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Comparative Study of the Separation of a Binary Mixture Ethanol-Water and 2G-Ethanol in a Pilot-Scale Thermosyphon-Assisted Falling Film Distillation Unit

Rodrigo Battisti*, Ricardo A. F. Machado, Cintia Marangoni

Chemical Engineering Graduate Program, Federal University of Santa Catarina, Trindade Campus, 88040-900, Brazil
rodrigo.battisti@ifsc.edu.br

Aiming to reduce energy expenditure, our research group recently proposed an innovative technology of falling film distillation assisted by a two-phase closed thermosyphon, patented as Destubcal. Second generation (2G) ethanol, produced from lignocellulosic materials is considered the biofuel with the highest potential to replace fossil derivatives. The objective of this study is to verify the effect of viscous components (such as glycerol and sugars) present in 2G-ethanol on the Destubcal distillation performance, in comparison to ethanol-water binary mixture. Two forms of heat supply in the steam chamber were evaluated: isothermal and temperature-profile, besides evaluating the influence of feed flow rate and evaporator temperature. When the thermosyphon's steam chamber is operating in isothermal mode, temperatures of the bottom and the top of the distillation tube were higher with the 2G-ethanol mixture. This feedstock contains components with higher boiling temperature (as glucose and glycerol), which have influenced the temperature profiles. Unlike distillation with binary ethanol-water, lower evaporator temperatures favor 2G-ethanol distillation when the steam chamber is operating in temperature-profile mode. In all cases, the mass fraction of ethanol was favored in the 2G-ethanol distillation, indicating that the presence of components such as glucose and glycerol allows better recovery of the most volatile components in a falling film distillation process. The separation was similar with ethanol-water and 2G-ethanol mixture. However, the presence of components such as sugars and glycerol allowed better recovery of ethanol in the distillate. The imposition of a temperature-profile condition promoted higher ethanol mass fractions in the distillate, being the more suitable mode of operation.

1. Introduction

With the increasing need to improve the energy efficiency of chemical processes concomitantly with higher yields and purities in the industrial separations, many alternative distillation technologies are being studied. Integrated approaches have been developed in order to minimize energy consumption, especially in the distillation of multicomponent mixtures, originally carried out in multicolumn units. As stated by Kim (2016), there are three main proposals for structural modifications in distillation columns that allow the reduction of energy demand: the divided wall column (DWC), the diabatic distillation, and the HIDiC (heat-integrated distillation column). In the first case (DWC), also referred to as Petlyuk columns, industrial use has already been applied because the proposal has proved to be more efficient than the conventional process. However, the application is still limited to multicomponent mixtures (Zhai et al., 2015). In the case of diabatic columns, the temperature difference between the reboiler and the condenser is reduced by the introduction of successive heat exchangers in the column trays (Mello et al., 2020; Zierhut et al., 2020). With minor temperature differences, the thermodynamic efficiency of the process increases. However, this concept is still more theoretically and experimentally studied on a small scale than industrially applied (Pinto et al., 2011). In this sense, the third proposal (HIDiC) uses the concepts of diabatic distillation associated with the recovery of the heat released by the condenser, supplying it in the reboiler. This process is carried out by raising the operating pressure of the rectifying section, thus also coupling the concept of heat pumps in distillation columns, already tested and industrially used (Shenvi et al., 2011).In line with these proposals is the concept of miniaturization of engineering systems, which, as mentioned by Monnier et al. (2012), is interesting from an

