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Synthesis of biodiesel from soybean oil through alkaline transesterification

Síntese do biodiesel a partir de óleo de soja por meio da transesterificação alcalina

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RESUMO

Os impactos ambientais, resultantes do uso de combustíveis fósseis, tem intensificado a necessidade de desenvolver fontes de energia renováveis. O biodiesel é um combustível alternativo aos combustíveis fósseis e pode ser definido como um combustível renovável normalmente produzido da transesterificação de óleos vegetais. Este vem sendo usado para diminuir os problemas ambientais, como o aquecimento global. Este trabalho consiste na produção de biodiesel utilizando como matéria prima principal o óleo de soja, por meio da transesterificação alcalina, seguida de algumas características físico-químicas: pH, densidade, índice de corrosão. Os resultados após a pré-lavagem do óleo resultou em um biodiesel de melhor qualidade. Sendo isto confirmado pelos ensaios de caracterização, com um pH de 7,5, uma densidade de 871,2 kg/m^3 e um fator de corrosão 1b, esses dados apresentaram valores próximos e outro dentro dos parâmetros da ANP.

Palavras-chave: Biodiesel, transesterificação alcalina, fator de corrosão.

ABSTRACT

The environmental impacts resulting from the use of fossil fuels, has intensified the need to develop renewable energy sources. Biodiesel is a fuel alternative to the fossil fuels and can be defined as a renewable fuel normally produced from the transesterification of vegetable oils. It has been used to diminish the environmental problems, such as global warming. This work consists in the production of biodiesel using as main raw material the soybean oil, through alkaline transesterification, followed by some physical-chemical characteristics: pH, density, corrosion rate. The results after pre-washing the oil resulted in better quality biodiesel. This being confirmed by the characterization tests, with a pH of 7,5, density of 871,2 kg/m^3 and corrosion factor 1b, these data present values close to or within the parameters of ANP.

Keywords: Biodiesel, alkaline transesterification, corrosion factor.

1 INTRODUCTION

The search for energetic sources of minor environmental impact due to the crescent social, economic and technological development attached to the increase of the population and pollution, results in a huge energetic consumption. One of the alternative technologies most promising is the use of biodiesel, which proves being a viable source of renewable energy (Knothe et al., 2006).

Biodiesel is perfectly miscible and physical-chemically similar to the mineral diesel oil, can be, as well, used as a natural substitute to the petroleum diesel, being able to be added to this one or completely replace it, and can be obtained through vegetable oils, residual oils such those from frying, and animal fat (Ramos, 2011; Pereira, 2007). Some of the characteristics of the biodiesel which make possible its utilization in diesel engines are the presence of high concentration of cetanes, suitable viscosity among some others (Machado, 2013).

In December 2018, soybean was the main raw material used in the national production of biodiesel (67,75%), and following were other raw material such as bovine fat (12,30%), other fatty materials, that correspond to traditional raw material in tank, and reprocessing of by-products generated in the production of biodiesel (11, 67%), palm tree (3,22%) and etc. (ANP, 2019).

Biodiesel presents several advantages, such as be produced from natural sources and when compared to the mineral diesel, for example, has low toxicity, it is not inflammable, it is biodegradable, does not have sulfur in its composition, can diminish the level of emission of pollutant gases, among others. However, biodiesel also has some disadvantages, such as: less speed and bigger wear of the engine, higher emission of nitrogen oxide (NOx) etc. (Paiva, 2010).

The obtaining of biodiesel can be through micro-emulsion, catalytic cracking and transesterification reaction, although, according to Petrobrás, there are other methodologies, such as: acid esterification, thermo-catalytic cracking, hydro-treatment-route. (Esalq/USP, 2019). There is also the production of biodiesel by subcritical hydro-esterification/chemical done in two phases: oils hydrolysis in fatty free acids (FFAs) in subcritical water and chemical esterification of FFAs in biodiesel (Santos et al., 2019).

