Evaluation of mechanical vapor recompression in the reactive distillation of the N-butanol esterification process

Avaliação da recompressão mecânica de vapor na destilação reativa da esterificação do N-butanol

Evaluación de la recompresión mecánica de vapor en la destilación reactiva del proceso de esterificación con N-butanol

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Abstract
The process of producing esters is usually performed through esterification in a reactor followed by a distillation column to separate the products. However, this design limits the reagent conversion. Reactive distillation is an alternative to get around this issue as it allows greater reagent conversions in reactions limited by chemical equilibrium. It is one of the most famous process intensification techniques. On the other hand, mechanical vapor recompression has been used to recycle waste heat to improve efficiency of conventional distillation columns. In this context, this work evaluated the inclusion of a mechanical vapor recompression system in a reactive distillation process to obtain n-butyl acetate via n-butanol esterification with acetic acid. Systems with and without recompression were simulated in an Aspen Plus™ environment. The addition of recompression resulted in a reduction of 33.65% in the annual cost of the process, while not significantly affecting the purity of the desired product and the reagents' conversion. From an environmental point of view, the mechanical vapor recompression system adoption resulted in a 12.69% reduction in CO_2 emissions, contributing positively to meeting the requirements of the environmental regulations.
Keywords: N-butyl acetate; Esterification; Reactive distillation; Vapor recompression; Simulation.

Resumo
O processo de produção de ésteres geralmente é realizado por meio de esterificação em reator seguida de coluna de destilação para separação dos produtos. No entanto, esta configuração limita a conversão do reagente. A destilação reativa é uma alternativa para contornar esse problema, pois permite maiores conversões de reagentes em reações limitadas pelo equilíbrio químico. É uma das mais famosas técnicas de intensificação de processos. Por outro lado, a recompressão mecânica de vapor tem sido usada para reciclar o calor residual e melhorar a eficiência das colunas de destilação convencionais. Nesse contexto, este trabalho avaliou a inclusão de um sistema mecânico de recompressão de vapor em um processo de destilação reativa para obtenção de acetato de n-butila via esterificação de n-butanol com ácido acético. Os sistemas com e sem recompressão foram simulados em um ambiente Aspen Plus ™. A adição da recompressão resultou em uma redução de 33,65% no custo anual do processo, sem afetar significativamente a pureza do produto desejado e a conversão dos reagentes. Do ponto de vista ambiental, a adoção (ou inclusão?) do sistema de recompressão mecânica de vapores resultou na redução de 12,69% nas emissões de CO_2, contribuindo positivamente para o atendimento aos requisitos da regulamentação ambiental.
Palavras-chave: Acetato de N-butila; Esterificação; Destilação reativa; Recompressão de Vapor; Simulação.

Resumen

El proceso de producción de ésteres se realiza habitualmente mediante esterificación en un reactor seguida de una columna de destilación para separar los productos. Sin embargo, este diseño limita la conversión de reactivo. La destilación reactiva es una alternativa para solucionar este problema, ya que permite mayores conversiones de reactivos en reacciones limitadas por el equilibrio químico. Es una de las técnicas de intensificación de procesos más famosas. Por otro lado, se ha utilizado la recompresión mecánica de vapor para reciclar el calor residual y mejorar la eficiencia de las columnas de destilación convencionales. En este contexto, este trabajo evaluó la inclusión de un sistema de recompresión mecánica de vapor en un proceso de destilación reactiva para obtener acetato de n-butilo mediante esterificación de n-butanol con ácido acético. Los sistemas con y sin recompresión se simularon en un entorno Aspen Plus ™. La adición de recompresión resultó en una reducción del 33,65% en el costo anual del proceso, sin afectar significativamente la pureza del producto deseado y la conversión de los reactivos. Desde el punto de vista medioambiental, la adopción del sistema de recompresión mecánica de vapor resultó en una reducción del 12,69% en las emisiones de CO_2, contribuyendo positivamente al cumplimiento de los requisitos de la normativa medioambiental.

Palabras clave: Acetato de N-butilo; Esterificación; Destilación reactiva; Recompresión de vapor; Simulación.

1. Introduction

n-Butyl acetate (n-BuAc) is an ester used mainly in the manufacture of paints, coatings, and solvents, to adjust viscosity and improve fluid properties (Bravim Junior & Pires Afonso, 2019). Usually, it is produced through the esterification reaction of acetic acid (HAc) with n-butanol (n-BuOH) in the presence of an acid catalyst. The increasing consumption of n-BuAc is justified by its lower impact on the environment compared to other esters (Cho et al., 2014; Giwa & Giwa, 2017; Tian et al., 2012; Venimadhavan et al., 1999).