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industrial point of view since small volumes are used, and in the case of exothermic reactions, safety can be improved. Using this concept, Saifutdinov et al. (1999) presented a proposal for a falling film distillation unit operating under vacuum, whose heat source is a thermal fluid. The authors demonstrated a reduction in the size of the unit as well as an improvement in energy efficiency. Due to the energy supply being distributed along the distillation tube, the amount of reflux is changed, in addition to the use of the condensation heat of the mixture that does not occur conventionally. Thus, the total energy needed to separate the desired mixture is minimized. From this conception, our research group has been developing a distillation unit assisted by a two-phase closed thermosyphon, patented as Destubcal. In this apparatus, the distillation occurs by falling film in an internal tube, called distillation tube, and whose heat supply no longer occurs in the conventional form, but by a steam chamber-type thermosyphon (Battisti et al., 2020a). Due to the characteristics of the two-phase closed thermosyphon, the mode of energy supply can be performed either isothermally or by imposing a temperature-profile longitudinally. In both cases, heat is supplied throughout the length of the distillation tube (Battisti et al., 2020b). The proposal that has been developed is characterized by operating at atmospheric pressure, and with reduced dimensions with only one meter of height (Marangoni et al., 2011).

Consolidated experimental studies by the research team of this work have pointed to the viability of separating different mixtures with this new technology, as ethanol-water (Marangoni et al., 2019a, 2019b), aromatic mixture of toluene, para-xylene, meta-xylene, ortho-xylene, and ethylbenzene (Silva Filho et al., 2018), multicomponent mixture of synthetic naphtha (Querino et al., 2018), and monoethyleneglycol-water (Pires et al., 2020). In all cases, the same quality of separation was compared with a conventional column, and it was shown that the thermosyphon-assisted falling film unit is more energy-efficient, requiring less energy load. Thus, these results encouraged more detailed studies about different mixtures on the pilot-scale unit, since the condition of operation under atmospheric pressure characterizes it as different from the already conventional processes of molecular distillation and the patent of Saifutdinov et al. (1999), which operates under vacuum.

Second generation (2G) ethanol, produced from lignocellulosic materials, is considered the biofuel with the highest potential to replace fossil fuels because it has less impact than conventional first-generation bioethanol (Dias et al., 2012). In addition to being cheaper and abundant, lignocellulosic materials such as agro-industrial and urban waste have no competition with food production, therefore, they do not compromise food security in countries (Alvira et al., 2010). Conventional distillation of 2G-ethanol is a highly energy-intensive process and can account for more than 50 % of unit operating cost (Kiss et al., 2012).

The objective of this work is to evaluate, for the first time, the feasibility of purifying 2G-ethanol through the Destubcal thermosyphon-assisted falling film distillation unit and comparing the results with the ethanol-water binary mixture distillation. The ethanol-water binary mixture has been evaluated since the beginning of the construction of the pilot-scale unit, as it is a model mixture that can simulate the output of fermentation bioreactors, and whose behavior in a distillation process is already well known (Battisti et al., 2019). The 2G-ethanol mixture, consisting of ethanol, water, glycerol, sugars, some other higher alcohols, and polyphenols is important due to the need to verify the effect of the presence of more viscous components (such as glycerol and sugars) in the formation of the falling film, and consequently in the quality of separation.

2. Materials and methods

2.1 Brief description of the pilot-scale unit

Figure 1(a) shows the photograph of the pilot-scale unit highlighting the main equipment. Figure 1(b) shows a schematic diagram of the thermosyphon-assisted column operation. The pilot-scale unit is built in stainless steel and designed for a maximum feed capacity of 60 L/h. The distillation process occurs through a falling liquid film formed from a mixture fed on the top of the column, which flows over the internal surface of a vertical tube (called heat and mass transfer tube). The liquid film flows in a symmetrical laminar flow in counter-current with the enriched vapor generated at a certain pressure and temperature, while the tube wall is kept radially at a constant temperature by means of a steam chamber-type thermosyphon. Therefore, the steam chamber is responsible for providing energy for the process. The so-called isothermal condition refers to maintaining an equal temperature longitudinally in the steam chamber by removing the non-condensable gases, while the so-called temperature-profile refers to the imposition of a profile of temperature of about 20 °C in the steam chamber due to the presence of non-condensable gases. The unit operates continuously, where the bottom stream leaves the unit by gravity and the top vapors are condensed and collected by gravity. These two streams are mixed in an accumulator tank, which has the purpose of dampening fluctuations over time due to the variation in the concentration caused by the separation. Then, this stream is sent back to the storage tank. In the steam chamber, 10 (ten) temperature sensors were installed in order to allow visualization of the energy distribution throughout the unit. Also, the temperature acquisition is carried out in the feed, bottom, and top of the distillation unit. The unit is manually controlled. The feed flow rate is controlled by a rotameter, and the top and bottom flow rates are acquired manually at the time of sample collection.

