

# Distillation Columns with Multiple Phase Divisions: How They Improve Thermodynamic Efficiency and Decrease Energy Consumption

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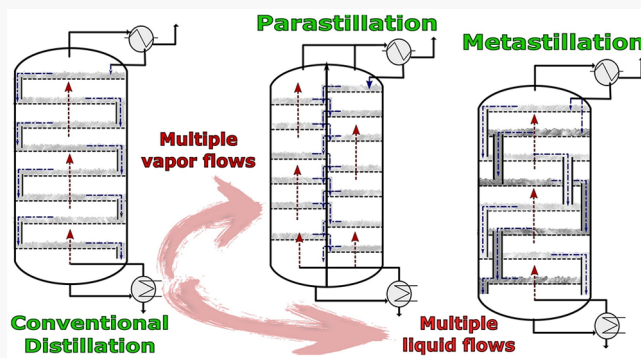


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**ABSTRACT:** Distillation efficiency can be improved by columns with multiple phase divisions, also known as parastillation (vapor division) and metastillation (liquid division). Although, previous studies demonstrate that these configurations improve separation efficiency, little is known about the mechanisms that cause this improvement. These mechanisms are elucidated through exergetic and driving force analyses. Methanol-ethanol and multicomponent hydrated bioethanol purifications were investigated. Thermodynamic efficiency and exergy losses are improved when the number of phase divisions is increased. In methanol-ethanol distillation, the increase of the number of phase divisions from one to eight decreases both the operational costs and CO<sub>2</sub> emissions by 34% and increases thermodynamic efficiency by 23%. Considering a more feasible number of phase divisions, from the construction point of view, four divisions improve operational costs by 31%, over one division. In the production of hydrated bioethanol, four-vapor divisions lead to a reduction in energy consumption by 18% when compared with conventional distillation. This study shows that it is possible to reduce operating costs to a value close to the theoretical minimum, without a significant increase in capital costs. This observation contrasts with the conventional process, in which the reduction in operating costs necessarily leads to higher distillation columns and capital costs.



## 1. INTRODUCTION

The U.S. Energy Information Administration projects that the U.S. industrial energy consumption will increase from about 27 to 38 EJ between 2019 and 2050.<sup>1</sup> Currently, most of the U.S. industrial sector energy consumption is attributed to the bulk chemical and refining industries, representing, respectively, 29% and 18% of total U.S. industrial energy consumption.<sup>1</sup> The global CO<sub>2</sub> emissions in 2019 from these two industries, were 541 million metric tons of CO<sub>2</sub> (MMmtCO<sub>2</sub>), representing 37% of the total U.S. industrial emissions.<sup>1</sup> In both industries, separation processes represent almost 60% of the total energy consumption, nearly 95% of these processes are distillation operations.<sup>2</sup>

Although, distillation is energy intensive, it is one of the most used separation processes in the world,<sup>3</sup> because of its high mass transfer rate and the fact that it requires no inert solvents or solid matrices.<sup>3</sup> Due to these characteristics, distillation is the focus of numerous studies aimed at improving its energy efficiency.<sup>4</sup> Reactive distillation,<sup>5</sup> internally heat-integrated distillation,<sup>6</sup> and dividing-wall columns (DWC)<sup>7</sup> are examples of promising alternatives to improve the efficiency of conventional distillation. However, currently such processes are only used for specific applications. For example, DWC is

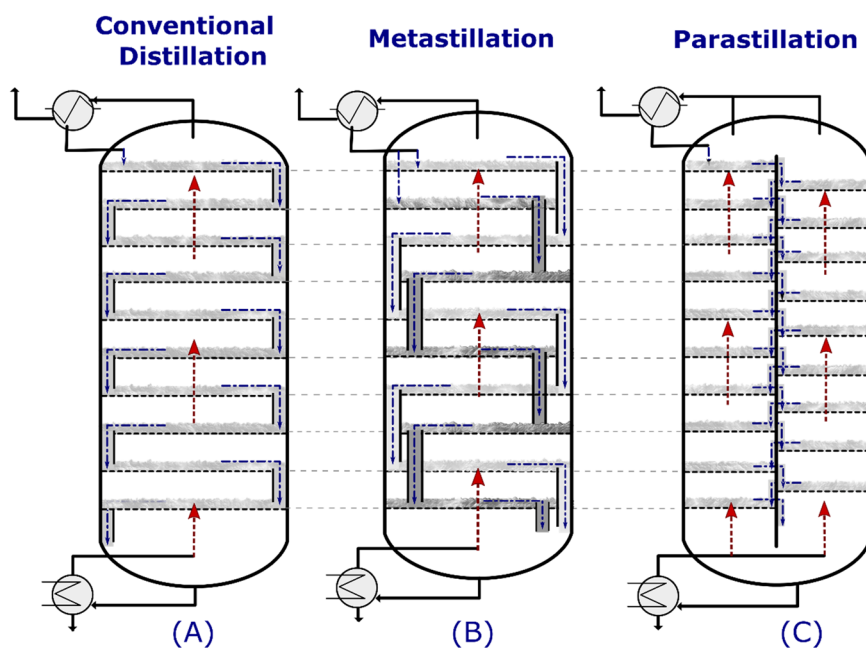
used for the separation of three product streams in a single column. It includes the integration of two conventional columns of the Petlyuk system into a unique column shell. In comparison with conventional distillation, DWC reduces operational and capital costs up to 40% and 30%, respectively.<sup>8</sup>

Distillation with multiple phase divisions is a less well-known technology, which can result in substantial operational and/or capital costs savings and can be used for a wide range of applications. Distillation with multiple phase divisions, or with parallel streams, as it is also known, includes the parastillation process, with division of the vapor phase, metastillation, with liquid division. Note that the phase division is also present in the DWC column, where both liquid and vapor phases are divided. Parastillation and metastillation columns are compared with a corresponding conventional column in Figure 1.

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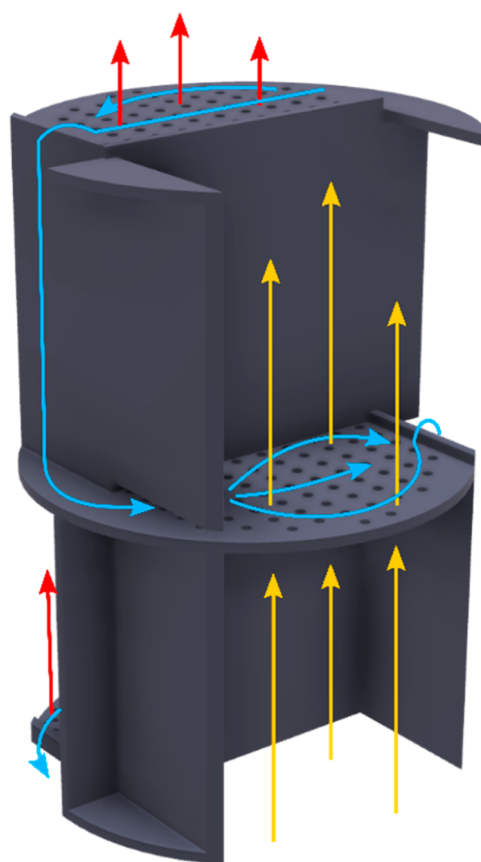


**Figure 1.** (A) Conventional distillation, (B) metastillation, and (C) parastillation columns of same height.

All columns of Figure 1 have the same height, but in parastillation, it is possible to include almost twice the number of stages compared to the other two configurations, considering the construction scheme suggested by Jenkins,<sup>9</sup> which is illustrated in Figure 2. Considering a fixed column height, parastillation columns may reduce the reflux ratio by 7.7%–48.4%, when compared with conventional columns.<sup>10</sup> This reduction depends on the selected range of ratios for the real reflux to the minimum one.<sup>10</sup> In metastillation, two liquid divisions in hydrocarbon distillation decrease the stage area up to 30%, compared to a conventional column,<sup>11</sup> but with an increase of 50% in the number of theoretical stages.

In the bioethanol concentration, a parastillation column, with two vapor phase divisions, reduces the operational and total annual costs up to 42% and 35% when compared to a conventional column of same height.<sup>12,13</sup> For fixed reflux ratio, two vapor divisions promote a reduction in column height of up to 26% over conventional distillation.<sup>14</sup> A metastillation column applied to neutral alcohol distillation, as a replacement for the hydroselction column, reduces the equipment diameter by 10%, keeping the same number of stages.<sup>13</sup> These results are better than those presented by Mizsey et al.<sup>11</sup> due to the greater internal liquid/vapor ratio present in the hydroselction column.

The construction of laboratory-scale parastillation columns for ethanol-water distillation was reported by Belincanta et al.,<sup>15,16</sup> de Moraes,<sup>17</sup> and Di Domenico.<sup>18</sup> Belincanta et al.<sup>15,16</sup> did not have operational problems related to the division of phases, in parastillation columns with 12 stages. The authors reported that in the parastillation column, a foam (cellular and homogeneous) regime occurred more often than expected for a conventional column. de Moraes<sup>17</sup> compared columns of conventional distillation and parastillation, both with six stages. The authors reported that the operating range is different in both columns and that parastillation has a higher overall efficiency than conventional distillation. This difference in the operability may be attributed to the fact that both columns have the same number of stages. For example, Di Domenico<sup>18</sup>



**Figure 2.** Construction scheme of parastillation trays, with the liquid flow represented by the blue arrows and the two vapor flows represented by the red and yellow arrows.

reported that conventional distillation column, with four stages, and parastillation column, with six stages, have a very similar operating range. de Moraes<sup>17</sup> and Di Domenico<sup>18</sup> reported that the parastillation column was less sensitive to

variations in the reflux ratio than conventional distillation columns. Canfield and Jenkins<sup>19</sup> reported the commercial installation of three parastillation columns. Few details are provided, once the authors claimed that they were confidential. However, they reported that the parastillation columns met design expectations for increased purities and increased capacity, resulting in satisfied clients. In one of the columns, the reduction in the reflux ratio was 40% in relation to conventional distillation.

Even with the advantages of para- and metastillation, there is only one report about the industrial installation of three parastillation columns<sup>19</sup> and none about metastillation. According to Biasi et al.,<sup>12</sup> this can be assigned to the deficit of technological and scientific information concerning columns with multiple phase divisions in comparison with conventional distillation equipment. The authors also mentioned previous specific difficulties of simulating para- and metastillation processes, which have been overcome by the unified model proposed by them. This model can be used to simulate columns with any integer number of phase divisions.