The esterification process to produce n-butyl acetate may be carried out through a reactor followed by a distillation column. Another option is to use a reactive distillation column, which combines the reactor and the distillation column in a single equipment. As the reaction is reversible, the conversion of n-BuOH is limited by chemical equilibrium. Reactive distillation is better suited to this type of process for two reasons: 1) constant recycling of unconverted raw material; and 2) continuous removal of products, promoting an increase in the conversion of reagents (Andrade, 2012; Muthia *et al.*, 2018).

The reactive distillation (RD) process is one of the most important in the intensification field; since it can increase production and require less invested capital, due to the reduction in the number of equipment. The application of RD to the esterification process was first reported by Backhaus through a series of patents published in 1921, 1922, and 1923 (Arthur A Backhaus, 1921, 1922, 1923). The first industrial column was implemented in 1980 by the Eastman Chemical Company to produce methyl acetate. There are already more than 150 RD in operation in the chemical and petrochemical industries (G. JanHarmsen, 2007). RD systems comprise homogeneous and heterogeneous, irreversible and reversible, catalyzed reactions, and may include hydrogenation, hydrodesulfurization, esterification, and etherification reactions (Kiss *et al.*, 2019). Studies that evaluated different intensified processes such as pervaporation, pressure swing distillation and reactive partition wall column, indicate that reactive distillation is one of the most suitable configurations in esterification systems for the production of acetates (Martínez *et al.*, 2020).

In the literature, there is an increasing number of studies focused on the production of n-BuAc through reactive distillation. Hanika *et al.* (1999) experimentally studied the synthesis of n-BuAc through RD. The authors developed a computational model based on phase and chemical equilibrium and validated it with experimental data. Considering the production of n-BuAc through transesterification between n-butanol and ethyl acetate, Giwa (2012) compared the performance of the temperature and composition profiles of a system combining a reactor and a column with those of RD. The author found simulation results that pointed to the greater efficiency of the integrated system in comparison to the conventional configuration, as RD was able to provide a higher conversion and greater product purity. Zheng *et al.* (2018) used residual curve maps for the conceptual design of the synthesis of n-butyl acetate. From the obtained project, the authors calculated the

energy consumption and the total annual cost. Through tests in a pilot plant, Steinigeweg & Gmehling (2002) evaluated the RD process to produce n-BuAc using a strongly acidic ion exchange resin as a catalyst. The authors analyzed the thermodynamic and kinetic aspects of the system.
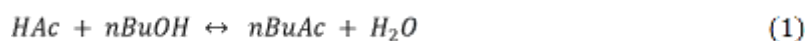
Due to the energy-intensive nature of distillation, several heat integration techniques may be used to reduce energy consumption. Mechanical vapor recompression (MVR) is one of these techniques. In this case, an external cycle is added to the column, aided by compressors and heat exchangers, resulting in an energy-efficient scheme. The use of MRV can reduce distillation energy requirements by 20 to 70% (Gao *et al.*, 2014, 2015; PeterMizsey, 1995). he application of mechanical vapor recompression to reactive distillation to obtain n-butyl acetate was not found in the consulted literature. In this context, this work brings two ideas that are on the edge of the chemical engineering state-of-the-art: the intensification of a process using RD and the use of MRV to achieve greater energy integration. The esterification of n-butanol using RD was simulated in Aspen Plus™. The configurations with and without MRV were compared from the perspective of energy consumption, total annual cost, and CO_2 emissions.

2. Methodology

The methodology used in this paper was theoretical-computational (Souza *et al.*, 2021). The esterification process of n-butanol is the process under evaluation. This research was developed in Aspen Plus software, which is a suitable tool for designing, optimizing and monitoring process performance for the chemical industry. The first step is the definition of thermodynamic and kinetic model. The next phase comprises the flowsheet development of the conventional reactive distillation and the reactive distillation with mechanical vapor recompression. The last step is the comparison between the two configurations. It is important to say that all the parameters and input data were obtained from literature, and they are highlighted in the following sections.

2.1 Kinetic and Thermodynamic Model

N-butyl acetate is produced by the esterification of acetic acid with n-butanol according to the following second-order reversible reaction:

$$HAc + nBuOH \leftrightarrow nBuAc + H_2O \tag{1}$$

Acetic Acid + n-Butanol ↔ n-Butyl acetate + Water

This reaction is catalyzed by the ion exchange resin (Amberlyst-15) and the pseudo-homogeneous model represents the reaction rate:

$$r = \frac{1}{m_{cat}} \frac{1}{v_i} \frac{dn_i}{dt} = k_1 a_{HAc} a_{nBuOH} - k_{-1} a_{nBuAc} a_{H_2O} \tag{2}$$

The reaction rate was modeled using activity terms (a_i) instead of the concentrations or molar fractions, due to the strong non-ideality of the mixture. The kinetic model (Eq. 2) assumes a linear relationship between catalyst mass (holdup) and

reaction rate. The temperature dependence on the kinetic constant (k_i) is described by Arrhenius' Law (Eq. 3) and the kinetic parameters $k_1^0, k_{-1}^0, E_{A,1}, E_{A,-1}$ are shown in Table 1 (Steinigeweg & Gmehling, 2002).

$$k_i - k_i^0 exp \left(\frac{-E_{A,i}}{RT} \right) \qquad (3)$$

Table 1. Kinetic parameters of n-butanol esterification.

	i	k_i^0 (mol/g.s)	E_A (kJ/mol)
Esterification	1	6.1084 x 10^4	56.67
Hydrolysis	-1	9.8420 x 10^4	67.66

Source: Steinigeweg and Gmehling (2002).

