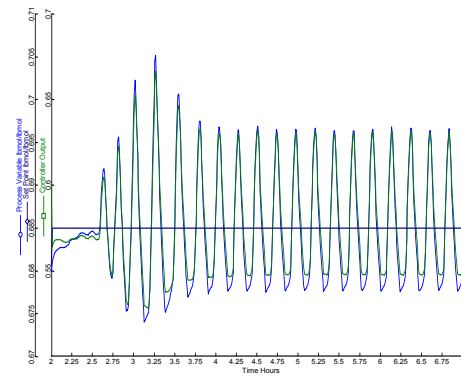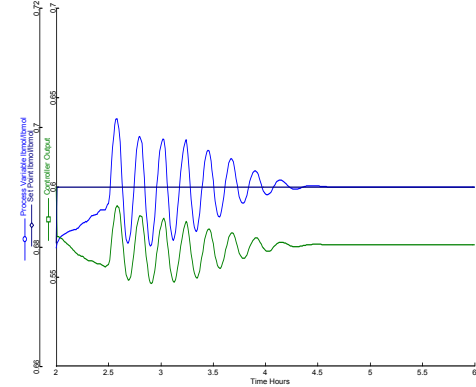

Figure 2 Continuous oscillatory responses.   Figure 3 Dynamic closed-loop responses.

In order to complete the study, the component mole flows in the feed were subjected to disturbances of different magnitudes (5 to 10%). The dynamic responses showed that in general the reactive Petlyuk column eliminated the effect of the disturbance on the mole fraction of ethyl acetate in the organic liquid phase. For negative disturbances of the same magnitude, again, the system eliminated the effect of the disturbance.

3. Conclusions

From these results, one may conclude that thermally coupled distillation systems present significant advantages over the classical process used to produce ethyl acetate. In particular the Petlyuk column turned out to be the most convenient system because of the lower energy demand in achieving a production yield of ethyl acetate similar to those obtained in the thermally coupled distillation sequences with side columns. Also, the results indicate that simple PI controllers are sufficient to provide reasonable control of the mole fraction of the ethyl acetate in the organic liquid phase of the reactive Petlyuk column.

Acknowledgements

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