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Influence of oil quality on biodiesel purification by ultrafiltration

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ABSTRACT

In the present study, biodiesel was produced by ethylic transesterification of soybean and canola oils using sodium hydroxide as a catalyst. It was evaluated the influence of oil quality on the biodiesel and glycerol separation by ultrafiltration. The experiments were carried out with tubular a-Al_2O_3/TiO_2 membranes with average pore diameter of 0.05 μm and 20 kDa, varying the transmembrane pressure and the concentration of the feed mixture. The comparison among the use of degummed soybean oil, refined soybean oil, crude canola oil, and refined canola oil, demonstrated that free fatty acid presented in the oils influence the formation of droplets containing glycerol. The separation was efficient when reaction mixture was produced from degummed soybean oil and crude canola oil, both with a higher acidity value. The highest free fatty acid content in the crude canola oil, not only favored the formation of a dispersed phase containing glycerol, which was retained by the membrane, but also resulted in the lowest flux decline rates. The ultrafiltration was efficient in removing glycerol, since the highest glycerol content in the permeate was 0.013 wt%. This novel refining process of biodiesel showed the advantage of not requiring previous decantation to separate the two phases obtained after transesterification and the reduction in the amount of water used in the washing steps. The properties of the biodiesel produced, which were evaluated, meet the ANP biodiesel standards required for marketing.

1. Introduction

Biodiesel is considered a renewable fuel, as vegetable oil and animal fat are the main raw materials for its production. It has higher flash point than mineral diesel, ensuring greater safety in use and also presents appropriate viscosity for burning in diesel engines. It is biodegradable, non-toxic and has excellent lubricity, providing longer life to components of engines [1].

The most common method for producing biodiesel is the transesterification, a reaction between a triacylglycerol, from vegetable oils or animal fats, and a short chain alcohol producing alkyl esters of fatty acids and glycerol as a co-product [2,3]. Biodiesel has similar physicochemical properties to that of mineral diesel and can be used in engines without modification [3].

The potential use of a raw material in biodiesel production depends on several factors, such as availability, cost, storage properties and performance as fuel [4]. Given the high biodiversity, large territory, climate diversity and soil conditions, Brazil contains different oil sources for biodiesel production including soybean, canola, castor, babassu, cotton, palm and sunflower [5]. Since Brazil has a well stablished soybean production, presently most of biodiesel produced in the country used soybean oil [5,6]. Canola presents a high percentage of seed oil, 34–40%, which is approximately twice the value found in soybeans and correspond to 84% of all raw materials used in global biodiesel production [7,8].

Regarding the alcohol used in the process, in Brazil, the use of ethyl route has a strategic importance, since the availability of raw materials and technology allows an economically viable production of ethanol by fermentation processes, resulting in a cheaper product than the methanol. In biodiesel production, the use of vegetable oils and ethanol derived from sugarcane makes the process completely independent from petroleum, providing environmental benefits and generating a socio-economic development program [9,10].

After transesterification, the final mixture is mainly composed of alkyl esters of fatty acids, residual alcohol, glycerol, catalyst, mono-, di- and triglycerides. These and other contaminants in the biodiesel can cause operational and environmental problems and must be separated so that esters can be used as fuel [9,11]. The quality of B100 biodiesel in Brazil is specified by the National Agency of Petroleum, Natural Gas and Biofuels (ANP), based on the American ASTM D6751 and European EN14214 standards, with some modifications to meet the Brazilian raw material requirements [12].

One of the most important parameters for quality control of

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biodiesel is the amount of free glycerin, which has a maximum allowed limit of 0.02%. A high concentration of free glycerin can result from the separation of glycerin, causing problems during storage and in the fuel injection system [9,13].

Thus, besides controlling all the parameters influencing the reaction of biodiesel production, the stage of glycerol separation is very important to achieve a quality product, free of impurities and no risk of corrosion to the engine. Conventional purification procedures use a large volume of water, which varies depending on the impurities present, and provides the generation of a large amount of effluent that must be properly treated and disposed [14].

Studies in the literature [15–19] indicate that distinct methods have been applied for glycerol removal and biodiesel purification. Among the alternative methods of separation, the process with membranes has many advantages and good prospects for use in the separation and purification of biodiesel. The use of membranes can provide high quality and purity biodiesel, and environmental and economic advantages for reducing the amount of water used and eliminating the use of adsorbents. Apart from the reduction of costs related to effluent treatment, studies indicate that the use of membranes in the processing of biodiesel provides reduced power consumption, enabling the application of this process in industrial scale [20].

Regarding the use of membranes for biodiesel production, the published studies have focused on the use of membrane reactors to improve conversion into esters [21–23] and the use of membranes in the purification step, after separation by decantation [18,24–28]. Direct use of micro- and ultrafiltration after transesterification for the separation of phases, without previous decantation, was studied in previous works developed by our research group. The first experiments [29] were carried out with microfiltration membranes using synthetic mixtures of biodiesel, glycerol, and ethanol. They were evaluated the effects of the membrane porosity, transmembrane pressure, and the ethanol concentration in the mixture. The results indicated the influence of ethanol on behavior of the emulsion and the potential of applying ceramic membranes in the separation of glycerol and biodiesel.

