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Energy Study of Reactive-HIDiC Simulation for Ethyl Acetate Synthesis from Acetic Acid

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In this paper the concept of Heat Integrated Distillation Column (HIDiC) and Reactive Distillation (RD) were used to study the ethyl acetate process by the simulation in Aspen Plus. The intensification concept of reactive-HIDiC was developed applying simulation concepts for the representation of the heat transfer phenomenology. An analysis of binary mixtures involved in the process was developed to determine the thermodynamic model. The thermodynamic properties were calculated with the NRTL-RK (Non-random two-liquids modified by Redlich-kwong) model to estimate the properties. The energy consumption was studied in a reactive distillation column and the intensified configuration r-HIDiC. The parameters of simulation and column configuration were established in order to compare the two configurations. The results showed the amount of energy consumed between the reactive distillation column and r-HIDiC column and compared to determine the energy savings. With the r-HIDiC column presented a decrease of energy consumption and increased concentration of valuable product on the top of column of the 7.8% compared to the reactive distillation column.
Keywords: Reactive distillation, simulation, r-HIDIC, intensification process.

1. Introduction

Reactive distillation is a process where chemical reaction and separation process occur in parallel at the same unit. The advantages of reactive distillation process are the intensifying system, operate in single equipment, recovering products and recirculation of unconverted reactants. This arrangement of equipment present a potential to reduce operation costs, allows less energy consumption and environmental impacts (Gao *et al*, 2014). Researchers throughout the world present the potential to improve the conversion, the selectivity and mass transfer in reactive distillation processes. The reactive distillation is a technology used in reactions limited by chemical equilibrium (Hangx *et al*, 2001).

Different processes have been proposed in order to improve the conditions of thermal balance in distillation columns. A lot of information and research that demonstrate the possibility of approach the energy in separation systems. Basically different methods and arrangements presented coupled columns that allow using the available energy in the condenser with external connection to reboiler and other arrangement with others columns. Other concepts such as diabatic and adiabatic distillation present the possibility of operating with embedded systems within the equipment (Mukherjee *et al*, 2013).

Other possibility of process is the internal heat integrating configurations, called Heat Integrated Distillation Column (HIDiC), this configuration combines the advantages of vapour compression and diabatic distillation (Huang *et al*, 2005). The column HIDiC transferred the heat from the hottest section to the coldest section, rectifying to stripping section, leading to a gradual evaporation along the length of the stripping section and

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progressive condensation along the length of the rectifying section. Currently, novel methods have it emerged, the reactive distillation and concepts of heat integration was used, resulting in a Heat Integrated Reactive Distillation Column (r-HIDiC), this configurations present the advantages of reactive distillation and heat approach in distillation columns (Pulido *et al*, 2012).
The ethyl acetate is an industrial product used for many process, products, artificial essences, solvent, varnishes and lacquers. The ethyl acetate is a colorless liquid, less dense than water. It is obtained conventionally by slow process of distillation of a mixture of acetic acid, sulphuric acid and ethyl alcohol or acetaldehyde in the presence of aluminium ethoxide. This production requires reactor units and separation operations. In this paper, a study of reactive distillation to produce ethyl acetate is compared to a novel configuration of Heat Integrated reactive Distillation Column (r-HIDiC) using simulation techniques to describe a configuration and the internal arrangement. The production of ethyl acetate was developed in r-HIDiC configuration in order to get an energy comparison between the two systems.

2. Description of Heat Integrated Reactive Distillation Column (r-HIDiC)

The concept of r-HIDiC consists in making use of the hot section of column and transfer the energy to the cold section of the column. This exchange is simulated from energy flowing between the two sections. Although several arrangement of columns have been proposed, in this work, it is compared the reactive distillation with r-HIDiC. This disposition represents a concentrically configuration, rectifying within the stripping section. The rectifying section operated at higher pressure and temperature compared to the stripping section. The concept of r-HIDiC approaches the heat available in the rectifying section to evaporate the liquid in the stripping section, which decreases the energy charge on the reboiler. A schematic diagram of the concentric stage concept is shown in Figure 1.

