

Parastillation and metastillation applied to bioethanol and neutral alcohol purification with energy savings

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ARTICLE INFO

Keywords:

Parastillation

Metastillation

Biofuel

Neutral alcohol

Process intensification

ABSTRACT

Bioethanol is an important biofuel with high potential to be a safety environmental alternative to fossil fuels. However, bioethanol production involves many distillation steps, which is one of the most energy consuming separation processes. Unconventional distillation techniques were proposed, aiming to reduce energy cost and CO₂ emissions on bioethanol production. Parastillation and metastillation processes and novelty combinations of these techniques were explored. In all proposed configurations the liquid or vapor phase was divided inside the column. For the first time, parastillation columns with multiple condensers and columns with different distillation techniques combined into one unique column shell, here denominated as combined columns, were studied. Multiple condensers set, in parastillation columns, avoids the non-necessary mixed of the vapor phases. Combined columns are composed of parastillation trays in the rectifying section and of metastillation or conventional trays in the stripping section. The new configurations reduce total annual costs and CO₂ emissions up to 35 % and 42 %, respectively, when compared with traditional distillation. Reduction in the column diameter by using metastillation instead of conventional distillation was possible without an increase in the column height, differently from previously results. Therefore, biofuel and neutral alcohol production can be even more economical and sustainable.

1. Introduction

Decrease of fossil fuel reserves and increase of the greenhouse effect contribute to growing interests in renewable energy. Bioethanol and biodiesel are important sources of renewable energy, contributing to reductions in CO₂ emissions. The United States and Brazil are the world's largest producers of bioethanol. In 2019, the United States and Brazil produced together 95.5 billion L of ethanol, corresponding to 83 % of the world's bioethanol [1,2]. In 2020, the productions of the United States and Brazil are estimated at 52 and 30 billion L, respectively [3]. From 2019 to 2020, there was a decrease in the biofuel production due to the COVID-19 pandemic [3].

Most of the bioethanol is produced by a fermented from sucrose of sugarcane (in Brazil) and corn (in United States). The fermented

product, industrially referred to as wine, is concentrated by a series of distillation columns aiming to obtain a product with a minimum specific ethanol grade of 92.5 mass% in Brazil [4]. This product, known as hydrous bioethanol, can be used in flexible fuel or ethanol-powered engines. Furthermore, the hydrous ethanol can be purified by three additional distillation columns in order to produce neutral alcohol [5,6]. The neutral alcohol is a kind of hydrated alcohol with high ethanol concentration (94 % in mass) and low level of contaminants [5]. Neutral alcohol has some specific applications as in the food, beverage, pharmaceutical, and cosmetics industries. In addition, bioproducts, such as neutral alcohol, will probably be the main input material for alcohol chemistry in future biorefineries.

The hydrous bioethanol production mostly uses two distillation columns, separated into five sections [7]. For the neutral alcohol

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<https://doi.org/10.1016/j.cep.2021.108334>

Received 21 November 2020; Received in revised form 25 January 2021; Accepted 6 February 2021

Available online 12 February 2021

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production, three additional distillation columns are required beyond those used to hydrous bioethanol [5,6]. Although, bioethanol may contribute to global environmental goals, distillation operation is one of the worldwide energy intensive process. Approximately 50 % of the world industrial energy is consumed by separation processes, and distillation is responsible for 49 % of this amount [8].

Several technologies have been proposed to reduce energy consumption in distillation processes. Some examples are thermally coupled distillation, double-effect integration distillation, conventional and extractive dividing-wall columns (DWCs) etc. In DWC the liquid and the vapor phase are divided inside the column shell. In the bioethanol dehydration the use of DWC permits to reduce the number of condensers and reboilers, in relation to the use of conventional columns, and thereby leading to energy savings up to 40 % [9,10]. The replace of the extractive distillation by thermally couple extractive operation may represent a reduction in energy consumption of up to 30 % [11]. The use of double-effect forward-integrated columns in the hydrous bioethanol distillation may present reductions in the total annual cost, even with increase in the investment costs [12].

Less known distillation techniques that may present energy savings are the columns with parallel streams. These columns involve the division of the liquid or vapor phase inside the column into two or more parts. In parastillation the vapor phase is divided in the bottom of the column into two or more ascending streams. On the other hand, in metastillation columns the division occurs in the liquid phase at the top of the column.

Distillation columns with parallel streams can reduce capital or operational costs, when used in the replacement of conventional distillation columns [13–16]. The mechanical arrangement of parastillation trays permits to reduce the height of this type of column in about 30 %, when compared with conventional distillation operating with the same reflux ratio [15–17]. It is also possible to replace a conventional distillation column by a parastillation one of same height, while reducing the reflux ratio in up to 48.4 % for hydrocarbon distillation [16] or in 24 % for multicomponent alcoholic distillation [18]. Metastillation columns

are preferred for processes with high internal liquid/vapor ratio since the division of liquid increases the contact between the phases. This characteristic of the metastillation columns permits to decrease the column diameter by up to 30 % in comparison with conventional distillation [13]. However, this diameter reduction, sometimes, may apply in increase of the number of stages and column height [13].

Parastillation and metastillation trays can be used alone or be combined inside the columns. The combination of more than one technique inside one unique column shell is referred to as a combined column. Combined columns are reported in the patent of Biasi et al. [19]. The combination of two techniques inside one column shell is illustrated in Fig. 1. In Fig. 1, the CC column represents the conventional distillation, with N_R^C and N_S^C stages in the rectifying and stripping sections, respectively, plus the feed tray. The combined columns are shown at Fig. 1-PC and -PM. In both configurations, N_R^P parastillation trays are present in the rectifying (above feed) section of the combined column. In Fig. 1-PC the stripping (below feed) section is composed of conventional trays (N_S^C) and in Fig. 1-PM of metastillation trays (N_S^M). The feed stage of either combined column is a conventional distillation tray, which receives the liquid from the rectifying section (with parastillation trays) and the vapor from the stripping section. Above the feed, the vapor is divided in two equal parts, each part flowing to one side of the parastillation section.

The combined column is better suited for processes that present high amount of liquid in the stripping section, while the rectification section is characterized for separations occurring under small relative volatility. This because the parastillation technique is indicated for processes with small relative volatility, but it is not indicated for processes with high internal liquid flows [14]. For processes that present high liquid/vapor ratio in the stripping section it is better to use combination of metastillation below the feed and parastillation or conventional distillation above the feed [19]. Since, this techniques are more appropriated for processes with high amount of liquid [13].

Another adaptation of parastillation columns refers to the use of multiple set of condensers. In this configuration, each vapor flow leaving

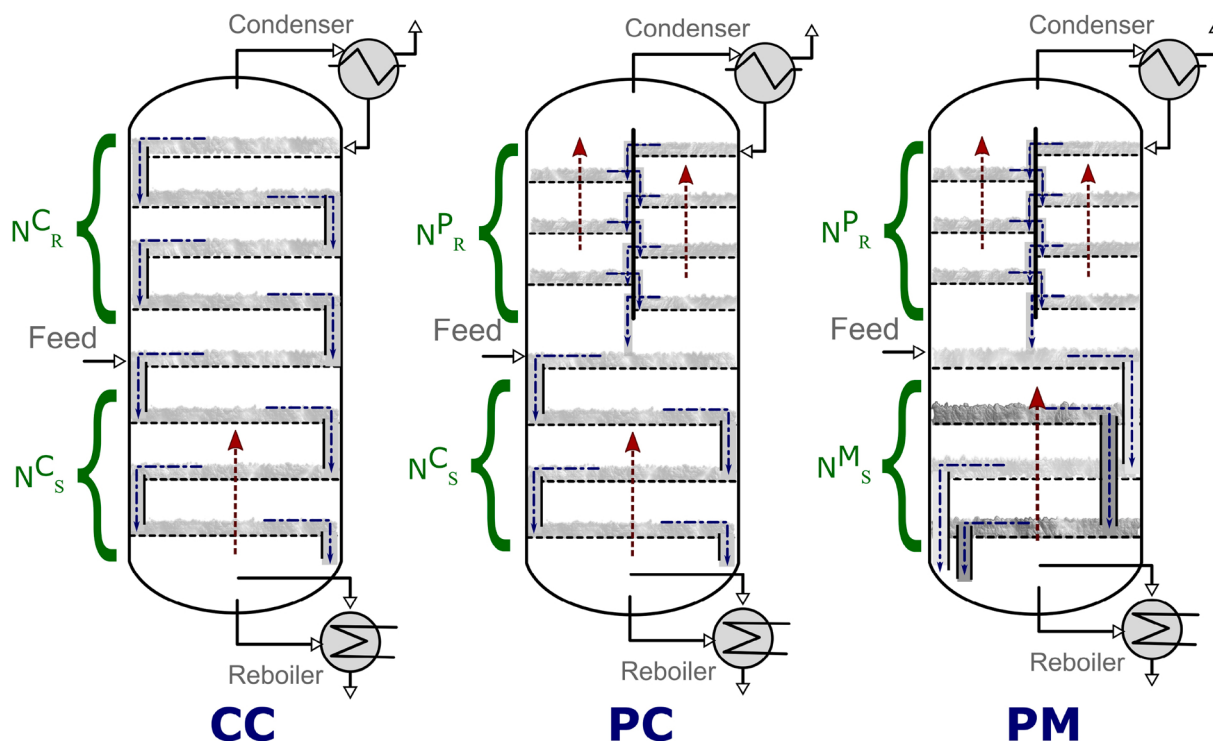


Fig. 1. Conventional distillation (CC) and combined columns composed of parastillation trays in the rectifying section and of conventional distillation (PC) or metastillation (PM) in the stripping section, N represents the number of stages of each section.

the top of the parastillation column enters in a different set of condensers. This means that the vapor flows are completely separated from the bottom to the top of the column. This procedure is illustrated in Fig. 2. In existing configurations, the multiple vapor flows inside the column are joined before entering in a unique condenser set [16,20]. Considering multiple sets of condensers, it is possible to withdraw two distillate flows, one from each condenser. It is also possible to operate one condenser under total reflux condition, while to remove the distillate from the other condenser. In both configurations, the reflux flows from both condensers are combined and fed to the last stage of the column. The first report of this configuration was mentioned in the patent of Biasi et al. [19].