Afterwards [30], the experiments were performed using the reactional mixture produced by ethylic transesterification of degummed soybean oil. Considering the emulsion behavior of the mixture produced in the transesterification of degummed soybean oil, it was developed a methodology of addition of acidified water, aiming to destabilize this emulsion and improve the retention of glycerol by the membrane. The results showed the key role of both ethanol and water in the formation of agglomerates in the dispersed phase, since the glycerol retention after adding water was significant, with glycerol mass content in the permeate below 0.02%, indicating the efficiency of the used methodology.

Continuing the study [31], it was evaluated the influence of the amount of acidified water added on the separation of glycerol and biodiesel using micro and ultrafiltration ceramic membranes. The results showed that the amount of acidified water added influences the emulsion properties and, consequently, the distribution of agglomerate size containing the glycerol.

The current work aimed at improving knowledge on the behavior of ultrafiltration with ceramic membranes in separating glycerol from biodiesel using different feedstock. To this end, it was evaluated the influence of oil quality on ultrafiltration of the reaction mixture produced after ethyl esterification of vegetable oils with different characteristics. The separation of glycerol was performed using ultrafiltration membranes, and the best operating condition was evaluated in terms of permeate flux and quality of the product.

2. Experimental section

2.1. Production of biodiesel

The reaction mixtures needed for the experiments were prepared by alkaline ethyl transesterification of vegetable oils. They were used degummed soybean oil and crude canola oil donated by Cocamar (Maringá, Paraná State, Brazil), and commercial refined soybean and canola oils. The anhydrous ethanol (99.4% purity) was donated by Cocafé, Astorga, Paraná State, Brazil and sodium hydroxide (NaOH) was purchased from Biotec.

The previous results of the study of the yield of esters as a function of reaction parameters [30] indicate that the reaction temperature for obtaining a high ester yield depends on the acidity of the oil. In this way, when used refined oils, the reaction temperature was 45 °C, and when used crude and degummed oils, the transesterification was carried out at 30 °C. For all oils, the oil: alcohol molar ratio used was 1:7.5 and the amount of catalyst was 1% of mass of oil. The reaction was prepared in a 2 L batch reactor and the reaction time was 1 h. The reactor contents were mixed using a mechanical stirrer.

2.2. Ultrafiltration runs

The experimental equipment consisted of a micro- and ultrafiltration pilot unit UF NETZSCH, Pomerode, Santa Catarina State, Brazil, model 027.06-1C1/07-0005/AI, operating in cross-flow conditions. A detailed description of the experimental unit was presented in a previous study [30].

The hydrophilic ceramic membranes used in the experiments were made of tubular α-Al_2O_3/TiO_2 (Shumacher GmbHTi 01070), 250 mm long, 7 mm in diameter, and 0.005 m^2 filtration area, purchased from Andritz, Pomerode, Santa Catarina State, Brazil. The tests were carried out with ultrafiltration membranes of 0.05 μm and 20 kDa. All ultrafiltration experiments were performed at 50 °C.

In the first step, ultrafiltration of the mixture obtained from refined canola oil was evaluated. For all tests, before ultrafiltration of the mixture, the addition of acidified water (0.5% HCl) was evaluated in the mass concentrations varying from 0% to 20% in relation to the total mixture mass, under transmembrane pressure of 0.5–2.0 bar. As previously discussed [31], addition of water affords the formation of dispersed phase containing water, glycerol, catalyst, salts and other water-soluble substances, distinct from the continuous phase rich in ethyl esters and unreacted oil.

Next, ultrafiltration experiments were run with reaction mixtures produced with refined soybean, degummed soybean, refined canola and raw canola oils. The experiments were performed only with the 0.05 μm membrane, under pressure of 1.0 bar, with prior addition of 10% acidified water.

Finally, it was evaluated the separation of glycerol from the mixture produced with raw canola oil. In these experiments were used the membranes of 0.05 μm and 20 kDa, under pressures of 1.0, 2.0 and 3.0 bar and water concentration of 10%.

Approximately four liters of the mixture were poured into the feed tank of the module for each run. After heating to 50 °C, the mixture was pumped into the membrane and the pressure was set to begin the permeate flux. All the runs were undertaken with a flow rate of 700 L/h, corresponding to a tangential velocity of about 8 m/s. The permeate was collected and the concentrate was completely recirculated to the feed tank.

The performance of the glycerol separation process by ceramic membranes were characterized in terms of glycerol rejection, stabilized permeate flux, percentage of flux decline and flux with pure water after membrane cleaning.

The reaction mixture obtained after adding acidified water was