Most of the published works considered the distillation of binary mixtures in parastillation and metastillation columns with two vapor phases. The experimental works of Belincanta et al.,<sup>15,16</sup> de Moraes,<sup>17</sup> and Di Domenico<sup>18</sup> considered the binary ethanol-water distillation in parastillation columns with two phase divisions. Gouvêa et al.<sup>14</sup> simulated parastillation columns for separation of benzene-toluene, methanol-water, methyl alcohol-water and benzene-styrene mixtures. The methanol-water system was also simulated by Canfield and Frank,<sup>20</sup> considering parastillation columns under total reflux ratio. Hydrocarbon multicomponent mixtures were investigated by Meszaros and Fonyo<sup>10</sup> and Mizsey et al.<sup>11</sup> Biasi et al.<sup>13</sup> evaluated the application of parastillation and metastillation columns with two phase divisions to the binary and multicomponent bioethanol purification. All these works considered up to two phase divisions.

Previous authors reported columns with only two phase divisions, except for Meirelles et al.<sup>21</sup> and Biasi et al.<sup>12</sup> Meirelles et al.<sup>21</sup> adapted the McCabe–Thiele method to represent parastillation and metastillation columns with any number of phase divisions. Analytical results were also presented, assuming certain process simplification, as constant molar overflow and constant relative volatility. A linear relation between the minimum number of ideal stages and the number of phase partitions was presented.<sup>21</sup> The authors indicated a possible increase in the driving force of the alternative columns, in relation to the conventional one.<sup>21</sup> However, this increase was not thoroughly investigated, as the mechanisms involved in the mass transfer improvement were unclear. Biasi et al.<sup>12</sup> enabled the rigorous simulation of columns with up to two phase divisions. The Naphtali and Sandholm<sup>22</sup> method was adapted and a new set of MESH equations were formulated. The proposed model simulates different column configurations, just by specifying the number of phase partitions.<sup>12</sup> Their work focused on the model development and its validation, giving valuable simulation tips. However, only brief results were presented, which considered only two phase divisions. To the best of our knowledge, there are no reports in the open literature about the use of more than two phase divisions on the separation of multicomponent mixtures or of binary mixtures considering rigorous simulation procedures. The present work deals with this lack of information.

In previous works, we studied different variations of the parastillation and metastillation columns and the combination of these techniques with the conventional one. Results for binary and multicomponent separations show that the separation is slightly sensitive to the split ratio (percentage of division) of the internal liquid (metastillation) and vapor (parastillation) flows in the extremes of the columns, being more influenced by the Murphree efficiency, indicating that it is better to improve tray efficiency than to control the phase split ratio.<sup>23</sup> The division of the liquid or vapor flows into two equal portions (split ratio of 50:50% for two internal streams) presented better results, improving the separation.<sup>23</sup> Additionally, the use of multiple condensers in parastillation and multiple reboilers in metastillation avoids the non-necessary mix of the internal phases in the outlet of the columns, increasing the separation.<sup>13,24</sup> This is because the internal flows may have different compositions, with one of them being richer with the component of interest. At least, we introduced the concept of combined columns in which different distillation techniques are combined into one unique column shell.<sup>13,24</sup> Combined columns are composed of parastillation trays in the rectifying section and of metastillation or conventional trays in the stripping section.<sup>13,24</sup> These configurations of trays highlight the advantages of each technique, reducing the operational and/or the capital costs in relation to the conventional distillation columns. Note that, usually, the volume of liquid passing in the stripping section is greater than in the rectifying section, making advantageous the use of metastillation or conventional trays in this section. On the other hand, the use of parastillation stages in the rectifying section increases the total number of trays without increasing the column height, while allowing a possible lower total pressure drop. This combination of more stages with reduced pressure drop is particularly important in the case of separating mixtures with low relative volatility, which is common in the rectifying section. These works show it is possible to increase even more the advantages of the alternative columns in relation to the conventional one. However, the mechanisms involved in these improvements is not clear yet, but this subject is covered in the present manuscript.

Most research on parastillation and metastillation processes points to an increase in mass transfer due to the flow division.<sup>10,11</sup> However, the mechanisms underlying this increase are still not entirely clear. In this work, these mechanisms are elucidated thorough exergetic analyses and investigation of mass driving forces. For the first time, thermodynamic efficiency and global and stage-by-stage exergy losses were applied to parastillation and metastillation columns. These exergetic analyses elucidate the mass transfer effects that lead to the improvement of separation efficiency achieved through phase division. In fact, our systematic analyses have proven that this improvement is associated with an increase in the mass transfer driving force and thermodynamic efficiency due to the rearrangement of vapor or liquid streams and how this effect can be adequately explained. The improvement on the thermodynamic efficiency reduces operating costs to a value close to the theoretical minimum, required for a specific separation, without significantly increasing the capital costs. This observation contrasts with the conventional process, where decreases in operational costs lead to higher distillation columns and capital costs. Therefore, as far as we know, this is the first time that a work studies the columns with parallel streams with more than

two phase divisions, considering rigorous simulation procedures and binary and multicomponent mixtures. We studied columns with up to eight internal streams, determining the optimum number of liquid and vapor streams. The effect that increasing the number of phase divisions has on separation and on the capital and operational costs is also investigated.

The principle of phase division can be applied to biofuels production. Biofuels have received growing interest in the present energy scenario, especially regarding the reduction of greenhouse gas emissions.<sup>25</sup> To achieve the 2030 IEA's Sustainable Development Scenario (SDS) target, in accordance with the Paris Agreement on climate change, the use of biofuels needs to triple, considering reductions in production costs and CO<sub>2</sub> emissions.<sup>26</sup> Up to four phase divisions were here considered, while previously multicomponent hydrocarbon<sup>10,11</sup> and alcoholic<sup>13</sup> parastillation separations only considered two phase partitions. Our results show that phase divisions may contribute to cost reductions in biofuels production. Considering the hydrous ethanol production, two and four vapor divisions may reduce the energy consumption by 14% and 18%, respectively, when compared with conventional distillation. The CO<sub>2</sub> emissions are reduced by the same magnitude as the operational costs. Overall, phase division is a promising technology to reduce the high-energy demand of distillation processes, and it can be successfully applied to biofuels production and to other separations.

## 2. METHODS

### 2.1. Process Simulation and Column Configurations.

All columns were simulated, in MatLab, considering the mathematical model developed and validated in our previously work.<sup>12</sup> This model is based on the MESH (mass and enthalpy balances and equilibrium relations) equations. It is an adaptation of the Naphtali and Sandholm<sup>22</sup> method, which was originally proposed for simulation of conventional distillation columns. In addition to the conventional column, our model can simulate parastillation and metastillation columns with any number of phase divisions. The method considers  $\beta$  vapor and  $\theta$  liquid internal flows. Conventional columns correspond to the setting  $\beta = \theta = 1$ , that is, one liquid and one vapor internal stream. Parastillation columns consist of one liquid stream ( $\theta = 1$ ) and  $\beta \geq 2$  vapor streams. Metastillation columns consist of one vapor stream ( $\beta = 1$ ) and  $\theta \geq 2$  liquid streams. Details about the MESH equations, the model implementation, and its validation can be found in Biasi et al.<sup>12</sup>

In parastillation, it is possible to allocate more stages per column height than in the conventional and metastillation columns,<sup>12,27</sup> considering the parastillation construction scheme patented by Jenkins<sup>9</sup> and shown in Figures 1 and 2. In Figure 1, the height of a parastillation column with 21 stages (19 trays plus reboiler and condenser) is comparable to the height of a conventional column with 12 stages. We considered parastillation columns of the same height as the conventional ones but with different numbers of stages. The reflux ratio was adjusted to achieve the separation specifications. The tray spacing is the same for all column types. The total number of stages in a parastillation column ( $N_S^{P/\beta}$ ), with  $\beta$  vapor divisions, is related to total number of stages in a corresponding conventional distillation column ( $N_S^D$ ) of same height, by eq 1:<sup>12</sup>

$$N_S^{P/\beta} = \beta \cdot N_S^D - [3 \cdot (\beta - 1)] \quad (1)$$

Eq 1 includes the condenser and the reboiler as stages. The number of stages used in the metastillation columns were the same as the number of stages in a corresponding parastillation, with the number of vapor divisions in parastillation equal to the number of liquid divisions in the metastillation column.

**2.2. Configuration of the Separation Processes.** The main core of this paper is based on the methanol-ethanol separation. This process was adopted to illustrate the effect of increasing the number of phase divisions, while explaining the separation mechanisms involved in these processes. The column specifications were based on the work of Meirelles et al.<sup>21</sup> This separation system was chosen because of its simplicity and its behavior close to the ideal, enabling the observation of effects associated with the phase division, without the interference of the mixture nonideality. These characteristics are also preferred for exergy analyses, where nonidealities require more advanced properties calculations, otherwise the results may be inconsistent with the laws of thermodynamics.<sup>28</sup> However, the methanol-ethanol mixture represents a simplified separation system, it is present in different processes. As in the production of neutral alcohol, where a smaller content of methanol must be separated from the mixture mostly composed of ethanol.<sup>29</sup>

For the methanol-ethanol distillation, a feed of 450 kmol/h ( $\sim 17,575$  kg/h) is used, composed of 50 mol % ( $\sim 41$  mass%) of methanol (Table 1). In a metastillation column with  $\theta$  liquid

**Table 1. Specifications for Binary and Multicomponent Distillation**

| parameter                         |                 | binary                         | multicomponent                                             |
|-----------------------------------|-----------------|--------------------------------|------------------------------------------------------------|
| feed temperature                  |                 | 69.97 °C                       | 94.00 °C                                                   |
| feed thermodynamic state          |                 | saturated liquid               | saturated liquid                                           |
| molar/mass fractions of feed flow | methanol        | 225 kmol/h (7209 kg/h)         | —                                                          |
|                                   | ethanol         | 225 kmol/h (1036.4 kg/h)       | 14.36 kmol/h (661.37 kg/h)                                 |
|                                   | water           | —                              | 518.04 kmol/h (9329.92 kg/h)                               |
|                                   | isoamyl alcohol | —                              | $1.62 \times 10^{-2}$ kmol/h (1.42 kg/h)                   |
|                                   | ethyl acetate   | —                              | $8.73 \times 10^{-4}$ kmol/h ( $7.69 \times 10^{-2}$ kg/h) |
|                                   | glycerol        | —                              | $4.72 \times 10^{-2}$ kmol/h (4.35 kg/h)                   |
| vapor distillate rate             |                 | 225 kmol/h ( $\sim 7367$ kg/h) | 17.00 kmol total/h ( $\sim 707$ kg/h)                      |
| liquid side stream                |                 | —                              | 0.30 kmol/h ( $\sim 6$ kg/h)                               |
| column pressure                   |                 | 1 atm                          | 1 atm                                                      |
| Murphree efficiency               |                 | 100%                           | 70% (trays and condenser) and 100% (reboiler)              |

phase divisions, internal liquid flows were fed into  $\theta$  consecutive trays, each one receiving  $1/\theta$  of the feed flow. This procedure was adopted to equally distribute the feed effect to all internal flows of the column, avoiding an imbalance among the amount of liquid in the  $\theta$  internal flows.<sup>12</sup> The vapor distillate (top product) flow was 225 kmol/h ( $\sim 7367$  kg/h), with a molar methanol content of 95.00 mol % ( $\sim 93$  mass%) and the bottom product with 95.00 mol % of ethanol (Table 1).

