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Comparison of Different Separation Methods for Solids Removal in an Ethanol Fermentation Broth from Banana Culture Waste

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New alternatives for alcohol production from low-cost feedstocks, such as lignocellulosic biomasses, have been proposed. Banana wastes are an example of these substrates. Existing applications involve the use of the fruit, leaves and other residues, such as the pseudostem. Centrifugation is commonly used for the separation of the solids in the fermentation broth. However, due to the presence of banana residues in the broth, it is necessary to evaluate whether the solid-liquid separation method interferes with the composition of the clarified broth (wine) that is sent to ethanol recovery by distillation. Based on this scenario, the objective of this study was the characterization of the liquid and solid phases for three separation methods: centrifugation, vacuum filtration and microfiltration. Centrifugation was performed at 3800 rpm.min^{-1} for 20 min and vacuum filtration was conducted with the fermentation broth poured through a filter paper in a Buchner funnel. Microfiltration was performed using a capillary membrane module (polyimide) at room temperature with a flow rate of 90 L.h^{-1}. The loss of ethanol in the liquid phase was evaluated for each method; no differences among the methods were observed. Few differences in the clarified broth composition were verified after centrifugation compared with vacuum filtration and microfiltration. For the removal of solids, microfiltration resulted in a minor presence of total solids in the liquid. These results support microfiltration as a potential method for the separation of solids and liquids in fermentation broth from banana waste. Similarly, the moisture content, Chemical Oxygen Demand (COD), Total Nitrogen (TN) and pH were determined for the solid phase that was discarded after the separation. The highest COD and moisture contents and the lowest value of TN were obtained with microfiltration. The solid residue should be characterized with respect to other constituents and properties to assess their use in processes such as biogas production.

1. Introduction

In the pursuit of alternative raw materials for biofuel production, certain social and economic issues are paramount, especially regarding the use of biomass as a source in the production of biofuels, which can produce potential food shortages due to a lack of productive land. Thus, various biomasses from lignocellulosic residues, such as forest by-products (Fischer et al., 2013), paper and wood residues, sweet sorghum and agriculture residues (Pirozzi et al. 2013) are being evaluated worldwide. Banana culture waste—especially the pseudostem, leaves and rejected fruits—are attractive for ethanol production due to their significant potential as a low-cost and abundant raw material. Brazil is considered to be the second largest producer of fruit. The cultivation of fruit in all states in Brazil results in the generation of a substantial amount of residues, which are usually disposed in fields for simple decomposition. The use of such residues enables the reduction of environmental pollution and increases the value of banana culture, which has experienced losses in recent years due to fluctuation in the product price in the internal Brazilian

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market (Fernandes et al., 2013). Studies show that the ethanol yield and productivity from the fermentation of rejected fruit, banana peels (Souza et al., 2012) and banana plant pseudostems (Gonçalves Filho et al., 2013) are promising.

The process of ethanol production from banana culture residues differs from the process in which sugarcane is employed as biomass (extensively employed in Brazil), especially regarding the use of the pulp from the rejected fruit. These residues are included *in natura* in the fermentation broth due to their active and inactive yeast cells, as well as the presence of a fraction of suspended solids, which gives the broth a lower fluidity. In addition, the fermentation broth from lignocellulosic residue contains ethanol, sugar, and salts, as well as oil and suspended solids, which could subsequently influence the efficiency of the ethanol recovery process (Zhang et al., 2012).

Solid residues are present in high concentrations in the pre-treatment and enzymatic hydrolysis of lignocellulosic biomass and in the broth that is directly fermented from residues. Solid residues also exhibit an extensive distribution of particle sizes in these mediums. These solids, for which the removal from solution can be difficult, exert a negative impact on fermentation and subsequent ethanol separation.

