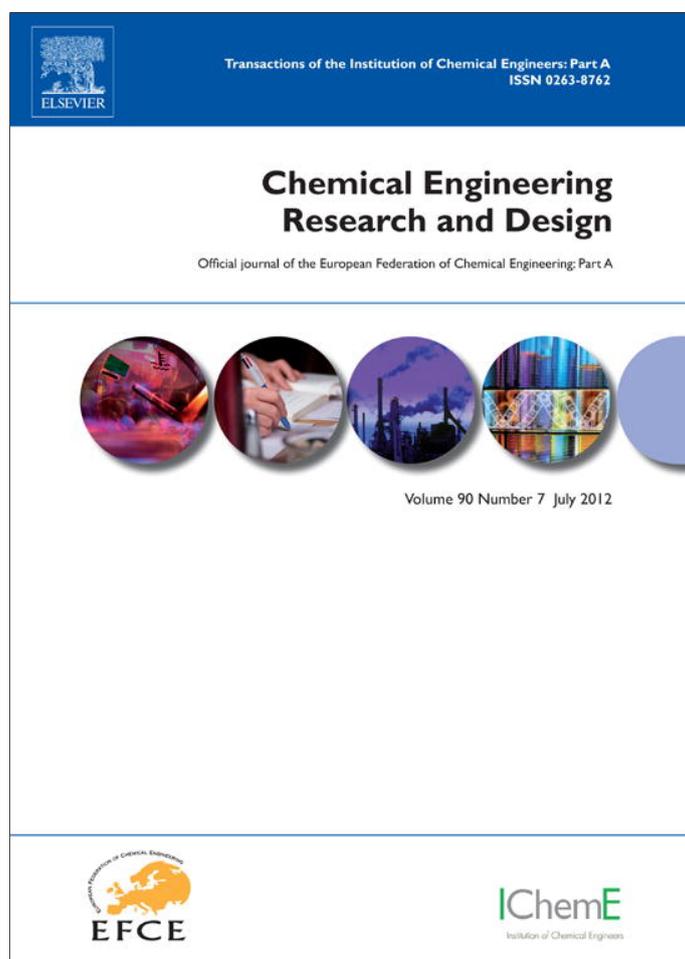


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From simulation studies to experimental tests in a reactive dividing wall distillation column

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ABSTRACT

The design and control of thermally coupled distillation sequences have been studied since many years, but the real implementation occurred until middle of the 1980s using a single shell divided by a wall named dividing wall distillation column. In this work, experimental results for the production of ethyl acetate in a reactive dividing wall distillation column are presented for first time. The experimental results are in agreement with those obtained using steady state simulations with AspenONE Aspen plus. These experimental results are important since it is possible to validate most of the previous results generated using simulations.

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Keywords: Reactive distillation; Thermally coupled distillation; Production of ethyl acetate

1. Introduction

Distillation has been widely used in chemical process industries over the years; however its versatility to carry out separations is linked to high-energy requirements and low thermodynamic efficiency.

Wright (1949) made one of the first studies reported in the literature, about energy savings in complex distillation columns, in 1949. He proposed a distillation column considering a shell and an internal wall for separating the feed stream and the side stream.

In 1965 Petlyuk et al. carried out a thermodynamic analysis of a column known after as Petlyuk distillation column (Fig. 1) to separate a ternary mixture (A,B,C). This column seemed an excellent option to reduce the energy consumption in distillation processes. Tedder and Rudd (1978) presented a parametric study of eight distillation sequences including conventional distillation sequences and some new designs with liquid and vapor recycles to replace some condensers and reboilers. These distillation sequences with material and energy recycles were known as distillation sequences with thermal coupling (Fig. 2). The results showed that distillation

sequences with thermal coupling could achieve energy savings up to 30% in comparison with conventional distillation sequences for the separation of some ternary mixtures. However, despite of the potential energy savings, the industrial implementation of the distillation sequences with thermal coupling was limited, with only some applications in oil industry.

Alatqi and Luyben (1986) reported a comparison about the control effort between a conventional direct distillation sequence and a distillation sequence with thermal coupling. The results showed that there was not a significant difference in the operation and control between conventional and thermally coupled distillation sequences. In addition, they reported that the recycled streams improved the control properties because they helped to diminish the effect of disturbances in the distillation sequences.