Transesterification is the most used process for the production of biodiesel and presents the Best efficiency (Demirbas, 2003; Zhang et al., 2003; Ferrari et al., 2005; Keera, Sabagh and Taman, 2018; Navas et al., 2018), defined as a reaction that aims the reduction of viscosity of the triglycerol. Its process occurs in the presence of homogeneous and heterogeneous catalysts – which can be acids or bases (Stone, 1992), where one lipid react with an alcohol (generally methanol or ethanol), obtaining as product the alkyl ester (biodiesel) and the glycerin. (Felizardo et al., 2006). Also other catalysts such as enzymatics, done through liquid enzyme and the one of immobilizing enzyme are used in the transesterification process (Andrade et al., 2019).

The global process of synthesis of biodiesel is a sequence of three consecutive and reversible reactions in which diglycerides and monoglycerides are formed as intermediaries. Normally, transesterification is made by basic or acid cathalysis. However, in homogeneous cathalysis, alkaline catalysts (sodium hydroxide, potassium hydroxide) allows faster process than the acid cathalisys (Knothe et al., 2006; Santana, 2008).

The route of synthesis of biodiesel that will be studied is related to the transesterification process, which can be an alternative to the reduction of the production coast of the wanted product (Machado, 2013).

Commonly used as an example is the junction of the oil with methanol and the NaOH as the catalyst of this reaction, showed in Figure 1.

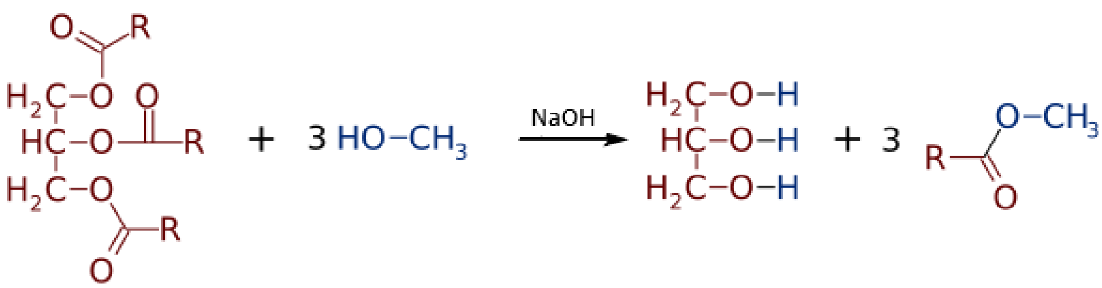


Figure 1: Transesterification reaction in alkaline mean.

A methyl ester of fatty acid is obtained in this process (Biodiesel) and glycerine as by-product, that is removed by the means of decantation. The two products of the reaction have different densities.

The glycerin formed is used by pharmaceutical, cosmetics and explosive industries (Geris, 2007). The purification system of the glycerin and the reuse of the methanol and fatty acids pointed clearly an economic alternative and environmentally viable to the biodiesel industry (Stracke et al. 2018).

Therefore, the objective of this work was to produce biodiesel from the vegetal soybean oil, being necessary produce some characterization of the raw material before beginning the production process. Then, we have got the biodiesel, determining some physical and chemical characteristics such as density, pH and corrosion in copper.

2 METHODOLOGY

2.1 ANALYSIS OF RAW MATERIAL

In the analysis of the raw material (soybean oil) the acidity was observed to determine the percentage of fatty acids and the density of the vegetable oil.

2.1.1 acidity and density

To determine the acid number was weighed 2.0g of soybean oil in an Erlenmeyer. Soon after, 25 mL of methanol was added to the oil. Subsequently, titration of the solution with 0.1M potassium hydroxide, previously standardized with potassium biftalate, was carried out .

Phenolphthalein was used as indicator. Then the titration was carried out on white, or 25 mL of methanol without the presence of oil. With the data found, it was possible to obtain the acidity index for soybean oil, from Equation 1, as a percentage of free fatty acids.

$$AGL = \frac{(V\ Sample - V\ blank\ ) \times\ \ M\ fat\ acid\ \times C\ \ alkaline\ \times 100}{m\ \ sample}$$

At where:

- $V_{(sample)}$: Volume of KOH solution used in the titration of the sample (mL);
- $V_{(white)}$: Volume of KOH solution used in titration of blank (mL);
- $m_{(sample)}$: Oil mass (g);
- $C_{(base\ )}$: Molar concentration of KOH solution (mol/L);
- $M_{(\ fatty\ acid\ )}$: Molar mass of linolic acid (g/mol).
- The density for pure oil was determined by pycnometry at a temperature of 25 °C.