For this mixture, the thermodynamic properties were calculated by the Peng–Robinson equation-of-state, as detailed

in the Supporting Information, Appendix A. This means that enthalpies and  $k$ -values were calculated using the same thermodynamic package, being more appropriate for the exergy analyses.<sup>30</sup> Since equilibrium and physical properties can be calculated using a unique thermodynamic package, the use of different thermodynamic packages may lead to numerical destruction of entropy, which violates the second law of thermodynamics. The mixture enthalpy calculation significantly impacts the exergy loss profiles, although it has a small effect on the overall energy balance of distillation columns.<sup>28</sup> Additionally, the Peng–Robinson method was accurate to represent the methanol–ethanol equilibrium. Equilibrium results obtained with the Peng–Robinson package and with NRTL, with parameters adjusted by Batista et al.<sup>31,32</sup> for industrial alcoholic distillation, presented great accordance.

Conventional distillation, parastillation, and metastillation columns were investigated. The study used parastillation columns with same height as the conventional ones, with the number of stages being correlated by eq 1. For metastillation columns, this study uses the same number of stages as in the corresponding parastillation columns, even if this led to different column heights. We compared parastillation and metastillation of same number of stages, because these corresponding columns require approximately the same reflux ratio to achieve a specified separation.<sup>33</sup>

In a second part of this work, a multicomponent separation was considered. The aim of this part is to illustrate a case study with configurations close to those found in industrial processes. For this purpose, the hydrous ethanol distillation was considered. The studies of Biasi et al.<sup>12</sup> and Batista et al.<sup>32</sup> were adopted as the base for the column specifications investigated here. Parastillation columns with up to four phase divisions were compared with a conventional distillation column of same height. The process specifications are reported in Table 1. The vapor phase was considered ideal. The nonideality of the liquid phase considered the NRTL model, which is more accurate to the present mixture than the Peng–Robinson package. The NRTL parameters used here were previously adjusted by Batista et al.<sup>32</sup> and are reported in Batista,<sup>34</sup> being validated against an industrial bioethanol plant. The NRTL parameters and details used for the enthalpy calculation are given in the Supporting Information, Appendix A.

**2.3. Exergetic Analyses Economic Evaluation and Carbon Dioxide Emissions.** Exergy balances, usually applied to whole equipment, were applied to each stage of the column, using the methodology proposed by Ognisty<sup>35,36</sup> and described in Zemp.<sup>37</sup> This methodology was used in later works also for conventional columns, but considering nonideal<sup>28</sup> and multicomponent mixtures,<sup>38</sup> and in the optimization of columns by adding side heat exchangers.<sup>30</sup> It was also adopted by Suphanit et al.<sup>39</sup> for the investigation of the DWC equipment. As proposed by Zemp,<sup>37</sup> equilibrium and physical properties were calculated using a unique thermodynamic package, the Peng–Robinson equation-of-state. For more details about exergy and thermodynamic efficiency, see Supporting Information, Appendix B.

The columns were also assessed using their economic costs, measured by total annual cost (TAC). The TAC considers a normalized capital cost for a payback period of 3 years and the operational costs associated with 8000 operating hours per year. This payback period was considered because it is classically used<sup>40,41</sup> and satisfactory for alternative columns.<sup>42</sup>

The column height was calculated considering the tray spacing of 0.6 m, with a 10% of tolerance, according to Treybal.<sup>43</sup> Parastillation trays of the same column side present the same tray spacing as conventional and metastillation columns. However, consecutive trays are connected by the liquid flow present  $(1/\beta)$  of the distancing, where  $\beta$  is the number of vapor divisions. Thus, it is possible to allocate more parastillation trays per column height than in conventional distillation, as reported by eq 1. However, parastillation columns also present more downcomers per horizontal cut. Jenkins<sup>9</sup> presented the construction of parastillation trays with two phase divisions. Based on this construction scheme, but considering more than two phase divisions, the total downcomer area in parastillation can be calculated as  $[(\beta - 1) + (1/\beta)] \cdot A_d$ , where  $A_d$  is the downcomer area calculated for a conventional tray designed for the same liquid and total vapor flows. Note that for conventional distillation ( $\beta = 1$ ), the equation reduces to  $1 A_d$ .

For all columns, the material of construction was stainless steel ( $F_c = 3.67$ ). The capital cost included heat exchangers, column shell, and tray values, and it was calculated based on equations reported by Douglas<sup>44</sup> and Kiss.<sup>7</sup> Although, these equations were originally designed for conventional columns, recent works have been used them to estimate the cost of alternative columns, as the DWC,<sup>42</sup> that also present phase division and an internal wall, as in parastillation. The calculation of the heat exchange areas considered a heat-transfer coefficient of 0.852 and 0.568 kW/(K·m<sup>2</sup>) for the condenser and reboiler, respectively. No instrumental cost was considered. The operational cost considers the hot and cold utilities. The analyses considered a steam costing of \$8.22/GJ and the cold-water costs of \$0.354/GJ.<sup>41</sup> Douglas<sup>44</sup> used the Marshall and Swift index (M&S) to correct the price for the actual inflation. We adopt the value of the M&S index of 1537<sup>45</sup> for 2012. Then, the Chemical Engineering Plant Index (CEPCI) was used to update the cost to 2019, due to unavailability of M&S index for subsequent years. The adopted CEPCI for the years of 2012 and 2019 were 585<sup>45</sup> and 607.5,<sup>46</sup> respectively.

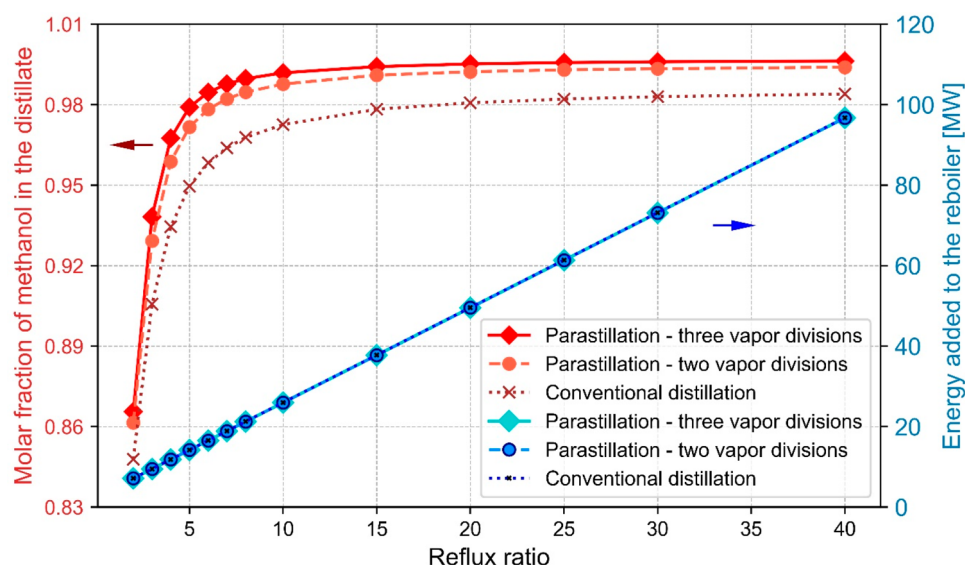
The CO<sub>2</sub> emissions in distillation columns are primarily associated with the heat supplied to the reboiler. The emission from steam boilers can be calculated as indicated by Gadalla et al.<sup>47</sup> Assuming that air is assumed to be in excess to ensure complete combustion, so that no carbon monoxide is formed, the CO<sub>2</sub> emissions (kg/s) are related to the amount of fuel burned,  $Q_{\text{fuel}}$  (kW), in a heating device by eq 2:

$$\text{CO}_{2\text{emiss}} = (Q_{\text{fuel}}/\text{NHV}) \cdot (\text{C}\%/100) \cdot \alpha \quad (2)$$

where  $\alpha = 3.67$  is the ratio of molar masses of CO<sub>2</sub> and C, and NHV (kJ/kg) is the net heating value of a fuel with a carbon content of C%.<sup>47</sup> For heavy fuel oil, NHV and C% are 39,771 kJ/kg and 86.5, respectively.<sup>47</sup> Thus, the amount of fuel burned is represented by eq 3:

$$Q_{\text{fuel}} = (Q_R/\lambda_{\text{proc}}) \cdot (h_{\text{proc}} - 419) \cdot [(T_{\text{FTB}} - T_0)/(T_{\text{FTB}} - T_{\text{stack}})] \quad (3)$$

where  $\lambda_{\text{proc}}$  (kJ/kg) and  $h_{\text{proc}}$  (kJ/kg) are the latent heat and enthalpy of steam delivered to the process, respectively. For this work, a saturated steam at 160 °C ( $\lambda_{\text{proc}} = 2082.55$  kJ/kg and  $h_{\text{proc}} = 2758.10$  kJ/kg) was assumed. The flame temperature of the boiler flue gases is represented by  $T_{\text{FTB}}$  (°C), while  $T_{\text{stack}}$  and  $T_0$ , both in °C, are the stack and ambient temperatures, respectively. This work assumes stack, flame, and



**Figure 3.** Influence of the reflux ratio on product purity and energy consumption for columns with different number of phase divisions, but the same height (9.90 m), as calculated by eq 1.

**Table 2.** Parastillation Columns with Different Numbers of Phase Divisions

| no. of phase divisions                                 | 1      | 2      | 3      | 4      | 5      | 6      | 7      | 8      |
|--------------------------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| total no. of stages (including condenser and reboiler) | 17     | 31     | 45     | 59     | 73     | 87     | 101    | 115    |
| reflux ratio                                           | 5.04   | 3.60   | 3.29   | 3.16   | 3.09   | 3.04   | 3.01   | 2.99   |
| column height (m)                                      | 9.90   | 9.90   | 9.90   | 9.90   | 9.90   | 9.90   | 9.90   | 9.90   |
| column diameter (m) <sup>a</sup>                       | 1.73   | 1.55   | 1.56   | 1.62   | 1.71   | 1.83   | 1.98   | 2.20   |
| downcomer area (m <sup>2</sup> ) <sup>a</sup>          | 0.21   | 0.25   | 0.39   | 0.59   | 0.85   | 1.19   | 1.67   | 2.37   |
| active area (m <sup>2</sup> ) <sup>a</sup>             | 2.16   | 1.63   | 1.53   | 1.48   | 1.45   | 1.43   | 1.42   | 1.41   |
| total tray area (m <sup>2</sup> ) <sup>a</sup>         | 2.37   | 1.88   | 1.92   | 2.07   | 2.30   | 2.62   | 3.09   | 3.78   |
| operational cost (\$10,000/year)                       | 361.45 | 274.72 | 256.29 | 248.40 | 244.01 | 241.30 | 239.49 | 238.16 |
| capital cost (\$10,000)                                | 202.38 | 168.64 | 162.46 | 161.12 | 161.80 | 163.89 | 167.35 | 172.53 |
| total annual cost (\$10,000/year) <sup>b</sup>         | 428.91 | 330.93 | 310.45 | 302.11 | 297.94 | 295.93 | 295.27 | 295.67 |
| exergy loss (kW)                                       | 248.4  | 155.6  | 136.0  | 127.7  | 123.1  | 120.2  | 118.3  | 116.9  |
| thermodynamic efficiency (%)                           | 64     | 74     | 76     | 77     | 78     | 78     | 79     | 79     |
| CO <sub>2</sub> emissions (kg/h)                       | 4995   | 3805   | 3553   | 3444   | 3384   | 3347   | 3322   | 3304   |

<sup>a</sup>The column diameter or area corresponds to the diameter or area of the enriching section, slightly larger than the corresponding stripping section diameter or area. <sup>b</sup>Payback period of 3 years.

ambient temperatures of 160, 1800, and 25 °C, respectively.<sup>47</sup> The heat added to the reboiler is dependent on the process and is represented by  $Q_R$  (kW).