Fidowski and Krolikowski (1986) compared the vapor flows generated in the reboilers of the direct and indirect distillation sequences with those of the Petlyuk and a pseudo Petlyuk column under minimum reflux conditions. The optimal vapor flows were determined using analytical expressions based on the Underwood equation and the necessary stages to carry out

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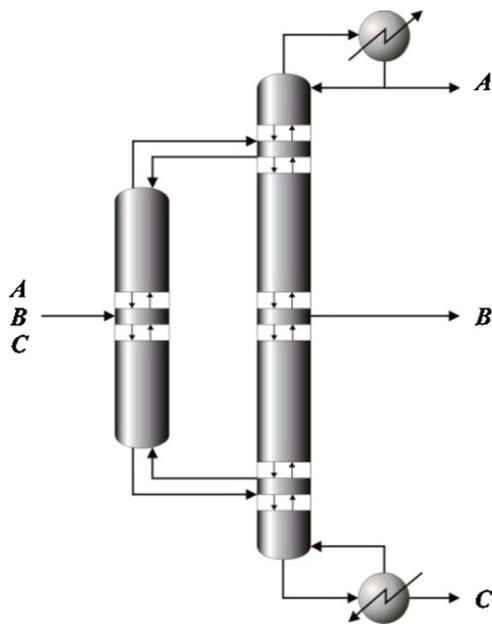


Fig. 1 – Petlyuk distillation column.

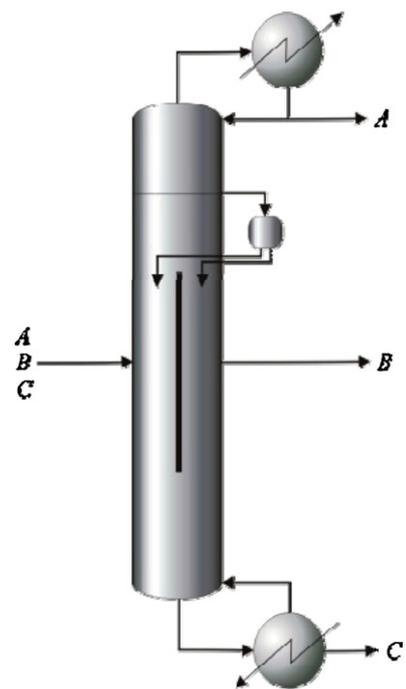


Fig. 3 – Dividing wall distillation column.

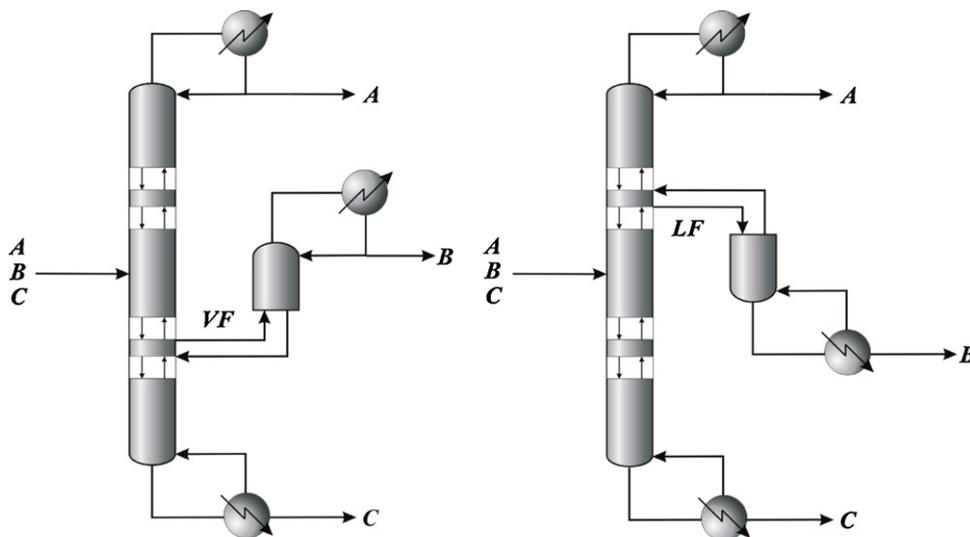
the separation were not considered. According to this comparison, the Petlyuk column showed significant savings in the total minimum vapor flow to achieve the separation of a ternary mixture.

Kabel (1987) patented the dividing wall distillation column shown in Fig. 3, which is thermodynamically equivalent to the Petlyuk distillation column studied by Petlyuk et al. (1965). However, this equivalence is only valid when there is no heat transfer across the dividing wall.