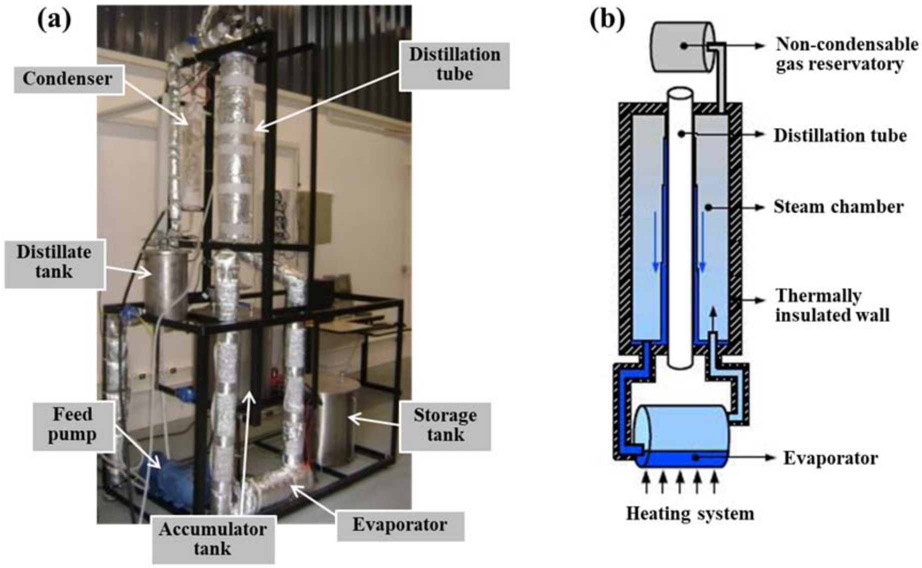

Figure 1: Photograph (a) and schematic diagram (b) of the thermosyphon-assisted falling film distillation unit.

2.2 Experimental procedures

The analysis of ethanol recovery from both the binary ethanol-water mixture and 2G-ethanol was performed by evaluating two forms of heat supply by the thermosyphon: isothermal and temperature-profile. The influence of the feed flow rate (Q_f) and the evaporator temperature (T_{evap}) were also investigated, as shown in the experimental conditions (based on preliminary studies) presented in Figure 2. The feed temperature (T_f) was kept constant at 81 °C in all experimental runs. The experiments carried out with the ethanol-water binary mixture were conducted with a feed composition of 10 wt% ethanol and 90 wt% water. For the 2G-ethanol, in addition to ethanol and water, several components are present in smaller amounts such as higher alcohols, different sugars, glycerol, furfural, acetaldehyde, and polyphenols. In order to verify whether the presence of these components could affect the formation of the liquid film, only sugars and glycerol were selected to perform the experimental tests since these components could affect the viscosity of the mixture, or have a thermal degradation resulting from the heating of the distillation tube wall. The values of the 2G-ethanol feed composition were defined according to the average composition of second-generation ethanol widely available in the literature, as 88.29 wt% water, 9.32 wt% ethanol, 1.86 wt% glucose, and 0.53 wt% glycerol.

