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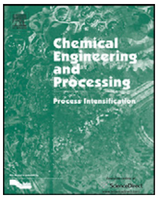

Reactive dividing wall distillation columns: Simulation and implementation in a pilot plant[☆]

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ABSTRACT

We performed steady state and dynamic simulations of a reactive Petlyuk column through an equivalent reactive dividing wall column (RDWDC). In the case of the reaction between ethanol and acetic acid catalyzed by sulfuric acid to produce ethyl acetate and water, we have found that the reactive Petlyuk column can achieve set point changes in two control loops of temperature. Also, for load rejection, the control loops can eliminate the effect of the disturbances in the feed composition. These results and previous knowledge reported about thermally coupled distillation columns and reactive distillation were considered to design and implement a RDWDC.

1. Introduction

Distillation is a unit operation widely used to separate multicomponent mixtures in spite of its high energy consumption and low thermodynamic efficiency. As a result, engineers and researchers are interested in developing new configurations capable of reducing and improving the use of energy. It has been demonstrated that thermal linking can reduce energy demands between 30 and 50% depending on the composition of the mixture to be separated. The three thermally coupled distillation sequences (TCDS) that have been explored in detail are the TCDS using a side rectifier, the TCDS involving a side stripper and the fully thermally coupled distillation sequence or Petlyuk system. Because of the reduction in the oil reserves and polices of reduction in carbon dioxide emissions [1], significant research has focused on the design, optimization and control of the TCDS. Regarding the design of TCDS, Christiansen et al. [2] reported a design and optimization procedure for the Petlyuk distillation column that involves the search for the values of the interconnecting streams of the system. Hernández and Jiménez [3] presented a design method that minimizes the energy consumption for a given structure of the Petlyuk distillation column. Dunnebier and Pantelides [4] reported a formal procedure based on mathematical programming for detecting the optimal design of integrated distillation columns. Also, dynamic studies have been reported for the TCDS; for instance, Jiménez et al. [5] compared the theoretical control properties and closed-loop dynamic responses of conventional and thermally coupled distillation sequences, and they found that the TCDS schemes presented theoretical control properties and dynamic responses better than those of the conventional distillation sequences. In the same context, Serra et al. [6] compared the controllability of different distillation arrangements and showed that some operation conditions different from those of the optimum energy consumption favored the operation of the heat-integrated systems.

The implementation of TCDS systems has been more noticeable in Europe and Japan, in part because of their dependence on imported crude oil. The Petlyuk system has been successfully implemented by using a dividing wall inside a distillation column; the resulting configuration is known as the dividing wall distillation column (DWDC, see Fig. 1). Practical implementations of the DWDC have reported savings of up to 40% in both energy and capital costs [7–10]. Because of polices in process intensification, we are interested in carrying out reactions in thermally coupled distillation sequences. Based on results about steady state design, optimization and control obtained by using simulations, we have designed and implemented a reactive dividing wall distillation

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

Azeotrope	Type	Mole fractions	Temperature (°C)
Ethanol–ethyl acetate	Homogeneous	(0.462, 0.538)	71.81
Ethanol–water	Homogeneous	(0.9037, 0.0963)	78.17
Ethyl acetate–water	Heterogeneous	(0.6885, 0.3115)	70.38
Ethanol–ethyl acetate–water	Homogeneous	(0.1126, 0.5789, 0.3085)	70.23

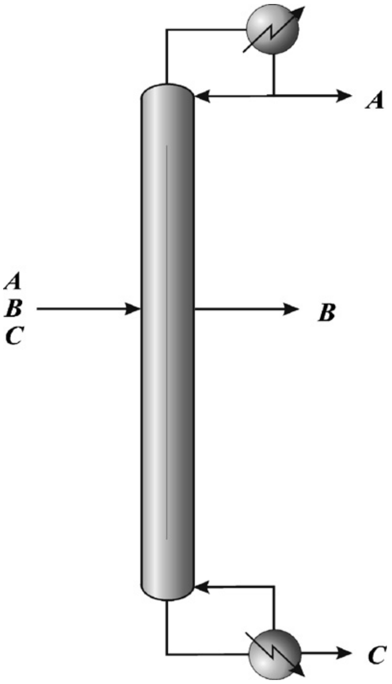


Fig. 1. Petlyuk column as a dividing wall distillation column (DWDC).