Glinos and Malone (1988) obtained analytical expressions to determine the minimum flow necessary to separate a ternary mixture (A,B,C) using alternative separation designs, including the Petlyuk column. According to the results, they recommended using the Petlyuk distillation column when the molar fraction of the middle component B is low. Also, they found that the maximum savings achieved in the vapor flows were close to 50% in comparison with the conventional

distillation sequences. In addition, they showed that distillation sequences thermally linked to side columns can operate successfully when the mole fraction of the middle component on the feed stream is lower than 0.3.

Triantafyllou and Smith (1992) gave an explanation about the higher thermodynamic efficiency of the Petlyuk distillation column. For the case of the conventional direct distillation sequence, for the separation of a ternary mixture, in which each component is removed as overhead product, an analysis of the composition profile of the middle component (B) in the first column shows how it reaches a maximum value below the feed stage and then diminishes as the bottom is reached (Fig. 4). This phenomenon is known as remixing, because the composition of middle component always is low at the bottom of the column. This bottom stream with lower content of



(a) Thermally coupled distillation sequence with a side rectifier.

(b) Thermally coupled distillation sequence with a side stripper.

Fig. 2 – Thermally coupled distillation sequences with side columns.

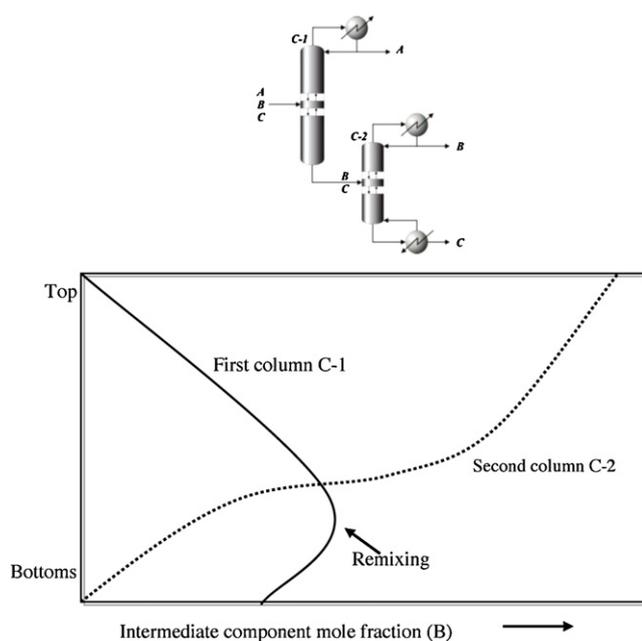


Fig. 4 – Remix effect in the conventional distillation sequences.

the intermediate component is sent to a second column to be purified, where additional energy is necessary, increasing the total energy consumption. In the case of the Petlyuk distillation column, the composition profile of the middle component in the main distillation column presents a maximum; therefore the side stream should be taken from the stage where this maximum is presented. Also, in this work, a short-cut method to design the Petlyuk column was presented using the Fenske–Underwood–Gilliland equations. It is important to mention that, a total preliminary design including stages, reflux ratio and distributions of the middle component can be calculated using the methodology proposed.

During the 1990s, different works about the design and optimization of distillation sequences with thermal couplings were published (Hernández and Jiménez, 1996, 1999a; Dünnebier and Pantelides, 1999). Hernández and Jiménez

(1996) reported a dynamic model used to obtain the minimum energy consumption for a given tray structure in thermally coupled distillation sequences with side columns. Also, the same model was used for dynamic studies. For the Petlyuk distillation column, Hernández and Jiménez (1999a) determined the minimum energy consumption varying the interconnections flows. Dünnebier and Pantelides (1999) used mathematical programming for calculating the optimal design for the Petlyuk distillation column. Hernández and Jiménez (1999b) and Jiménez et al. (2001) studied the control properties of distillation sequences with thermal coupling using the singular value decomposition technique and closed-loop dynamic responses under proportional-integral controllers. The results showed that the distillation sequences with thermal couplings could be as controllable as the conventional distillation sequences. When the dynamic responses under feedback control were obtained, both types of distillation sequences presented good responses for set point tracking and load rejection.

Around those years, motivated by the previous oil crisis, the chemical process industry achieved the first successful implementation of a dividing wall distillation column, with savings on both energy and capital costs. BASF SE made this first implementation in 1985.

Some improvements for dividing wall distillation columns like catalytic packing and non-welded walls have been proposed (Asprion and Kaibel, 2010; Dejanović et al., 2010).

