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EXTRACTION AND CHARACTERIZATION OF FUSEL OIL FRACTIONS, FOR THE PRODUCTION OF BIODIESEL

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Abstract: Interest in alternative and renewable energy sources that meet global demand is constantly increasing. This factor associated with the environmental impacts caused by fossil fuels has stimulated research and interest in the development of renewable fuels, such as ethanol. In this context, Brazil, in addition to having favorable conditions and biomass diversity, dominates the technology for producing ethanol through fermentation, which gives the country economic advantages. The sugarcane industry has tradition and importance in the national economy, even contributing to the reduction of negative environmental impacts. However, in the ethanol manufacturing process, some residues are generated, including fusel oil, which is part of this range of by-products generated through the processing of sugarcane. Some mills sell this by-product, but the vast majority see sugarcane oil as a residue. Most biodiesel is produced via methyl or ethyl, However, in this work it was proposed the extraction, purification and characterization of fusel oil fractions, for the production of sample biodiesel, as well as the physical-chemical characterization of biodiesel samples, here called biofuel. Purification and fractional distillation of the fusel oil were carried out, in alcohol/oil proportions of 9:1, 12:1 and 13:1. To obtain biodiesel, transesterification was carried out by basic catalysis. Ten samples were prepared, with different proportions and reaction times. The physical-chemical characterizations of the samples were determined, as well as the indices regulated by the ANP and ASTM . It was found that some indices, as well as physical-chemical parameters, for some samples, are in accordance with what is established by the ANP. As for the reaction yield, an average value of 75.3% was obtained, which is below the expected yield for ethyl biodiesel, which is in the range of 95%.
Keywords: Sugarcane Industry, industrial residues, fusel oil, biofusel.

INTRODUCTION

The interest in renewable energy sources and alternatives that can meet a global demand is constantly increasing. This factor associated with the environmental impacts caused by fossil fuels has been stimulating research and interest in the development of renewable fuels such as ethanol. In this context, Brazil, in addition to having favorable conditions and a diversity and productivity of biomass, dominates the technology of ethanol production through fermentation processes, which gives the country competitive advantages.

The sugar and alcohol industry, despite all the tradition and importance in the national economy, has been the target of concerns and judgments regarding the negative environmental impacts that its industrial processes operate on the environment (RODRIGUES, REBELATO & MADELENO. 2016).

In the ethanol manufacturing process, various residues are generated, including fusel oil, more popularly known as sugarcane oil, which is part of this range of by-products generated through the processing of sugarcane. Some mills sell this by-product, but the vast majority see sugarcane oil as a waste disposal.

The growing demand of reusing waste from sugar and alcohol processes minimizes the degradation of natural resources (FERREIRA, JAGUARIBE & SILVA, 2020). In this sense, it is of great importance, in countries where there is a large production of ethanol such as Brazil, meet alternatives for the use of waste generated in the process, making ethanol production less pollutant and more profitable.

The Northeast region of Brazil is one of the major producers of sugarcane. The sugar and alcohol industry is very rich, as it uses practically everything from the plant. In the processing of sugarcane, products such as cachaça, sugar, ethanol, brown sugar, molasses are obtained, as by-products we can mention

vinasse, bagasse, biodegradable plastic, fusel oil, among others. (FERREIRA, JAGUARIBE & SILVA, 2020)

Fusel oil is a viscous liquid, yellowish in color and unpleasant odor, being the least known residue of the sugarcane industry. For every thousand liters of ethanol produced, an average of 2.5 liters of fusel oil is generated, which is burned or discarded. Annually, over 80 million of this waste is wasted a year. Of this compound, formed by several long-chain alcohols, only one of them is still used in other types of chemical industry: isoamyl alcohol (CARDOSO et al. 2020). Its disposal causes damage to the environment, as well as to health, fauna and flora. With its fractional distillation, higher alcohols can be obtained, such as propanol, butanol and pentanol, alcohols being one of the ingredients of biodiesel. The production of biodiesel from these fractions of long-chain alcohol, which becomes a good substitute for diesel, being a green, renewable fuel that does not pollute the environment and can be used in any diesel-powered machine. Biodiesel is produced from vegetable cooking oil, but the intention would be to reuse residual oils.