Esterification reactions present many azeotropes (and of various types), which makes the thermodynamic validation of properties a challenge. The quality of the binary parameters of the thermodynamic model is essential to ensure the correct prediction of composition and temperature. The UNIQUAC thermodynamic model was used to represent the non-ideality of the liquid phase; the vapor phase was considered ideal. The binary interaction parameters U_{ij} are shown in Table 2 and were obtained from the vapor-liquid equilibrium database provided in DECHEMA (Chemistry Data Series edited by J. Gmeling and U. Onken).

Table 2. Binary interaction parameters for the UNIQUAC model (cal/mol).

$U_{11} - 0$	$U_{21} = 68.0083$	$U_{31} = -343.593$	$U_{41} = 685.71$
$U_{12} = 581.1417$	$U_{22} = 0$	$U_{32} = -131.7686$	$U_{42} = 24.6386$
$U_{13} = 527.9269$	$U_{23} = 148.2833$	$U_{33} = 0$	$U_{43} = 712.2349$
$U_{14} = 461.4747$	$U_{24} = 82.5336$	$U_{34} = -298.4344$	$U_{44} = 0$

Components: (1) water; (2) n-butanol; (3) acetic acid; (4) n-butyl acetate. Source: Cho *et. al.* (2014).

The phase equilibrium results predicted by the UNIQUAC model are in accordance with Luyben (2008) and the highest percentage error found was 1.11%, as shown in Table 3.

Table 3. Prediction of azeotrope composition and temperature at atmospheric pressure.
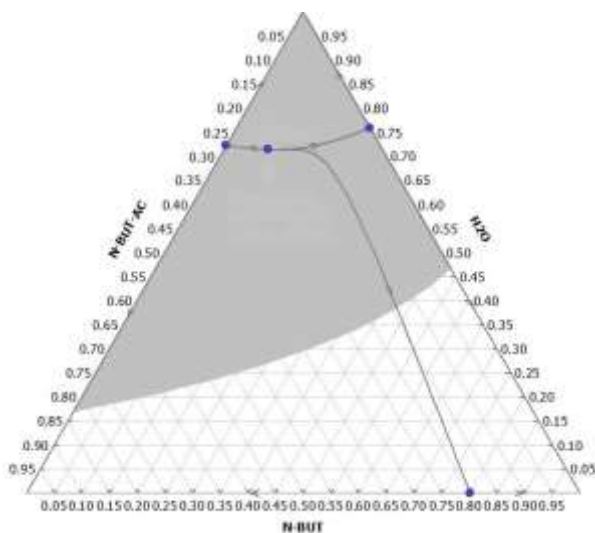
Component	H₂O	n-nBuOH	nBuAc	Temperature (ºC)	Type	Highest Error (%)
H₂O – nBuAc	0.7234		0.2766	91.21	Heterogeneous	1.11
H₂O - nBuOH	0.7595	0.2405		92.87	Heterogeneous	0.18
H2O-nBuAc-nBuOH	0.7142	0.0805	0.2053	90.99	Heterogeneous	0.34
nBuOH-nBuAc		0.8015	0.1985	117.08	Homogeneous	0.19

Source: Authors (2021).

The description of the composition and temperature of the azeotropes based on experimental data may be visualized in a ternary diagram, as shown in Figure 1. The two-liquid phase region represents more than 50% of the diagram and the minimum boiling ternary azeotrope is located within the liquid-liquid envelope. In esterification processes, the appearance of two liquid phases is common, therefore, a decanter is usually used (Luyben, 2008). In this case, the decanter has the function

of removing pure water in the aqueous phase and completely recycling the organic phase to remove the n-butyl acetate in the column base stream.

Figure 1. Ternary diagram for n-butanol/water/n-butyl acetate mixture.

Source: Authors (2021).