In the present work, parastillation, metastillation and combined columns are applied to hydrous bioethanol and neutral alcohol production. The use of combined columns was suggested for the hydrous bioethanol distillation. In the neutral alcohol production, both hydroselection and demethylizer columns were investigated. The hydroselection column was replaced by a metastillation one. Parastillation technique with multiple condensers was used for the ethanol-methanol separation in a simplified process representing the demethylizer column. The alternative columns with multiple phase divisions lead to cost savings and CO₂ emission reductions in all investigated processes in comparison to conventional distillation columns.

2. Methods

2.1. Computational simulation

The columns were simulated using the mathematical model described in our previous work [18]. The model is an adaptation of the Naphtali and Sandholm [21] method, commonly used for conventional

columns. This method considers the simultaneous solution of the mass and enthalpy balances and of the equilibrium relations, which are usually known as MESH equations. These equations were previously reported by Mizsey, Mészáros and Fonyó [13] for simulation of metastillation columns, and by Meszaros and Fonyo [16] for parastillation columns. The MESH equations for conventional distillation column were reported by Naphtali and Sandholm [21], by Seader, Henley and Roper [22], and by many other authors. Biasi et al. [18] enabled the simulation of all these columns using a unique set of equations just by specifying the number of vapor or liquid phase divisions.

The main difference among the equations for conventional distillation and those for para- and metastillation is the internal vapor (in parastillation) or liquid (in metastillation) flows division into two or more parts, each one flowing into alternative stages. These differences require small modifications on the indexes of the MESH equations. There is no report on the open literature about the simulation of combined columns or parastillation columns with multiple condensers. However, combined columns can be simulated considering a blend of equations from the combined processes with minor modifications in the regions where the techniques are joined. In the present paper, the techniques were joined in the feed region. For the simulation of parastillation columns with multiple condensers, one must consider each additional condenser as a stage of the column adjusting the MESH equations in this region. The MESH equations for combined columns and for parastillation columns with multiple condensers are reported in Appendix A. The mathematical models were implemented in MatLab® and the Newton-Raphson method was used to solve the set of nonlinear equations, for more details see the Appendix A. The simulation tips proposed by Biasi et al. [18] were used. There are no experimental report of combined columns or columns with multiple condensers. However, the MESH equations for parastillation and metastillation columns were validated in our previous work [18].

Regarding the thermodynamic properties, the NRTL model was selected for calculation of activity coefficients of the liquid phase. The adopted parameters of the NRTL model were previously adjusted by Batista et al. [7] for alcoholic distillation. The vapor phase was considered ideal, with fugacity coefficients equal to the unit. The extended Antoine equation was used to predict the vapor pressure with coefficients obtained from Aspen Plus®. The enthalpies were calculated using COCO (Cape-Open to Cape-Open) [23], for more information and a validation procedure see Supplementary Material – Appendix B.

2.2. Combined columns applied to bioethanol production

The hydrous ethanol is concentrated in two distillation columns, industrially separated into five sections, as shown in Fig. 3. The first column is composed of sections A, A1, and D, from base to top (Fig. 3). This column is known as AA1D column. The second column, known as BB1, is composed of sections B1 and B, from base to top (Fig. 3). These sections aim to concentrate and purify the ethanol from water and minor compounds. According to their relative volatility in relation to water, the minor compounds present in the ethanol distillation can be classified into three groups of components: light components with lowest minor relative volatility, heavy ones with higher relative volatility, and the intermediate ones [7].

The wine (fermented wort) is fed on the top of section A1. This section decreases the wine contamination of light components. Section D, above A1, is used for concentrating these light components. The section A, below section A1, is responsible for exhausting the wine and for removing the heavy components, recovering almost all ethanol feed into the process (Fig. 3). Two side streams are withdrawn from column AA1D and fed to the bottom tray of section B, which is present in the second column. One of the side streams is withdrawn from the bottom of section D (liquid phase) and the second, known as phlegm (vapor phase), from top of section A. Section B finishes the ethanol

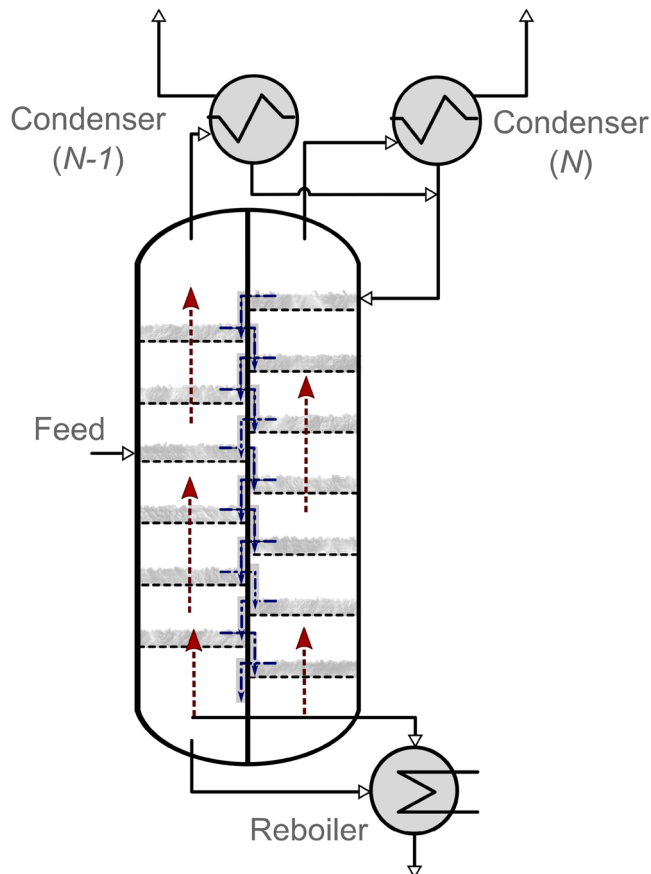


Fig. 2. Parastillation column with multiple condensers.

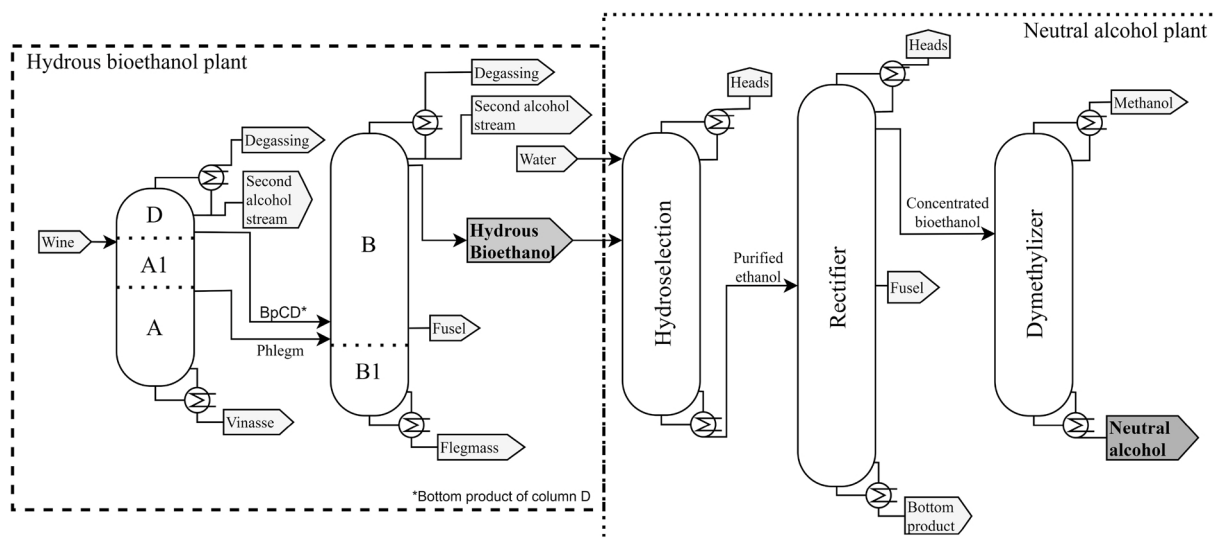


Fig. 3. Typical hydrous bioethanol and neutral alcohol industrial plants.

concentration to the legislation levels. From section B, the fusel oil is withdrawn as side stream. This stream is composed mostly of heavy alcohols and are necessary to guarantee the required ethanol level in the product. Section B1 (bellow section B) is responsible to recovery almost all ethanol fed into column BB1. More details about this purification process can be found in the work of Batista et al. [7]. The process specifications here adopted are based on the work of Batista et al. [7]. Binary and multicomponent distillations were considered.

2.2.1. Binary distillation

On the first part of this work, it was investigated the simple effect of the combined column in the binary distillation for hydrous bioethanol production. The wine was considered a binary mixture of ethanol and water. The tray (Murphree) efficiency was 100 % for all stages. This part of the work aims to identify major influences with no interference of minor components, understanding the effect of the use of two types of techniques in one unique column shell. For this, different feed concentrations were considered, exploring ethanol grades present in both AA1D (the wine feed flow) and BB1 (the phlegm feed flow) columns (Table 1).

For all columns, the feed was performed at 101.3 kPa as saturated

Table 1
Specifications for the binary bioethanol distillation.