Broth clarification is usually performed by centrifugation, which is a conventional and well-established method. However, to optimize the process and reduce energy consumption, alternatives to the classic separation process for solids are being proposed. Evaluation of the separation methods for solids in the fermentation broth is critical for improving the quality of the produced alcohol and decreasing energy consumption and the cost of effluent treatment. Flocculating yeasts have been used to facilitate biomass recovery in processes that operate continuously for long periods (Zhao and Bai, 2009). A pre-treatment method with flocculation, which incorporates chitosan and sodium alginate, was employed by Gao et al. (2013) to facilitate subsequent filtration for the recovery of acids in fermented broth. Flocculants such as polyelectrolytes can be used to improve the solid-liquid clarification of lignocellulosic biomass, as demonstrated by Burke et al. (2011). The potential use of hydrocyclones for yeast separation was investigated by Habibian et al. (2008) to reduce energy consumption. Membrane processes are also suggested by authors such as Bello et al. (2012), who employed polyimide membranes to perform the microfiltration of fermentation broth. Another study conducted by Wojciech (2013) includes the tangent microfiltration of fermentation broth from a given saccharification process and simultaneous fermentation.

Despite the focus on a reduction in energy consumption or the optimization of the recovery process for a given component, observations show that the selected method can alter the composition and properties of the stream destined to the ethanol recovery process. Thus, the purpose of this study consisted of the evaluation of three different separation methods (centrifugation, microfiltration and vacuum filtration) to characterize resultant liquid and solid fractions. Due to the properties of the fermentation broth obtained from rejected fruits (banana), the evaluation of solid-liquid separation methods is necessary to identify the effects on the composition of the broth that is sent to fractional distillation columns.

2. Methodology

2.1 Fermentation

The fermentation broth used in the separation tests was developed in a bioreactor with a working volume of 3 L and 20 % v/v of inoculum. The study used *Saccharomyces cerevisiae* yeast and *in natura* pulp from banana waste on a substrate concentration of 500 g MU/L. The fermentation processes were conducted at 30 °C for 12 h with an agitation frequency of 150 min^{-1} according to the method presented by Schulz (2010).

2.2 Solid-liquid separation methods

Centrifugation tests were conducted in a model 280-R refrigerated centrifuge (Excelsa 4) with a frequency of 3800 min^{-1} for 20 min (time defined for reach visually a limpid liquid after the separation process). After centrifugation, the supernatant was immediately removed, and the solid and liquid fractions were frozen for posterior analysis.

In the vacuum filtration tests, the fermented broth was fed by a Buchner funnel containing filter paper and connected to a Kitasato flask. The set was attached to a DV 142 N 250 Vacuum Pump (J/B Industries) for pressure reduction. The test was performed at room temperature for approximately 5 h (time defined with same criteria as with centrifugation).

For the microfiltration tests, the fermentation broth was fed at room temperature by an FE 611 (B. Braun) gear pump with a flow rate of 90 L/h. Figure 1 presents a diagram of the microfiltration module. The microfiltration module was composed of polyvinyl chloride (PVC), and its interior, which contained hollow polyimide membranes, comprised a total area of 0.08 m^2.

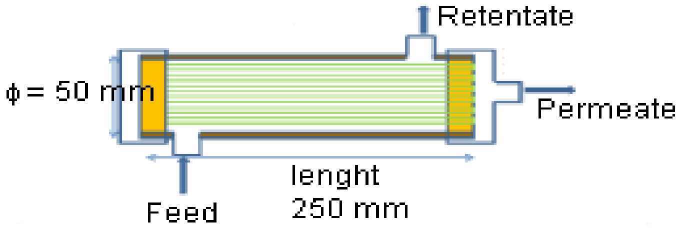

Figure 1: Diagram of microfiltration module

The experiments were performed in batches, with a duration of one hour for each batch (time defined by the viscosity of the retentate that is increasing as the test was carried out).