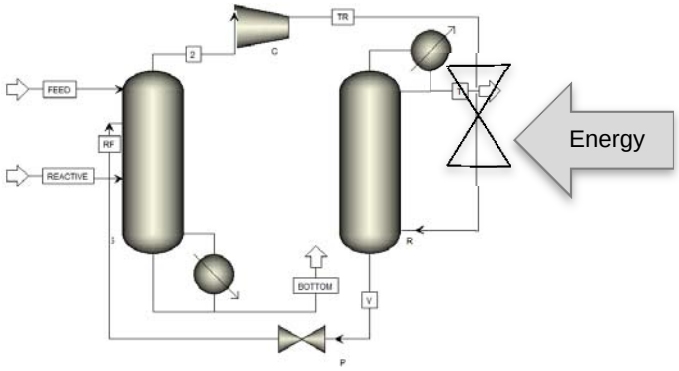

Figure 1: Configuration of r-HIDiC

The new configuration applied the reactive distillation column and internal heat integration concepts, the arrangement locate a reactive zone placed in HIDiC column in specified stage range. R-HIDiC column is fed in two points of the stripping section, this occurs at the place where the reaction occurs. The top product of this section is fed to the rectifying section while the bottom of the rectifying section is feedback to the stripping section. The disposition unit presents a reduction in the cost operations and combines two processes in a single vessel (Jie *et al*., 2009). The reactive column and r-HIDiC configuration are modelled in Aspen Plus software, the conventional process of reactive distillation includes a reactive section in a conventional system and the r-HIDiC include an internal configuration for heat transfer. The reactive distillation merges two processes: reaction and distillation in a single unit. The reaction area depends on the nature of the reaction.

3. Synthesis of Ethyl Acetate Process the Case of Study

The ethyl acetate production is obtained by esterification reaction between acetic acid and ethanol mixture. This mixture is preheated and fed to the esterification column, the bottom product takes another column for the treatment of azeotrope based in ethyl acetate. A conventional process was developed using a RCSTR reactor available in a model library of Aspen Plus. The reaction between acetic acid and ethanol is an equilibrium process, this is presented in the Equation 1.

$$CH3COOH+C2H5OH \leftrightarrow CH3COOCH2CHE+H2O \quad (1)$$

The equilibrium is influenced to the left by the water, the ethanol usually is used dry in the process and this requires additional energy and associated process. The esterification reaction obtains ethyl acetate and water by acetic acid and ethanol. The amount of heat transferred between the sections was calculated based on the concept of enthalpy. The reaction present an endothermic behaviour, the reaction area are located in the stripping section. The kinetic parameters used in the simulation study are presented below. The parameters of the esterification reaction to ethyl acetate production were studied by *Anil et al.*, 2007. These are presented below at the Table 1.

Table 1. Kinetic Parameters of Ethyl Acetate Production by Reactive Distillation

Parameter	Unit	Value
	Temperature (65°C)	
Keq	-	5.51
k1	mol $kg_{cat}^{-1}s^{-1}$	0.147
K1,o		$4.24x10^{6}$
K2,o		$4.55x10^{8}$
EA,1	kJ mol^{-1}	48.3
EA,2		66.2
k2	mol $kg_{cat}^{-1}s^{-1}$	0.0268

In the r-HIDiC configuration the reactive zone is localized in the stripping section, this section is designed with the characteristics necessary for the process to ensure that the reaction occurs under the conditions set by kinetics at a given temperature.

4. Simulation Study of Reactive Distillation (RD) and r-HIDiC Column

The reactive distillation with internal heat integration is composed of a reactor and a separation column that is configured to use the heat available in the equipment. The reactive distillation and r-HIDIC are fed by the reagents of the esterification reaction (ethanol and acetic acid) under the same conditions and concentrations. Then a section located in series allows separating the resulting mixture, the distillate product obtained is ethyl acetate.

The thermodynamic model used for simulations of the reactive distillation and r-HIDIC were selected through the comparison and study between the behaviour of binary mixtures involved in the process from experimental data obtained from the database of professional network of Chemical Engineering and Biotechnology (DECHEMA) and Aspen Plus software analysing different thermodynamic models compared with the conventional behaviour. The NRTL-RK (Non-Random-Two-Liquid modified to Redlich-Kwong) was used for property calculations in both systems. The simulation studies were modelled assuming not pressure drop in the column. The simulation was performed under steady state.

The esterification reaction occurs along of column. The simulation was developed using equilibrium stage model, the energy is totally transferred in the r-HIDiC column. The condition of simulation was established for perfect mixing and azeotropic convergence.

Table 2. Parameters of Simulation

Item	**RD**	**r-HIDiC**	**Item**	**RD & r-HIDiC**
Stage	13	16	***Mole Frac***	
Rectifying	6	8	*Temperature:* 65 °C	
Stripping	7	8	Water	0.0229
Reacting Stages	1 to 13	8 Stripping stages	Ethanol	0.4808
Feed Flow (Kmol/s)	1,076	1,076	Acetic Acid	0.4962

4.1 Simulation Parameters of Reactive Distillation (RD) and Heat Integrated Reactive Distillation Column (r-HIDiC)

The reactive distillation column was developed using RadFrac model. The conditions of simulation was presented in the Table 2. For this simulation the reaction occurs along the column, the set of condenser and reboiler are total and kettle type accordingly. The r-HIDiC simulation used the same characteristics of the reactive distillation. The feed conditions in the two configurations are the same for concentration, type of reaction and no pressure drop along the column. In the r-HIDiC column the energy provided in the rectifying section is transferred to the stripping section. A compressor is used for increase the pressure in this section and a valve is used between the two sections to ensure the pressure conditions (Pulido *et al*., 2011). The Figure 2 presents a conventional scheme of the reactive distillation column.