Study Case	1	2	3	4
Molar percentage of ethanol in the feed [mol%]	3.0	5.0	20.0	20.0
Mass percentage of ethanol in the feed [mass%]	7.3	11.9	39.0	39.0
Alcoholic graduation in the feed [°GL]	9.0	14.4	44.4	44.4
Molar feed flow [kmol/h]	5,500	5,500	5,500	5,500
Mass feed flow [kg/h]	103,713.07	106,799.09	129,944.23	129,944.23
Feed pressure [kPa]	101.3	101.3	101.3	101.3
Vapor Percentage in the feed	0%	0%	0%	100 %
Molar distillate flow [kmol/h]	196.78	327.97	1,311.87	1,311.87
Mass distillate flow [kg/h]	8,174.07	13,623.46	54,493.83	54,493.83
Column pressure [kPa]	101.3	101.3	101.3	101.3
Tray (Murphree) efficiency	100 %	100 %	100 %	100 %

liquid. The 20 mol% ethanolic grade is close to that of the alcoholic phlegm, which is fed into the BB1 column, usually as vapor phase. Thus, for this ethanolic concentration, it was also considered the feed as saturated vapor. Two types of combined columns were considered containing parastillation in the rectifying section, while the stripping section was composed of metastillation (this column is shown in Fig. 1-PM) or of conventional distillation trays (shown in Fig. 1-PC). The ethanol percentage in the distilled flow was fixed in 93.00 mass% (~83.86 mol%). The ethanol loss in the bottom product was less than 0.02 mass% (~8.10⁻³ mol%). In this way, the ethanol recovered in the distillate was 99.7 %. The vapor distillate flow was adjusted to achieve the specific ethanol degree and recover percentage, as shown in Table 1. The reflux ratio was adjusted to meet the quality parameters.

Four study cases were considered, see Table 1, each one with different feed and operational conditions. For each specification, one conventional column was simulated based on the work of Batista et al. [7]. These are the reference columns for each study case. The reflux ratio was set to be close to 4.0, which are the optimal for this kind of process, as mentioned in early works [7] after a series of optimization techniques. The number of stages was then adjusted to achieve the specific ethanol degree at distillate (93.00 mass%) and recover percentage (99.7 %). The number of trays varied from 16 to 36 (see results). The feed tray position was optimized to increase the ethanol recovery. The conventional columns were compared with combined columns PC and PM of Fig. 1 keeping constant the column height. For study case one, it was also considered a PC column (Fig. 1) operating with same reflux ratio as the corresponding conventional one but having a smaller height.

2.2.2. Multicomponent distillation

In a second approach, it was considered the presence of minority components and a decrease in the separation efficiency from 100 % to 60 %. These considerations bring the study closer to the real industrial case. This part of the work is focused on the BB1 column of Fig. 3. It was investigated the replacement of the conventional trays of section B (rectifying section) by parastillation trays, while keeping the B1 section (stripping section) with conventional distillation trays. This combined column configuration is shown in Fig. 1-PC.

The phlegm fed was composed of ethanol, water, and by other three congeners, one of each volatility class present in alcoholic distillation [7]. Ethyl acetate represents the light components, which concentrate in the column top. Isoamyl alcohol is the main component with intermediate volatility, withdraw in the side-stream flow. Glycerol stands for the heavy ones, being recovery in the bottom of the column. The feed flow,

based on the work of Batista et al. [7], was fixed in 5,500 kmol/h (~130,034 kg/h), with composition described in Table 2. Partial condenser, with distillate as vapor, and a liquid side stream - for the withdrawal of intermediate volatility components (heavy alcohols) - were considered (Table 2). The reflux ratio and the number of stages of the conventional column were based on the work of Batista et al. [7]. The authors optimized the hydrous bioethanol distillation process using conventional distillation columns. The feed tray was optimized to be at its best position. The columns were adjusted to achieve the specific ethanol degree at distillate (93.00 mass%) and recover percentage (99.7 %), see Table 2.

2.3. Metastillation and parastillation applied to neutral alcohol production

The hydrous bioethanol can be extra purified to produce neutral alcohol. This extra purification takes place into three additional distillation columns: hydrosselection, rectifier and demethylizer columns. These columns and all flows and connections are shown in Fig. 3. The hydrosselection column aims to separate superior alcohols from ethanol. Potable water is fed in the top of this column, it dilutes the superior alcohols, increasing their activity coefficients and, for consequence, their volatilities. Thus, the superior alcohols can be separated from ethanol, being concentrated in the column heads [5,6]. The bottom product of the hydrosselection column, mostly composed of ethanol and water, is then concentrated in the rectifier column, to about 94 mass% of ethanol. Besides the ethanol purification, the rectifier column also aims the removal of the remained volatile compounds, as distillate, and of the superior alcohols in an additional fusel oil stream. The concentrated bioethanol is withdrawn from a tray located two or three positions below the column top. The last column, the demethylizer one, aims to eliminate the methanol contamination from the neutral alcohol. Neutral alcohol is obtained as the bottom product of the demethylizer column, while a methanol-rich stream is withdrawn as distillate. Decloux and Coustel [6] and Batista et al. [5] describes in details this set of columns. Their works are the base of this study. In the present study, it is proposed the use of metastillation column in the hydrosselection process and of parastillation column with multiple condensers in the demethylizer process.

2.3.1. Metastillation in hydrosselection process

The hydrosselection column (Fig. 3) presents high internal liquid/vapor ratio being indicated for metastillation process. Metastillation was investigated as an alternative distillation apparatus considering a feed mixture with eight components (water, ethanol, methanol, propanol,

isobutanol, isoamyl alcohol, and acetaldehyde). The minor components selected for this investigation were the same chosen by Decloux and Coustel [6]. Batista et al. [5] used the same eight components, here adopted, plus others eleven ones. However, the flow of each component in the feed (Table 3), as well as the column specifications, were obtained from the work of Batista et al. [5]. This procedure was adopted to continuous the example using the same base as the one of the previous section. Batista et al. [5] classified the minor components into light, intermediate and heavy ones, depending on their volatilities in relation to ethanol and water. Based on this classification, only the heavy component class is not included in the present investigation, since the heavy components tend to be separated in the early columns used in hydrous bioethanol production. The intermediate compounds are the most important class of minor components to be withdrawn during the hydrosselection purification step. Isoamyl alcohol, propanol and isobutanol represent the main components of this class.

The first step was to simulate a conventional hydrosselection column based on previous works [5,6]. The hydrosselection column is illustrated in Fig. 3. This column was composed of 52 stages (including condenser and reboiler) with two feeds: (i) cold potable water, free of congeners, into stage 51 (bottom-top), and (ii) fuel hydrated bioethanol into stage 32 (bottom-top). The alcoholic content of the bottom product was 10 % in volume. The ethanol loss in the distillate was less than 2% of the total ethanol fed to the column, and the total steam consumption was less than 2 kg of steam per liter of alcohol fed into the column. The reflux ratio was adjusted to meet the quality parameters. The specifications of this process are indicated in Table 3.

After simulating the conventional hydrosselection column, the use of a metastillation apparatus with two liquid divisions was investigated. For the metastillation operation, it was considered the same total number of trays (52) and operational conditions of the conventional equipment. Each feed was split into two equal parts and fed into the column in two consecutive trays, to equally distribute the feed between the internal liquid flows. The bioethanol fuel was fed in stages 31 and 32, and the cold water in stages 50 and 51. The results obtained for both processes were analyzed considering ethanol loss in distillate flow, total steam consumption, concentration of ethanol and minor components in the bottom product, column diameter, and total annual costs.

Table 2
Specifications for the multicomponent bioethanol distillation.

Parameter	Value
Total feed flow	5,500 kmol/h (~130,034 kg/h)
Water	79.98 mol% (60.94 mass%)
Ethanol	20.00 mol% (38.97 mass%)
Isoamyl alcohol	$2.36 \cdot 10^{-2}$ mol% ($8.81 \cdot 10^{-2}$ mass%)
Molar/Mass fractions of feed flow	
Ethyl acetate	$1.27 \cdot 10^{-4}$ mol% ($4.74 \cdot 10^{-4}$ mass%)
Glycerol	$1.45 \cdot 10^{-4}$ mol% ($5.67 \cdot 10^{-4}$ mass%)
Feed temperature and pressure	97.5 °C and 101.3 kPa
Vapor distillate flow	1,310 kmol/h (~54,490 kg/h)
Liquid side stream	8 kmol/h (~235 kg/h)
Tray (Murphree), condenser and reboiler efficiency	60 % (all trays and condenser), 100 % (reboiler)
Column pressure	101.3 kPa
Ethanol concentrations at the column top	93.00 mass% (~83.87 mol%)
Ethanol concentrations at the column bottom	0.02 mass% (~ $8 \cdot 10^{-3}$ mol%)

Table 3
Specifications for the multicomponent hydrosselection distillation.

