Analysis of the reflux ratio on the batch distillation of bioethanol obtained from lignocellulosic residue

T. C. Coelho\textsuperscript{a}, O. Souza\textsuperscript{a,b}, N. Sellin\textsuperscript{a,b}, S. H. W. Medeiros\textsuperscript{a,b}, C. Marangoni\textsuperscript{a,b} \textsuperscript{*}

\textsuperscript{a}Department of Chemical Engineering/Universidade da Regi\~{o} de Joinville (UNIVILLE), Rua Paulo Malschitzki 10, Zona Industrial. Joinville/SC CEP: 89219-710, Brazil

\textsuperscript{b}Masters in Process Engineering/Universidade da Regi\~{o} de Joinville (UNIVILLE), Rua Paulo Malschitzki 10, Zona Industrial. Joinville/SC CEP: 89219-710, Brazil

Abstract

Aiming for sustainable and low-cost production, bioethanol production using lignocellulosic wastes, such as sugarcane bagasse and waste from banana crops, has been extensively explored. The recovery step is usually carried out during the distillation process and is challenging, particularly regarding energy issues. This study aimed to evaluate the bioethanol recovery from banana culture waste as a function of the reflux ratio in a process employing a batch distillation column. Tests were performed using a standard mixture of ethanol and water and using total reflux and ratios 0.5, 1 and 2. As expected, the best result was obtained with the highest reflux ratio, and it was under this condition that the broth obtained from the fermentation process was distilled. The maximum ethanol t in the distillate was 67\% (wt\%), which is less than the 93\% composition that was obtained using the standard mixture; however, this is a promising result because inferior values are typically obtained in distilleries using a single column. Also, this value is close to others reported in literature for bioethanol distillation obtained with different residues and higher reflux ratio. Batch distillation is appropriate and feasible for implementation in the production of bioethanol from banana waste in small production units intended for the production of biofuels, beverages or commercial alcohol.

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* Corresponding author. Tel.: + 55 47 34619180 ; fax: + 55 47 34730131.
E-mail address: cintia.marangoni@univille.br.

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1. Introduction

Ethanol is produced during the fermentation of sugars and is used to produce alcoholic beverages such as cachaça, spirits, vodka and beer as well as perfume products. With the current concern about carbon emissions to the atmosphere, the use of this component as fuel has great energy and environmental appeal. Worldwide, the gradual increase in oil prices and concerns about reducing man-made environmental impacts has encouraged the search for new sources of renewable energy, such as those originating from biomass [1]. Among the products obtained from such sources, ethanol has been shown to be a viable alternative to fossil fuels because of its ecological appeal. In this context, we highlight lignocellulosic wastes, which, in addition to being abundant, have great potential in the production of industrial products, such as bioethanol, glucose and protein.

The need to expand the supply of raw materials for ethanol production without harming the lands that are currently used for food production is the main factor for the development of research in clean technologies, which are increasingly using waste products for bioethanol production [2]. Several studies have addressed the use of agricultural or forestry wastes for the production of ethanol [3]. These waste products are called residual biomass and include sugarcane bagasse and straw, corn fiber and straw, rice and wheat straw, eucalyptus wood and wheat straw waste, as well as fruit cultures, such as bananas, grapes and apples. In the case of bananas, applications have been developed to use the fruits, leaves and other wastes, such as the pseudostem. The importance of the banana culture in Brazil, specifically in the State of Santa Catarina, as well as the impact of waste generated in banana cultivation were described by Federizzi [4]. The author mentioned that there is a daily loss of 15 tons of fruit at the Ceasas (Supply Centers) across the country, and another 14 tons are discarded in the retail process, even before the bananas reach the consumer. We obtained data that indicated that in this state, for every ton of bananas harvested, there are approximately 4 tons of lignocellulosic waste (i.e., 3 tons of pseudostem, 160 kg of stems, 480 kg of leaves and 440 kg of bark).

The process of converting lignocellulosic biomass to bioethanol requires five distinct steps: (1) biomass delignification to release cellulose and hemicellulose from the lignin-cellulose-hemicellulose complex, (2) depolymerization of the cellulose and hemicellulose carbohydrates to produce their respective free sugars (pentoses and hexoses), (3) fermentation of the free sugars to produce ethanol, (4) ethanol recovery and (5) effluent treatment [5]. Regardless of the substrate used, the fermented broth or must (wine) that comes from the fermentation process is generally composed of up to 10% by volume of alcohol, along with other liquid, solid and gaseous components. The broth also contains many other components in small quantities that are derived from the fermentation process and affect the final quality of the product. The ratio of these components varies depending on the operating conditions of the fermentation process as well as the substrate used. Regardless of its use, either as fuel or for something else, the ethanol that is obtained during fermentation must meet quality standards in addition to providing the required alcohol content. The components derived during the fermentation process influence these criteria and affect the distillation purification process.