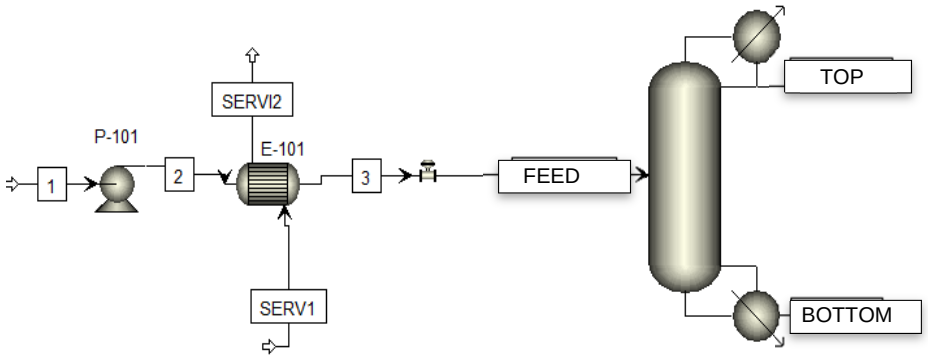

Figure 2: Configuration of Reactive Distillation

The use of the pump (P-101), the heat exchanger (E-101) and the valve are entirely to represent the conventional reactive process. All studies are focused on the configuration of column, feeding conditions, reflux ratio, energy consumption for reactive column and r-HIDiC. The r-HIDiC configuration represent a concentrically arrangement because the software does not have this model.
The energy exchange occurs between the stripping and rectifying section from energy interconnections stage to stage, a compressor was used to increase the pressure and temperature in the rectifying section and a valve to decrease the pressure of flow to stripping section. The esterification reaction of acetic acid with ethanol leads in the stripping section and is endothermic. Therefore, the available heat of the rectifying section is used to transfer to the stripping section. The compressor is isentropic and operates with an efficiency of 80%. The number of stage in r-HIDiC was obtained of RD column and increased by 20% to ensure the concentration of the output products. The quantity of energy transferred was calculated based on the enthalpy difference of each stage.

Table 3. Mol flow of Reactive Distillation (RD)

ITEM	FEED (kmol/hr)	TOP (kmol/hr)	BOTTOM (kmol/hr)	TOP (kmol/hr)	BOTTOM (kmol/hr)
		RD		r-HIDiC	
Water	89,093	435,777	1062,872	615,326	986,98
Ethanol	1862,427	374,049	78,822	205,057	144,13
Acetic Acid	1922,08	88,936	423,589	1,094	407,74
Ethyl Acetate	0	980,542	429,013	1057,9	455,44

5. Results and Analysis of RD and r-HIDiC Columns

The initial configuration of column was developed using DSTWU and Distil models provided by Aspen Plus Software. The flow of RD column was presented in the Table 3. The parameters estimations and reaction were developed along the column with the RadFrac model available in the Aspen library (Pulido *et al.*, 2012). The bottom product from reactive distillation and r-HIDiC column is high-purity. Because the presence of azeotropes between water-ethyl acetate and ethanol components, the distillate product has a 35 mol % of the components and the rest is the ethyl acetate obtained. The reactive distillation composition and temperature profiles are shown in Figure 3. The compression ratio between stripping and rectifying section is 1:2, respectively, in the r-HIDiC column.