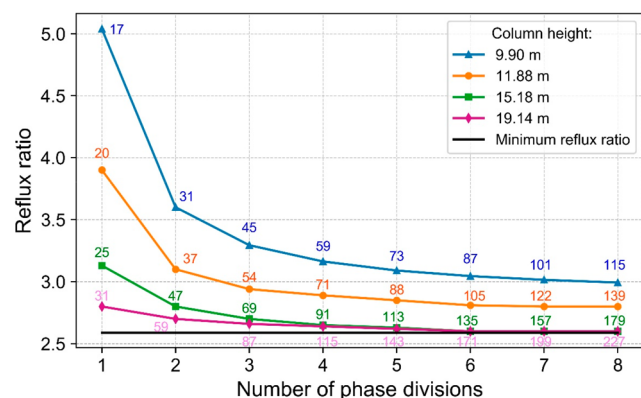
### 3. RESULTS AND DISCUSSION

**3.1. Improvement of the Thermodynamic Efficiency by Phase Division.** The improvements in thermodynamic and separation efficiency, associated with phase division, are demonstrated, in a first moment, considering the methanol-ethanol distillation. A mixture similar to the one adopted here but containing much smaller amounts of methanol (still far much above the toxic level for human consumption) and small amounts of water is the feed stream for the demethylation step of the neutral bioethanol production. Neutral bioethanol is a very pure ethanolic product with applications in the food, beverage, pharmaceutical, and cosmetic industries and with a potential application in the future biorefineries based on bioethanol chemistry.<sup>29</sup> In a second moment, the parastillation columns were applied to a more complex multicomponent distillation, the bioethanol (hydrous ethanol) production.

In a first part, conventional distillation columns were compared with parastillation columns of same height. Figure 3 compares three columns with the same height (9.90 m) but different numbers of vapor divisions and stages: (i) conventional distillation with 17 stages; (ii) parastillation columns with two vapor divisions and 31 stages; and (iii) parastillation columns with three vapor divisions and 45 stages. The distillate purity is defined by the reflux ratio, which is linearly dependent on the amount of energy added to the reboiler. Given the desired purity of the distillate, industrial columns are usually designed to operate in the lowest range of reflux ratios, for instance, the range from 5 to 10 (Figure 3). Note that, for a distillate purity equal to 95 mol % of methanol, the conventional distillation column requires a reflux ratio of 5.04. In contrast, parastillation equipment, with two vapor divisions, achieves the same distillate purity with a reduction of 29% in reflux ratio (3.60) over conventional distillation. A parastillation column with three vapor divisions and using the same reflux ratio of 5.04 allows a higher distillate concentration ( $\approx 98$  mol %) or produces the desired purity with a lower reflux ratio (3.29). A summary of the result of the columns of Figure

3 for a distillate with 95 mol % of methanol is reported on Table 2.

Reduction in reflux ratio leads to energy savings. Using a parastillation column with two vapor divisions to achieve a distillate purity equal to 95 mol % results in a reduction in the energy added to the reboiler of 24% compared to conventional distillation. Using a parastillation column with three vapor divisions results in an energy reduction of 29% when compared with the conventional column. The reduction in the energy added to the reboiler may be even more significant for columns with the same height than the corresponding conventional column but with larger numbers of phase divisions. For example, a parastillation column with eight vapor divisions reduces the amount of heat added to the reboiler in 34%, through a reduction in reflux ratio of 41% (Figure 4), when



**Figure 4.** Required reflux ratio to obtain a distillate with 95 mol % of methanol for columns of same height and different numbers of phase divisions; the annotations represent the number of stages in each column according to eq 1.

compared with a conventional column of same height. CO<sub>2</sub> emissions depend linearly on the energy demand of the reboiler, which means that it is possible to reduce the emissions by 34% by increasing the number of phase divisions from one to eight (Table 2).

Although additional vapor phase divisions always decrease energy consumption, the relative improvements are more significant for the lower range of the number of partitions, that

is, by increasing the number of phases from one (conventional column) to two, one can reduce the reflux ratio more significantly than by increasing the number of phases from two to three, as seen in Figure 4. According to Figure 4, the energy savings decrease with larger number of divisions until becoming asymptotic. This fact is useful from a construction point of view. This is because more divisions require more downcomers, reducing the tray area available for mass transfer and/or increasing the column diameter. Actually, the area required by one downcomer is typically around 9% of the total area of a conventional distillation tray.<sup>43</sup> However, the parastillation tray area corresponds to approximately  $(1/\beta)$  of the area of a conventional distillation tray, where  $\beta$  is the number of vapor divisions.

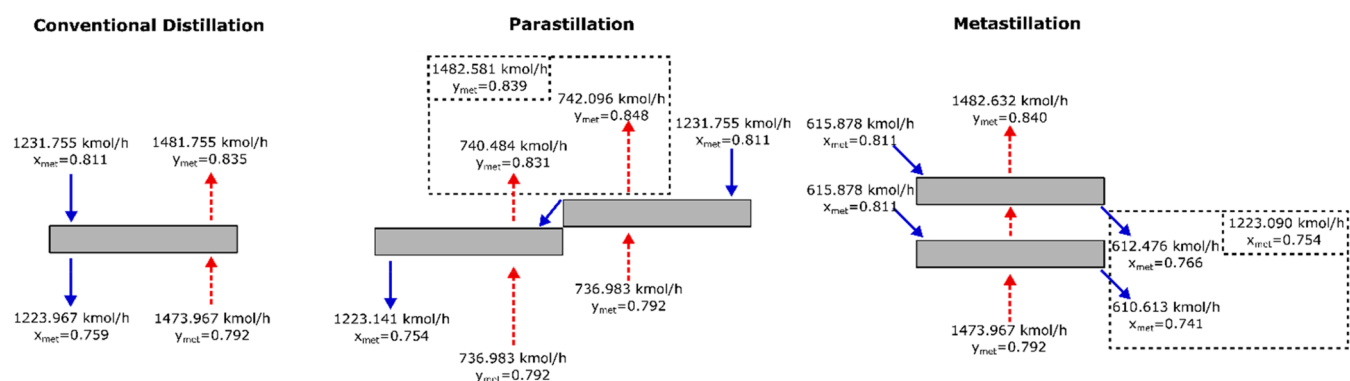
The downcomer area is related to the amount of liquid flow. Therefore, the allocation of downcomers in parastillation stages tends to occupy a larger fraction of the tray area, in comparison to conventional distillation, a value that increases in proportion to the vapor phase divisions. This problem can partly be overcome by increasing the column diameter and avoiding a possible reduction of the active tray area. However, it is important to highlight that in contrast to conventional distillation, parastillation columns usually operate with smaller reflux ratios. The reduction of the reflux ratio contributes to a decrease in the internal flow of liquid and consequently the required tray and downcomer areas. The optimization of parastillation columns, considering only capital costs, must consider these two effects on the column diameter. It is important to note, however, that reducing the reflux ratio always contributes to lower operating costs.

Theoretically, there is no limit in the maximum number of phase divisions that the alternative columns can have. Meirelles et al.<sup>21</sup> determined the minimum number of stages for para- and metastillation columns with different numbers of internal flows. The authors simulated, using an adaptation of the original McCabe–Thiele methodology, columns with up to 100 phase divisions. Note, however, that 100 internal phases is a theoretical number used by the authors to represent the linear behavior of the minimum number of ideal stages as a function of the number of partitions. The construction of para- and metastillation columns with this number of phase partitions is practically impossible considering the currently adopted construction designs, as the one proposed by Jenkins<sup>9</sup> for

**Table 3. Metastillation Columns with Different Numbers of Phase Divisions**

| no. of phase divisions                                 | 1      | 2      | 3      | 4      | 5      | 6      | 7      | 8      |
|--------------------------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| total no. of stages (including condenser and reboiler) | 17     | 31     | 45     | 59     | 73     | 87     | 101    | 115    |
| reflux ratio                                           | 5.04   | 3.60   | 3.28   | 3.15   | 3.08   | 3.04   | 3.01   | 2.99   |
| column height (m)                                      | 9.90   | 19.14  | 28.38  | 37.62  | 46.86  | 56.10  | 65.34  | 74.58  |
| column diameter (m) <sup>a</sup>                       | 1.73   | 1.47   | 1.39   | 1.35   | 1.33   | 1.31   | 1.30   | 1.29   |
| downcomer area (m <sup>2</sup> ) <sup>a</sup>          | 0.21   | 0.15   | 0.13   | 0.13   | 0.12   | 0.12   | 0.12   | 0.11   |
| active area (m <sup>2</sup> ) <sup>a</sup>             | 2.16   | 1.54   | 1.39   | 1.31   | 1.27   | 1.23   | 1.21   | 1.19   |
| total tray area (m <sup>2</sup> ) <sup>a</sup>         | 2.37   | 1.69   | 1.52   | 1.44   | 1.39   | 1.35   | 1.33   | 1.30   |
| operational cost (\$10,000/year)                       | 361.45 | 274.30 | 255.63 | 247.92 | 243.58 | 240.87 | 239.06 | 237.80 |
| capital cost (\$10,000)                                | 202.38 | 191.50 | 203.28 | 218.19 | 233.57 | 248.97 | 264.24 | 279.31 |
| total annual cost (\$10,000/year) <sup>b</sup>         | 428.91 | 338.13 | 323.39 | 320.65 | 321.44 | 323.86 | 327.14 | 330.90 |
| exergy loss (kW)                                       | 248.4  | 156.4  | 136.9  | 129.0  | 124.6  | 121.8  | 120.0  | 118.8  |
| thermodynamic efficiency (%)                           | 64     | 73     | 76     | 77     | 78     | 78     | 78     | 78     |
| CO <sub>2</sub> emissions (kg/h)                       | 4995   | 3800   | 3543   | 3438   | 3378   | 3341   | 3316   | 3299   |

<sup>a</sup>The column diameter or area correspond to the diameter or area of the enriching section, slightly larger than the corresponding stripping section diameter or area. <sup>b</sup>Payback period of 3 years.