2.2. Evaluated Process Flow Diagrams

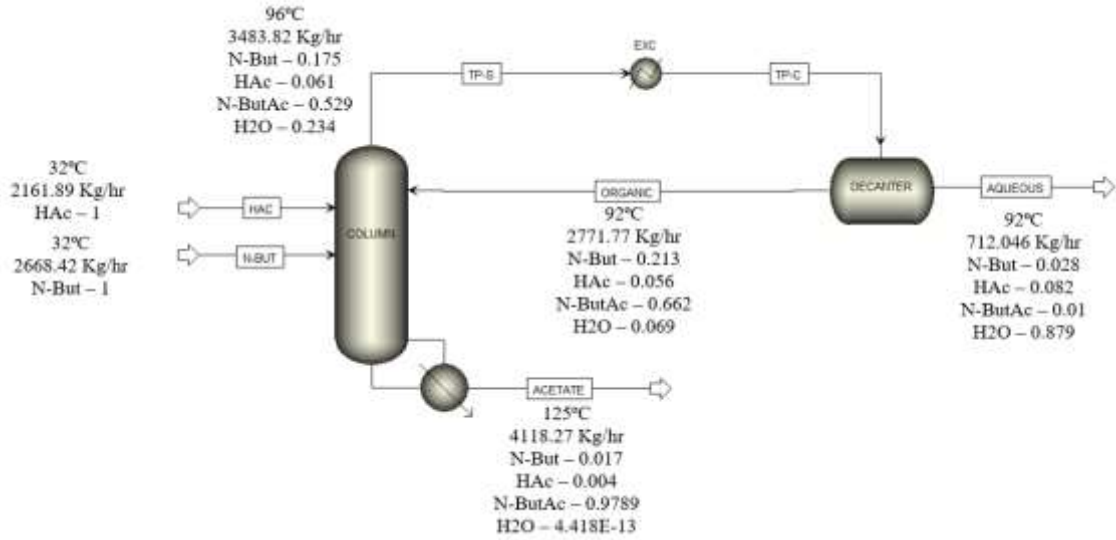### 2.2.1 Conventional Reactive Distillation (RD)

The conventional flowsheet of the reactive distillation process designed to produce n-butyl acetate was simulated in Aspen Plus™ and is shown in Figure 2.

The distillation column was modeled using the RADFRAC routine, which solves the MESH equations (mass and energy balances, sum of compositions, and equilibrium relations). The column operates at 101325 N/m^2 and the pressure drop across it has been neglected. The top product is condensed and then separated into aqueous and organic phases in a decanter. The aqueous phase mainly containing water is withdrawn as distillate, while the organic phase mainly containing n-butyl acetate is returned to the column in the first stage as reflux.

The equipment design and feed conditions used to simulate the flowsheet for the conventional configuration can be seen in Table 4 (Cho *et al.*, 2014).

To achieve a countercurrent flow (liquid-vapor) at each stage of the column's reactive section, it is common for the reagent with a lower boiling point to be fed below this section, while the reagent with a higher boiling point is fed above it. However, the two reagents of the current chemical system of interest have similar boiling points (HAc: 117.86ºC and n-BuOH: 117.38ºC). Then, the feeding of the two reagents occurs in the same stage (#8), resulting in a high concentration of these components in that section.

Figure 2. PFD for n-butyl acetate synthesis via reactive distillation.

Source: Authors (2021).

Table 4. Reactive Distillation column design data.

Number of stages	28
Number of reactive stages	11 (8-18)
Number of stages of the rectfication section	7 (1-7)
Number of stages of the stripper section	10 (19-28)
Feed stage of the reactants (NBUT/HAC)	8
Feed stage of organic reflux (ORGANIC)	1
Pressure (N/m^2)	101325
Distillate mass flowrate (kg/hr)	3483,82

Source: Authors (2021).

The desired composition (purity) of n-butyl acetate at the bottom of the reactive column is achieved using the Aspen Plus™ Design Specification tool:

$$x_{nBuAc}(wt\%) - 0.9789 \tag{4}$$

To meet the desired purity, the manipulated variable chosen is the holdup of the equilibrium stages. The initial uncertainty range is shown in Eq. 5:
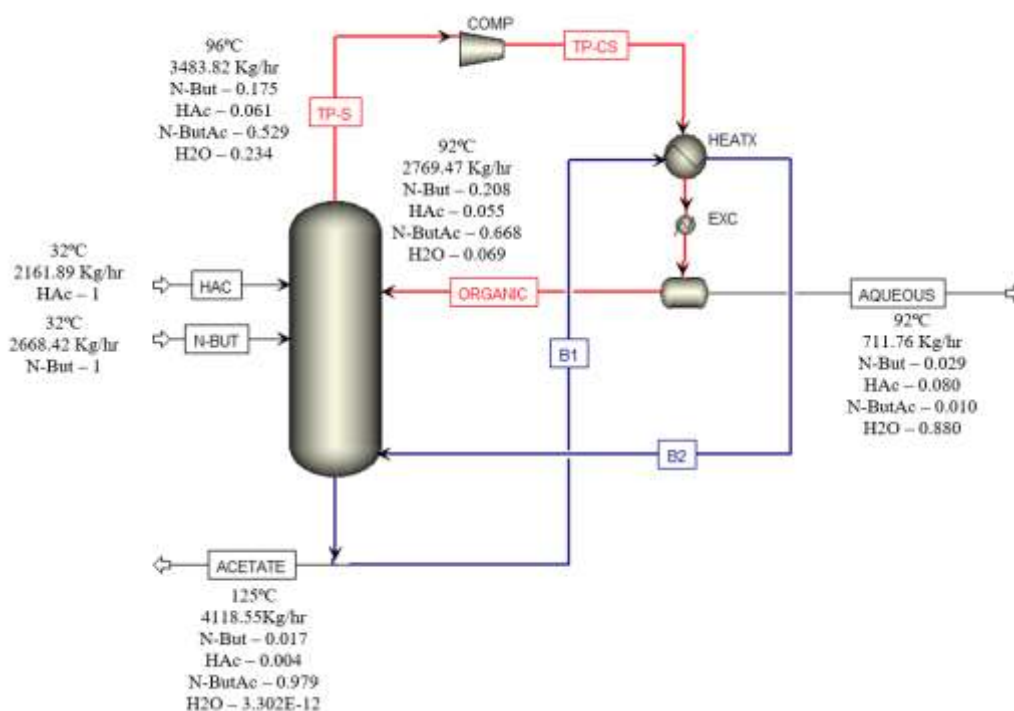
$$0.1 < Holdup\ (kg) < 300 \tag{5}$$