During this decade, new applications for dividing wall distillation columns have been reported; perhaps one of the most important is the possibility to combine chemical reactions and separations simultaneously inside the dividing wall column according to process intensification principles. Following this topic, some applications for biodiesel production by the acid route have been proposed using reactive distillation and thermal coupling (Kiss, 2011; Kiss and Bildea, 2011; Hernández et al., 2011).

In these works the intention to include reaction and separation in the same equipment is evident, taking as advantage the *in situ* integration of the heat of reaction. Moreover, higher conversions for equilibrium reactions are achieved, because

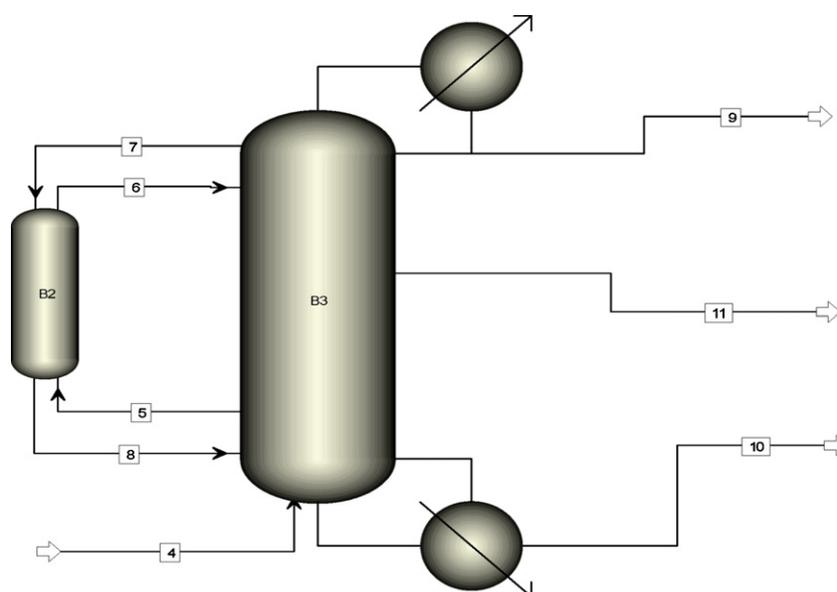


Fig. 5 – Implementation of the RDWDC in AspenONE Aspen Plus.

Table 1 – Azeotropes in the ternary system of ethanol–water–ethyl acetate at 1 atm.

Azeotrope	Composition (mol.%)	Boiling point (°C)	Type
Ethyl acetate–ethanol–water	58.7, 15.9, 25.4	70.1	Homogeneous, minimum boiling point
Ethyl acetate–water	69.0, 31.0	70.6	Heterogeneous, minimum boiling point
Ethyl acetate–ethanol	55.4, 44.6	71.8	Homogeneous, minimum boiling point
Ethanol–water	90.8, 9.2	78.2	Homogeneous, minimum boiling point

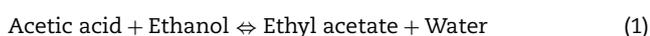
the products are removed from the system as soon as they are formed. For the case of biodiesel production, a fatty organic acid, typically oleic acid, is fed near the top of the column while a methanol feed stream is introduced as vapor in the reboiler. A methyl ester with the required composition to be used as biodiesel is obtained as bottoms product.

An environmentally friendly application of the dividing wall columns has been their use in extractive distillation, mainly to produce high purity bioethanol in order to either substitutes or combines it with gasoline. As it is known, the final stage of the process to produce bioethanol generates an aqueous stream with no more than 10% weight of ethanol that should be purified. For this case, the mixture is introduced to a conventional distillation column some stages above the reboiler to obtain a distillate product with a composition close to the azeotrope and later this stream is fed to a complex distillation column like a dividing wall column. An entrainer as ethylene glycol or glycerol is introduced into the top of this column to perform the separation; there are three streams: ethanol with purity higher to 99.5% weight is collected as distillate; water is extracted as side stream and the entrainer can be recovered in the bottoms and recycled to the column (Hernández, 2008; Murrieta-Dueñas et al., 2011; Sun et al., 2011).

Almost all the research efforts about dividing wall distillation columns have been done using process simulators. However the information reported in the open literature about experimental studies for these columns is meager (Kiss et al., 2009), because the *know how* for this technology has been developed by some companies like BASF, Montz and Akzo Nobel. Because of this lack of information, a dividing wall distillation column was designed and implemented to study reactive distillation in a pilot scale. Also, the results can be used to validate our previous results obtained using simulations.