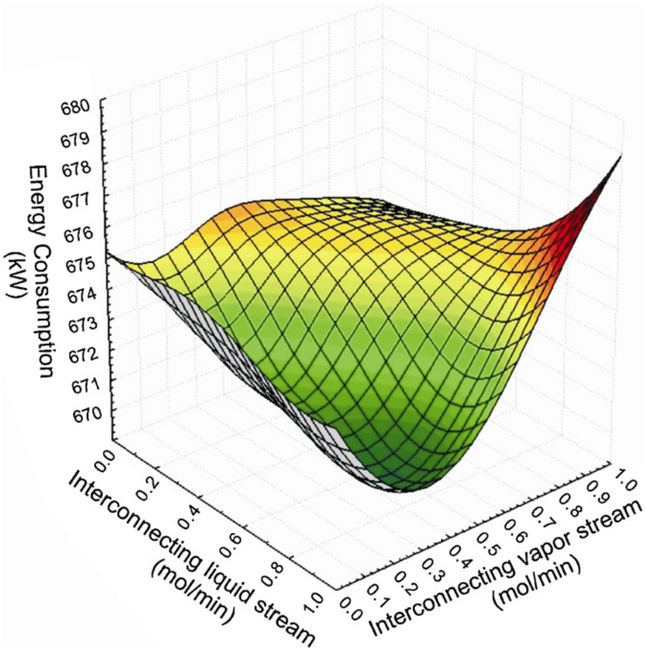
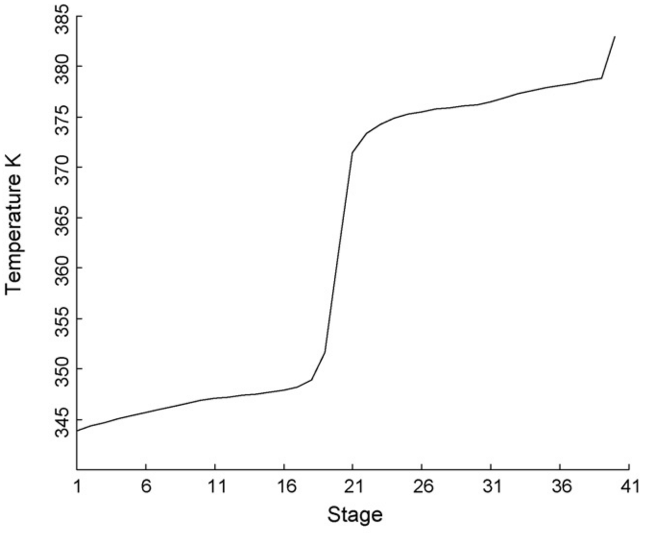
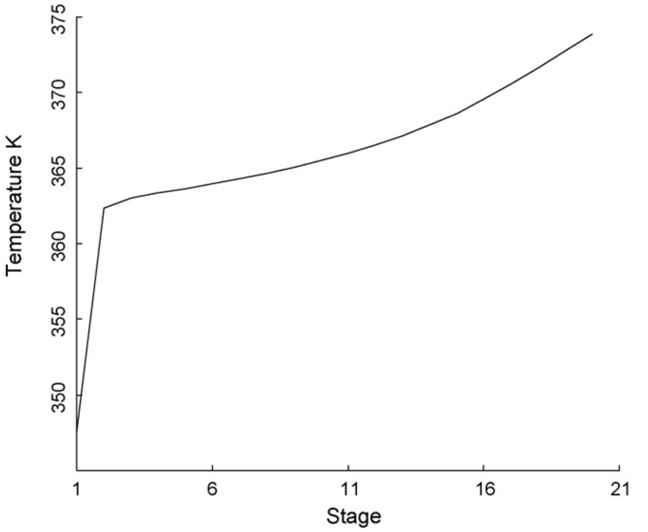


Fig. 2. Energy optimization of the design of the reactive Petlyuk column.



(a) Main distillation column.



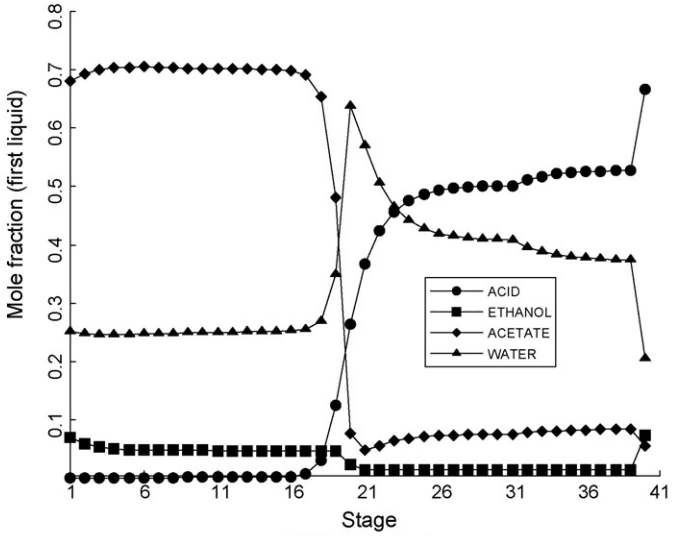
(b) Prefractionator.

Fig. 3. Temperature profiles in the steady state design of the reactive Petlyuk distillation column.

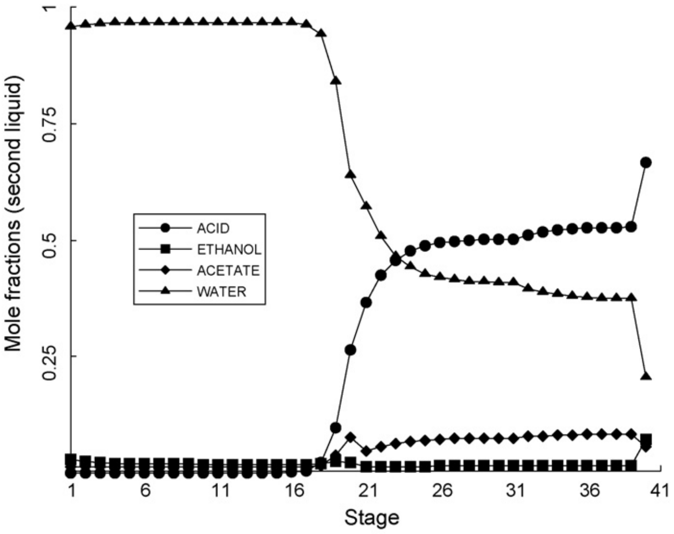
column (RDWDC) in a pilot plant. The column was designed to carry out the equilibrium reaction between ethanol and acetic acid to produce ethyl acetate and water catalyzed by sulfuric acid. Hence, significant information (Kloker et al. [11], Lai et al. [12]) regarding the production of ethyl acetate via reactive distillation was also considered during the design process.

2. Base case: the reaction-separation process

The process involves a reactor-column where ethanol and acetic acid are introduced to the reboiler, and the chemical reaction pro-



(a) First liquid phase.



(b) Second liquid phase.

Fig. 4. Liquid composition profiles of the main column in the reactive Petlyuk distillation column.