Parameter	Value
Total feed flow	326.5 kmol/h (~13,598 kg/h)
Water	15.96 mol% (6.82 mass%)
Ethanol	84.02 mol% (93.15 mass%)
Methanol	$5.312 \cdot 10^{-4}$ mol% ($4.096 \cdot 10^{-4}$ mass%)
Molar/Mass fractions of feed flow	
Propanol	$1.171 \cdot 10^{-2}$ mol% ($1.693 \cdot 10^{-2}$ mass%)
Isobutanol	$3.074 \cdot 10^{-3}$ mol% ($5.484 \cdot 10^{-3}$ mass%)
Isoamyl alcohol	$5.859 \cdot 10^{-12}$ mol% ($1.243 \cdot 10^{-11}$ mass%)
Acetaldehyde	$3.905 \cdot 10^{-3}$ mol% ($4.140 \cdot 10^{-3}$ mass%)
Ethyl acetate	$1.459 \cdot 10^{-3}$ mol% ($3.093 \cdot 10^{-3}$ mass%)
Feed temperature and pressure	78.17 °C and 101.3 kPa
Total cold water feed	7794.7 kmol/h (~140,424 kg/h)
Cold water feed temperature and pressure	25 °C and 101.3 kPa
Vapor distillate flow	30 kmol/h (~540 kg/h)
Tray (Murphree), condenser and reboiler efficiency	70 % (all trays and condenser), 100 % (reboiler)
Column pressure	101.3 kPa

2.3.2. Parastillation columns with multiple condensers in demethylizer process

To illustrate the use of multiple condensers in parastillation columns the methanol/ethanol distillation was considered. The simulations were based on the ethanol/methanol separation studied by Meirelles et al. [14]. In this work the authors compared conventional distillation with para- and metastillation, using a procedure based on the McCabe-Thiele approach. For this present work, the same column specifications as Meirelles et al. [14] were adopted. However, the column was simulated considering a rigorous mathematical procedure (see Appendix A). The methanol separation from ethanol is characteristic of the demethylizer column. This column removes methanol contamination from neutral alcohol, which is rich in ethanol [5,6]. The feed, of 450 kmol/h, was performed at 101.3 kPa as saturated liquid, containing an equimolar ethanol/methanol mixture. Note that, the percentage of methanol in the feed is much higher than the one usually presents in the demethylizer column. Batista; Follegatti-Romero; Meirelles [5] pointed for an initial methanol content of 20 mg.L⁻¹, being reduced for 5 mg.L⁻¹ after the distillation process. However, we adopted a higher methanol content in the feed, to better illustrate the effect of multiple condensers, which can be applied to different processes, not only in the demethylizer column. A column pressure of 101.3 kPa and a tray (Murphree) efficiency of 100 %, for all the stages were adopted. The methanol percentage in the distillate flow was fixed in 95.0 mol%. The distillate flow was 225 kmol/h, and the reflux ratio was adjusted to meet the quality parameters.

Counting the stages from 1 (reboiler) to N (last condenser), all distillate was withdrawn from condenser of stage N , while condenser of stage $N - 1$ operated under total reflux condition (see Fig. 2). This means that there is no distillate flow from stage $N - 1$ and all liquid condensed is returned to the column as reflux. The parastillation columns with one and two condensers contained 31 and 32 stages, respectively (including the reboiler and the condensers). This additional stage represents the extra condenser, note that in this stage no separation is performed. Thus, in the parastillation column with multiple condensers, the main condenser is the stage $N = 32$ and the total condenser is stage $N - 1 = 31$.

2.4. Economic analyzes and carbon dioxide emissions

For the economic analyzes the total annual cost (TAC) was considered. The TAC is the sum of operational and capital costs, which can be calculated based on the equations reported by Douglas [24] and Kiss [25]. These equations were originally proposed to conventional columns, but they were recently used to calculate the cost of dividing-wall columns (DWC) [26]. DWC also considers phase division and an internal wall, as in parastillation. The inflation are originally corrected in these cost equations using the Marshall & Swift index (M&S) [24,25]. However, this index is only available until 2012. After this, the Chemical Engineering Plant Cost Index (CEPCI) was adopted. Thus, the costs were first updated to 2012, using the M&S index of 1537,36 and then to the year 2019, using the CEPCI for the years 2012 and 2019 of 585 [27] and 607.5 [28], respectively. An annualization period of 3 years and 8760 operating hours were considered.

The column height was calculated considering the tray spacing of 0.6 m, with a 10 % of tolerance, in accordance with Treybal [29]. The tray spacing is the same for all processes. However, in parastillation, it is possible to allocate about twice the number of stages than in conventional distillation [14,18,20]. In parastillation, consecutive trays of the same column side present the same tray spacing as conventional and metastillation columns. However, consecutive trays connected by the liquid flow present half of this distancing [20].

The column diameter was calculated as indicated by Treybal [29], considering the liquid and vapor flow that pass through each stage. In metastillation, the trays are constructed as conventional distillation trays. Parastillation trays, however, are divided by a central wall and contains more downcomers than the conventional distillation tray,

considering the construction scheme of Jenkins [20]. Thus, the considered total downcomer area in parastillation was $1.5A_d$, where A_d is the downcomer area calculated for a conventional tray designed for the same liquid and total vapor flows.

The adopted construction material was stainless steel ($F_c = 3.67$), the steam cost was \$8.22/GJ, and the heat-transfer coefficients were 0.852 and 0.568 kW/(K.m²) for the condenser and reboiler, respectively.

CO₂ emissions in distillation columns are, specially, associated with the heat added to the reboiler and can be calculated by the procedure indicated by Gadalla et al. [30]. Assuming an excess of air in a heating device, the CO₂ emissions (kg/s) are related to the amount of fuel burnt (Q_{fuel} in kW), as indicated in Eq. (1).

$$CO_{2,emiss} = (Q_{fuel}/NHV) \cdot (C\%/100) \cdot \alpha \quad (1)$$

Where $\alpha = 3.67$ is the ratio of molar masses of CO₂ and C, NHV (kJ/kg) is the net heating value of a fuel with a carbon content of $C\%$. For heavy fuel oil, $NHV = 39771$ kJ/kg and $C\% = 86.5$. The amount of fuel burnt (Q_{fuel} in kW) is indicated by Eq. (2).

$$Q_{fuel} = (Q_R/\lambda_{proc}) \cdot (h_{proc} - 419) \cdot [(T_{FTB} - T_0)/(T_{FTB} - T_{stack})] \quad (2)$$

Where Q_R (kW) is the heat added to the reboiler, T_{FTB} (°C) is the flame temperature of the boiler flue gases, T_{stack} (°C) is the stack temperature, T_0 (°C) is the ambient temperature, and λ_{proc} (kJ/kg) and h_{proc} (kJ/kg) are the latent heat and enthalpy of steam delivered to the process, respectively. In this work, a saturated steam at 160 °C ($\lambda_{proc} = 2082.55$ kJ/kg and $h_{proc} = 2758.10$ kJ/kg) was assumed. The considered flame, stack, and ambient temperatures were 1800 °C, 160 °C, and 25 °C, respectively. The heat added to the reboiler depends on the process.

3. Results and discussion

3.1. Combined columns applied to bioethanol production

Bioethanol (hydrous ethanol) is industrially distilled in two distillation columns, the AA1D and BB1 column, see Fig. 3. Both columns were investigated considering a combination of parastillation with conventional distillation or metastillation. In the investigation of the binary distillation, the main differences between a conventional column and a combined one is pointed. In the second moment the BB1 column was investigated, considering a multicomponent distillation, which proximate the example with the industrial case.

3.1.1. Binary distillation

For the binary distillation, it was considered the liquid feed with three different ethanol contents: 3.0 mol%, 5.0 mol%, and 20.0 mol%. Results are reported in Table 4. Considering the feed with 3.0 mass% of ethanol, it is necessary a conventional distillation column (CC-1 in Table 4) with 25 stages (counting the condenser and reboiler) and a reflux ratio of 4.28, to obtain a distillate with 93.00 mass% of ethanol. This column contains 10 conventional stages ($N^C_R = 10$ in Fig. 1 - column CC) in the rectifying section, which can be replaced by parastillation trays. Keeping the same reflux ratio (4.28), it is necessary 16 parastillation trays in the rectifying section ($N^P_R = 16$ in Fig. 1 - column PC) to obtain a distillate with 93.01 mass% of ethanol. This is the column PC-1^A, in Table 4, with a total of 31 stages: 13 conventional stages in the stripping section, 16 parastillation trays in the rectifying section, plus one condenser and one reboiler. The PC column is represented in Fig. 1, where it is possible to observe the arrangement of the stages. More parastillation stages ($N^P_R = 16$ in Fig. 1 - column PC) in the rectifying section are required to reach the same separation as the initial 10 conventional stages ($N^C_R = 10$ in Fig. 1 - column CC). However, PC-1^A column is 10.9 % smaller than the corresponding conventional one (CC-1).

Table 4
Binary alcoholic distillation in conventional (CC) and combined columns (PC and PM).

Study Case	1			2			3			4		
	3.0 mol% (7.3 mass%)			5.0 mol% (11.9 mass%)			20.0 mol% (39.0 mass%)			20.0 mol% (39.0 mass%)		
Column sort ¹	CC-1	PC-1 ^A	PM-1 ^B	CC-2	PM-2 ^B	PC-2 ^B	CC-3	PM-3 ^B	PC-3 ^B	CC-4	PM-4 ^B	PC-4 ^B
mass% of ethanol - distillate	93.00	93.00	93.00	93.00	93.00	93.00	93.00	93.00	93.00	93.00	93.00	93.00
mass% of ethanol - bottom product	2.610 ⁻³	7.210 ⁻⁴	3.310 ⁻³	1.210 ⁻⁵	2.910 ⁻³	2.510 ⁻⁴	1.010 ⁻²	4.910 ⁻³	2.210 ⁻³	1.410 ⁻²	1.410 ⁻²	9.110 ⁻³
Number of stages in the rectifier section ($N_R^{C/P}$) ²	10	16	21	10	21	21	9	17	17	9	17	17
Number of stages in the stripping section ($N_S^{C/P}$) ²	12	12	14	12	12	12	4	5	5	4	5	5
Total number of stages (including condenser and reboiler)	25	31	36	25	36	36	16	25	25	16	25	25
Feed tray (bottom to top)	14	14	14	14	14	14	6	7	7	6	7	7
Reflux ratio	4.28	4.28	3.50	4.10	3.00	2.80	4.00	3.70	3.10	5.00	5.00	4.30
Heat added to the reboiler [MW]	11.72	11.72	10.05	18.75	14.83	14.11	71.80	67.52	58.97	23.71	23.71	13.73
Relative heat added to the reboiler ³ [MW]	-	100.0%	85.8%	-	79.1%	75.3%	-	94.0%	82.1%	-	100.0%	57.9%
Relative diameter ³ [m]	1.22	98.9%	92.3%	1.50	86.8%	88.1%	2.98	88.9%	90.0%	1.68	95.6%	76.5%
Stripping	1.45	99.6%	89.4%	1.85	87.2%	85.9%	3.70	95.6%	90.3%	4.02	96.9%	92.2%
Stripping	8.58	100.0%	100.0%	8.58	100.0%	100.0%	3.30	120.0%	120.0%	3.30	120.0%	120.0%
Rectifying	6.60	75.0%	100.0%	6.60	100.0%	100.0%	5.94	88.9%	88.9%	5.94	88.9%	88.9%
Total relative height ³ [m]	15.18	89.1%	100.0%	15.18	100.0%	100.0%	9.24	100.0%	100.0%	9.24	100.0%	100.0%
Capital [10,000\$]	164.11	97.2%	89.1%	219.54	84.7%	82.2%	467.34	95.6%	87.2%	377.13	99.1%	84.6%
Operational [10,000\$/year]	323.87	100.0%	85.6%	517.33	78.9%	75.0%	1988.89	94.0%	82.0%	718.39	100.0%	61.3%
Total annual [10,000\$/year]	378.22	99.6%	86.1%	591.23	79.6%	75.9%	2141.05	94.1%	82.3%	844.47	99.9%	64.8%
CO ₂ emissions ³ [kg CO ₂ /s]	6.09	100.0%	85.8%	9.74	79.1%	75.3%	37.29	94.0%	82.1%	12.34	100.0%	57.9%
Relative CO ₂ emissions ³ [kg CO ₂ /kg product]	4.47.10 ⁻²	100.0%	85.8%	4.29.10 ⁻²	79.1%	75.3%	4.11.10 ⁻²	94.0%	82.1%	1.36.10 ⁻²	100.0%	57.9%