2. Case study

Based on the previous experience on design, simulation and control of dividing wall distillation columns (Hernández and Jiménez, 1996, 1999a; Jiménez et al., 2001; Hernández et al., 2009, 2011), an experimental dividing wall distillation column was designed and implemented to study esterification reactions. The equilibrium reaction to produce ethyl acetate using sulfuric acid as catalyst was chosen and it is shown in Eq. (1).



For this reactive system, the azeotropes shown in Table 1 can be present. To avoid corrosion problems in the equipment because the nature of the substances used for this reaction in addition to temperature, the experimental reactive dividing wall distillation column (RDWDC) was built with stainless steel 316 L and Teflon™ for the random packings. A limitation during the construction of the column was the height inside our unit operations lab.

2.1. Simulation of the RDWDC

Before of the real implementation, the RDWDC was simulated using 3 stages for prefractionator and 11 stages for the main distillation column. The numbers of stages were set to these values because of the height inside our experimental lab (approximately 4 m). The same molar flow of 60 mol/h was used for both the acetic acid and ethanol streams that were fed into the reboiler. These values of the fed flows were fixed according to a residence time of 5 min in the reboiler. Also, the endothermic equilibrium chemical reaction is carried out in the liquid contained in the reboiler of the main distillation column, since reactants and catalyst are introduced in this part where the highest temperature is presented.

The module RadFrac of AspenONE Aspen Plus™ was used for the rigorous simulation that includes material and energy balances and summations constraints for each equilibrium stage. The NRTL model was chosen to calculate the equilibrium data, because it is well known that for this reactive system two liquid phases can be formed in equilibrium with the vapor phase. The implementation in AspenONE Aspen Plus is depicted in Fig. 5.

It has been reported previously, that the energy consumption depends strongly on the interconnecting liquid and vapor flows (Hernández and Jiménez, 1996, 1999a); therefore, it is very important to find the optimal values for those flows to minimize the energy consumption.

2.2. Simulation results of the RDWDC

For the search of the minimum energy consumption of the RDWDC, the method SQP (sequential quadratic programming), implemented as part of the simulator AspenONE Aspen Plus, was used. The target was to minimize the reboiler duty taking the liquid and vapor interconnecting flows as search variables, including the ethyl acetate molar composition of 0.65 in the organic phase obtained at the top of the column as constraint. This composition is closed to the heterogeneous azeotrope ethyl acetate–water, as it can be seen in Table 1. It is important to highlight that during the search for the minimum energy consumption, the number of trays remains unchanged since the size of the RDWDC is fixed.

Fig. 6 shows how the SQP method converges to the minimum value for the reboiler heat duty. From this design with the minimum energy consumption: the condenser and reboiler duties, optimal values of the interconnecting streams, column diameter, as well as bottom and top temperatures can be obtained. These important values for the design variables are shown in Table 2 and they were used for the mechanical design and detailed engineering design of the RDWDC. Also, the material balance in the optimal solution is presented in Table 3, and from these results an overall conversion of 86% can be calculated.

Regarding the composition profile for ethyl acetate, it can be observed two liquid phases in the first stage of the column; one phase is rich in ethyl acetate (Fig. 7) and the other

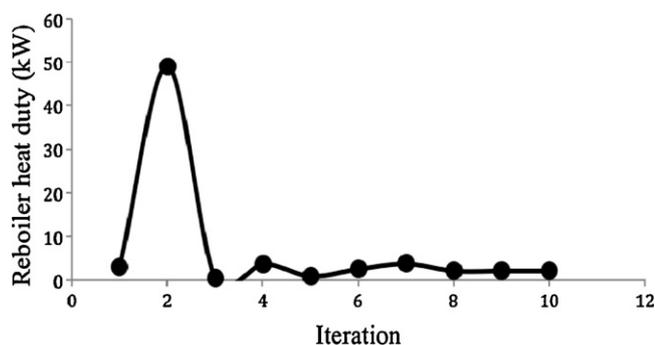


Fig. 6 – Optimization of the energy consumption of the RDWDC.

Table 2 – Simulation results of the RDWDC.