**Figure 5.** Mass transfer and concentrations calculated for corresponding stages of conventional distillation, parastillation, and metastillation, total molar flows, and methanol molar fractions.

parastillation. Furthermore, Figure 4 shows that there is no need to increase this value above six partitions, as there is no significant reduction in the reflux ratio after this value. To determine the best number of phase divisions, for a determined system, one must consider the most advantageous capital/operational cost ratio, as the total annual cost. This is because the increase in the number of partitions reduces the operational cost (reducing the reflux ratio), but may increase the capital cost. Additionally, this analysis must consider the difference in the construction of parastillation and metastillation columns. Parastillation columns permit to reduce the column height, while metastillation reduces the column diameter but with a possible increase in column height, in relation to the conventional column. For the present study case, this analysis is reported in the Tables 2 and 3 and discussed further.

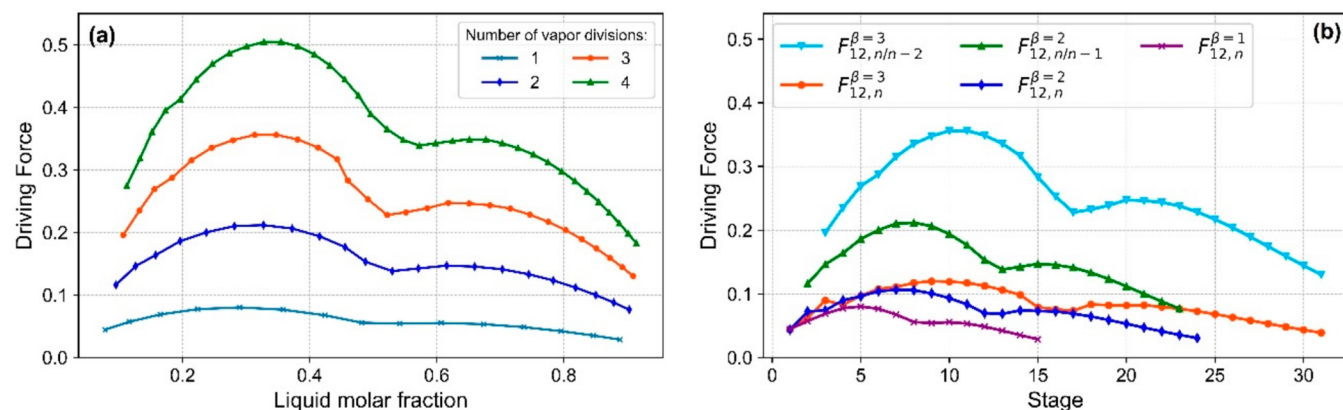
The reflux ratio needed to achieve a desired purity with conventional distillation can be reduced by increasing the number of stages. However, this increase results in taller columns and increased capital cost, as seen in Figure 4. For instance, in the case of the methanol-ethanol separation (Figure 4), a conventional 25-stage distillation column requires a reflux ratio of 3.13, which is 38% less than that needed by a conventional 17-stage distillation column. However, the height of the 17-stage column is approximately 2/3 of the height of the 25-stage column (Figure 4). In contrast, parastillation with multiple vapor streams reduces the reflux ratio while keeping the column height the same. For example, an 87-stage parastillation column with six vapor divisions has a height equal to the 17-stage distillation column but needs a reflux ratio of 3.04, as seen in Figure 4. This value is 40% lower than that required by the conventional equipment with 17 stages and 3.5% lower than the conventional 25-stage column. Metastillation columns, having the same number of stages and phase divisions as the corresponding parastillation columns of Figure 4, were also simulated. The differences between the reflux ratios required by these metastillation columns and those values for parastillation reported in Figure 4 were <0.3%.

In practice, the operational and capital costs must be balanced. The operational costs decrease linearly with the reflux ratio, but in conventional distillation, a reduced reflux ratio requires additional trays and increases column height and capital costs. It is important to note that the minimum reflux ratio value is independent of the number of phase divisions,<sup>21</sup> being the same for conventional distillation and columns with parallel streams, a value of 2.59 in the present separation case.

The best cost balance for conventional distillation is achieved with processes operating with reflux ratios between 1.2 and 1.5 times the minimum reflux ratio.<sup>43</sup> In contrast, the internal arrangement of stages in parastillation allows the construction of equipment with a high number of stages without increasing its height and makes it possible to operate it close to the minimum reflux ratio without a very significant increase in the capital cost. As mentioned earlier, the decrease in the required reflux ratio becomes less for larger number of phase divisions. For instance, the minimum reflux ratio value, for the above-mentioned separation, is only 13% smaller than the reflux ratio required for a 115-stage parastillation column with eight divisions and the same height of a 17-stage conventional equipment (Figure 4). An 87-stage parastillation column, with three vapor divisions and the same height of a 31-stage conventional equipment, demands a reflux ratio of 2.66, a value close to the minimum ratio, while the corresponding column with eight divisions requires a reflux ratio almost equal to the minimum value (Figure 4).

Figure 4 significantly contributes to understanding the correlation of the number of phase divisions with the reflux ratio for parastillation columns with fixed height. Except for the work of Meirelles et al.,<sup>21</sup> there are no reports in the open literature about the evaluation of columns with more than two phase divisions. Meirelles et al.<sup>21</sup> studied simplified systems represented by McCabe–Thiele procedure. The authors reported a linear increase in the minimum number of stages with the increase of the phase divisions. The minimum number of stages also depends on the relative volatility of the components to be distilled. However, the authors did not compare columns of same height. Figure 4 brings an important contribution to distillation designs. In parastillation columns, the phase division possibilities to achieve the specified purification while using a reflux ratio are almost equal to the minimum required for that separation. A conventional column operating with the same reflux ratio would require 55 stages, which represents a column of 36.3 m. Otherwise, a parastillation column, with six phase divisions, and same reflux ratio, requires 135 stages, which can be arranged in a column of only 15.18 m. The capital cost of this parastillation column is 15% lower than the cost of the corresponding conventional column.

**3.1.1. Effect of the Phase Division on the Driving force.** The improvement in separation efficiency observed in parastillation columns has been attributed to the Jenkins effect.<sup>20,21</sup> According to this effect,  $2N$  parastillation ( $\beta = 2$ )



**Figure 6.** Aggregated driving force for (A)  $\beta$  consecutive stages and (B) driving forces for distillation and parastillation columns with two and three vapor streams, for the methanol + ethanol mixture. The present definition incorporates the main way of changing the mass transfer driving force for distilling a specific mixture in a conventional column, namely by altering its reflux ratio. In the case of distillation with parallel streams, a similar effect is obtained without changing the reflux ratio.

stages lead to a better separation than  $N$  conventional distillation stages.<sup>20</sup> The Jenkins effect is based on the higher concentration gradient between the liquid and vapor streams entering each tray in parastillation columns. Our results show that the Jenkins effect is also present in metastillation columns. In fact, a given stage  $n$  in meta- or parastillation receives the liquid or vapor streams coming from the  $n + \theta$  or  $n - \beta$  trays, respectively.

The analysis of the Jenkins effect, usually associated with parastillation trays, can be extended to metastillation by analyzing the mass transfer phenomenon occurring in isolated stages of the column. This can be achieved by comparing the mass transference associated with one tray of a conventional column with two consecutive trays of para- or metastillation, considering two phase divisions. For this purpose, the stream amount, temperature, and composition of the inlet liquid and vapor flows were fixed, and the outlet flows were compared. For the parastillation trays, the vapor flow was divided equally into two parts, with each tray receiving one-half. The liquid flow was entirely fed sequentially into both parastillation trays. Analogously, in the case of metastillation, the liquid flow was divided equally into two parts, and the vapor was fed into the first stage, flowing into the second one afterward. The total flow, composition, and temperature of the inlet liquid and vapor streams were the same for the three cases, but the total outlet vapor flows of the alternative arrangements were richer in methanol, in comparison to the conventional way distillation trays are arranged. The control volume and the results are shown in Figure 5.

In the investigated cases, the concentration difference was slightly smaller for the first alternative stage; this stage being responsible for a lower level of separation than the conventional tray. However, the concentration difference for the second alternative stage was greater, leading to a higher total mass transfer rate. The sum of the mass transfer rates of the two alternative stages was about 1% larger than the transfer rate observed in the conventional distillation tray. This value is significant when entire columns are considered. Distillation columns normally have many stages, and the final effect in the entire equipment is cumulative. Furthermore, the difference observed in this example is less expressive than what really occurs in most of the trays of a column with divided vapor or liquid streams. In the present case, the inlet vapor or liquid

streams have the same composition for each different tray configuration. In the real column, this situation occurs only at the bottom of the parastillation column (vapor division) or at the top of the metastillation column (liquid division). In other stages, the inlet vapor of a parastillation tray comes from  $\beta$  stages below. In metastillation stages, the liquid comes from  $\theta$  stages above, counting from bottom to top. Therefore, the concentration differences (driving force) observed in most divided-stream column trays are, in fact, higher than that indicated in the present example. This can be observed when analyzing the driving force inside the columns.

The greater the number of phase divisions ( $\theta$  or  $\beta$ ), the greater are the concentration differences, increasing the mass transfer driving force (Figure 6). The internal streams rearrangement in para-/metastillation trays increases the difference of chemical potentials between the components of the phases. This means that it is possible to increase the mass transfer driving force without changing the proportion of the liquid/vapor flows within the equipment. As long as changes in relative volatility between components are excluded, the same effect on a conventional distillation column can be achieved exclusively by increasing the reflux ratio.

Considering the tray  $n$  of a conventional column for distilling a binary mixture containing compounds 1 and 2, we define the driving force as

$$F_{12,n} = y_{1,n}^* - y_{1,n-1} \quad (4)$$

Assuming a mixture with constant relative volatility  $\alpha_{12}$  and the enriching section of a McCabe–Thiele diagram, eq 4 corresponds to eq 5:

$$F_{12,n} = \left[ \frac{x_{1,n} \cdot \alpha_{12}}{1 + x_{1,n} \cdot (\alpha_{12} - 1)} \right] - \left[ \frac{r}{r + 1} \cdot x_{1,n} + \frac{x_{1,D}}{r + 1} \right] \quad (5)$$

Note that, in the case of a distillation column operating at total reflux ( $r \rightarrow \infty$ ), the operation line reduces to  $y_{i,n-1} = x_{i,n}$  and the above definition leads to eq 6:

$$F_{12,n} = y_{1,n}^* - x_{1,n} \quad (6)$$

This means that, at total reflux, the definition used here is the same proposed by Gani and Bek-Pedersen,<sup>48</sup> which corresponds to the highest possible driving force according to the

definition given by eq 4. In fact, the driving force measured as the difference between the equilibrium and the mass balance concentrations, both for the vapor phase, achieves its maximum for a column operating at total reflux.