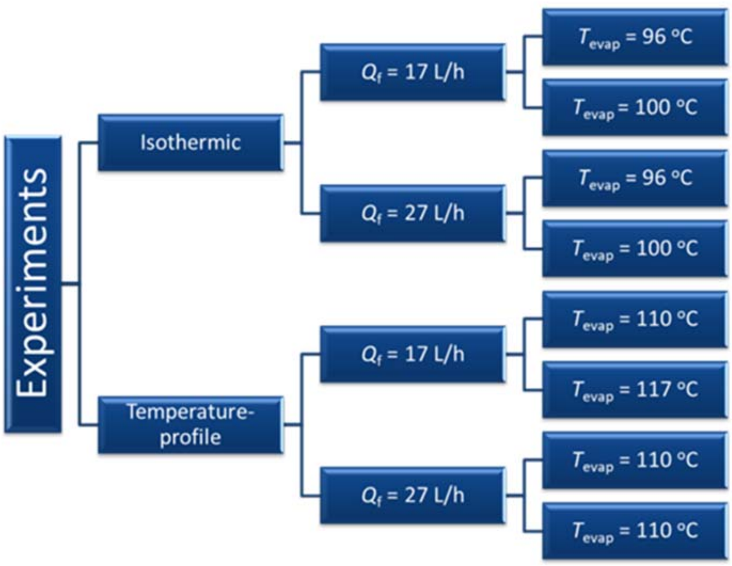

Figure 2: Experimental operating conditions performed in the pilot-scale unit.

The volume fraction of ethanol in the distillate was determined by gas chromatography and the results obtained were converted to mass fraction in order to allow comparison with the ethanol-water binary mixture. Glucose and glycerol were determined by high-performance liquid chromatography as well as by colorimetric method (DNS).

3. Results and discussion

3.1 Isothermic operation

Figure 3 shows the comparison results between the distillation of the ethanol-water binary mixture and 2G-ethanol mixture with the thermosyphon's steam chamber is operating in isothermal mode. According to Figures 3(a) and Figure 3(b), all the bottom (T_B) and top (T_T) temperatures of the distillation tube were higher with the 2G-ethanol mixture when compared to those obtained with the binary ethanol-water mixture. In fact, the 2G-ethanol contains components with a higher boiling temperature (especially glucose and glycerol), which, even in small quantities, may have influenced the profile of temperature.
When evaluating the results for distillate flow rate (Q_D) shown in Figure 3(c), and ethanol mass fraction in the distillate stream (x_D) shown in Figure 3(d), it is observed that for Q_D an increase only occurred in the case where Q_f = 27 L/h and T_{evap} = 100 °C. As for ethanol recovery, Q_f = 27 L/h, T_{evap} = 96 °C and Q_f = 17 L/h, T_{evap} = 96 °C, both variables increased the x_D when the distilled mixture was 2G-ethanol. This observation indicates that, unlike distillation with ethanol-water binary mixture, lower values of evaporator temperature favor the distillation of 2G-ethanol. However, it is important to note that the highest value of ethanol mass fraction was obtained with a higher feed flow rate.