A = columns with same reflux ratio; B = columns with same height as the corresponding conventional one; 1 = Configuration of the techniques used in the column: CC = conventional column in the stripping and rectifying section; PM = parastillation in the rectifying section and metastillation in the stripping section (Fig. 1 - PM); PC = parastillation in the rectifying section and conventional distillation in the stripping section (Fig. 1 - PC); 2 = see Fig. 1; 3 = The percentage values are calculated in relation to the corresponding conventional distillation column of each study case.

As proposed by Jenkins [20], it is possible, in comparison to conventional columns, to allocate approximately twice the number of parastillation trays in the same column height, with the same tray spacing. In fact, the 10 conventional stages ($N_R^C = 10$ in Fig. 1 - column CC), of column CC-1 (Table 4) can be replaced by 21 parastillation stages ($N_R^P = 21$ in Fig. 1 - column PC), without affect the column height. This combined column is shown as PC-1^B in Table 4 and as PC column in Fig. 1). This procedure makes possible to reduce the reflux ratio from 4.28 to 3.50, while keeping the column height constant. This reduction in the reflux ratio decreases the heat added to the reboiler in 14.2 % (Table 4). The CO₂ emissions is decreased in the same order of magnitude (14.2 %), while the total annual cost (TAC) is reduced in 13.9 %, in comparison with the corresponding conventional column (CC-1). Similar results were obtained for the other percentages of ethanol in the feed.

The replacement of the conventional trays by parastillation ones is a good alternative to the retrofit of the conventional process. In this case, the external structure and the column shell are preserved, modifying only the internal part of the column, i.e., the trays of the rectifying section. Although, there are just one report of the industrial construction of parastillation trays [15], we believe that this is not a difficult task. The control of the liquid flow on the stage by a central division is an ancient and known subject, as well as the construction of downcomers on the same side of the column tray. These techniques are contemplated in the reverse flow tray illustrated by Treybal [29] in Fig. 6.11 (page 165) and used in conventional distillation. The industrial acceptance of dividing-wall columns (DWC) is also an indication of the feasibility of building parastillation stages. In DWCs, as in parastillation, an internal wall divides the stages in half, each part being on one side of the column. The knowledge acquired with these techniques can be used to build parastillation stages.

For 5.0 mass% of ethanol in the feed, the combined column (PC-2^B in Table 4) reduces the operational cost in 25.0 %, when compared to the corresponding conventional distillation column (CC-2) with the same height. Additionally, the reduced reflux ratio present in the combined column PC-2^B decreases the liquid and vapor internal flows, allowing a reduction in the column diameter, decreasing the capital costs in 17.8 %, in relation to the column CC-2. Reductions in operational and capital costs lead to a total annual cost (TAC), of column PC-2^B, 24.1 % smaller than the TAC of the conventional column CC-2.

With the increase of ethanol content in the feed, less stages are required to perform the same operation. For 20 mol% of ethanol in the liquid feed, the conventional distillation column (CC-3 in Table 4) requires 16 stages and a reflux ratio of 4.0. This column presents 9 stages in the rectifying section ($N_R^C = 9$ in Fig. 1-CC), which can be replaced by 17 parastillation trays ($N_R^P = 17$ in Fig. 1-PC), without affecting the column height. The corresponding combined column (PC-3^B) decreases the reflux ratio and the TAC in 23.0 % and 17.9 %, respectively, in relation to the corresponding conventional one (CC-3).

The replacement of the conventional trays, in the rectifying section, by parastillation trays was an advantageous procedure. Another combination is the replacement of the remaining conventional trays (in the stripping section) by metastillation trays. Results of these new combined columns, with parastillation and metastillation techniques, are reported in Table 4, being referenced by the initials "PM". It is important to highlight, that n metastillation stages are allocated in the same height as n conventional distillation trays, considering the same tray spacing. Thereby, the metastillation does not present the mechanical advantage of parastillation, where more stages can be arranged per column height. However, the liquid division in metastillation, permits to reduce the internal liquid/vapor ratio, contributing with a diameter reduction, as seen in Table 4. This effect is intensified for column PM-2^B with 5.0 mol % of ethanol in the feed. The "PM" configuration that presented more advantage, from an energetic point of view, was also the one with 5 mol % of ethanol in the feed. This combined column PM-2^B (Table 4) allowed a decrease in the energy consumption of 20.9 %, in relation to the

corresponding conventional distillation (CC-2), reducing the operational cost in 21.1 %. Nevertheless, the combined columns composed of conventional distillation and parastillation (initials “PC” in Table 4) represented better results for all the studied cases, presenting the lowest TAC values. For this case study in which the “PM” column showed better results, Fig. 4 compare the composition profiles inside the columns. From Fig. 4 it is possible to observe similar composition profiles for the different columns.

For alcoholic wines, the usual ethanolic grade is approximately 6–12 °GL. However, there are efforts to develop fermentative procedures targeting wines with higher alcohol content (up to 16°GL). In this work, conditions up to 44.4°GL were also tested (Cases 3 and 4 in Table 4). This ethanolic grade is close to that of the alcoholic phlegm, the more concentrated stream of ethanol leaving the first ethanol concentration column (from section A) and then fed into the second column (consisting of sections B and B1), to complete the purification process [12]. In this case, the feed, of column BB1, is usually done in vapor phase. Thus, for this ethanolic concentration (44.4°GL), it was considered both liquid phase (0% steam) and vapor phase (100 % steam) feed.

As Table 4 indicates, the combination of conventional distillation with parastillation (PC-3^B) allows substantial reduction in both equipment cost and energy consumption, when the ethanol feed content is 20.0 mol% in liquid phase. The savings were even more significant in the case of vapor phase feeding, Case 4 in Table 4, which corresponds to the column BB1. The combined column, PC-4^B reduced the total annual cost and the CO₂ emissions in 35.2 % and 42.1 %, respectively, in comparison with the corresponding distillation column (CC-4). Therefore, the advantages of the combined columns occur in at least one case, for 9.0°GL wine (PC-4^B column), becoming larger for higher alcohol contents in the feed (14.4°GL) and assuming very significant values for the typical distillation conditions of the alcoholic phlegm (column BB1).

From Table 4 parastillation and metastillation trays presented better performance than distillation trays. It can be associated with different factors, as the Jenkins effect and the flow arrangements [17]. The Jenkins effect was first attributed to the better performance of parastillation trays over conventional ones [14,17], but it can also be extended to metastillation. According to this effect, 2*N* parastillation/metastillation trays lead to a better separation than *N* conventional distillation ones [17]. Biasi et al. [18] showed that for a specific separation the parastillation column required 36 % more stages than the conventional one operating with the same reflux ratio. Even with this increase in the number of stages, this parastillation column has a height 33 % smaller than the corresponding conventional column. Canfield [17] and Gouvêa [31], analyzing different systems, observed an increase in the required number of parastillation trays of 33 % and 55 % in comparison to a conventional column with same reflux ratio.

The Jenkins effect represents the higher concentration gradient between the inlet streams of parastillation and metastillation trays, in comparison to the ones of conventional trays. This because while a given conventional tray *n* receives the vapor and liquid streams from the stages

immediately above (*n* + 1) and below (*n* – 1) it, the alternative columns receive the inlet flows from farthest stages. The parastillation tray receives the vapor stream coming from the (*n* – 2) tray. The metastillation tray *n* receives liquid from the (*n* + 2) tray. This represents greater concentration differences than in conventional trays, also representing an increase in the mass transfer driving force of the alternative columns in relation to the conventional one. Meirelles et al. [14] compared the concentration difference for two consecutive parastillation and distillation trays on the methanol-ethanol distillation. The authors showed that the difference in composition could be improved by increasing the reflux ratio or the number of phase divisions.