In fact, in the case of parastillation with  $\beta$  partitions, whose tray  $n$  receives the vapor phase leaving the stage  $(n - \beta)$ , the above definition should be modified to eq 7:

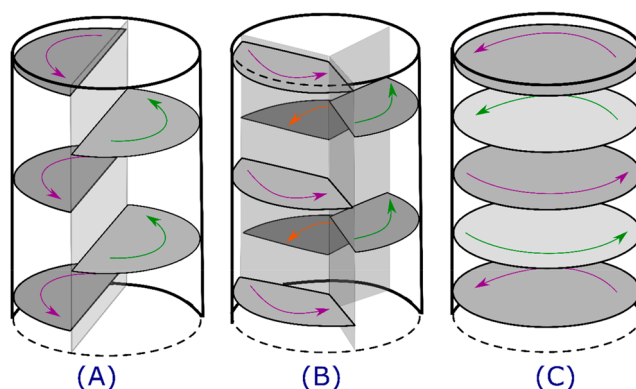
$$F_{12}^{\beta} = y_{1,n}^{*} - y_{1,n-\beta} \quad (7)$$

To do a fair comparison between the driving forces obtained in both tray arrangements, their values, for parastillation trays, must be added over all  $\beta$  stages, as indicated in eq 8, since these trays together correspond to the number of stages necessary for the liquid phase flow  $L$  to contact with the entire vapor phase stream  $V$ :

$$F_{12,n/n-\beta+1}^{\beta} = \sum_{k=n-\beta+1}^n (y_{1,k}^{*} - y_{1,k-\beta}) \quad (8)$$

Figure 6a shows the values of the aggregated driving forces (eq 8) as a function of the liquid phase molar fraction for vapor partition numbers varying from 1 to 4. For this procedure, columns of same reflux ratio were considered but with different heights. On the other hand, Figure 6b shows some of the observed driving forces as a function of the trays. Note that the values for the added driving force (eq 8) always increase with the  $\beta$ -values and are much larger than the driving forces for conventional trays. This occurs in a similar way for two as well as three vapor phase partitions. However, the driving force values for each parastillation tray are in the same order of magnitude or only slightly higher than the corresponding values in a conventional column. This slight effect observed in every para-tray is caused by the fact that the entire liquid phase  $L$  contacts only part of the vapor phase  $V/\beta$ . On the other hand, when all  $\beta$  stages are considered, the Jenkins effect is clearly confirmed, and the total sequence of  $\beta$  parastillation trays can conduct a greater separation than the corresponding conventional distillation stage. This behavior should be attributed to the better driving force distribution achieved by the different tray arrangements.

Para- and metastillation trays showed similar results, indicating that the Jenkins effect explains the improvement in separation for both column types (Figure 5). The mass transfer improvement in parastillation columns has also been attributed to its liquid flow arrangement over the trays,<sup>20</sup> which is illustrated in Figure 7. In this type of equipment, the liquid flows in the same direction on consecutive trays of a given vapor side, classifying this column as the Lewis case II.<sup>49</sup> Figure 7a,b illustrates a simplified scheme to represent parastillation trays with two and three vapor streams. Note that in Figure 7a,b, the arrows represent the direction of the liquid flow inside the column, and the color scheme represents the trays receiving the vapor flow from one specific stream. Note that trays with arrows of same color flow in parallel (same direction), which is characteristic of the Lewis case II.<sup>49</sup> In traditional distillation columns, the liquid flows in opposite directions on consecutive trays (Lewis case III). The distribution of the mass transfer driving force over a specific tray is better in Lewis case II than in case III, improving the tray mass transfer efficiency.<sup>49</sup> In metastillation, the liquid of  $\theta$  consecutive trays flows in the same direction, but the next  $\theta$  stages flow in the opposite direction, as illustrated in Figure 7c for  $\theta = 2$ . In Figure 7c, the arrows illustrate the direction of the

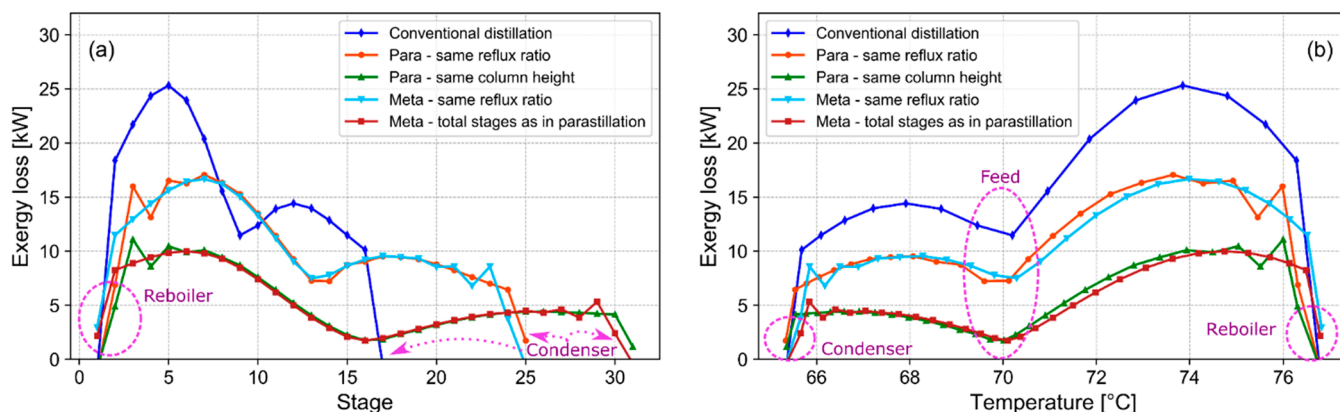


**Figure 7.** Simplified scheme of parastillation trays with (A) two ( $\beta = 2$ ) and (B) three ( $\beta = 3$ ) vapor streams and of (C) metastillation trays with two liquid streams ( $\theta = 2$ ).

liquids flows inside the column, and its colors scheme represents each of the liquid stream (in this example two streams).

By simulating equilibrium stages, we aimed to differentiate the effects arising from the rearrangement of the internal streams from those specific effects of the efficiency of mass transfer. This procedure permits us to focus on the first type of effect that does not depend on the mass transfer efficiency of each tray. In such a manner, we highlighted the effects associated to the way the liquid and vapor currents contact each other, that is, the mechanical arrangement of the internal flows, which is different in para- or metastillation compared to conventional distillation. Note, however, that a good tray design allows high mass transfer efficiency in any type of tray, regardless of whether it is a conventional, parastillation, or metastillation one. Considering the phase equilibrium, para- and metastillation trays achieve a better separation of the components than the conventional trays. This indicates that the rearrangement of the internal streams allows to increase the driving force of mass transfer (as confirmed in Figure 6) in relation to the conventional distillation, regardless of the mass transfer efficiency of the tray. In this way, the inlet currents at each stage of the alternative columns are further away from equilibrium than in the conventional case, and if all possible mass transfer is performed (currents reach equilibrium in the output of each stage) at each stage of the nonconventional columns as well as in the conventional ones, the separation will necessarily be greater in the nonconventional columns. Finally, the consideration of mass transfer efficiency can further improve, in relative terms, the performance of nonconventional columns over conventional columns since nonconventional columns have a Lewis best-case style tray design. In the alternative columns, the liquid flows in the same direction in consecutive trays (Lewis case II). This has the advantage that there is a mass concentration gradient in the stage, with a decrease of light components in the liquid from the inlet to the outlet of the stage, and this gradient is more advantageous in currents that run in parallel, as it increases the driving force (greater gradient).

It is important to highlight that the classification of parastillation trays as case II is not intrinsic to this type of column. Distillation columns can be constructed in such a way to improve tray efficiency.<sup>43</sup> In fact, the different Lewis cases are related to the tray mass transfer efficiency. On the other hand, we assume in the present example that each tray,



**Figure 8.** Stage-by-stage exergy loss profile for conventional distillation, parastillation ( $\beta = 2$ ), and metastillation ( $\theta = 2$ ), as function of the (A) stage number and (B) temperature

regardless of whether it is a conventional column or a divided-stream apparatus, has the same Murphree mass transfer efficiency of 100%. This means that the improvement in separation observed in parastillation trays is, in the present case, related exclusively to the rearrangement of the streams that come into contact on each tray, increasing the mass transfer driving force and the corresponding thermodynamic separation efficiency. Considering that parastillation and metastillation, with the same number of stages and reflux ratio, present almost the same results and that the Murphree efficiency was fixed as 100% for the three investigated cases (Figure 5), the flow arrangement over each tray is not the mechanism involved in the improvement of the separation efficiency. This improvement was caused exclusively by the greater mass transfer driving force generated by the division of the vapor or liquid streams.

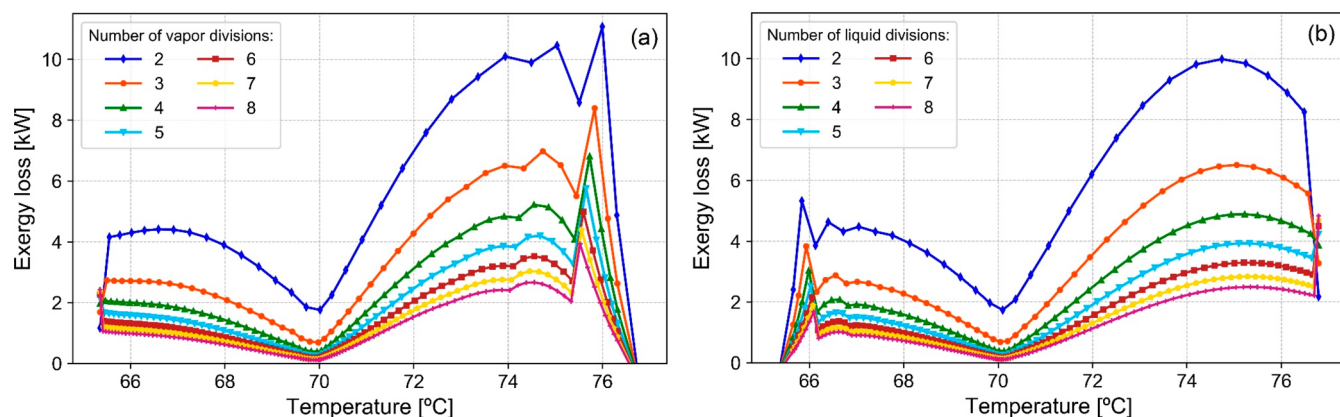
**3.1.2. Effect of the Phase Division on the Thermodynamic Efficiency.** Exergy analysis is a thermodynamic tool for pinpointing inefficiencies of the processes. It combines the first and second laws of thermodynamics, evaluating the irreversibility of the process. The main advantage in using exergy (from the combination of the first and second laws) instead of the entropy generation (from second law) is the fact that exergy was a more feasible unit (power) than entropy.<sup>50</sup> For more details about the definitions, see Supporting Information, Appendix B. Reversible processes present the theoretical minimum energy requirement for that process to occur. In the case of reversible processes, the generation of entropy (second law) or the exergy loss (first and second laws) in the system is zero. This value increases with the increase of the irreversibility of the system. A reversible distillation process is represented by a column with an infinite number of stages and infinitely many side exchangers. In this case, the operating line coincides with the equilibrium line along the whole column, representing a condition of zero driving force.<sup>30</sup> However, this is a theoretical condition that is not practical in the industry due to capital cost limitations. Thermodynamic analysis can then assess how far a process deviates from the reversible case.