Some authors [6,7] indicated that to reduce the cost of bioethanol processing, new raw materials must be evaluated. However, with the use of new substrates, all of the stages of production must be re-evaluated because these new substrates will result in the generation of fermentation broths with different compositions. The ethanol distillation process is well established, especially when raw materials and wastes such as sugarcane, starch and corn are used. In this regard, many proposals for the unit operation and control of this process have been presented. In many cases, the goal is to reduce the energy consumption because the total thermodynamic efficiency of a conventional distillation process is only approximately 5-20% [8]. One of the greatest energy expense of a fermentation plant is the distillation process. Therefore, different operational and control configurations have been proposed from the energy
analysis and process sustainability standpoints [9]. Examples are studies [10,11] where a configuration using vacuum extractive fermentation with triple-effect distillation proved to be an interesting alternative to minimize the energy demand. Other proposals include the use of thermally coupled columns [12,13] and the cogeneration of energy [14]. Furthermore, the concept of a biorefinery has been extensively explored [15,16].

However, few studies have presented results from bioethanol recovery from fermentative processes using banana waste as a substrate. Velásquez Arredondo et al. [17] performed an energy assessment of the production of bioethanol from bananas, but the work did not emphasize the operating conditions used in the process. It is necessary to evaluate the distillation based on the constituents of the fermentation broth once they influence the operating conditions employed in the process, even in small quantities. Furthermore, the resulting ethanol compositions are quite different depending on which part of the banana is used, for example, banana pulp or skin waste. This choice may result in different process adjustments to improve the quality of the distillate. Similarly, few studies have evaluated batch distillation because the primary interest is for the use of bioethanol as a biofuel. However, it is important to consider the small producers, for whom batch distillation can be an attractive and viable alternative for small-scale production.

The use of batch distillation is indicated when smaller investments are needed, and this process is well-suited to establish new operating conditions that are often specified according to the need for the recovery of a particular component [17]. Batch distillation is also used when the mixture has a high solids content [18] and it has the advantage of being able to separate multi-component mixtures in a single operation [19]. Thus, the use of batch distillation columns for refining bioethanol can be a viable alternative for small-scale farmers. Moreover, we cannot discard the possibility of refining ethanol from bananas for the production of alcoholic beverages.

Thus, the objective of this study was to evaluate different reflux conditions during the separation of ethanol produced in the fermentation of banana culture waste using batch distillation. The focus of this work is to assess the recovery process of ethanol obtained from lignocellulosic waste (banana) and not to study the parameters that influence the process of distillation, which are well-known.

2. Methodology

Experimental tests were first conducted with a binary standard mixture (ethanol and water) and then with the fermentation broth. The ethanol concentration used in both cases was approximately 3% (wt%). The experimental distillation process, shown schematically in Figure 1, consisted of a glass distillation column that was heated at the base by an electric mantle and cooled at the top by a condenser.

The column contained 8 equilibrium stages, which were constructed in jacketed, glass fractionation modules that were 7.5 cm tall with an inner diameter of 5 cm and filled with Rasching rings (8 mm characteristic size). In addition, temperature sensors (thermocouples) were installed throughout the column to monitor the column’s temperature. The flask-type column reboiler had a capacity of 5 L, and the initial volume used was 2 L. To heat the flask, an electric heating mantle, with a maximum power of 698 W and controlled by a power controller, was used. The tests were conducted with full power with the goal of a faster stabilization of the process. The total-type condenser used public water as a refrigerant. The reflux rate of the system was determined by a refluicer module (a drive system with an electromagnet that directs the condensed steam).

The experiments were performed with the standard mixture (ethanol/water) and used reflux ratios (the ratio of the reflux flow rate and the distillate flow rate) of 0, 0.5, 1 and 2. Using the best reflux ratio determined, we distilled the fermented banana culture broth to evaluate the recovery of ethanol.
The distillation process was initiated at constant reflux until the unit temperatures stabilized (stationary state), and then the studied reflux condition was set. At this point, 10 mL samples of the distillate current were removed consecutively, and composition analyses were carried out using a pycnometer to determine the density of the samples. This procedure was continued until the ethanol in this stream was exhausted. The best operational condition was used to evaluate the distillation of ethanol obtained from banana culture.

3. Results and discussion

3.1. Determination of stationary state

The batch unit operation used in this work was a conventional process with constant reflux. Thus, the unit was operated at total reflux until steady-state was reached, at which point the reflux was modified. Attainment of the steady-state condition was determined by the temperature progression from the beginning of the distillation operation, which was detected with ten thermocouples distributed throughout the tower, as shown in Figure 2a. To determine the time necessary for process stabilization (startup), the derivative of the temperatures in the unit was analyzed (Figure 2b). Thus, it was possible to precisely determine the transient state and the stationary state.
For operation with a total reflux ratio and using a binary mixture (3% by weight ethanol), a vapor volumetric flow of 0.36 mL/s was obtained, with a total stabilization time of approximately 50 min.