Table 2
Important design variables of the reactive Petlyuk system

Design specifications for Petlyuk column			
Main column			
Feed composition	Ethanol		22.7 kmol/h
	Acid acetic		22.7 kmol/h
Number of stages		40	
Feed Stage		40	
Pressure	Top		117 kPa
	Bottom		144.5 kPa
Extraction stage		20	
Column diameter (m)		0.61	
Reactive stages		40	
Prefractionator (dividing wall)			
Number of stages		20	
Pressure	Top		117 kPa
	Bottom		144.5 kPa
Column diameter (m)		0.37	

Table 3
Component flows in the main products of the reactive Petlyuk distillation column

Stream	Feed	Bottoms	Distillate	Side stream
Ethanol (kmol/h)	22.7	0	2.726	0.260
Acetic acid (kmol/h)	22.7	0	0	2.984
Ethyl acetate (kmol/h)	0	0	18.845	0.864
Water (kmol/h)	0	0	12.472	7.238

ceeds as it is catalyzed by sulfuric acid according to the reaction at equilibrium given by Eq. (1).

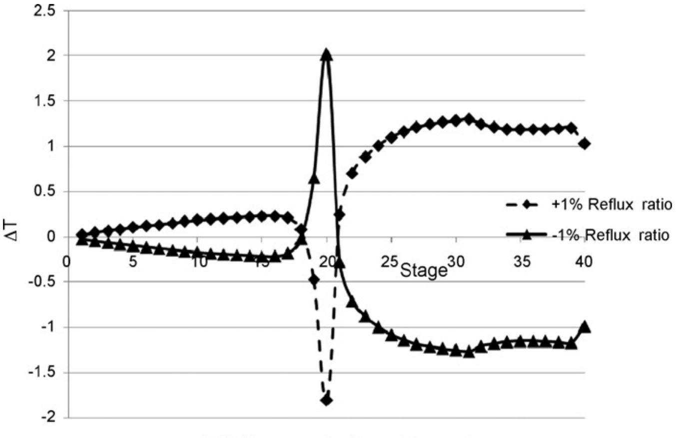
$$CH_3COOH + C_2H_5OH \overset{H_2SO_4}{\rightleftarrows} H_2O + CH_3COOC_2H_5 \quad (1)$$

For the steady state study, an equilibrium reaction can be used, but for dynamic simulations the model kinetics was taken from Tang et al. [13].

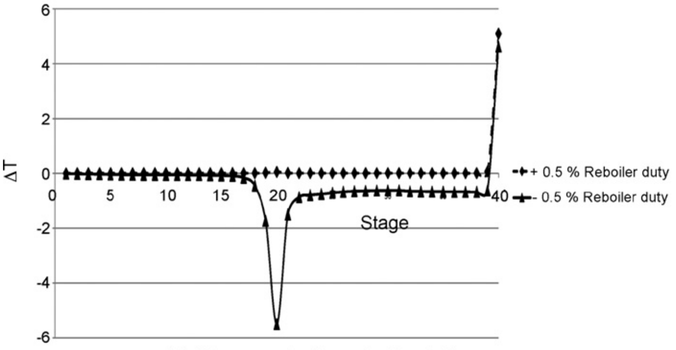
$$K1 = 0.485\ \exp\left(\frac{-59774}{RT}\right) \quad (2)$$

$$K2 = 0.123\ \exp\left(\frac{-59774}{RT}\right) \quad (3)$$

The distillate is introduced into a decanter tank where two liquid phases are present. The organic phase is fed into the purification column of the reactor-column system to obtain a high purity ethyl acetate (99.5% weight at) whereas the separated aqueous phase is fed into a different conventional distillation column to recover the ethanol which is then returned to the reactor-column. It is important to highlight that two inconvenient aspects in the operation can be observed in this process: (i) the chemical reaction yield is limited by the thermodynamic chemical equilibrium (representing a limit to the production of ethyl acetate) and (ii) the system presents



(a) Changes in the reflux ration.



(b) Changes in the reboiler duty.

Figure 5. Gains in the trays of the main distillation column.

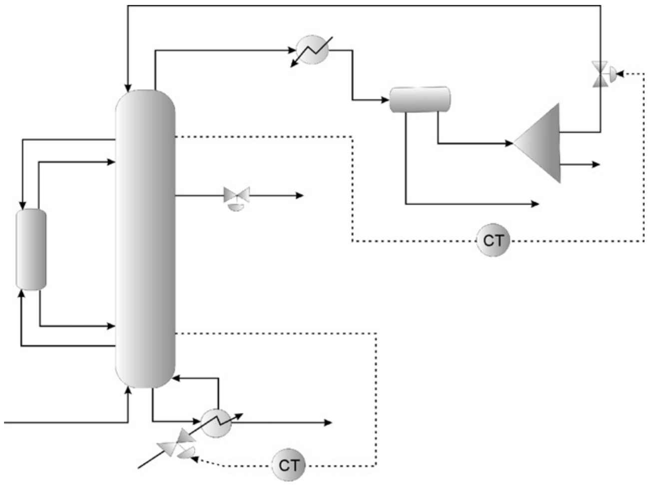


Fig. 6. Control loops of temperature in the Petlyuk system.