Para- and metastillation allow improvements in thermodynamic efficiency up to 23% by increasing in the number of phase divisions from one to eight. It is a consequence of the higher driving forces obtained by the alternative tray arrangements. This increase is directly related to the reduction of the exergy provided by the utility system. The thermody-

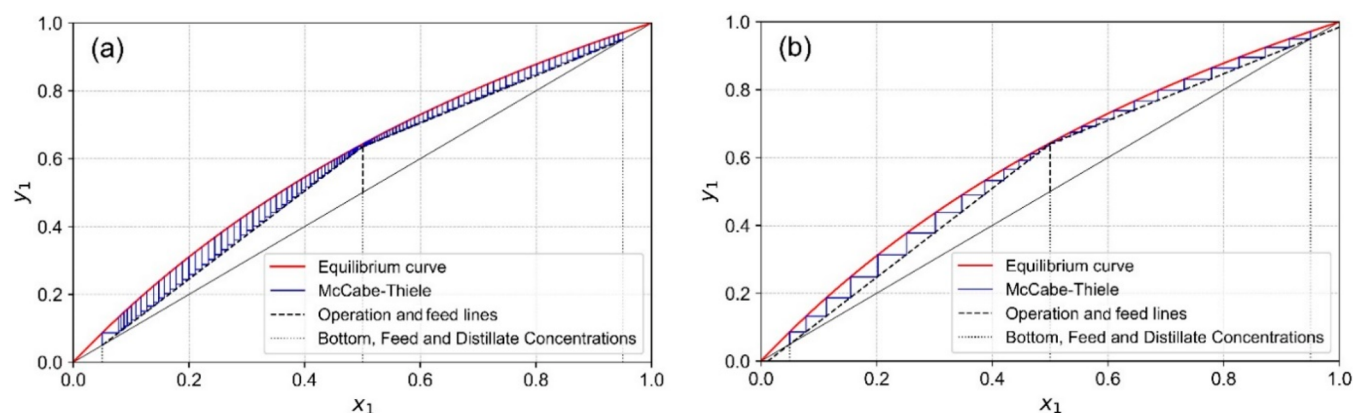
amic efficiency for a separation process is calculated as the ratio between the minimum exergy required to separate a mixture (work of separation) and the energy provided by the utility system (heat fed to the reboiler and rejected at the condenser), see Supporting Information, Appendix B. Fixing the feed conditions and the product specifications, the exergy associated with the inlet and outlet streams are the same for all different column configurations, meaning that the separation exergy is the same for all columns. However, the energy provided by the utility system decreases with an increasing number of parallel streams, because the higher mass transfer driving force allows a reduction of the reflux ratio. As shown in Tables 2 and 3, the thermodynamic efficiency increases for both column configurations as the number of divisions increase.

Global exergy analysis points to thermodynamic efficiency of the process. However, it does not illustrate what is happening inside of the columns. This can be observed in the stage-by-stage exergy loss profiles, which will be used to illustrate the effects of phase division in distillation columns. The stage-by-stage exergy losses along the column for conventional distillation and para- and metastillation with 2 phase divisions are shown in Figure 8. Figure 8a represents the exergy loss per column stage. However, the columns have different numbers of stages, making the comparison difficult. We propose to represent the exergy loss as a function of the stage temperature, as seen in Figure 8b. This facilitates the comparison of the columns aligning the condenser, feed, and reboiler stages. The sum of the stage-by-stage exergy losses for all stages represents the global exergy loss per column and is reported in Tables 2 and 3. Figure 8 compares columns operating with the same reflux ratio: a second parastillation column of same height as the conventional one but with smaller reflux ratio, and a second metastillation with same number of stage and reflux ratio as the second parastillation column.

For columns operating with same reflux ratio, the stage-by-stage exergy losses decrease as the number of phase divisions increases (Figure 8). However, the global exergy losses of these columns are the same as in the corresponding conventional column with same reflux ratio. This is because the exergy of the inlet and outlet streams is the same (same composition, temperature, and duty in the heat exchangers) in this case. However, the second parastillation column presents a global exergy loss 34% smaller than the conventional column of same height, as seen in Table 2. Note that the global and stage-by-



**Figure 9.** Stage-by-stage exergy loss profile for (A) parastillation columns with fixed height and different number of phase divisions and (B) metastillation columns with same number of stages as the parastillation columns



**Figure 10.** McCabe–Thiele diagrams for (A) a parastillation column with eight vapor divisions and (B) a conventional distillation near the minimum reflux condition.

stage exergy losses are similar in the parastillation and metastillation columns with the same reflux ratio and same number of stages (Figure 8). The exergy loss profiles, as a function of the number of phase divisions, of para- and metastillation columns from Tables 2 and 3 are illustrated in Figure 9.

Figure 9a compares exergy loss profiles for parastillation columns with fixed heights and different numbers of phase divisions. The selected height corresponds to a conventional column with 17 stages (9.90 m), and the number of parastillation stages is calculated according to eq 1. The reflux ratio was adjusted for each column to obtain 95.00 mol % of methanol in the distillate and 95.00 mol % of ethanol in the bottom product. In Figure 9b, the comparison is between metastillation columns with the same number of stages as the corresponding parastillation ones shown in Figure 9a. We considered metastillation columns with same number of stages, then same height of the parastillation columns because of the proximity of this columns. Parastillation and metastillation columns of same number of stages require almost the same reflux ratio to achieve the desired purification. In fact, as indicated in Figures 8 and 9, the stage-by-stage exergy loss profiles are very similar for the evaluated para- and metastillation columns. However, these metastillation columns are higher than the corresponding conventional column (17 stages). This is because the internal constructing scheme of metastillation trays is similar to those of conventional columns,

meaning that  $N$  metastillation stages occupy the same height as  $N$  conventional stages. This can be seen in Figure 1, which compares conventional, para- and metastillation columns of same height. In Figure 1 conventional and metastillation columns have 12 stages each, and the parastillation column has 21 stages (including the condenser and reboiler).

From Figures 8 and 9, we see some outliers near the parastillation reboiler or near the metastillation condenser. This occurs because the mixture of streams with different temperatures and compositions causes irreversibility. The greater the difference in composition and temperature between the inlet streams, the greater the exergy loss is. For example, in a parastillation with two partitions, 50% of the vapor leaving the reboiler (stage  $n = 1$ ) enters in the stage  $n = 2$  and 50% in stage  $n = 3$ . The composition and temperature of the vapor leaving the reboiler are closer to the characteristics of the stage  $n = 2$  than of stage  $n = 3$ . Thus, the exergy loss in stage  $n = 3$  is greater than the loss in stage  $n = 2$ . In the same way, the exergy loss in the parastillation condenser or in the metastillation reboiler increases with the increase of the number of phase divisions. This occurs because the multiple parallel streams are mixed in these heat exchangers, as illustrated in the Supporting Information, Appendix B. This can be avoided by using multiple condensers in parastillation or multiple reboilers in metastillation.<sup>24</sup> Note, however, that even with these increases in the exergy losses due to irreversible mixtures, the columns

with parallel streams present a global exergy loss lower than the conventional column.

The thermodynamic efficiency improvement (Figures 8 and 9) is more pronounced for columns with smaller numbers of phase divisions, confirming the results shown in Figure 4. This is a novelty per se, as once for the first time parastillation and metastillation columns were analyzed from a thermodynamic point of view. However, from Figure 9, it is possible to obtain another interesting conclusion. For five to eight phase divisions, a zone of exergy loss approaching zero is observed near the feed region. This effect is associated with the decrease of the mass transfer driving force due to the reflux ratio reduction. A similar behavior near the feed region is also observed in conventional processes operating close to the minimum reflux ratio.<sup>30</sup> This means that the reflux ratio can be reduced by the increase of the phase divisions until a limit.

After six phase divisions, the reduction, in relation to five phases, in the reflux ratio is too small to justify more partitions. This is a good result from a construction point of view. More phase divisions require more downcomers, reducing the active area and/or increasing the column diameter. Additionally, there is an increase in the number of internal walls for more phase divisions. The number of internal walls in parastillation is equal to the number of vapor phase divisions. These walls present a width of the column radius and height almost equivalent to the column height. Jenkins<sup>9</sup> and Meirelles et al.<sup>21</sup> illustrated, respectively, a possible construction of trays with two and three phase divisions.

To understand why more phase divisions do not reduce the reflux ratio below its minimum value, let's analyze Figure 10. This figure compares a conventional distillation column near the minimum reflux ratio (2.6) to parastillation equipment with eight vapor divisions (reflux ratio of 2.99). The graphics are based on the adapted McCabe–Thiele methodology described by Meirelles et al.<sup>21</sup> and the equilibrium line was traced based on the Peng–Robinson thermodynamic package. In both McCabe–Thiele diagrams, the operating lines are very close to the equilibrium curve within the feed zone (Figure 10). The operating lines are functions of the reflux ratio, and the minimum reflux ratio does not depend on the process type, be it conventional distillation, para- or metastillation.<sup>21</sup> The difference of about 15% in the reflux ratios between a parastillation ( $\beta = 8$ ) and a conventional distillation operating at the minimum reflux ratio (Figure 10) corresponds to a very small difference in the operating lines. This analysis (Figure 10) together with the exergetic profiles demonstrate that the increase in the number of phase divisions tends to lead to a minimum exergy loss profile, comparable, approximately, to the minimum energy required to evaluate a separation (the minimum reflux ratio condition).

Improvements in the driving force and in the thermodynamic efficiency due to phase divisions affect, in a positive way, the process costs and CO<sub>2</sub> emissions. Tables 2 and 3 summarize the costs, CO<sub>2</sub> emissions, and thermodynamic efficiencies of columns of Figure 9, with one to eight vapor and liquid divisions, respectively. Note that, one phase division ( $\beta = 1$ ) refers to the conventional distillation column.