Extraction stage number of the liquid stream in the main column	5
Extraction stage number of the vapor stream in the main column	7
Diameter of the RDWDC	0.17 m
Condenser heat duty	-2.37 kW
Reboiler heat duty	2.13 kW
Interconnecting liquid flow	6 mol/h
Interconnecting vapor flow	8 mol/h
Condenser temperature	338.47 K
Reboiler temperature	370.28 K
Mole flow of acetic acid	60 mol/h
Mole flow of ethanol	60 mol/h
Reboiler pressure	0.795 atm

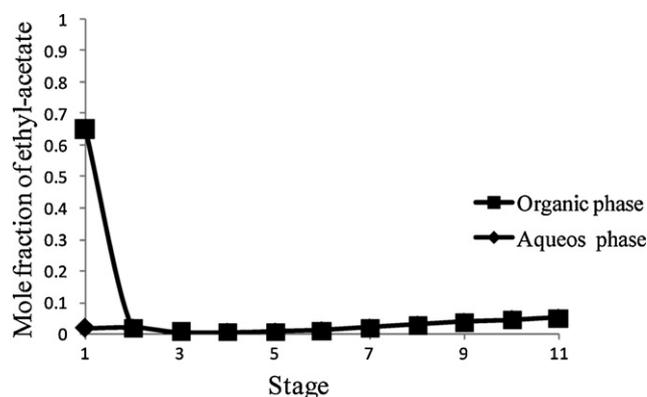


Fig. 7 – Mole fraction of ethyl acetate in the two liquid phases.

one in water (Fig. 8). Another important aspect about the temperature profiles showed in Fig. 9 is the higher temperature in one side of the wall. This implies heat transfer across the wall if it is not insulated. Related to this aspect, Lestak et al. (1994) showed by a pinch analysis that insulation is not necessary because the heat transfer is beneficial in some part of the wall, and the total increment in the energy requirement of the dividing wall distillation column is not superior to 10%.

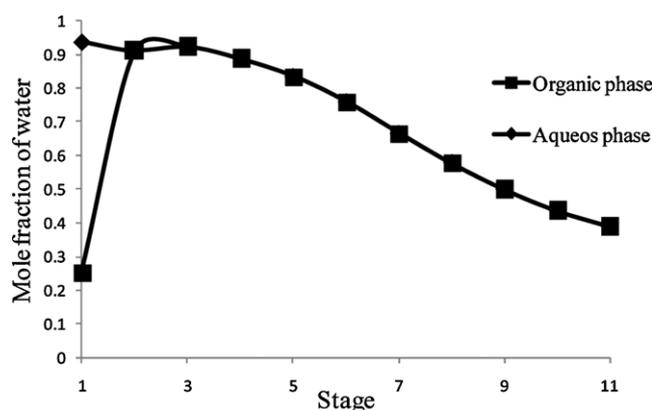


Fig. 8 – Mole fraction of water in the two liquid phases.

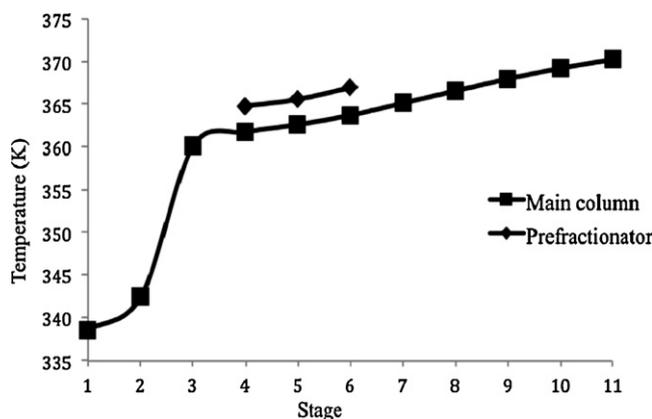


Fig. 9 – Temperature profiles of the RDWDC.

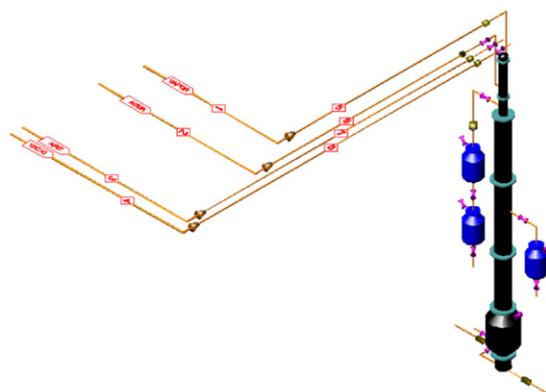
2.3. Important aspects to be considered in the implementation of the RDWDC

The column has three packed sections (numbered from reboiler to condenser) with a total height of 2.5 m filled with random packing made of Teflon™; and the key piece for a correct performance, the dividing wall, is located inside the second packed section. The column has been instrumented with six thermocouples in different sections of the column: one located in the reboiler, one in the section on top of the reboiler, two in the second section on both sides of the dividing wall, one in the third section under the condenser and the last one in the condenser (Fig. 10a and b). At the bottom of the column an automatic control valve was implemented to control the temperature at this location (Fig. 11a). To record the six temperatures and for manipulating the control loop, SIMATIC WinCC of SIEMENS was installed in a laptop (Fig. 11b).