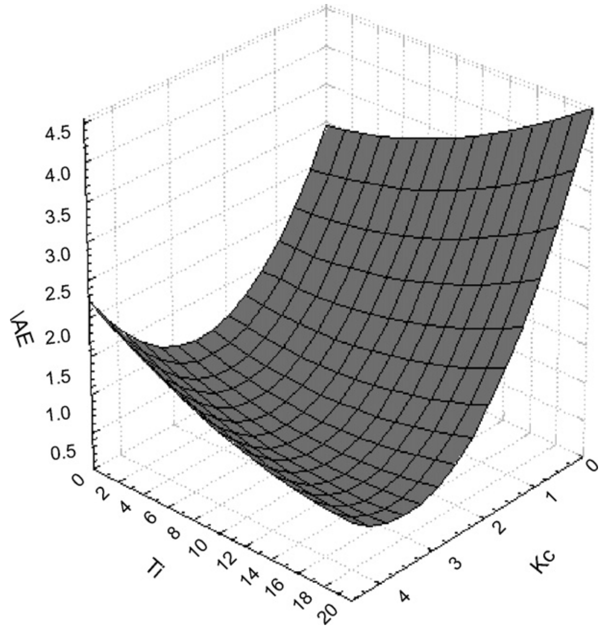
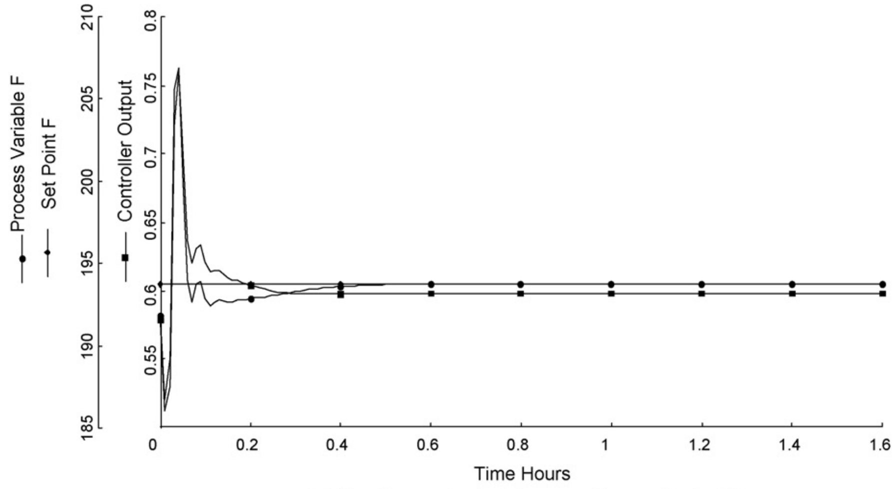
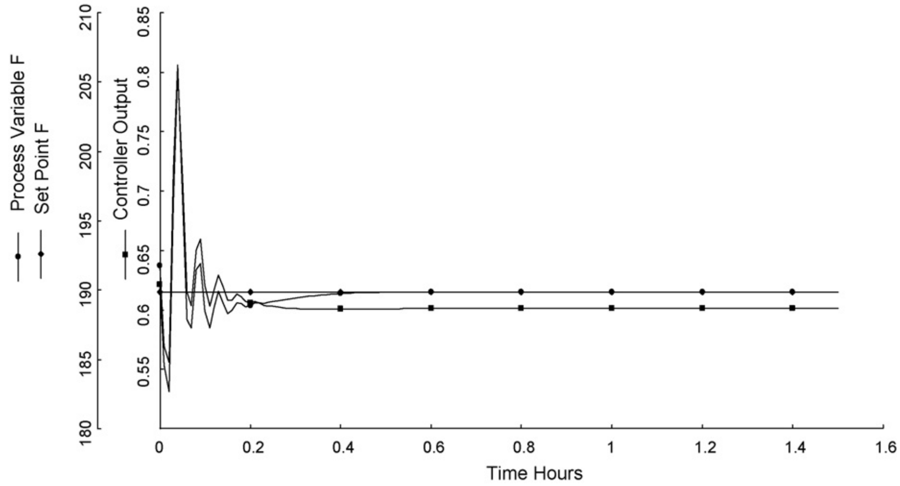


Fig. 7. Minimization of the IAE for the first control loop.



(a) Positive set point change of magnitude 1°F.



(b) Negative set point change of magnitude 1°F.

Fig. 8. Dynamic responses of the first control loop.

two binary homogeneous azeotropes, one ternary homogeneous azeotrope and one heterogeneous binary azeotrope (Table 1).

3. Steady state simulation of the reactive Petlyuk distillation column

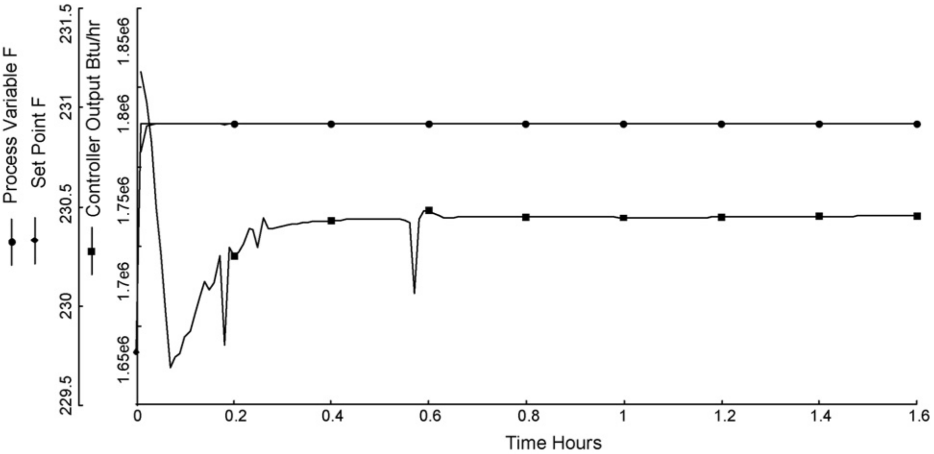
The design and optimization methods reported in Hernández and Jiménez [3] were used through the Aspen Plus process simulator. The thermodynamic properties were calculated using the NRTL model and an equilibrium reaction was considered for the production of the ethyl acetate. The equilibrium stage model included in the radfrac model of Aspen Plus^{TM} was used for both steady state and dynamic simulation.