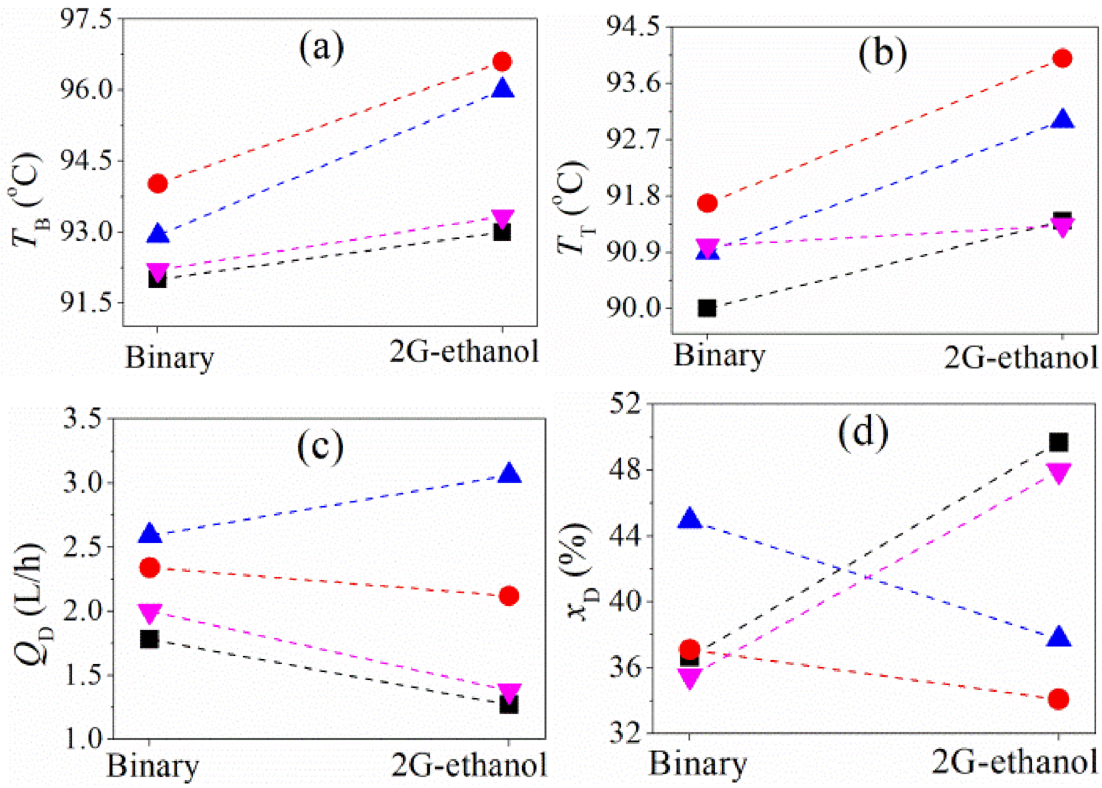

Figure 3: Isothermic operation: (■) Q_f = 27 L/h, T_{evap} = 96 °C; (●) Q_f = 17 L/h, T_{evap} = 100 °C; (▲) Q_f = 27 L/h, T_{evap} = 100 °C e (▼) Q_f = 17 L/h, T_{evap} = 96 °C.

3.2 Temperature-profile operation

In Figure 4, the comparison results between the distillation of the ethanol-water binary mixture and 2G-ethanol are presented when the steam chamber was operated in the temperature-profile mode. As observed for the isothermal case, the values obtained for the steam chamber temperatures were not discrepant. For the temperature-profile operation, lower values of bottom (T_b) and top (T_T) temperatures of the distillation column were obtained with the 2G-ethanol mixture, as illustrated in Figure 4(a) and Figure 4(b), respectively. In this case, when a temperature difference is imposed in the steam chamber, whose purpose is to supply energy to the distillation tube, the influence of heavy components in the mixture is no longer verified. This behavior can directly influence the recovery of ethanol, resulting, therefore, in obtaining a good separation with the conditions Q_f = 27 L/h, T_{evap} = 117 °C (Figure 4(c) and Figure 4(d)), higher than observed isothermally.

