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STUDY OF THE ULTRAFILTRATION BEHAVIOR OF MIXTURES CONTAINING GLYCERIN

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Abstract: The intense search for renewable energy sources and sustainable processes aimed at reducing environmental pollution and global warming has stimulated the global market for biofuels. Biodiesel has great prominence in the national energy matrix, however, its large-scale production generates large amounts of glycerin. Glycerin has many industrial applications when it is purified. Purification through membranes has many advantages, especially in terms of the environment. With the use of mixtures containing glycerin, it is possible to study the behavior of filtration, since the consequences in the use of ethanol and biodiesel, for example, are different. Analyzing mixtures with similar compositions, varying the composition of biodiesel and ethanol only, the filtration flow is greater with greater presence of biodiesel, but the membrane clogging is greater, and therefore the filtration time is also smaller.
Keywords: Glycerin.

INTRODUCTION

From the recent interest in the development of renewable energies, biodiesel has attracted numerous researchers around the world as a viable alternative to reduce the consumption of fossil fuels. This great interest attributed to biodiesel is due to the fact that it is a renewable, biodegradable fuel with low levels of pollutant gas emissions (GOMES et al., 2012).

The increase in biofuel production implies an excess of glycerol in the market, contributing to lower marketing costs. (QUISPE, CORONADO and CARVALHO, 2013). According to Tan et al. (2013) for the production of 10 kg of biodiesel through the transesterification process, approximately 1 kg of crude glycerin is produced. In addition, according to Quispe, Coronado and Carvalho (2013), the crude glycerin produced contains a large amount of contaminants, which reduces its quality. Therefore, purification alternatives are sought in order to further increase the economic viability of biofuels. (HUNSON, 2013).

The study by Mota et al. (2009) states that glycerol is called glycerin when purified commercial products contain at least 95% glycerol.

According to Ardi, Aroua and Hashim (2015) it is possible to find several techniques for glycerin purification, for example, vacuum distillation, ion exchange adsorption, adsorption using activated carbon, membrane separation technology, among others. In the membrane separation process, the existence of a driving force is essential, which can be a pressure or concentration gradient. In processes that use porous membranes, such as microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF), the driving force is the pressure gradient across the membrane (HABERT et al., 2006).

Glycerin blends are composed of several compounds possibly found in the biodiesel industry. These blends are made to simulate glycerin which is a by-product of the biodiesel reaction. By simulating the mixtures, it is possible to carry out the purification by relating the glycerin that is produced industrially, but using mixtures made in the laboratory itself.

In this work, the objective is to analyze the ultrafiltration of a synthetic mixture using ceramic membranes, seeking to know the behavior of each component in the filtration.

METHODOLOGY

MATERIALS

The crude glycerin was donated by the biodiesel producer BSBIOS (Marialva, Paraná). Biodiesel was produced in the laboratory with soybean oil from the company Cocamar (Maringá, Paraná), ethanol from Distillery Melhoramentos (Jussara, Paraná), and sodium hydroxide in P.A. of the brand

F. Maia Indústria e Comércio. The acidified water was made with distilled water produced in the laboratory and phosphoric acid 85% P.A. of the brand F. Maia Indústria e Comércio.

METHODS

Biodiesel production: Biodiesel was produced by the transesterification reaction, following the results obtained from the experimental design of biodiesel production as presented by GOMES et al. (2011)

Biodiesel purification: Biodiesel was separated by wet washing, following the results obtained in the biodiesel purification experiments as presented by Geris et al. (2007).

Purification of glycerol by ultrafiltration: Ceramic membranes of α-Al_2O_3/TiO_2 (Shumacher GmbH-Ti 01070) purchased from NETZSCH, of the tangential flow tubular type, with a length of 250 mm, diameter of 7 mm and a filtration area of 0.005 m2, with an average diameter of 5 kDa pores. The experiments were carried out in the pilot ultra/microfiltration unit UF NETZSCH model 027.06-1C1/07-0005/AI, installed in the Separation Processes Laboratory II in the Chemical Engineering Department, as shown in figure 1.