The design of the reactive Petlyuk column was carried out in two stages: in the first stage, we adopt values of theoretical stages and interconnecting stages in the two distillation columns. The equilibrium chemical reaction is conducted in the reboiler of the main distillation column.

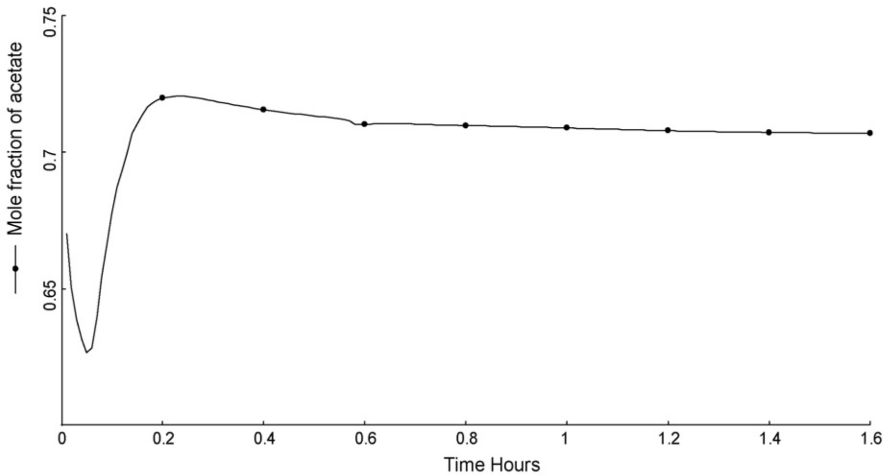
In the second stage of the design and optimization procedures, a value of the interconnecting vapor stream is assumed and a complete search is conducted in the interconnecting liquid stream until the local minimum energy consumption is detected for the assumed value of the interconnecting vapor stream. The strategy is conducted for other values of the interconnecting vapor stream until the optimal energy consumption is obtained for the initial trays of the reactive Petlyuk column. It is important to highlight that this procedure is repeated in Aspen Plus until the optimum in terms of number of stages and energy consumption is found. This procedure can be carried out using mathematical programming but the complexity of the system can lead to severe numerical control problems.

Fig. 2 presents the minimization of the energy consumption of the distillation column; it can be seen that the energy consumption depends strongly on the values of the interconnecting streams. Appropriate values of the interconnecting streams are important to obtain the minimum energy consumption in the reactive Petlyuk distillation column. After the search for the optimum values of the recycle streams was conducted, values of 13.62 and 27.24 kmol/h for the liquid and vapor streams respectively were detected. Table 2 provides the values of the main design variables of the reactive Petlyuk distillation column.

At this stage important information can be obtained from the steady state simulations; for instance, Fig. 3 presents the temperature profiles of both columns in the reactive Petlyuk distillation column, this temperature profiles can be used to detect the optimal location of the sensors of temperature. Also, it is really important to know the composition profiles because we are introducing ethanol



(a) Temperature and manipulated variable.



(b) Mole fraction of the ethyl acetate in the product stream.

Fig. 9. Dynamic responses of the second control loop for a positive set point change of magnitude 1 °F.

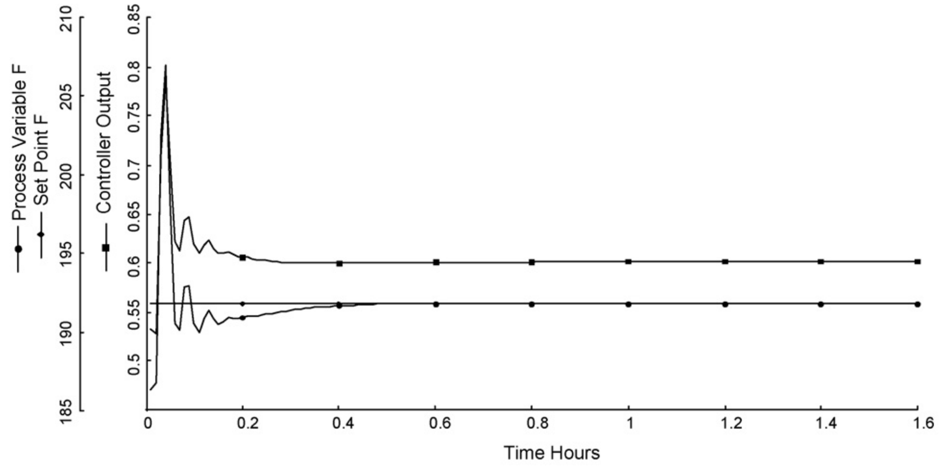
and acetic acid as feeds and the ethyl acetate and water are produced in the reboiler. According to Fig. 4, two liquid phases are obtained, one rich in the ethyl acetate product and the second liquid phase contains water as the main component. Table 3 contains the flows of components in the main streams of the Petlyuk reactive column. This table shows that the ethyl acetate and water produced in the reaction are obtained in the distillate and side stream products, because it is assumed that no bottoms product is obtained.