The reaction rate is directly affected by the holdup. The software Aspen Plus™ allows the user to change each stage holdup individually. The Calculator tool was used so that the holdup values of the other reactive stages were updated as the manipulated variable changed.

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2.2.2 Conventional Reactive Distillation with Direct Vapor Recompression (RDVR)

The mechanical vapor recompression was included in the PFD of reactive distillation, as shown in Figure 3, to evaluate the reduction in energy consumption. In the RDVR configuration, the top stream of the column goes to the compressor (COMP), which increases its pressure. Assuming the column pressure is 101325 N/m^2, and using a compression ratio of 4, the compressor outlet temperature increases from 96 to 171°C. The bottom stream of the column is split into two parts. One part is the product n-butyl acetate, while the other flows to the heat exchanger (HEATX), where it is heated by the compressor output stream (TP-CS), which generates the boil-up stream (B2) through its latent heat.

Figure 3. PFD for n-butyl acetate synthesis via reactive distillation with vapor recompression (RDVR).

Source: Authors (2021).

After thermal integration, the saturated liquid stream goes to the cooler (EXC), where the pressure and temperatures are reduced to 101325 N/m^2 and 92°C, respectively. This stream goes to the decanter where it is separated into aqueous and organic phases. The aqueous phase is removed as distillate, while the organic phase returns to the column as reflux.

To assess the energy impact in the reactive distillation process due to the addition of the MRV system, the design data for the distillation column and feed were the same as those of the RD conventional configuration. To ensure purity specifications, the Design Specification tool was also used.

This flowsheet presents additional difficulty in converging the mass and energy balances. The main obstacle is the presence of two recycles, which increases the non-linearity of the mathematical model. To get around this, the results obtained in the conventional configuration of the RD were used as an initial estimate. In this case, the stream TP-S has been specified. The use of an adequate initial estimate facilitates the search for the model's solution.

2.3 Economic and Environmental Analysis

The most common way to account for all the process' costs in a single function is by calculating the total annual cost (TAC), defined as the sum of all the costs with utilities (operational) and the cost with capital (equipment) divided by the time needed to recover the investment (payback). This is expressed by Eq. 6:

$$TAC = \frac{capital\ cost}{payback} + operacional\ cost \tag{6}$$

It was considered a payback of 3 years and the total annual cost was calculated in $/year, based on the equations specified by Luyben (2008) and Douglas (1998). Calculations were performed using the Aspen Plus™ *Calculator* tool. An annual operating time of 8150 hours was considered. Table 5 provides more details about the equations used to calculate the TAC.

Environmental pollution has become one of the biggest global issues of the century. Carbon dioxide (CO_2) plays a critical role in global warming, accounting for about two-thirds of the increase in the greenhouse effect (M.Gadalla; Ž.Olujić; R.Smith, 2006). In this case, reductions in greenhouse gases, in particular CO_2, emissions have been encouraged.

Since distillation is one of the largest energy consumers in the chemical industries – and the steam used in reboilers comes from the combustion of natural gas or coal (Vivek Kumar; Bandaru Kiran; Amiya K. Jana; Amar Nath Samanta, 2012) –, it also directly contributes to the increase in CO_2 emissions.

CO_2 emissions are related to the amount of fuel burned (Q_{fuel}) which is calculated from the energy balance of the electric power and/or steam generation process, as shown in Eq. 7:

$$[CO_2]_{emission}(kg/s) = \frac{Q_{fuel}\,(kW)}{NHV} \frac{C\%}{100} \alpha \tag{7}$$

where α (= 3.67) is the ratio of the molar masses of CO_2 and C, while *NHV* (Net Heat Value, kJ/kg) represents the net heating value of a fuel with a carbon content of *C%* (dimensionless). The *NHV* and *C%* values depend on the type of fossil fuel used in the process. For the processes evaluated in this work, natural gas was considered.