Two key aspects should be considered in the design and construction of the RDWDC, both related to the minimum energy consumption. First, the liquid flow from the third section should be split to both sides of the dividing wall using a side tank (Fig. 12a) with two valves to manipulate the liquid flows. Second, the vapor flows on both sides of the dividing wall depend on the dividing wall position along the column

Table 3 – Material balance for the RDWDC.

Component mole flow (mol/h)	Feed (stream 4)	Distillate (stream 9)	Bottoms (stream 10)	Sidestream (stream 11)
Ethanol	60	7.590	0.011	0.216
Acetic Acid	60	0.580	0.606	6.630
Ethyl Acetate	0	51.772	0.056	0.356
Water	0	28.960	0.426	22.798



(a) 3D presentation of set up.



(b) Implemented prototype of the RDWDC.

Fig. 10 – Schematic representation and real implemented RDWDC.

diameter (Fig. 12b) and the pressure drop inside the packed section.

2.4. Experimental tests in RDWDC

For the experimental tests, 98.14 and 73.93 mol of acetic acid and ethanol, respectively, were fed to the reboiler with 3 mol of sulfuric acid as catalyst for the esterification reaction. After the initial charge to the reboiler of the RDWDC, using the control loop for the heating, the hot utility in the reboiler is activated in order to start the chemical reaction. When the temperature recorded by the thermocouple close to the condenser increases, a flow of cooling water to the condenser is allowed. It is important to mention that most of the reaction takes place in the liquid retained in the reboiler, but hydrolysis reaction may occur in the rest of the packed column.

Initially the column is kept at total reflux until a steady state temperature profile is registered. This happens after 50 min according to the data shown in Fig. 13. At this point, the valve to extract product at the top of the column is open but only a fraction of the condensed vapor is extracted as product (approximately 40%) while the rest is returned to the column.



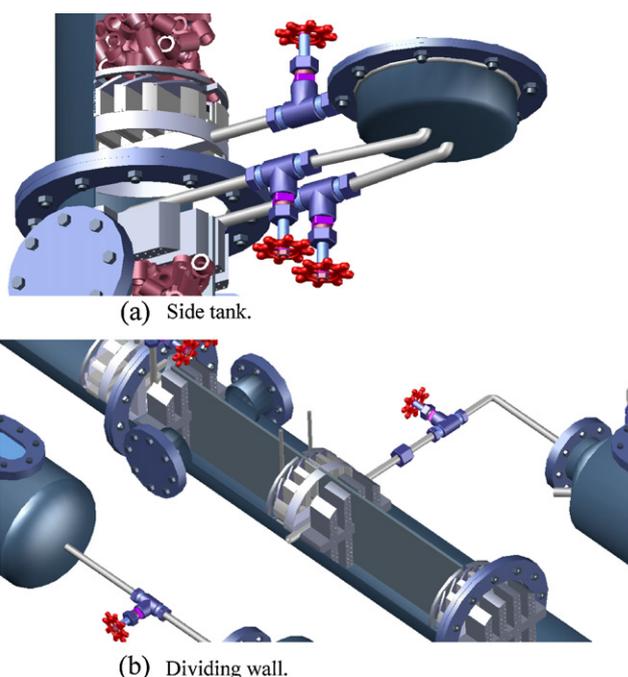
(a) Automatic control valve.



(b) Interface of the control system.

Fig. 11 – Control system of the RDWDC.

During 30 min, the temperature is approximately constant, obtaining a distillate with two liquid phases: an organic phase and an aqueous phase, this indicates that the heterogeneous azeotrope ethyl acetate–water is obtained according to the ternary diagram shown in Fig. 14. Also, the temperature registered in the third packed section is around 65 °C that is



(a) Side tank.

(b) Dividing wall.

Fig. 12 – 3D presentation of key components in the design of the RDWDC.