For non-reactive systems, it is well-known that the Petlyuk distillation column can reduce energy demands between 30 and 50% depending on the composition of the mixture to be separated. Also, for the specific case of production of ethyl acetate, Barroso-Muñoz et al. [14] found that similar energy savings can be obtained in the reactive Petlyuk distillation column in contrast to those obtained in non-reactive systems. Regarding control schemes, we anticipated that, in practice, it is difficult to implement gas chromatography on line to measure compositions due to additional costs as well as delays in the measurements. Hence, we considered inferential control instead, since the installation of thermocouples does not represent a significant problem in practice. Nevertheless, such an option requires finding the stages that are more sensitive to changes in the reflux ratio and the heat duty supplied to the reboiler. As recommended by Kaymak and Luyben [15], changes of 0.5% were assumed in the manipulated variables and the gains in the stages were obtained. Fig. 5a presents the gains for positive and negative changes in the reflux ratio of the main column of the reactive Petlyuk system. Stage number 20 is the most sensitive; as a result, the first control loop of temperature was established between the temperature of stage number 20 and the reflux ratio. It is important to highlight that this change has also an important effect in the stages between the stage 25 and the reboiler. When changes of 0.5% in the reboiler duty were implemented, the most sensitive stage was the stage number 40 (Fig. 5b); therefore, a second control loop can be considered between the temperature of the stage 40 and the heat duty supplied to the reboiler of the Petlyuk column. Notice, however, that this change also causes a significant gain in tray 20. According to this analysis of the gains of temperature in the trays, interaction between the two control loops can be expected. The proposed control loops of temperature are depicted in Fig. 6.

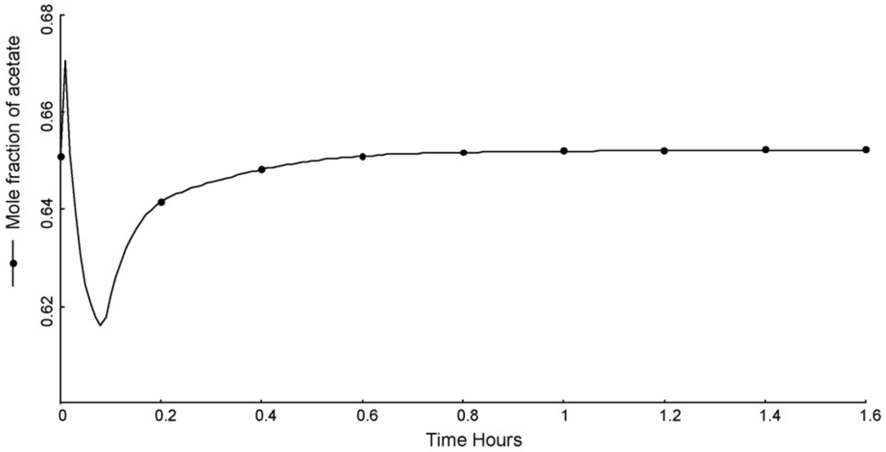
4. Dynamic simulation of the reactive Petlyuk distillation column

4.1. One closed loop

The dynamic simulations were conducted in Aspen Dynamics and the kinetics for the reaction was taken from Tang et al. [13]. The dynamics of the reactive Petlyuk distillation column was studied for one and two closed loops of temperature. In the first part of the study, we studied one closed loop of temperature for both changes



(a) Temperature and manipulated variable.

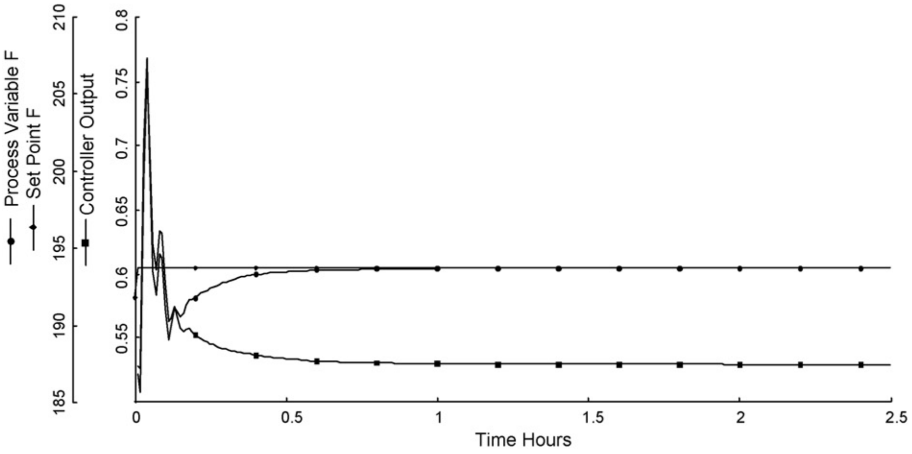


(b) Mole fraction of the ethyl acetate in the product stream.

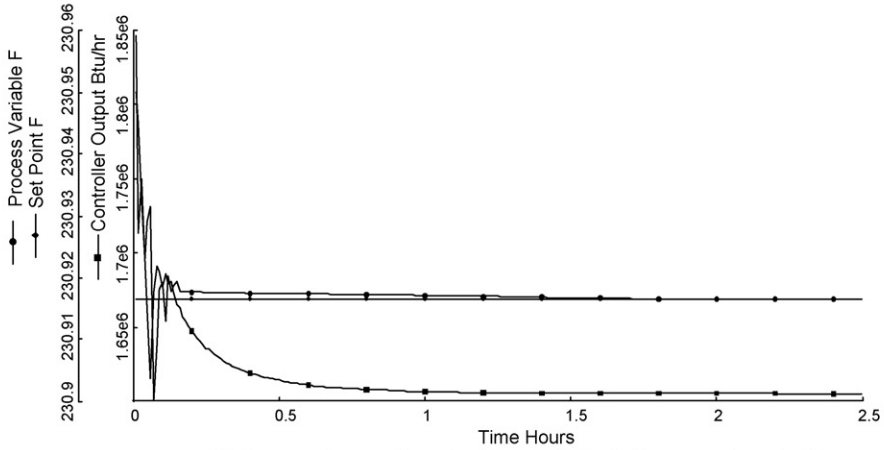
Fig. 10. Dynamic responses of the first control loop of temperature for a positive disturbance of 5% in the composition of the acetic acid.

in set point and load rejection. Proportional integral controllers were used and tuned to minimize the integral of the absolute error (IAE). For instance, for the first control loop, Fig. 7 shows the minimization of the IAE with optimal values of 3 and 18 min for the gain and integral time, respectively. For the second control loop a similar response surface can be obtained for the PI controller, and optimal values of the gain and integral time of 100 and 0.2 min, respectively, are derived.