3.2. Reflux variation tests with a binary mixture

Figure 3 shows the ethanol mass fraction of the samples when the reflux condition of the standard mixtures (ethanol and water) was varied. As expected, as the samples were removed, the ethanol mass fractions decreased. It shows that a reflux ratio of 0.5 and 1 established a greater distillate flow rate in relation to the reflux, and for this reason, the recovery curve is close to that obtained with a total reflux. Comparing reflux ratios of 1 (equal reflux and distillate flow rates) and 2 (reflux flow rate greater than the distillate flow rate), the ethanol composition in the initial samples is greater when a reflux ratio of 2 is used, suggesting that this condition facilitates the recovery of ethanol in the distillate. In fact, reflux helps to maintain an ethanol enrichment of the vapors in the top portion of the column.

Table 1 shows the distillate volumetric flow rate, distillation time and theoretical number of plates calculated for each condition of separation, and Figure 4 shows the instantaneous ethanol mass fraction in the distillate over time. More time is needed to distill a large quantity of ethanol when a greater reflux ratio is used. The ethanol concentrations in the distillate current remain higher for a longer time because the vapor current formed inside the column is enriched in the more volatile component because of the greater amount of reflux introduced.

Table 1. Flow rate, distillation time and number of real plates for the experiments performed when varying the reflux ratio using a standard mixture.

<table>
<thead>
<tr>
<th>Reflux</th>
<th>Volumetric flow rate of distillate (mL/s)</th>
<th>Total time of distillation (h)</th>
<th>Number of plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.36</td>
<td>3.11</td>
<td>8</td>
</tr>
<tr>
<td>0.5</td>
<td>0.24</td>
<td>3.58</td>
<td>8</td>
</tr>
<tr>
<td>1</td>
<td>0.19</td>
<td>4.00</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>0.11</td>
<td>4.50</td>
<td>9</td>
</tr>
</tbody>
</table>

Fig. 3. Ethanol mass fraction as a function of the reflux ratio.
In a distillation column, the composition of the component of interest in the distillate is a function of the relationship between the number of plates and the reflux ratio. In this unit, while maintaining a fixed height of the column, the number of plates was increased when greater reflux conditions were used, resulting in improved ethanol compositions in the distillate as well as an increase in the distillation time.

In a batch distillation column, the objective may be to minimize the production time or maximize the production of the compound of interest. There is a nonlinear relationship between the reflux ratio and distillation time, as illustrated in Figure 5.

Little increase in this ratio is observed between reflux ratios of 1 and 2, suggesting that there may be a relationship between time minimization and product maximization.

3.3. Broth tests

In the experiments performed using the fermentative broth, the analysis of the stationary state was initially performed under conditions of total reflux, verifying the temperature stabilization along the column. The derivatives of these temperatures over time (Figure 6) indicated that there was an increase in the time required to reach the stationary state, corresponding to approximately double the time necessary for the standard mixture.
To compare the process with the broth distillation process, a reflux ratio of 2 was used. The volumetric flow rate of the distillate obtained in this experiment was 0.13 mL/s, which was slightly higher than that obtained using the standard mixture (0.11 mL/s). The total distillation time was also higher (4.82 h, compared to 4.50 h with the standard mixture), which was predominately due to the additional time needed for stabilization.

Figure 7 shows the ethanol composition (by weight) in the distillation current for the distillation of the broth and the standard mixture. Published works in the literature achieved an ethanol recovery of approximately 72% (wt%) in a batch distillation process using sugarcane bagasse and a reflux ratio of 6. Considering that this study used a reflux ratio of 2, these results are satisfactory because a purity of 67% (%wt) was achieved.

Furthermore, these results are interesting because usually, the ethanol distillation process is performed in two steps: an initial concentration step (to reach a composition of 37% ethanol) followed by the rectification of this alcohol to reach concentrations close to 95% [7]. In the case described in this work, a single unit achieved a concentration of 67% (wt%) ethanol.

Fig. 7. Comparison of the ethanol composition obtained in the experiments using a binary mixture or fermentative broth with a reflux ratio of 2.
In addition, this recovery corresponds to 72% of the maximum that could be obtained using a mixture of ethanol and water without interference from other constituents. Both the batch volume and alcoholic content of the broth influence the process efficiency. Baracho [20] reached a mass ethanol concentration of approximately 88% using the fermented broth from the huarango tree, which is also lignocellulosic, but the alcohol concentration in the feed solution was 20% by volume ethanol. In this work, the concentrations were approximately 3% by weight ethanol.

4. Conclusions

The operational results obtained from the distillation of the fermented broth compared to the standard mixture demonstrate the difficulty of this process for multi-component mixtures. However, they confirm the technical and economic feasibility of the proposal to recover ethanol using a batch distillation process because in continuous processes, it is necessary to use more than one column to obtain a similar distillate composition. Besides, the ethanol mass fraction in distillate obtained in this case is close to others reported in literature for bioethanol distillation obtained with different residues and higher reflux ratio.

Operation of this process under higher reflux conditions allows for better ethanol recovery. However, it is necessary to evaluate the energy of the best operating condition because the introduction of reflux increases the distillation time.

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