2.3 Performed analysis

The identification and quantification of the components present in the liquid phase of the broth after the separation process were performed by gas chromatography (GC). The equipment (Agilent, model 6890) was coupled to an automatic sampler (Agilent, model 7683) and a Hewlett-Packard HP-1 column with a length of 50 m, an outside diameter of 0.32 mm, a stationary phase of 100% polydimethylsiloxane and a film thickness of 1.05 μm. The eluent consisted of helium with a flow rate of 2.2 $mL.min^{-1}$. High-performance liquid chromatography (HPLC) was also performed using a Merck Hitachi D-7000 IF equipped with a refraction index detector (Merck RI-71). H_2SO_4 with a concentration of 8.5 mM was used as the eluent, with a flow rate of 0.5 mL/min. The studies of Bessa et al. (2012) and Batista and Meirelles (2011) were used for selection of the components to be analyzed. In these studies, alcohols, aldehydes, organic acids and other fermentation by-products were identified in a given industrial process for ethanol production.
The following items were also determined: Total Nitrogen (TN) using the method proposed by Hach and according to the Hach Company Instructions Manual; Chemical Oxygen Demand (COD) estimated using the Hach COD Reagent Kit in the range of 0 to 1500 mg O_2/L (code 212590) and according to the method proposed by the supplier; and Total Solid (TS) concentration tests performed by gravimetric analysis using porcelain crucibles dried in a stove (105 °C for 48 h) until a constant mass was obtained. Total Carbon (TC) was detected using a total organic carbon analyzer, and the pH was measured with a Mettler Toledo pHmeter model MP220 with a pH range of 0 to 14 and a 0.01 resolution.

3. Results

The characterization of fermentation broth from rejected banana cultures and the results after subsequent separation processes are presented in Table 1.

Table 1: Comparison of data in the literature and the experimental results of this study regarding composition (on a volume basis) of fermentation broth from banana residue (rejected fruit) after centrifugation, vacuum filtration and microfiltration

	Experimental Results			Batista and Meirelles (2011)	Bessa et al. (2012)
	Centrifugation	Microfiltration	Vacuum filtration		
Ethanol (%)	3.643	2.973	3.073	6.6	8.1
Isobutanol (%)	0.005	0.005	0.005	0.00278	0.00278
Methanol (%)	0.023	0.016	0.020	0.000032	0.000032
Pentanol (%)	0.017	0.007	0.006	-	0.0001
Propanol (%)	0.006	0.004	0.004	0.00336	0.003
Acetic acid (%)	0.045	0.013	0.013	0.04351	-
Succinic acid (%)	0.022	0.023	0.023	-	-
Isoamyl alcohol (%)	0.021	0.017	0.018	0.01425	0.01425

In addition to ethanol, seven other components from the fermentation of banana pulp were identified in higher quantities by chromatography analysis. According to Bessa et al. (2012), the identified components are among the most commonly cited components in the literature on alcohol fermentation. The quantities of the identified constituents were less than the quantities cited in the literature. Boscolo et al. (2000) indicate that more than 51 components of alcohols and esters are formed during the fermentation process for obtaining cachaça (the Brazilian sugarcane spirit). Therefore, the direct use of the rejected fruit in fermentation may have caused changes in the composition of the fermentation broth. Because the same constituents were obtained regardless of the separation method, this behavior was attributed to substrate processing or to laboratory-scale production.

Ethanol and by-product concentrations, which differ from data in the literature, are relevant factors. Particular attention is given to the notion that the studies used for comparison are aimed at the production of ethanol and not alcoholic beverages, which were prevalent in the literature. Considering that Batista and Meirelles (2011) and Bessa et al. (2012) used data from industrial-scale fermentation, a conventional separation process and different substrates, such as sugarcane and grapes, it can be inferred that the production of these compounds by alcohol fermentation is directly related to the substrate used in fermentation. This observation is also corroborated by Dragone et al. (2009), who characterized fermented broth from whey by focusing on the production of alcoholic beverages.