Lewis [32] classified distillation columns into three cases, depending on the liquid and vapor flow arrangements. Conventional distillation columns are classified as Lewis Case III, with the liquid flowing in opposite directions on consecutive trays. Parastillation columns can be classified as Lewis Case II [17,32], with the liquid flowing in the same direction on consecutive trays of a given vapor side. In metastillation, the liquid of two consecutive trays flows in the same direction, but the next 2 stages flow in the opposite direction, being a mix of Cases II and III. Lewis [32] demonstrated that the mass transfer driving force distribution is better in Lewis Case II than in Case III, improving the tray mass transfer efficiency. However, the Case II classification is not intrinsic to these types of column and trays can be constructed aiming an improvement in its efficiency [29]. Nevertheless, the present study used fixed Murphree efficiencies not considering possible improvements due to the arrangements of the streams. Thus, the mass transfer improvement can be attributed mainly to the Jenkins effect.

The division of the flows inside the column collaborates to a better distribution of the driving forces [14,33]. It is known that processes with better distribution of the driving forces present better performances for heat and mass transfer operations. This is what happens in counter-current over parallel-current heat exchangers. In the same way, it was showed that for parastillation and metastillation columns it is preferred to a wide range of processes the division of the internal flows into equal portions [33], equalizing the separation in the two internal currents. The better distribution of the driving forces inside the alternative techniques is another reason for the improvement of the performance of these columns in relation to the conventional ones.

3.1.2. Multicomponent distillation

Previously results shown that greatest total annual costs savings are obtained for processes with high ethanol content in the feed, feature presents in the column BB1 (Fig. 3) of the hydrous ethanol production. Therefore, this part of the work will focus on the BB1 column, assuming multicomponent distillation and a reduction in the tray efficiency. These assumptions approximate the study to industrial process. Results suggest that the conventional trays present in the section B1 (rectifying section) of column BB1 can be partially replaced by parastillation trays, as seen in Table 5 and Fig. 5.

According to Table 5, the PC-1 column, composed of parastillation and conventional distillation, has the same reflux ratio as the conventional column CC-1. However, PC-1 is about 20.4 % smaller than CC-1 column, as indicated in Fig. 6. Note that both columns produce a distillate with 93.01 mass% of ethanol and have similar ethanol losses in the bottom product, while requiring almost the same reboiler duty. The PC-1 column, with 61 trays, is compared in height with the conventional column CC-2 (Fig. 6). This second conventional column has 41 stages and demands an increase in operational cost of 20.2 %, in comparison to CC-1. Considering a new alternative column, PC-2, with the same energy consumption as CC-2, it is possible to obtain an additional reduction in equipment height of approximately 30.6 %, compared to the first apparatus (CC-1), as illustrated in Fig. 6. The concentration of the side stream (fusel oil) was almost the same for the four column configurations, indicating that the equipment configuration does not affect the extraction of isoamyl alcohol in a significant way.

From Table 5, we observe that the alternative columns can be

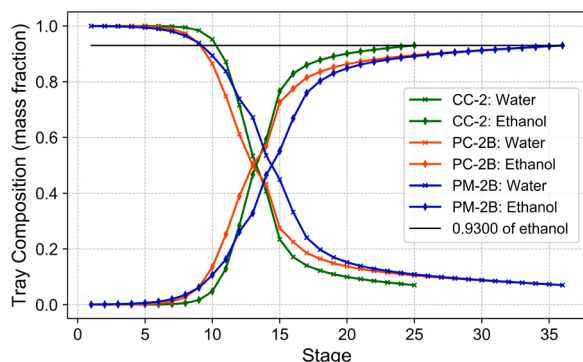


Fig. 4. Ethanol/water composition profile for the vapor phase of Case Study 2.

Table 5
Multicomponent hydrous ethanol distillation.

Column sort ¹		CC-1	PC-1	CC-2	PC-2
mass% of ethanol – distillate		93.01	93.01	93.01	93.01
mass% of ethanol – bottom		$2.17 \cdot 10^{-2}$	$2.16 \cdot 10^{-2}$	$1.79 \cdot 10^{-2}$	$2.05 \cdot 10^{-2}$
Number of stages in the rectifier section ($N^{C/P}_R$) ²		29	39	22	37
Number of stages in the stripping section ($N^{C/M}_S$) ²		19	19	16	15
Number of stages (including reboiler and condenser)		51	61	41	55
Feed tray (bottom to top)		21	21	18	17
Side stream tray (bottom to top)		24	24	21	20
Reflux ratio		6.2	6.2	6.8	6.8
Heat added to the reboiler [MW]		40.05	40.06	48.55	48.56
Relative heat added to the reboiler ³ [MW]		–	100.0 %	121.2 %	121.2 %
Relative diameter ³ [m]	Stripping	2.42	100.0 %	109.6 %	109.5 %
	Rectifying	4.19	102.4 %	106.4 %	106.9 %
Relative height ³ [m]	Stripping	13.20	100.0 %	85.0 %	80.0 %
	Rectifying	19.14	65.5 %	75.9 %	62.1 %
Total relative height ³ [m]		32.34	79.6 %	79.6 %	69.4 %
Cost ³	Capital [10,000\$]	647.75	92.9 %	99.8 %	95.5 %
	Operational [10,000\$/year]	1173.77	100.0 %	120.2 %	120.2 %
	Total annual [10,000\$/year]	1391.14	98.9 %	117.0 %	116.4 %
CO ₂ emissions ³ [kg/s]		20.80	100.0 %	121.2 %	121.2 %
Relative CO ₂ emissions ³ [kg CO ₂ / kg product]		$2.29 \cdot 10^{-2}$	100.0 %	121.2 %	121.2 %
Side stream flow rate ⁴ [kg/h]		232.78	237.37	234.81	237.64
	Water	48.8	46.8	47.3	46.6
	Ethanol	14.2	16.3	17.7	16.8
	Isoamyl alcohol	37.0	36.9	35.0	36.6
	Ethyl acetate	$2.4 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	$2.3 \cdot 10^{-5}$	$2.3 \cdot 10^{-5}$
	Glycerol	$2.1 \cdot 10^{-9}$	$5.0 \cdot 10^{-9}$	$1.8 \cdot 10^{-9}$	$4.5 \cdot 10^{-9}$

A = columns with same reflux ratio; B = columns with same height as the corresponding conventional one; 1= Configuration of the techniques used in the column: CC = conventional column in the stripping and rectifying section (Fig. 1 - CC); PC = parastillation in the rectifying section and conventional distillation in the stripping section (Fig. 1 - PC); 2= see Fig. 1; 3= The percentage values are calculated in relation to the conventional distillation column (CC1); 4=The side stream is fixed as 8 kmol/h; its value in kg/h depends on the stream concentration, causing the observed differences.

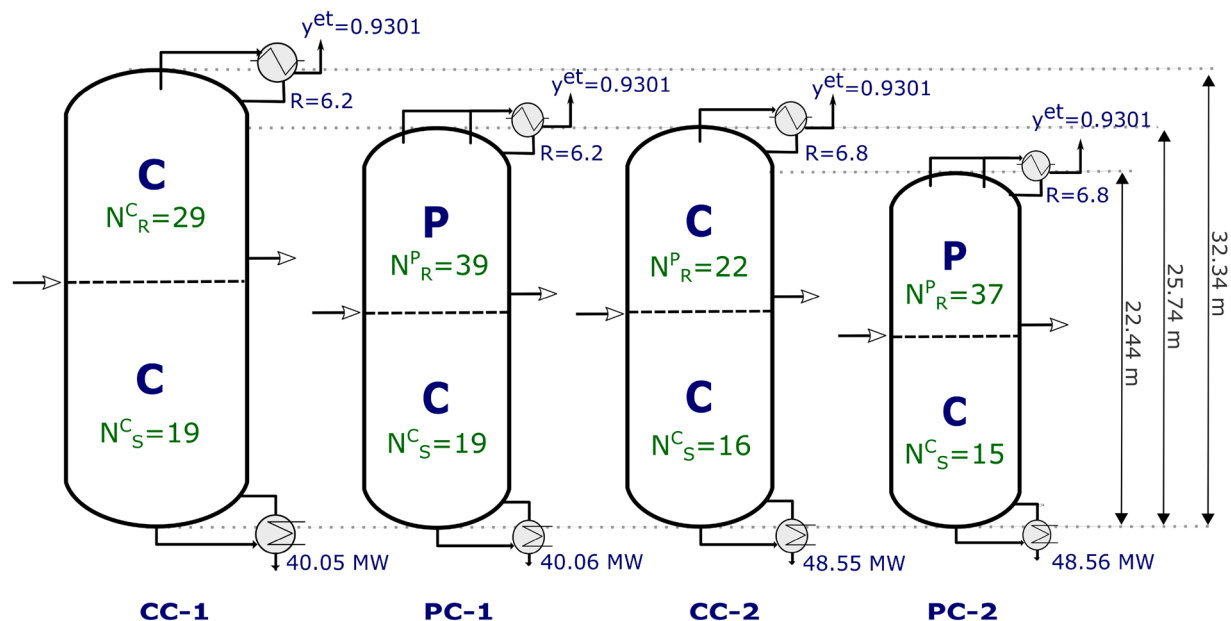


Fig. 5. Multicomponent hydrous ethanol distillation columns, where C and P represent, respectively, conventional distillation and parastillation trays, and N is the number of trays in each section.

correctly applied to multicomponent processes. It is important to note that the side-stream flow was able to withdraw the isoamyl alcohol without to increase the ethanol loss. Both alternative columns presented reductions in total annual cost in relation to its corresponding conventional column. In this way, parastillation stages can be used for retrofitting of existing columns or the construction of new ones.