Gadalla *et al.* (2006) developed the model to calculate the amount of necessary fuel Q_{fuel} for each form of energy used in the process. In RD systems, steam is used to provide energy to the reboilers, and the amount of fuel for heating this steam is calculated according to Eq. 8:

$$Q_{fuel} = \frac{Q_{process}}{\lambda_{process}} \left(h_{process} - h_f^{H2O} \right) \frac{T_{FTB} - T_0}{T_{FTB} - T_{stack}} \tag{8}$$

where $\lambda_{process}$ (kJ/kg) and $h_{process}$ (kJ/kg) are the latent heat and the enthalpy of the steam delivered to the process, respectively; T_{FTB} is the flame temperature of the boiler (1800°C); T_0 is the ambient temperature; T_{stack} is the fuel gases temperature (160°C); and $Q_{process}$ is the heat duty required by the process.

Table 5. Equations used to calculate the TAC.

Equation	Comments
Capital Costs	
Shell Cost (\$) $= 7640D_c^{1.066}L_C^{0.802}$, where $L_c - 0.73152N_T$	- Dc is the column diameter; - L_c is the column length;
Tray Cost (\$) $= 229D_c^{1.55}N_T$	- NT is the total amount of trays;
Reboiler Cost (\$) $= 7296A_R^{0.65}$, where $A_R = \dfrac{Q_R}{U_R\Delta T_R}$	- A_R is the heat transfer area of the reboiler (m²); - Q_R is the heat duty of the reboiler (kW); - U_R is the global heat transfer coefficient for the reboiler, assumed as 1.419 $\frac{kW}{m^2K}$; - ΔT_R is the temperature difference, considered constant in 20 K;
Condenser Cost (\$) $= 7296A_c^{0.65}$, where $A_c - \dfrac{Q_C}{U_C\Delta T_C}$	- A_c is the heat transfer area of the condenser (m²); - Q_c is the heat duty of the condenser (kW); - U_c is the global heat transfer coefficient for the condenser, assumed as 0.852 $\frac{kW}{m^2K}$; - ΔT_c (K) is the logarithmic mean temperature difference (LMTD), calculated as: $\Delta T_c = \dfrac{\Delta T_1 - \Delta T_2}{\ln\frac{\Delta T_1}{\Delta T_2}}$;
Compressor Cost (\$) $= \dfrac{M\&S}{280}517.5(bhp)^{0.82}(3,11)$ where $bhp = \dfrac{hp}{n_{comp}}$ $hp = \dfrac{3.03x10^{-5}\mu}{\mu - 1}V_iP_i\left[\left(\dfrac{P_0}{P_i}\right)^{\frac{\mu-1}{\mu}} - 1\right]$	- The Marshall and Swift (M&S) index of 1108.1 (2002) is used in the calculation; - hp (horse-power) is the theoretical power of the pump; - bhp (Brake horse-power) is the real power; - V_i is the steam flowrate ($\frac{ft^3}{min}$); - P_i is the inlet pressure ($\frac{lbf}{ft^2}$); - P_v is the outlet pressure ($\frac{lbf}{ft^2}$); - μ is the polytropic coefficient;
Operating Cost	
Steam Cost (\$/year)$- m_{steam}\$C_v h$, where $m_{steam} - \dfrac{Q_R}{q}$	- Q_R is the heat duty of the reboiler $\left(\frac{Kj}{hr}\right)$; - q is the latent heat $\left(\frac{Kj}{kg}\right)$; - \$Cv is the cost of medium pressure steam (14.50\$/1000kg) - h is the total amount of operating hours.
Cooling water Cost (\$/year) $= m_{CW}\$C_a h$, where $m_{CW} = \dfrac{Q_c}{C_p\Delta T}$	- Q_c is the heat duty of the condenser $\left(\frac{Kj}{hr}\right)$; - c_p is the heat capacity of water $\left(4.183\ \frac{Kj}{kgK}\right)$; - \$Ca is the cost of cooling water (0.02\$/1000kg); - ΔT is the temperature difference between the water entering and leaving the condenser;
Compressor eletrical cost = $\dfrac{0.045}{KWhr}\dfrac{1\ KW}{1.341hp}\dfrac{bhp}{n_m}h$	- The operating cost of a compressor is based on engine efficiency and energy cost. $\frac{0.045}{kwhr}$; - n_m is the efficiency of the compressor engine considered 0.6.

Source: Authors (2021).