Results showed that the operational cost always decreases with the increase of the number of phase divisions (Tables 2 and 3). However, the capital cost decreases for a small number of divisions, but increases after four vapor divisions or two liquid divisions. This increase is associated with the largest number of downcomers and stages in para- and metastillation,

respectively, even against the reduction in column diameter associated with the decreased reflux ratio. It is important to highlight that the total annual cost (TAC), which considers operational plus capital costs, decreases significantly in parastillation until seven divisions and in metastillation until four divisions. The reduction in TAC achieves 31% in parastillation and 25% in metastillation when compared with the conventional distillation. Additionally, in both processes, it was possible to obtain a reduction in energy consumption and in CO<sub>2</sub> emissions of 34% by increasing the number of phase divisions from one to eight. This is a significant reduction that can contribute to the global energy goals.

Considering the parastillation columns (Table 2), one can note a decrease in the column diameter as the number of phase divisions increases from one (conventional distillation) to two phase divisions, even with an increase in the downcomer area. The downcomer area in parastillation columns increases as the number of phase divisions increase. This occurs because the liquid amount is not divided, requiring more downcomer area, in relation to the parastillation tray area, than the conventional distillation, to flow from one stage to another. Additionally, parastillation columns have more downcomers than the conventional one. The total downcomer area in parastillation can be calculated as  $[(\beta - 1) + (1/\beta)] \cdot A_d$ , where  $A_d$  is the downcomer area calculated for a conventional tray designed for the same liquid and total vapor flows. Note that for conventional distillation ( $\beta = 1$ ), the equation reduces to  $1 A_d$ .

In parastillation, the downcomers area is larger than in conventional distillation, which may contribute to increase the diameter of parastillation columns. However, for the same separation, the increase of the number of phase divisions represents a decrease in the reflux ratio, which represents smaller internal flows, contributing to smaller diameters. This last effect is more pronounced for two and three phase divisions, as the reduction of the reflux ratio is greater in these cases. For a number of divisions greater than three, the increase in the downcomer area outweighs the reduction due the reflux rate. However, the reduction in the reflux ratio additionally contributes to a decrease in the heat added to the reboiler or removed from the condenser, which represents a reduction in the heat transfer area and, consequently, in the material costs. Despite these contradictory effects, TAC values continually decrease with a larger number of vapor divisions up to seven partitions (Table 2).

Table 3 shows the results of the corresponding metastillation columns. It was considered the same number of stages as the number adopted for the parastillation columns. However,  $N$  metastillation stages require the same height as  $N$  stages of conventional distillation, as illustrated in Figure 1. This means that the metastillation columns, of Table 3, have different heights, being higher as the number of stages increases.

One of the main advantages of metastillation columns is the reduction in the column diameter. In this column type, the liquid division contributes to a reduction in the required area. It is important to highlight that each tray of the metastillation column has one downcomer in the same way as a conventional column, which further contributes to the reduction of the area required by the flow of the partitioned liquid phase. Additionally, the material cost for the heat exchangers is smaller as the number of liquid divisions increases, which is associated to a reduced heat transfer area. However, the metastillation columns are taller than the conventional ones, and this fact contributes to an increase in capital cost. In fact,

after two phase divisions, the increase in capital cost due the column height is more significant than the decrease associated with the reduction of tray and heat exchangers area. However, the operational costs always decrease with the increase of the number of phase divisions, being in some cases more significant than the increase in the capital cost. In fact, the TAC, considering a payback period of 3 years, decreases with the increase of the liquid phase division up to four partitions (Table 3).

**3.2. Parastillation Application to Bioethanol Production.** The lack of information on the performance of parastillation and metastillation columns may contribute to their reduced industrial acceptance, in comparison to conventional or dividing-wall columns. In this way, the industrial-based examples of bioethanol distillation, together with the more comprehensive explanation on the advantages of partitioning the internal streams given above, aim to improve the knowledge and acceptability of these techniques.

The conclusions obtained with the methanol-ethanol system can be extended to more complex processes, as the bioethanol (hydrous ethanol) multicomponent distillation. For this study, parastillation columns of same height were considered, being the correspondent height calculated according to eq 1. The reflux ratio was adjusted to achieve at least 93 mass% of ethanol in the distillate flow, while the number of vapor divisions was varied from 1 to 4. Results are reported in Table 4.

**Table 4. Multicomponent Distillation Conducted in Conventional and Parastillation Columns of Same Height**

| no. of phase divisions                                 | Conventional distillation |         | Parastillation |         |
|--------------------------------------------------------|---------------------------|---------|----------------|---------|
|                                                        | 1                         | 2       | 3              | 4       |
| total no. of stages (including condenser and reboiler) | 36                        | 69      | 102            | 135     |
| reflux ratio                                           | 4.22                      | 3.48    | 3.30           | 3.24    |
| Ethanol mass percentage in distillate (%)              | 93.03                     | 93.03   | 93.03          | 93.03   |
| column height (m)                                      | 22.44                     | 22.44   | 22.44          | 22.44   |
| column diameter (m) <sup>a</sup>                       | 0.42                      | 0.39    | 0.38           | 0.37    |
| downcomer area (m <sup>2</sup> ) <sup>a</sup>          | 0.01                      | 0.01    | 0.01           | 0.01    |
| active area (m <sup>2</sup> ) <sup>a</sup>             | 0.13                      | 0.11    | 0.10           | 0.10    |
| total tray area (m <sup>2</sup> ) <sup>a</sup>         | 0.14                      | 0.12    | 0.11           | 0.11    |
| operational cost (\$100/year)                          | 635.33                    | 549.01  | 528.18         | 521.22  |
| capital cost (\$100)                                   | 2669.58                   | 2418.80 | 2352.10        | 2331.93 |
| total annual cost (\$100/year) <sup>b</sup>            | 1525.19                   | 1355.28 | 1312.22        | 1298.53 |
| CO <sub>2</sub> emissions (kg/h)                       | 369                       | 319     | 307            | 303     |

<sup>a</sup>The column diameter or area correspond to the diameter or area of the enriching section, slightly larger than the corresponding stripping section diameter or area. <sup>b</sup>Payback period of 3 years.

All columns of Table 4 present the same height (22.44 m), although it was possible to allocate almost four times as many trays in the parastillation column with four vapor divisions, compared to the conventional column. The increase of the phase divisions permits to reduce the reflux ratio in 18%, 22%, and 23% for two, three, and four phase divisions, respectively, when compared with the conventional distillation. This contributes to a reduction in the TAC up to 15% over conventional distillation. The most substantial relative

reduction in reflux ratio is related to the increase of the number of phase divisions from one to two. The operational cost for a parastillation with two phase divisions is 14% smaller than that of conventional distillation. However, the reduction of the operational cost associated with the increase of phase divisions from two to three is 4%. Increasing from three to four phase divisions, the energy cost reduces just 1%.

Form Table 4, the reduction in the required reflux ratio and in operational costs are more substantial from one to two phase divisions than from three to four and subsequent divisions. This is because the reflux ratio of the conventional column is already well optimized. In fact, considering columns with smaller numbers of stages the reductions in the reflux ratio are more substantial, as seen in Figure 4, for the methanol + ethanol mixture. The same observation can be extended to the multicomponent separation. Considering the above multicomponent mixture, but a conventional column with 22 stages (including the reboiler and condenser), requires a reflux ratio of 9.00 to achieve the separation specifications. This column is 41% smaller than the columns of Table 4. Keeping the same column height of the column with 22 stages and increasing the number of phase divisions from one to two, the operational cost decreases in 29%. The reduction of the operational cost associated with the increase of phase divisions from two to three is 8%. Increasing from three to four phase divisions, the energy cost reduces 4%.

The increase from one to two phase divisions contributed to a reduction in the energy and capital costs in all cases considered. However, up to two phase divisions, the reductions depend on the process specifications and the column height. Processes operating with reflux ratios significantly above the minimum permit a more substantial reduction of the reflux ratio by increasing the number of phase divisions. The reflux ratio can be reduced up to the minimum value, which does not depend on the number of phase divisions.

It is important to note that, although it was used here alcoholic systems to illustrate the advantages of the alternative columns over the conventional one, the conclusion can be extended to other mixtures. As far as we know, there is no limitation in the class of components that can be separated using the columns with parallel streams, these being suitable for separation of mixtures that are usually processed in conventional columns. Unlike the DWC, used to separate three or more high-purity product streams in a single column, parastillation and metastillation are more likely the most used conventional columns configuration, which are used to separate two product streams. Note, however, that before the implementation of the columns, for each system, a tailored study evaluating the ideal number of phase partitions (considering the balance between operational and capital cost) and the most suitable technique (parastillation or metastillation) for the separation is required. In general, metastillation is more adequate for processes with high internal liquid/vapor ratios, providing a reduction in the column diameter in relation to the conventional process. On the other hand, the parastillation is suitable to reduce the number of trays and consequently the column height in relation to the conventional column, being adequate, for example, for mixtures of low relative volatility.

#### 4. CONCLUSION

The division of phases inside distillation columns allows significant improvements in costs savings and CO<sub>2</sub> emissions.

These improvements are associated with the increase in the mass transfer driving force and thermodynamic efficiency, due to the rearrangement of the vapor or liquid streams inside the column. Exergy analyses confirm that thermodynamic efficiency and exergy losses are improved when the number of phase divisions is increased. Furthermore, without significant changes in the investment cost, phase divisions allow reducing the operational costs (reflux ratio) until near the minimum value required to perform a specific separation. In conventional distillation, this substantial decrease in operational cost is only possible with a significant increase in the capital cost, associated with the increment of the column height. The most expressive reduction in operational costs occurs from the increase of one to two phase divisions. However, operational costs reductions were observed for columns with up to six phase divisions. After six divisions, the reductions are remarkably little improved by the phase division increase. This is an interesting result from the construction point of view. This is because, as the number of phase divisions increase, the parastillation columns require more downcomers and internal walls to divide the vapor phase, while in metastillation, it demands longer downcomers.

The best number of phase divisions must be balanced with the column capital cost. In metastillation, more divisions require more stages, requiring higher columns. In parastillation, the column height may be maintained, but an increase in the column diameter may be necessary. Thus, for both cases, the diameter must be balanced with the column height to obtain the best capital cost. For the selected methanol-ethanol example, the total annual cost was optimized for seven vapor or four liquid divisions, where parastillation is more advantageous than metastillation.

We also demonstrated that phase division may have a significant potential to be applied to the biofuel production, reducing its energy demand and the corresponding CO<sub>2</sub> emissions.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.1c02548>.

Appendix A details the thermodynamics models and simulation data used. Appendix B reports the mathematical development and details about the exergy and thermodynamic efficiency calculation. Appendix B also features a detailed analysis of exergy losses near the heat exchangers (PDF)

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## Notes

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## ■ ABBREVIATIONS

DWC = dividing-wall column  
TAC = total annual cost  
NRTL = nonrandom two-liquid model  
M&S = Marshall and Swift

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