2.2 OBTAINING BIODIESEL

Firstly, a volume of 400 mL of the soybean oil was measured, then the sample was brought up to 60 °C. After reaching the desired temperature, was added an alkaline solution of methanol prepared with 100.4 mL of ethanol and 7.2 g of KOH. The ration medium remained under constant stirring at the quoted temperature for a further 30 minutes (Ma & Hanna, 1999).

After the homogenization time, the reaction product was placed in a settling funnel to allow separation of the phases, glycerol and biodiesel (Figure 2). This process was carried out in 24 hours , until there was no turbidity.

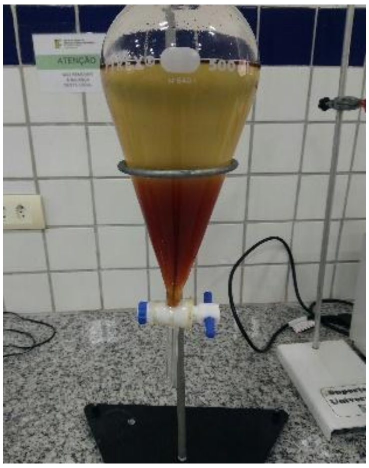


Figure 2: Separation of phases. Biodiesel on the top and glycerin on the bottom.
(Source – The Author)

We remove the more dense phase (glycerin), leaving the biodiesel together with the catalyst. After this, we started the washing process for pH correction and for the removal of the catalyst (KOH). A sodium chloride (NaCl) solution of 5% was added to the funnel. Still in the washing process was performed in duplicate, only with hot water, which is represented in Figure 3.

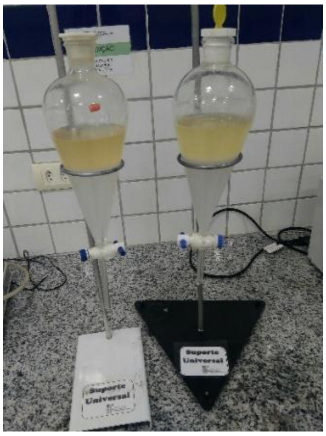


Figure 3: Washing procedure to remove KOH.
(Source – The Author)

Thereafter the washing product was withdrawn from the funnel and discarded. The biodiesel was placed in a Becker and taken to the hot plate under constant stirring at

110 °C in the range 45 minutes, so that there was evaporation of the water that was present in the medium. Figure 4 shows this process.

After cooling, the biodiesel was placed in a flat bottom flask. Subsequently, the product was subjected to physical-chemical analysis, such as: pH , density and corrosion potential in copper

(Source – The Author)

2.3 BIODIESEL ANALYSIS

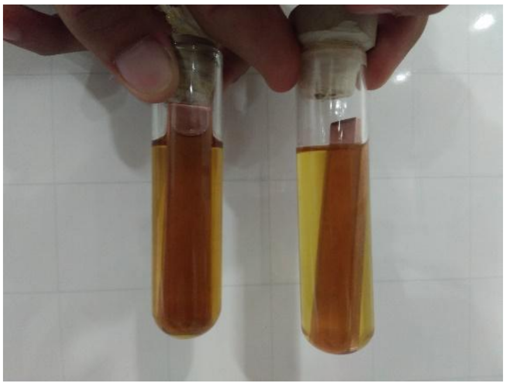
The physico-chemical analysis of biodiesel were carried out through pH, density and corrosion potential in copper.

2.3.1 PH and density

We removed a 20 mL aliquot of biodiesel to determine the pH. For this procedure we use the Mounting Plate for Water Solutions Mpa-210. To determine the biodiesel density, the method was used a pycnometry at a temperature of approximately 26 °C. This process were made in duplicate.

2.3.2 copper corrosion

In order to verify the corrosion potential of the biodiesel produced, we measured two volumes of approximately 30 mL and put them in two glass tubes together with the copper electrodes and then these tubes were brought to the thermostatic bath , at a temperature of 60 °C within metal capsules filled with water, about to 180 min. A Figure 6 shows these samples.



(Source – The Author)

3 RESULTS AND DISCUSSION

The results of the acidity of the raw material, the production of biodiesel and their respective characterizations are shown below.