In the RDVR configuration, the electrical energy used in the compressor may come from two sources, the local power grid or gas turbines. Considering the use of the gas turbines as power supply, the amount of fuel required is calculated from the ratio between the efficiency of a gas turbine (η_{GT}) and the Carnot factor (η_C), as described in Eq. 9. To calculate CO_2 emissions, the equations described above were implemented in the *Calculator* tool of Aspen Plus™.
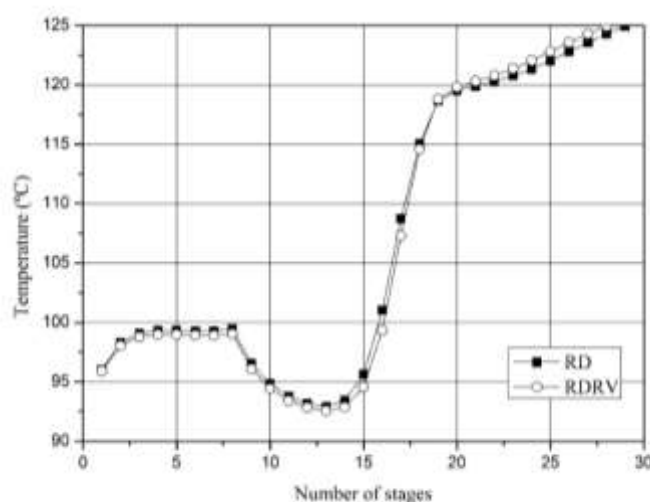
$$Q_{fuel} = \frac{Q_{process}}{\eta_{GT}} \frac{1}{1 - \eta_C} \tag{9}$$

3. Results and Discussion

The operating conditions obtained in the simulation of the two evaluated configurations are presented in Figures 1 and 2.

The temperature profiles for the RD and RDVR configurations are shown in Figure 4. The addition of the vapor recompression system did not affect the temperature profile of the n-butyl acetate production process. The azeotrope formation tends to lower the reaction temperature in the reactive section (Cho *et al*., 2014). This decrease prevents catalyst degradation and explains the temperature drop around stages 8-15. The temperature in the reactive section of the column varies between 99ºC and 115ºC. This range comprises the operating temperature values suitable for using the Amberlyst-15 catalyst. According to the manufacturer, the maximum recommended operating temperature is 125ºC (Steinigeweg & Gmehling, 2002).

Figure 4. Temperature profiles for RD and RDVR configurations.
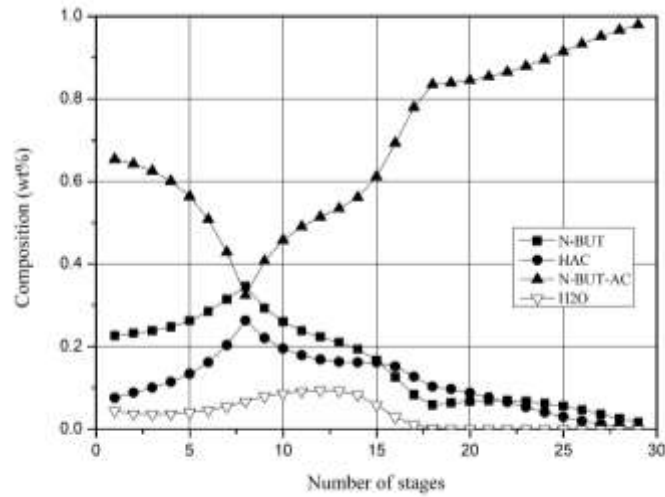

Source: Authors (2021).

Figure 5 presents the composition profile for the RD and RDVR configurations. The addition of the vapor recompression system did not affect the composition profile. In the reactive section, as acetic acid and butanol are consumed, acetate and water are formed. The maximum composition value of the reagents (n-But and HAc) occurs in stage 8 (feed stage).

N-butyl acetate is produced throughout the entire distillation column. As it approaches the bottom, where it is removed, its composition increases to the desired purity (around 97.9 wt%). The ternary azeotrope formed is responsible for dragging the water to the top of the column, shifting the equilibrium to favor the desired reaction. It is possible to see that the composition and temperature of the top are almost the same as those of the ternary azeotrope. A 96.6% n-butanol conversion was obtained.

An important variable to be analyzed in the RDVR system is the compressor output pressure. Two essential criteria were considered for choosing this pressure: 1) a minimum pressure sufficient to reach a temperature that vaporizes the entire boil-up of the column; 2) the lowest TAC value for the RVDR configuration, which minimizes costs. Figure 6 shows the behavior of TAC for the RDVR system as a function of the compressor output pressure. In all cases, the boil-up is completely
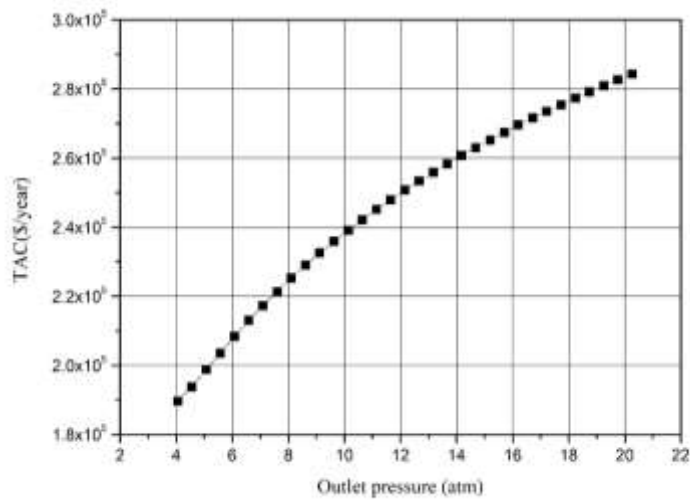
vaporized. As can be seen, the minimum compressor output pressure of 405300 N/m^2 allows full boil-up vaporization and results in the lowest annual cost for the RDVR system.