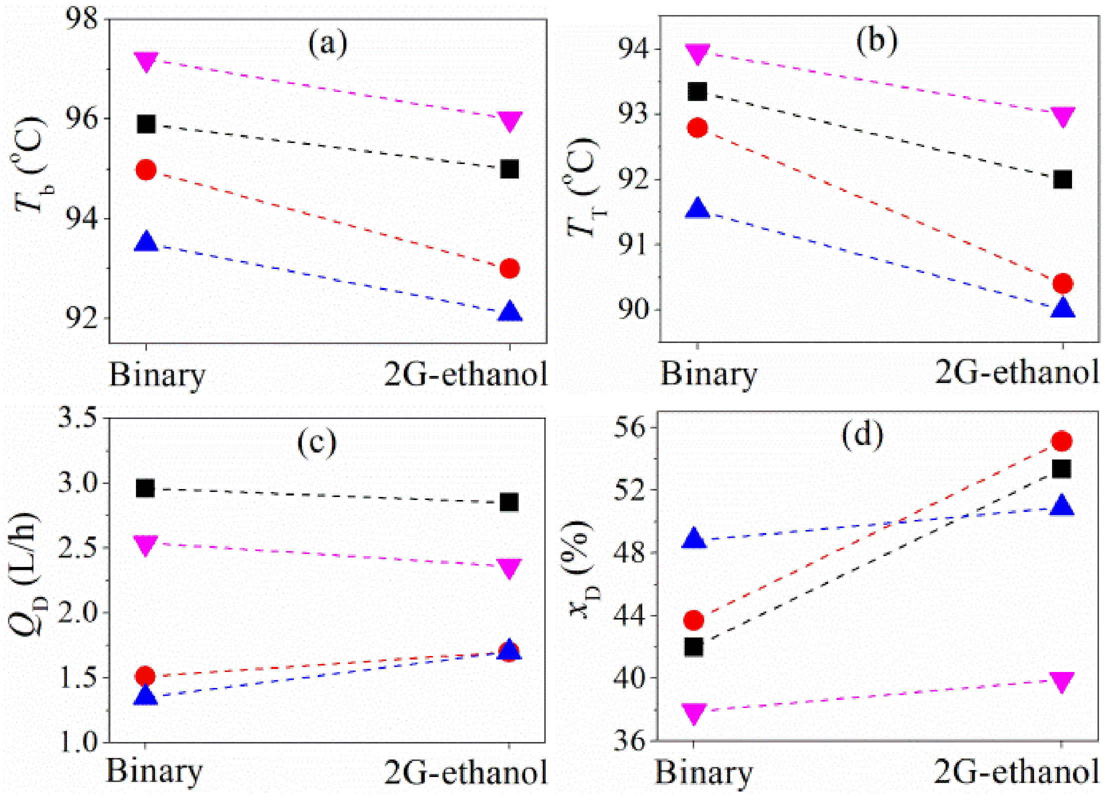

Figure 4: Temperature-profile operation: (■) Q_f = 27 L/h, T_{evap} = 117 °C; (●) Q_f = 17 L/h, T_{evap} = 110 °C; (▲) Q_f = 27 L/h, T_{evap} = 110 °C e (▼) Q_f = 17 L/h, T_{evap} = 117 °C.

For both modes of operation of the thermosyphon's steam chamber it was observed that, in general, the increase in the evaporator temperature allowed higher temperatures at the bottom and top of the distillation tube, leading to higher evaporation of the film and resulting in higher distillate flow rates, however, with a lower mass fraction of ethanol in this stream. The imposition of a temperature-profile mode in the steam chamber promoted higher values of ethanol mass fraction. It was expected, as it also favors the dragging of other components, there will be an improvement in the recovery of ethanol, due to the possibility of generating internal reflux in the unit and thereby improving the separation quality (Battisti et al., 2020b). It is important to consider that the analyzed samples of 2G-ethanol distillate did not show significant amounts of glucose and glycerol. This behavior demonstrates that the unit behaves like a conventional unit regarding the recovery of mixtures containing components such as sugars, allowing the production of vapor enriched in ethanol. Also, it was not observed the presence of dry spots in the film generated in the distillation tube that could be due to the effects of the mixture containing thermolabile components.

4. Conclusions

This comparative study allowed observing that the heat transfer in the thermosyphon-assisted falling film distillation unit was not affected by the characteristics of the 2G-ethanol mixture, since the temperature profiles obtained for this feedstock were similar to those obtained with the ethanol-water binary mixture. However, the presence of components such as sugars and glycerol allowed better recovery of ethanol in the distillate. Besides, the imposition of a temperature-profile condition in the steam chamber of the thermosyphon promoted a higher mass fraction of ethanol in the distillate, being the most suitable mode of operation. Therefore, the innovative distillation device, called Destubcal, can be used to recover 2G-ethanol with good separation quality, with the potential to be applied on a larger scale in the near future.

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