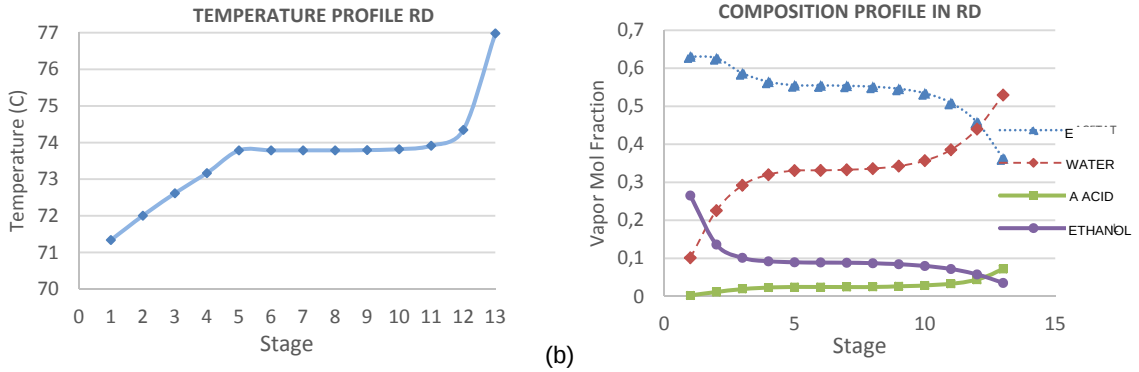

Figure 3: (a) Temperature profile of RD, (b) Composition profile in the RD

The molfrac (Kmol/h) profiles show a higher concentration of the most volatile compounds in the vapor phase, these are concentrated in the top of the column. A similar behavior occurs in the r-HIDiC configuration, this is presented in Figure 4.

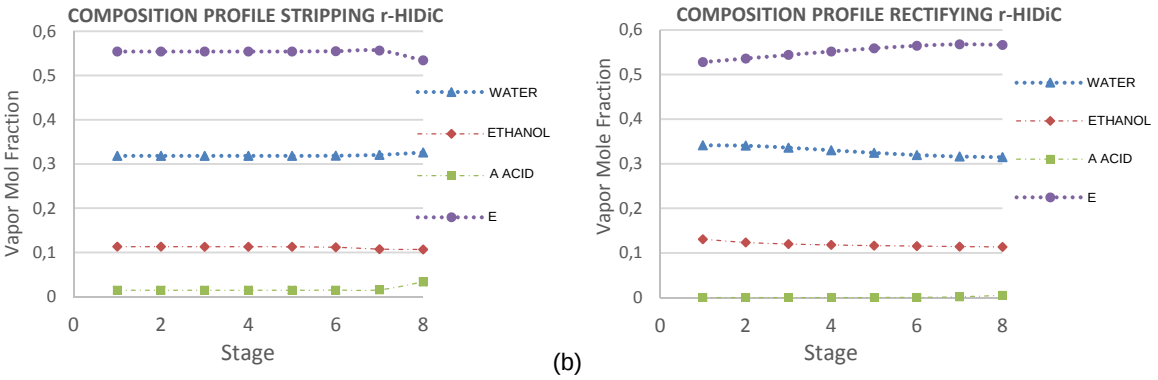

Figure 4: Composition profile in the r-HIDiC column, (a) Stripping Section, (b) Rectifying Section

The results obtained for the two configurations are advantageous over the conventional process (reactor and column separated). For the r-HIDiC column, the ethyl acetate is obtained in highest concentration in r-HIDiC column in 7.8 % respect to the reactive distillation.

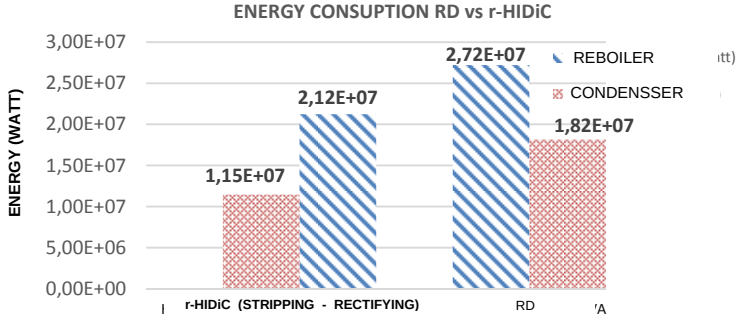

Figure 5: Energy consumption between RD vs r-HIDiC columns

Figure 5 present the energy consumption was compared for both columns. For r-HIDiC column the energy requirement is lower compared with RD column. The amount of energy potentially reduced by the r-HIDiC compared with RD is 11.792,3 KW considering that the compressor uses 0.9 KW for increasing the pressure and temperature in the rectifying section.

6. Conclusions

In this paper, simulation studies about reactive distillation column for ethyl acetate process was developed. The configuration and modeling simulation were developed in order to explore the r-HIDiC column, the feasibility of implementation and the potential for energy approach. Different studies about this technology are available in the literature. The simulation study was developed using the commercial software Aspen Plus. The r-HIDiC arrangements decrease the energy consumption in 7.8 % in relation to the conventional reactive distillation. The reaction takes places in the stripping section and approach the heat provided with the rectifying section. The r-HIDiC configuration present advantages to produce the ethyl acetate and present possibilities to treatment the azeotrope because their sections work at different pressures. The azeotrope mixtures difficulty of separation purity limited to 55% of ethyl acetate approximately. The energy diminution in the r-HIDiC column compared with the RD is 11.792,3 KW. Finally it was demonstrated about the potential of approach energy in reactive distillation systems and the advantage of internal heat arrangements.

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