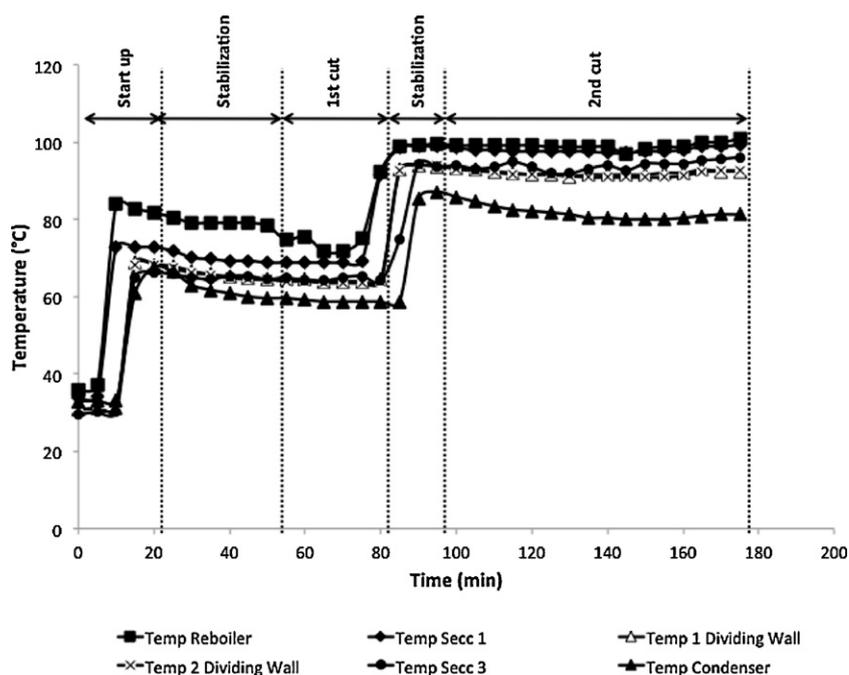


Fig. 13 – Experimental temperature profiles recorded during the operation of the RDWDC.

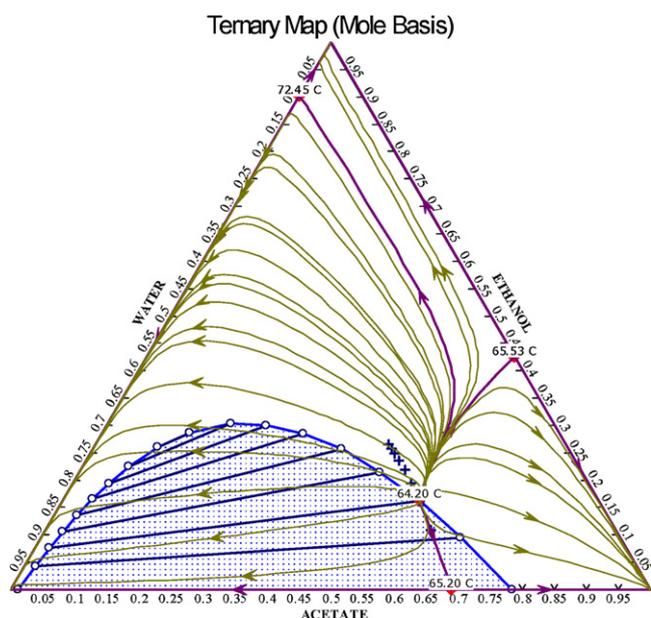


Fig. 14 – Ternary diagram for the system ethanol–water–ethyl acetate at 0.795 atm.

consistent with the boiling temperature of the heterogeneous azeotrope. Note that the ternary diagram is calculated at local ambient pressure of 0.795 atm.

This result is important because it allows validating the results found by simulation, because they show the formation of two liquid phases at the top of the column; one rich in ethyl acetate and the other one rich in water (Figs. 7 and 8). In addition, this result has been corroborated using gas chromatography.

After 100 min, the temperatures increase considerably which indicates that water produced by the chemical reaction as well as acetic acid are obtained as distillate.

These experimental tests allow validating the simulations of systems with thermal coupling and chemical reaction, showing how important the dividing wall distillation columns

can be to combine a chemical reaction and separation in the same unit, according to process intensification principles.

Maybe in near future the two most direct applications of this dividing wall distillation column are: first, the esterification of fatty organic acids and methanol to produce methyl esters that can be used as biodiesel and second, the application to purify bioethanol using entrainers like ethylene glycol, glycerol or ionic liquids.

3. Conclusions

The implementation, start up and operation of a dividing wall distillation column to carry out esterification reactions were achieved. The results predicted by simulation are in agreement with the data registered during the experimental tests and corroborated by gas chromatography. These results validate previous process simulation studies about design and control of these systems, emerging a new field to study experimental reactive distillation systems in process intensification.

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