Regarding the processes of centrifugation, vacuum filtration and microfiltration, a similar mass percentage of ethanol was observed for all processes, which suggests that product recovery is not influenced by the separation method. However, acetic acid and pentanol presented lower values for microfiltration and vacuum filtration, which is considered to be an advantage because there is a maximum allowed quantity of these components in ethanol fuel, which is established by regulatory organizations. According to Gamboa et al. (2012), different physicochemical compositions of vinasse are attributed not only to its raw materials but also to processes inherent to each substrate used to obtain ethanol. It is therefore believed that components obtained in smaller amounts in microfiltration and vacuum filtration processes can be adsorbed inside the solid mass retained by the microfiltration unit membrane and the filter paper in vacuum filtration tests.

Table 2 presents the results for COD, TN, TS, TC and pH for the liquid fraction after centrifugation, microfiltration and vacuum filtration.

Table 2 Characterization of the liquid fraction in fermentation broth obtained from banana residue (rejected fruit) separated by centrifugation, microfiltration and vacuum filtration

Parameter	Centrifugation	Microfiltration	Vacuum filtration
COD (mg/L)	88,200	13,300	58,400
TN (mg/L)	177	96	80.1
TS (mg/L)x	17,737	12,923	14,715
TC (mg/L)	793	631.9	616.3
pH	4.98	4.72	3.91

Lower concentrations of TN and TC were also obtained with vacuum filtration and microfiltration. Considering that both systems present a physical barrier (membrane or filter paper) and that nitrogen can be obtained in the form of dissolved gas or organic and inorganic combinations, the presence of nitrogen is assumed in the separated solid fraction.

Among all processes, the best result for broth clarification was obtained by microfiltration due to the highest removal of total solids (with a content approximately 30 % less than centrifugation and 12 % less than vacuum filtration), which demonstrates a higher potential for the solid-liquid separation process. The operating conditions for microfiltration are also attractive because they can provide a continuous-flow solid separation system.

COD, moisture content and TN analyses, which were aimed at future applications of residues from second-generation ethanol production, were performed using banana pulp as a substrate. These results are described in Table 3.

Table 3 Characterization of solid fractions in fermentation broth obtained from banana residue (rejected fruit) separated by centrifugation, microfiltration and vacuum filtration

Parameters	Centrifugation	Microfiltration	Vacuum filtration
COD (mg/kg)	8287.6	46,666.67	882.60
TN (mg/kg)	2,657.57	563.33	1,333.33
Moisture content (%)	86.84	93.60	91.20

In all cases, the formation of residues with high nitrogen contents and high CODs was evident. Thus, the direct disposal of this residue in soil is inadequate.

According to Gamboa et al. (2012), vinasse has a certain value as a fertilizer because it contains nutrients such as nitrogen. However, its high organic loads and high application doses render it vulnerable to soil contamination, changes in soil properties and water contamination, which can cause eutrophication due to high nitrogen enrichment (Junakova, 201). Anaerobic biodigestion has been shown to be an attractive pre-treatment for this residue in this scenario, which presents an important economic factor: the production of methane and its subsequent use in energy production. Szymansky (2010) proposed a system of upflow anaerobic sludge blanket digestion (UASB) reactors for the treatment of vinasse. This system presents an efficiency of 65% COD removal, which enables the use of this residue for irrigation because biodigested vinasse continues to exhibit potential for fertilization. This treatment system is appealing due to its biogas production, which exhibits high energy potential (close to the calorific value of natural gas).

4. Conclusion

The comparison of the classic centrifugation, vacuum filtration and microfiltration processes for liquid-solid separation of fermentation broth from banana culture residue (rejected fruit) revealed no significant differences in the composition of clarified broth. Observed differences due to the presence or absence of a given component and its concentration are attributed to the substrate. This finding is consistent with one of the contributions of this study.

The microfiltration of fermentation broth presented the highest potential regarding the use of centrifugation and vacuum filtration for separating total solids in the liquid fraction and for retaining TN and TS from alcohol fermentation, which makes it an attractive alternative compared with traditional methods.

Solid residues from the liquid-solid separation process for the fermentation broth exhibit high organic loads with high COD and TN concentrations; however, these quantities require treatment prior to their subsequent disposal.

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