3.2. Metastillation and parastillation applied to neutral alcohol production

Neutral bioethanol is a hydrated alcohol with higher ethanol concentration (94 mass%) and very low level of contaminants. It is obtained by extra purification of hydrous ethanol, conducted in three additional distillation columns [5], and has a wide application potential in future biorefineries. The relative absence of papers focused on the production of neutral alcohol [5,6] and some important applications of this product,

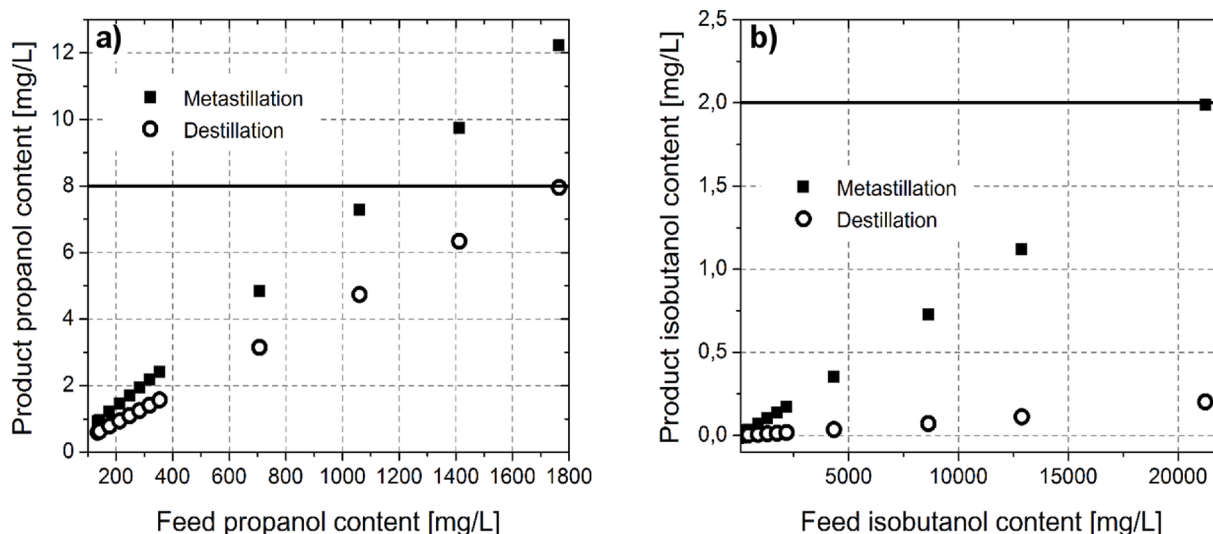


Fig. 6. Content of propanol and isobutanol in the product as a function of the content of these compounds in the feed stream, for conventional distillation and metastillation.

contribute to encourage research about this topic.

3.2.1. Metastillation in hydroselction

The first column used in the neutral alcohol production, known as hydroselction column, is an extractive distillation column, with about 50 trays, in which water is used as entrainer. This column is used to remove excess of superior alcohols present in hydrous ethanol. The dilution of bioethanol by water increases the superior alcohols activity coefficients, increasing its volatility, so that they can be concentrated in the vapor phase and withdrawn as top product. The purified bottom product, with an ethanol concentration around 10 vol%, is fed into a subsequent column to be concentrated once more.

The hydroselction column has high liquid/vapor ratio, impairing mass transfer and increasing column diameter. The division of the liquid phase decreases the liquid/vapor ratio, increasing separation efficiencies [13,31,34,35]. Our results showed that metastillation column could replace the conventional one, keeping the same height and reducing the equipment diameter in 10 %, representing a decrease about 15 % in investment costs. Results are reported in Table 6.

The alcoholic graduation of the bottom product, for both columns, was about 8% in mass (approximately 10 vol%), as shown in Table 6. This is in accordance with the specifications provided by Batista;

Follegatti-Romero; Meirelles [5]. The ethanol loss in distillate flow was around 1.7 % of the total amount of ethanol fed into the system of distillation columns. In both columns, the steam consumption was about 1.1 Kg of steam per liter of neutral alcohol.

For both columns simulated previously, the specifications required for neutral alcohol standard (see Table 6) were obtained using columns with the same size, i.e., same number of stages. This is an improvement over the results reported by Gouvêa [31] and by Mizsey et al. [13], who suggest that the metastillation column must be 50 % higher than the conventional distillation apparatus in order to obtain the same separation degree. The improvement showed in our results can be attributed to the characteristics of the hydroselction process. This column has a very high liquid/vapor flow internal ratio, a feature usually associated with a reduction in mass transfer efficiency and increase in the column diameter. In metastillation, the liquid is divided in two flows, reducing about 50 % the liquid/vapor flow internal ratio. Previous works do not considered processes with these characteristics, avoiding the main advantage of metastillation columns over conventional ones.

It is important to note that in the present work the separation efficiency (Murphree efficiency) is fixed and constant along the simulations. The alternative and conventional columns were compared using the same separation efficiency. This means that the columns were compared

Table 6
Hydroselction metastillation and conventional distillation columns.

Specifications	Units	Neutral alcohol standards ¹	Feed Composition	Distillation Column	Metastillation Column
Steam consumption	kg of steam/L alcohol fed at column	2	–	1.10	1.10
Alcoholic graduation	% (volume/volume)	10	–	10.00	10.00
Ethanol loss in distillate flow	% ethanol in respect to the ethanol fed to the equipment	2	–	2.49	2.49
Column diameter	m	–	–	1.35	1.30
Height	m	–	–	33	33
Capital cost	10,000\$	–	–	117.38	114.12
Operational cost	10,000\$/year	–	–	73.25	73.25
Total annual cost	10,000\$/year	–	–	111.94	110.86
Methanol	mg/L	5	3.28	$3.56 \cdot 10^{-1}$	$3.55 \cdot 10^{-1}$
Propanol	mg/L	8	135.53	$5.98 \cdot 10^{-1}$	$9.23 \cdot 10^{-1}$
Isobutanol	mg/L	2	43.90	$3.37 \cdot 10^{-4}$	$3.44 \cdot 10^{-3}$
Isoamyl Alcohol	mg/L	3	$9.96 \cdot 10^{-8}$	$1.08 \cdot 10^{-8}$	$1.08 \cdot 10^{-8}$
Acetaldehyde	mg/L	5	33.14	Trace ²	Trace ²
Ethyl Acetate	mg/L	5	24.76	Trace ²	Trace ²

1= Values reported by Batista et al. [5] and Decloux & Coustel [6].

2= Trace $\leq 10^{-9}$ mg/L.

on the same basis. Thus, the advantageous effect of the alternative columns over the conventional one is not due to greater efficiency, because even considering the same efficiency parastillation and metastillation presented better results than the conventional trays. The tower diameter is calculated to handle the vapor and liquid rates within the region of satisfactory operation. For this it is considered the flooding constant, which has been correlated for the experimental data available on flooding [29]. Conventional and metastillation columns were treated using the same procedure, thus the reduction in the diameter is due to the reduction in the internal flows. Mizsey et al. [13] also considering fixed separation efficiencies and equilibrium stages correlated the liquid/vapor ratio to the column diameter for conventional and metastillation columns. The authors reported a reduction in the metastillation diameter up to 30 % but with increases in the column height.

Both columns were analyzed considering the same operational conditions (reflux ratio, feed and distillate flow), which imply the same operational costs. Thus, the main difference that needs to be evaluated is the capital cost. For this comparison, the capital investment evaluated for both processes included the cost associated with the column shell and trays and with the heat exchangers.

The capital cost depends on the column height, diameter and correlations based on column material and operational conditions. Both simulated columns have same height, assuming same tray spacing and same number of stages [13,31]. Considering the same column height and same reflux ratio, the capital cost difference is based only on the different diameter. Since the variation in diameter between stripping and rectification sections was smaller than 20 % [29] for both columns, a unique diameter was considered for each column.

The internal vapor flow was about the same for both columns, with variations smaller than 5%. However, as expected, in metastillation, the internal liquid flow in each internal set of trays was roughly half of the conventional distillation one. This decrease in internal liquid flow represented a decrease about 5 % in metastillation diameter compared to that observed in the conventional column. Considering the column and tray cost correlations, the capital cost was about 3% smaller in the metastillation column, as shown in Table 6, what confers an economic advantage to the metastillation process.

Based on the results presented before, the metastillation column can be a potential substitute for the conventional apparatus in the hydroselection step for neutral alcohol production. However, more critical operational conditions need to be evaluated to confirm the potential of the metastillation equipment.

In a specific column case, the number of stages is a fixed variable that cannot be changed. The reflux ratio of the hydroselection column is very small, so it has little influence on operational costs. Based on the above findings, the contamination of the hydroselection column feed is the main influence on the bottom product contamination (main product of hydroselection column).

As the hydroselection column purpose is to remove superior alcohols, the most important congeners that need to be considered are propanol, isobutanol and isoamyl alcohol. Nonetheless, isoamyl alcohol is present in hydroselection column only in small amounts, since most part of this minor component is withdrawn in the fusel oil side stream during the fuel bioethanol production. For this reason, the feed stream contents of propanol and isobutanol were varied and the corresponding impact on the bottom product purity was analyzed for both columns, as shown in Fig. 6.

Fig. 6 shows that bottom product congeners content has a linear behavior in relation to the feed stream contents of propanol and isobutanol. For both components, the slope for metastillation is higher than the conventional distillation, indicating that, for higher contamination in the feed stream, metastillation has lower separation efficiency. However, in the range of feed contamination studied only for high propanol (> 1150 mg/L) and isobutanol (> 22,000 mg/L) concentrations metastillation cannot reach the required specification, expressed

by the full black horizontal line in Fig. 6. It should be considered that these very high contaminations of the feed stream with both congeners are completely unusual, so that it is possible to affirm that both processes are able to achieve the required quality standards.

The contaminant level in the product can be controlled by adjusting the reflux ratio or the number of stages. The metastillation and conventional distillation columns with same reflux ratio and same number of stages, presented in Table 6 and in Fig. 6, achieve the technical specification for neutral alcohol. However, the level of contaminants in the metastillation column is slightly larger than in the conventional distillation, especially regarding the propanol and isobutanol levels. For the same tray efficiency (70 %), keeping the same level of propanol in the distillate and the same reflux ratio, the number of stages required by the metastillation column, with the same specification than the conventional column reported in Table 6, is 60 stages. With the same number of stages (52 stages) and the same contaminants level as the conventional distillation (of Table 6), the adjusted reflux ratio for the metastillation column represents an increase in steam consumption of 7.6 %. Even with this increase, the steam consumption is still below the neutral alcohol standards.