The feeding system of the experimental module is composed of a reservoir with a capacity of 5 liters, in stainless steel, with double jacket and a positive displacement pump with frequency inverter, which allows the operation in different flow rates, that is, it makes it possible to vary the tangential

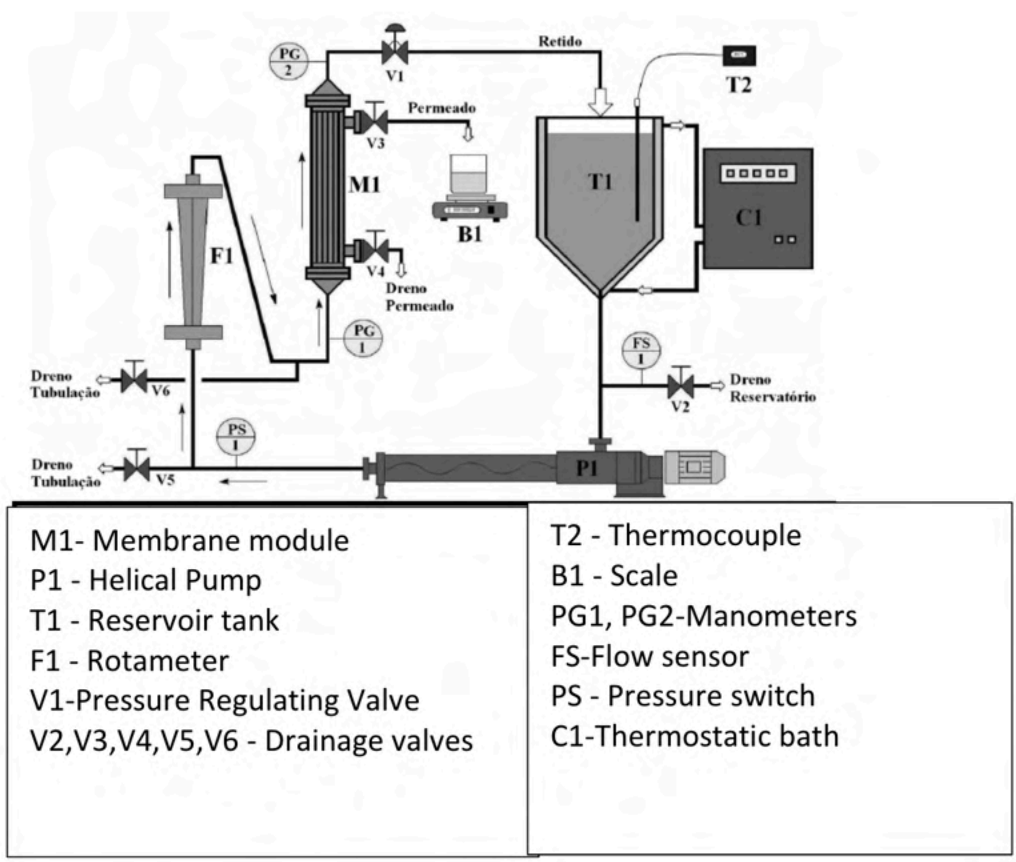

Figure 1. Schematic drawing of the micro and ultrafiltration pilot unit (GOMES, 2012).

filtration velocity. The instrumentation is composed of two pressure indicators (manometers) and a rotameter to indicate the flow of the feed pump. The safety devices present in the unit are a pressure switch, which limits the pump's operating pressure, and a device against dry running of the pump. The membranes used are installed in a stainless steel module, fixed to the pipeline by means of flanges.

For the purification of the mixture, they were heated to 60°C in the feed tank and then pumped into the pipeline. The pressure was adjusted by means of a manual valve and the temperature controlled with a thermostatic bath. The permeate was collected and the concentrate fully recirculated to the feed tank.

The permeate flux was obtained by determining the collected permeate mass as a function of time, measured on a semi-analytical balance (BG 4000-Gehaka), and calculated according to the equation.

$$J_{perm} = \frac{m_p}{A.t} \quad (1)$$

A: membrane permeation area in m^2.
t: time interval in hours;
J_{perm}: permeate flow ($kg/h.m^2$)
m_p: permeate mass in kg

Two mixtures with different compositions were made, the components were weighed and mixed, totaling a mixture between 3 and 4 liters. These mixtures were made to simulate the impurities present in glycerin as a co-product of the industrial production process of biodiesel. Table 1 presents the compositions used.

All experiments were performed at a flow rate of 700 L/h, which corresponds to a tangential velocity of approximately 8 m/s.

The average of all flows is called the average flow. In addition to the average flow, the stabilized flow was calculated, being the average of the last 10 flow values.