3.1 ACIDITY OF RAW MATERIAL

The Table 1 shows the mass and soybean oil volume values, together with the volumes found in the blank titration.

	SOYBEAN OIL	WHITE
V (mL)	0,7 ± 0,05	0,5 ± 0,05
m (g)	2,0537 ± 0,0001	-

According to the data in Table 1, based on the highest percentage of the oil composition, linoleic acid (Celante , Schenkel & Castilhos, 2018; Navas et al., 2018) and meeting their molar mass 280,474 g / mol, with the aid of Equation 1 were found % FFA. The mean value of the sample was 0.2731 ± 0.01 % for soybean oil.

According to the National Health Agency - ANVISA (2005) the acid value of refined soybean oil in grams linoleic acid per 100 g of oil is at most 0.3 %. Therefore, comparing the values with the one obtained for soybean oil, we observe that it is within the established norms.

The acidity indexes of the raw materials used in the production of biodiesel must have low values, since the free fatty acids and water impair the good performance of the biodiesel production process. Naik et al ., 2006, suggest that the amount of free fatty acids present in oils and fats should be less than 3% for transesterification to be efficient.

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3.2 OBTAINING BIODIESEL

After the oil is heated, it was observed the formation of two phase in the mixture, which consisted of a larger, less dense layer of a liquid similar to oil and another layer of a more viscous reddish liquid, these two f the s were biodiesel and glycerin, respectively.

After the washes, the catalyst was removed , leaving only biodiesel and moisture. By heating the product, the water will be evaporated leaving only the pure and free biofuel residues (Figure 7). Therefore, the physico-chemical characterization .

(Source – The Author)

3.3 PHYSICAL-CHEMICAL CHARACTERIZATIONS

The data of the density of soybean oil and biodiesel can be seen in Table 2.

Table 2: Mass, volume and density of soybean oil and biodiesel.

Substances	**m (g)**	**V (mL)**	**d (** kg/ m^3**)**
Refined-soybean oil	22,9883	25,0	9153
Biodiesel	6,1638	7,0712	871,2

According to the Technical Regulation for Fixation and Quality of Oils and Vegetable Fats, established by ANVISA (1999), the relative density of soybean oil at a temperature of 20 ° C remains between 919 and 925kg / m^3. Therefore, the density found in the procedure is close to the data of the required quality standards.

As to the density of biodiesel, we found a value of 871,2 kg/m^3 . This number is close to the values established by ANP (National Petroleum), which determines the density of biodiesel 875 kg / m^3 and 900 kg / m^3, at 20 ºC. Studies show that the density of biodiesel can vary between 865 kg / m^3 and 895 kg / m^3, that is, depends on the raw material they are produced (Veljković et al., 2018; Cesar et al., 2018).

Biodiesel density is directly linked to the molecular structure. The greater the length of the carbon chain, the greater its density, however, this value will decrease the greater the number of unsaturations present in the molecule.

The pH of the biodiesel sample, in duplicate, was in the range of 7.4. This value is close to that allowed by ANP Resolution 45/ 2014, which considers a neutral pH (7) .

As for the copper mass loss test, which was carried out according to a standardized color scale, biodiesel presented a classification corresponding to 1b, presenting a very low corrosivity to the copper blade, that is, within the established limit (Figure 8). In this case, biodiesel can be used in a diesel cycle engine, since the corrosivity to copper is an analysis in which it tends to determine if a fuel can cause corrosion in the engine or metal parts (Ferreira, 2009). Thus, it is perceived that biodiesel is a possible solution to reduce pollutant gases and does not cause corrosion in the engine.

Figure 8: Corrosion check on copper blade.
(Source – the author)

4 CONCLUSION

From the analysis of the raw material used it can be affirmed that the data obtained fit the standard values found in the literature. It is possible to emphasize that the stage of characterization of the raw material is fundamental importance as it influences the quality and preparation of biodiesel. The production of the products occurred as planned, forming a well-defined biphasic system.

The fact that the biodiesel obtained comes from a renewable source, whose raw material is abundant in Brazil, makes its study important, aiming at a reduction of the toxic gases to the environment. For this, it is necessary to continue the research to observe the gases emitted during the combustion, as well as a study on the economic viability.

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