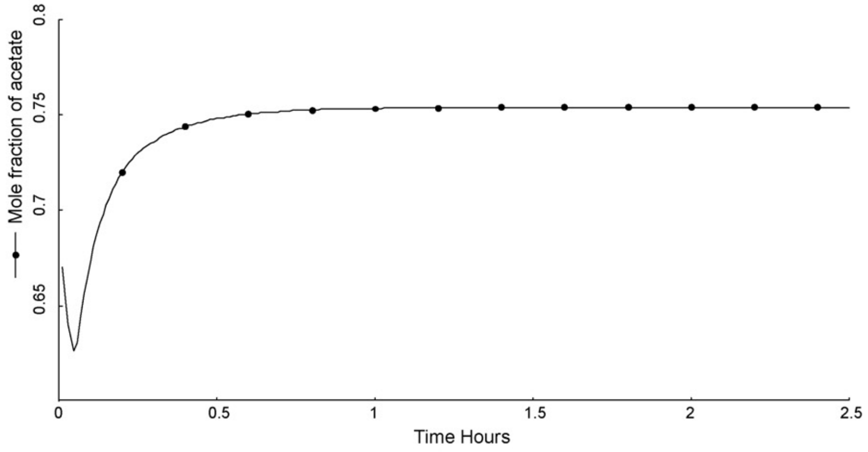
Fig. 8a presents the dynamic responses of the process variable (temperature of tray 20) and control variable (reflux ratio) for a positive set point change in the temperature of tray 20. According to Fig. 8a, the reactive Petlyuk column can achieve the change in the



(a) Temperature and manipulated variable in the first control loop.



(b) Temperature and manipulated variable in the second control loop.



(c) Mole fraction of the ethyl acetate in the product stream.

Fig. 11. Dynamic responses of the two control loops of temperature for a positive set point change of magnitude 1 °F in both controllers and a disturbance of 5% in the composition of the acetic acid.

set point in approximately 0.5 h. In the case of a negative set point change, Fig. 8b shows the dynamic responses, where the system reaches the new steady state in approximately 0.5 h; notice that, for a negative set point change, the responses present more oscillations in contrast to those obtained for a positive set point change. When the same changes were implemented in the second control loop, again the reactive Petlyuk column achieved the changes in the set point. Fig. 9a presents a typical response of the second control loop for a positive set point change, and Fig. 9b shows the dynamic response of the composition of ethyl acetate in the product stream. It can be seen that, in fact, the control of temperature has an important impact on the composition of the product stream.

When the system was subject to changes in the feed composition, the controllers also eliminated the effect of the disturbances. For instance, Fig. 10a presents the dynamic response of the first control loop when the composition of the acetic acid was increased 5% and the composition of the ethanol was reduced by the same amount. Also, Fig. 10b shows the stabilization of the molar composition of the ethyl acetate in the product stream. In general, the reactive Petlyuk column showed convenient dynamic closed-loop responses for both set point tracking and load rejection.

4.2. Two closed loops

In the second part of the study, the two control loops were closed simultaneously. In this control fashion, the first control loop was tuned while the second loop was kept open. Similarly, with the first control loop closed, the second control loop was tuned. Again, the reactive Petlyuk column was studied for both set point tracking and load rejection. In order to avoid a large number of dynamic simulations, the most difficult scenario was simulated. A positive set point change of magnitude 1 °F was assumed in both of the control loops, and a simultaneous disturbance with magnitude of 5% in mole fraction of the acetic acid in the feed stream was included. Fig. 11a and b display the dynamic closed-loop responses for the first and second control loop of temperature, respectively. According to these figures, it is clear that the system can achieve both set point changes and eliminate the effect of the disturbance. The dynamic response of the ethyl acetate is presented in Fig. 11c. The complete dynamic simulations let us establish that the reactive Petlyuk column has convenient dynamic closed-loop behavior for different scenarios. These results and the knowledge about non-reactive DWDC were considered for the design and implementation of a RDWDC in a pilot plant; the details are presented in the next section.

5. Description and operation of the reactive Petlyuk distillation column

It is important to highlight that the Petlyuk distillation column and the dividing wall distillation column are thermodynamically equivalent, but the industrial operation is different. Recently, Suphanit et al. [16] have found that the heat transfer across the wall can improve the operation of the dividing wall distillation column.

Fig. 12 depicts the RDWDC implemented in a pilot plant using stainless steel 316 L. We are interested in the control of the composition of the distillate but, as described above, this task is difficult to implement in industrial practice. Nevertheless, based on the simulation results, we know that it is possible to control the temperature at some points of the packed section instead. Both control objectives require the manipulation of the reflux rate in order to set either the composition or temperature in their set points. So, a valve was implemented inside the column in order to manipulate the reflux to the distillation column (Fig. 12, element 2; Fig. 13a).

Several collector and distributor trays were implemented in the three packed sections of the RDWDC to guarantee homogeneous liquid distribution in the packed bed (Fig. 12, elements 10 and 11). Special care needs to be taken between the first and second packed sections, since a collector tray (Fig. 12, element 11) is needed in the bottom of the first packed bed to send the liquid stream to a side tank (Fig. 12, element 4; Fig. 13b). This device plays an important role in the operation of the column because, during the steady state design and optimization, an important aspect is to detect the optimal splits of the liquid and vapor streams in the middle section of the DWDC to guarantee the optimal energy consumption in the reboiler. In practice, it is difficult to manipulate the splits of vapor streams; for that reason, the side tank has been implemented to split the liquid stream to both sides of the wall in the middle section of the distillation column and to extract the water decanted.