It is important to highlight that the results consider the same tray efficiency (70 %) for conventional distillation and metastillation. However, according to Mizsey; Mészáros; Fonyó [13], metastillation columns present greater Murphree efficiencies, than the conventional distillation. The Murphree efficiency depends on the point efficiency and the flow pattern on the tray. It could collaborated to a better performance of the metastillation column over the conventional one.

3.2.2. Parastillation columns with multiple condensers in demethylizer process

As demonstrated in the previous examples, parastillation and metastillation techniques may present capital and operational costs reductions. In this section, we show that an additional gain is possible with a simple modification of the columns, which consists of adding multiple condensers in parastillation or multiple reboilers in metastillation. This option was previously described in our patent [19] and is detailed here using a simple example. Meirelles et al. [14] evaluated the separation of a mixture of ethanol and methanol showing that it is possible to reduce the column height or the reflux ratio by replacing the conventional column by a parastillation one. Here we show that it is possible to reduce the reflux ratio even more, just avoiding the mixing of the vapor currents at the top of the column.

The removal of methanol from ethanol is present in the neutral alcohol production in the demethylizer column. In this separation, ethanol is the major component with 94–96 mass% and any methanol residual is withdrawn from the neutral alcohol. The present example, however, considered a separation of a feed composed of 50 mass% of methanol and 50 mass% of ethanol [14]. This is a simplified version of the process that will facilitate the observation of the effect of multiple condensers.

The parastillation column with one condenser that was simulated by Meirelles et al. [14] is compared with another parastillation column with two condensers in Table 7. The column with one condenser may

Table 7
Parastillation column with multiple condensers.

Parastillation column	1 condenser	2 condensers
Methanol contente in distillate (%)	95.01	94.99
Reflux ratio in condenser N	3.60	1.16
Reflux ratio in condenser N-1	–	Total
Reflux ratio, considering both condensers ^a	3.60	3.43
Heat added to the reboiler [MW]	10.424	10.398
Heat removed from the condenser [MW]	8.193	8.167
Operational cost [10,000\$/year]	68.76	68.59

^a Calculated as the sum of the two reflux flows (from condensers N and N-1) divided by the distillate flow.

present some differences against the column presented by Meirelles et al. [14], since the authors simulated the columns considering ideal separation and in a McCabe-Thiele based approach, while this work uses rigorous consideration and Newton's method.

By adding one additional condenser, it was possible to reduce the heat flow in the reboiler and condenser in 0.2 % and 0.3 %, respectively. It contributes to a reduction in the operational cost of 0.3 %, by increasing the number of condensers from one to two. Although, it seems not to be expressive, a further reduction of 0.3 %, in the operational cost, represents a saving of \$1.6.10⁷ dollars per year, for this distillation. The increase in the number of condensers also allows a reduction in the reflux. The reflux flow in the column with one condenser was 810.0 kmol/h, correspondent to a reflux ratio of 3.6. For two condensers, the reflux from stages N and $N - 1$ were 260.1 and 512.6 kmol/h, totalizing a reflux flow of 772.7 kmol/h. The reflux ratio of this column was calculated as the sum of the two refluxes flows divided by the distillate flow, as: $(772.7 \text{ kmol of reflux/h}) / (225 \text{ kmol of distillate/h}) = 3.43$. Thus, the addition of one condenser decreases the reflux ratio in 4.7 %. Note that this reduction requires more condensers, however, no additional cost is required for the construction of the column shell or trays.

Parastillation columns, with as many condensers as the number of vapor divisions, decrease further the energy consumption due to the avoidance of unnecessary mixing. In conventional parastillation columns (with just one condenser) all the vapor is mixed in the inlet of the condenser, decreasing the thermodynamic efficiency (irreversibility) due to the mixture of flows with different composition and temperature. In the parastillation column with multiple condensers this mixing is avoided. Furthermore, all distillate was withdrawn from condenser of stage N , which is richer in ethanol than the condenser of stage $N - 1$ (see Fig. 2). This because, the condenser N receives the vapor flow from the last stage of the column (stage $N - 2$), while the condenser $N - 1$ receive the current from the penultimate stage ($N - 3$). The counting scheme of the stages is shown in the figures of Appendix A.

In general distillation columns already have more than one condenser. Multiple condensers are used in series or as support if the main one stops working or needs maintenance or cleaning. This way, it does not take a lot of effort or extra expense to pass the vapor flows across different condensers. Therefore, it is an advantageous alternative, even if it does not present gains as significant as the replacement of conventional trays by parastillation ones. It is worth noting that the use of multiple condensers is not restricted to the demethylizer process. Multiple condensers can be used, for example, in the hydrous ethanol column. In this case the current with the highest content of volatile contaminants returns as reflux and the distillate is taken from the other vapor flow.

The increase in the number of flows inside the columns may raise doubts about their control. The dynamic behavior of parastillation and metastillation columns presents as a totally unexplored subject, without any scientific document within the open scientific literature. However, especially due to the constructive similarities between these types of columns with the dividing-wall column (DWC), it is believed that the dynamic performance of both columns, including process control, may be similar. Several articles reported that the main traditional controller design and tuning techniques could be applied satisfactorily in the development of different control loops in DWC columns [36–40]. In addition, the established control criteria (controller response speed, overshoot, stabilization time, etc.) was also very similar to the one of conventional distillation columns [37,38,41,42], indicating that DWC and, possibly, metastillation and parastillation columns, can directly replace conventional columns in industrial plants, with only minor adjustments to existing control systems.

The control of the phase split ratio is a common concern in this type of columns, especially when it concerns the vapor phase. The division of the liquid phase inside the column can be controlled by manipulating the cross-sectional area for the flow of the reflux current that returns to

the column as multiple liquid streams (as two streams in the present study). The vapor flow can be divided by controlling the position of the internal wall in the initial design. This division procedure does not provide flexibility for changes after the construction of the equipment. Additionally, the performance of this separation depends on factors as the pressure drop and number of stages in each side of the column, since this phase is compressible. Advanced devices were suggested to perform the vapor phase division in DWCs [41,43–45] since the separation in this type of column may depend on this variable [46–48]. In a previous work [33], we investigated the best split ratio of the vapor (in parastillation) and liquid (in metastillation) phases within the columns and how it affects the separation. We observed that for a wide range of processes, including alcoholic distillation, the best division of the vapor (in parastillation) and liquid (in metastillation) phases was into two equal portions (50:50 %), as adopted in the present work. Advantageous results were observed from the control point of view [33]. The separation processes were slightly sensitive to different split ratios, being more influenced by the Murphree efficiency [33]. Control systems were not required since fluctuations around the selected split ratio do not affect, in a significant way, the process performance [33].

Furthermore, due to the parastillation columns having a greater separation driving force, when compared with conventional columns [14], it is expected that the disturbance range in which the control system can operate satisfactorily, is substantially greater than in a conventional column, enabling a more robust control, guaranteeing an important advantage for the parastillation columns. However, as mentioned earlier, the absence of scientific material focused on the dynamic behavior of meta- and parastillation columns, allows only inferences to be made regarding this subject. Therefore, a complete study of the dynamics of these columns is being investigated by the research group responsible for this manuscript and will be published as soon as possible.

4. Conclusion

This work suggested the partial or total replacement of traditional distillation columns present in the bioethanol and neutral alcohol production, by parastillation and/or metastillation columns. We proposed and investigated innovative uses of parastillation and metastillation trays. For the first time, the combination of conventional distillation stages, parastillation and metastillation trays inside one unique column shell were investigated. These combinations were used to improve the hydrous bioethanol distillation by replacement or retrofit of the conventional columns, with savings on capital and operational costs and CO₂ emissions. The proposed technique is a viable alternative to the retrofit of distillation columns. In this case, just part of the conventional trays could be replaced by parastillation ones, thus allocating more stages per column height without affecting the overall column height and improving the separation. This is because two half parastillation trays present a better separation performance than one conventional distillation tray. Additionally, the remaining conventional trays can be replaced by metastillation trays. However, this replacement must be analyzed cautiously before since it was not advantageous for some processes, depending on the ethanol content in the column feed. The replacement of traditional trays by parastillation ones, however, was advantageous for all studied cases. These procedures proved that two different distillation techniques can be combined into one unique column shell, originating what was called combined columns. Combined columns present economic and environmental advantages, over conventional distillation.

Besides the hydrous ethanol production, the hydroselction and the demethylizer columns, present in the neutral alcohol production, were investigated. The conventional hydroselction column, an extractive distillation column, was replaced by a metastillation one, with decrease in the column diameter without increasing the column height. In previous works, the reduction in the column diameter, by using

metastillation instead of conventional distillation, was only possible with an increase in the column height. The results of this work were better than that of previous works because the metastillation column was applied to a process with high liquid/vapor internal ratio, contrary to what has been previously investigated. For the demethylizer process, the use of parastillation columns with multiple set of condensers was proposed. These columns presented economic advantages against the conventional parastillation, by avoiding unnecessary vapor mixture. The configurations presented in this paper are promising alternatives to reduce capital and operational cost in bioethanol and neutral alcohol production. Additionally, the construction modifications here presented – as the combined column, the parastillation with multiple condensers or the metastillation with multiple reboilers – can be applied to other processes of interest.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001; in part by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) - Financial Codes 140212/2017-5, 307398/2019-6, 406963/2016-9; in part by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) - Financial Codes 2014/21252-0, 2016/10636-8; and in part by NSF DMS 1819144.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.cep.2021.108334>.

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