Figure 5. Composition profile for RD and RDVR configurations.

Source: Authors (2021).

Figure 6. TAC behavior for RDVR configuration.

Source: Authors (2021).

The obtained polytropic coefficient (μ) was equal to 1.11. Considering that all the input data of the compression system remained fixed for every scenario, it is possible to state that the variation in the compression ratio (CR) directly influences the TAC, as shown in Eq. 10:

$$CR - \frac{P_0}{P_i} - \left(\frac{T_0}{T_i}\right)^{\frac{\mu}{\mu-1}} \qquad (10)$$

Considering a fixed input pressure (P_i) of 101325 N/m^2, the CR changing to achieve the desired output temperature (T_o) relative to a fixed input temperature (T_i) increases the required energy by compressor ($Q_{compressor}$) and the output pressure (P_o); therefore, increasing TAC.

Although there are no significant changes in the operating conditions of the process, the inclusion of the MVR impacts its costs. On one hand, there is the acquisition of equipment, and, on the other hand, there is the possibility of saving on utilities. In this context, the economic analysis provides a preliminary insight into the advantages of one process over another. Table 6 presents the operating and capital costs for the RD and RDVR configurations. It is observed that the inclusion of the vapor recompression system resulted in a reduction of 33.65% in the total annual cost, considering the n-butanol esterification process. Even though the RDVR configuration requires a greater capital investment and generates an electrical energy cost for compressor operation, there is a reduction in operating costs due to the decrease in the total utility consumption. The operating cost of steam is not required anymore, and the cost of cooling water is considerably reduced because the steam condensation takes place in the HEATX through heat exchange. This reduction reflects positively on the TAC, making the use of the RDVR system more advantageous.

Table 6. Costs for RD and RDVR configurations.

	RD	RDVR
	Capital Cost ($)	
Shell	175,373.95	170,102.31
Stages	5,317.98	5,116.89
Reboiler	64,386.60	68,807.22
Condenser	39,516.03	10,530.62
Compressor	-	302,999.30
	Operating Cost ($/year)	
Steam	169,108.42	-
Cooling water	22,893.02	3,670.43
Compressor electrical cost	-	67,495.83
Catalyst	1,565.591	1,842.37
	Total Annual Cost ($/year)	
TAC	288,431.90	191,364.92

Source: Authors (2021).

Due to the distillation's low efficiency, it is necessary to input high quality energy (steam) into the reboiler. The steam used in the reboiler for the RD configuration comes from boilers, which burn fossil fuels. The choice of natural gas is motivated by its lowest Fuel$_{fact}$ (0.05l kJ/h), calculated using the equations provided by Gadalla *et al.* (2006). The RD system presented a CO_2 emission of 168.02 kg/h.

While distillation requires an energy supply, a similar amount of heat is rejected in the condenser. In the RDVR configuration, that wasted heat is reused to provide energy to the reboiler. In this case, CO_2 is generated by a gas turbine responsible for supplying energy to the compressor. This RDVR system presented a CO_2 emission of 146.70 kg/h.

The inclusion of the vapor recompression system resulted in a 12.69% reduction in CO_2 emissions. This reduction is approximately 173 tons/year of CO_2 – considering 8150 hours of annual operation. Due to the reuse of wasted energy and, consequently, a lower energy consumption in the process, which directly impacts the required amount of fossil fuel for steam/energy generation, a significant reduction in CO_2 emission is achieved.

4. Conclusion

The n-butanol esterification process through reactive distillation was simulated in Aspen Plus™. Configurations with and without direct vapor recompression were compared. In both configurations, n-butanol conversion of 96.6% was achieved and an n-butyl acetate purity of 97.9% by mass was obtained. The addition of mechanical vapor recompression resulted in a 33.65% reduction in the total annual cost and a 12.69% reduction in CO_2 emissions when compared to conventional reactive distillation. As widely reported in the literature, mechanical vapor recompression reduces not only plant operating costs, but also the environmental impacts associated with energy generation.

As future work, it is suggested to evaluate more complex configurations of the classical mechanical vapor recompression in order to obtain higher savings in terms of TAC and CO_2 emissions.

Acknowledgments

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