After each processing, the experimental unit was immediately cleaned in order to preserve all equipment and restore the permeability of the membrane used. The module was cleaned with multiple washes with water, soap, 2% NaOH solution and finally deionized water. The membrane was cleaned with interspersed washes of a hot solution of 2% NaOH and 2% HCl.

RESULTS AND DISCUSSION

In figure 2, the permeate fluxes of mixture 1 and 2 are shown, using the 5kDa membrane and 3 bar pressure.

Mixture 1 had an average flow of 266.23 $kg/m^2.h$ and a stabilized flow of 198.50 $kg/m^2.h$. Unlike mixture 2, which had an average flow of 339.50 $kg/m^2.h$ and stabilized flow of 284.30 $kg/m^2.h$.

With the different compositions, it is possible to compare the influence of the increase in the percentage of biodiesel and

Composed	Mix 1	Mix 2
Crude Glycerin	70%	70%
Acidified water (0,5% H_3PO_4)	10%	10%
Ethanol	10%	1%
Biodiesel	10%	19%

Table 1 - Compositions of mixtures.

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the decrease in the percentage of ethanol present in the mixture. Ethanol, considered a co-solvent, causes glycerin to be dissolved in biodiesel, and thus, the lower the percentage of ethanol in the mixture, the greater the permeate flux. This is justified by the fact that when biodiesel is not dissolved in glycerin, flow is facilitated because of the presence of smaller particles. As in mixture 2 the percentage of biodiesel is higher and ethanol is lower than in mixture 1, the average and stabilized fluxes were higher than in mixture 1. However, in the presence of a higher percentage of biodiesel, and therefore, a greater amount of impurities, the flow decrease started more quickly, that is, the fouling effect was more evident in mixture 2 as there was an increase in biodiesel compared to the previous mixture. This characterizes a greater amount of impurities justifying the abrupt drop in the flow.

Over time, the accumulation of residues on the membrane, also known as fouling, causes the purification flux to drop, causing the stabilized flux to be less than average in both mixtures. This fouling process occurs due to the impurities present in crude glycerin and biodiesel, clogging the membrane pores causing a decrease in the permeation area and thus a reduction in the permeate flux over time.

CONCLUSION

Under the conditions in which the tests were conducted, it is concluded that:

Mixture 2, which has a higher percentage of biodiesel, showed a higher permeate flux due to the decrease in viscosity. On the other hand, the large amount of impurities that this mixture presents caused a shorter filtration time, due to the fact that the membrane pores are clogged more quickly.

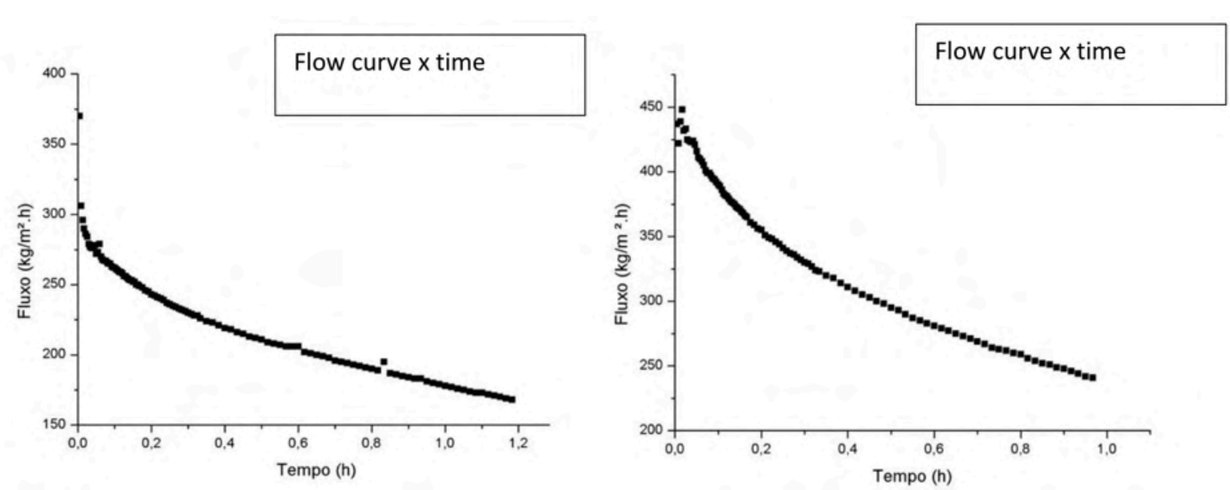

Figure 2 - Graphs of mixture 1 and 2, respectively.

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