The RDWDC contains three packed sections of Teflon rasching super-rings. In the middle section (Fig. 12, elements 6 and 7; Fig. 13c) of the distillation column, a wall (Fig. 12, element 5) was implemented so that it can be moved to three positions to manipulate the split of the vapor stream. This middle section is the key packed section in the energy-performance of the RDWDC, because the feed is introduced in one side (equivalent to the prefractionator in Petlyuk systems, Fig. 12, element 7) and a liquid side product (the side product stream in the main column of Petlyuk systems) is obtained in the other one (Fig. 12, element 6). As it can be seen, this section needs collector and distribution trays in the feed and side stream points.

The first and third packed sections are similar to those of a conventional distillation column, and only distributor and support trays are required for the appropriate performance of the RDWDC. At the end of the third packed section, a reboiler (Fig. 12, element 9; Fig. 13d) was placed so that it can be charged with the reacting mixture in the batch operation fashion. Finally, several thermocouples were implemented in the RDWDC to register the temperature profile. Current research work focuses on the experimental study of the hydraulics, steady state and closed-loop dynamics of the implemented RDWDC.

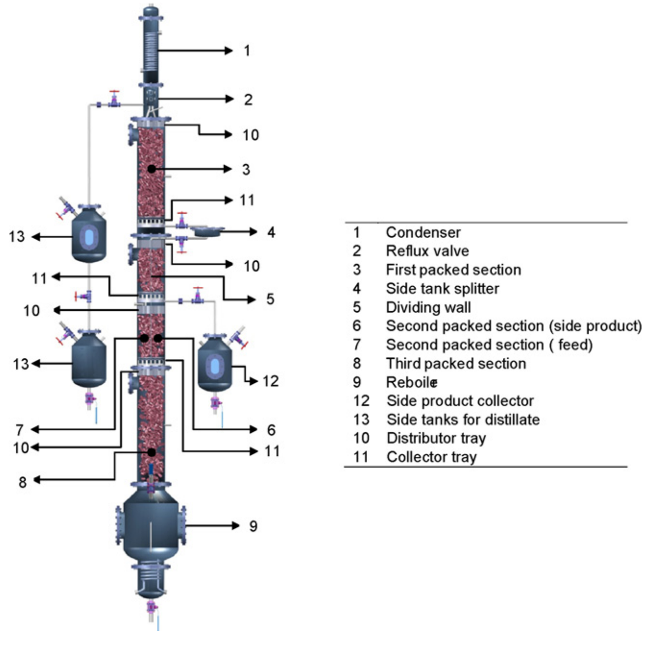
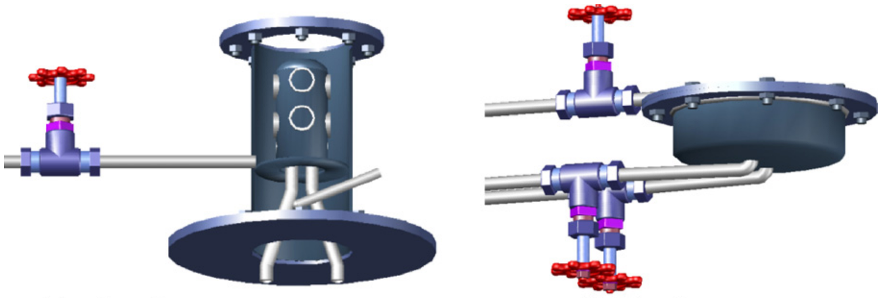
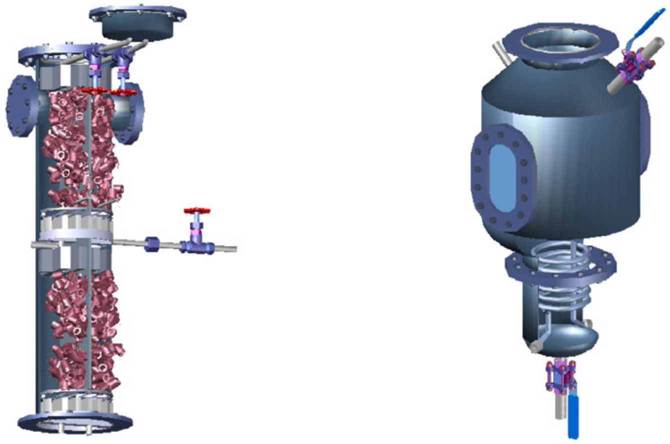


Fig. 12. RDWDC implemented in the pilot plant (patent in process).



(a) Reflux valve. (b) Side tank.



(c) Intermediate packed section. (d) Reboiler.

Fig. 13. Important devices in the RDWDC.

6. Conclusions

We have studied the dynamics of a reactive Petlyuk column for the production of ethyl acetate. Two control loops of temperature were implemented and tested for different scenarios. The results show that the system can achieve changes in the two set points and also eliminate disturbances in the composition of the feed stream. These results and the knowledge reported about TCDS for non-reactive mixtures were applied to design and implement a RDWDC for the production of ethyl acetate from acetic acid and ethanol. Important aspects derived from steady state simulation were considered. For instance, a side tank was used to split the liquid stream to both sides of the wall; also, a moving wall implemented inside the column allows one to fix the split of the vapor stream. The dynamic simulations indicate that it is possible to control either the composition of the top and bottoms products or two temperatures by manipulating the reflux rate and the heat duty supplied to the reboiler, respectively. The implementation of the RDWDC takes into account important issues like process intensification and minimum energy consumption.

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