Thus, fusel oil and residual oil to make biodiesel would be waste adding value to waste. The focus is the optimization of the production of this sample biofuel. which has presented a quality within the standards of the ANP and ASTM. Produced from longer-chain alcohols, there is energy savings and reduction in process time, as the shorter the chain, the greater the energy demand.

OBJECTIVE

Extraction, purification and characterization of fusel oil fractions, for the production of sample biodiesel, as well as physicochemical characterization of biodiesel samples, here called biofusel.

MATERIALS AND METHODS

The study was developed at the Federal University of Paraiba (UFPB) at the Center for Technology and Regional Development (CTDR). All analyzes were performed in duplication and the results are the averages.

Fusel oil was received from different plants the States of Paraiba and Pernambuco. The fusel oil chosen for this research was that one demanding a higher purification and had the most similar appearance to cooking oil.

The choice of basic transesterification was due to the fact that this type of reaction demands low temperatures (below 100 °C) and atmospheric pressure, yet providing high yield and low reaction time. Furthermore, the alkaline process is less corrosive than the acid transesterification process.

PURIFICATION AND DEHUMIDIFICATION OF FUSEL OIL

The oil used was commercial soybean oil, widely used in biodiesel derived from soybean oil, in combination with basic catalysts, presents a very expressive yield (Costa., 2011).

Approximately 250 mililiters of fusel oil samples were filtered through a vacuum system, in three repetitions. Was used a vacuum filtration system with a quantitative filter paper. Based on the filtered fusel oil, analyzes of specific mass, humidity, specific gravity, cloud point, flash point, viscosity at 40º C, NMR, and other indices were carried out.

FUSEL OIL DISTILLATION

In this step, 500 ml of the filtrate fusel oil was added to a round bottom distillation flask with a capacity of 1 liter. The distillation procedure was set up with an electric heating mantle, Vigreux distillation column, condenser with ground joint, claws, universal support and silicone hoses, coupled to a temperature controller. After assembling and feeding the entire system with fusel oil, heating

began, removing the fractions at 5 different temperatures. The analyzes were performed on the fractions.

The Vigreux column was chosen because its configuration allows exchanges between the gaseous phase and the thin layer of liquid flowing through the container wall (MAYER *et al*, 2015). In addition, it has advantages such as: (1) the amount of theoretical plates remains constant for wide ranges of load developed by the distiller, (2) it presents a high efficiency in the separation of substances constituted by several compounds, as is the case of fusel oil and (3) provides an even distribution of liquid flowing to the center, thus increasing separation efficiency.

The initial temperature was room temperature 25ºC, taking some time to reach the first desired temperature of 80ºC, the boiling point of ethyl alcohol. At each desired temperature, the first part of the Fraction was allowed to drain, subsequently collecting 100 ml of distillate. Fractions were named from F1 to F5. The fractions collected were respectively at temperatures of 80ºC, 93ºC, 100ºC, 117ºC and 138ºC. The intention was to start with ethanol and reach higher alcohols, including propanol, isopropanol and isoamyl alcohol.

CATALYST USED IN BIOFUEL SYNTHESIS

The choice of basic transesterification was due to the fact that this type of reaction demands low temperatures (below 100°C) and atmospheric pressure, yet providing high yield and low reaction time. Furthermore, the alkaline process is less corrosive than the acid transesterification process.

The alkaline catalyst chosen for the transesterification reaction in this work was sodium hydroxide (NaOH), as it increases the reaction speed by up to 4000 times.

SOYBEAN OIL CHOICE

The oil used in this work was commercial soybean oil, widely used in most studies dealing with the subject, and since biodiesel derived from soybean oil, in combination with basic catalysts, presents a very expressive yield (QUESSADA et al. , 2010)

BIOFUEL SYNTHESIS

Figure 1 shows the stages of the biodiesel production process from fusel oil, using soybean oil, synthesized by the ethyl route and basic catalysis. A certain fraction was chosen for making the fuel.

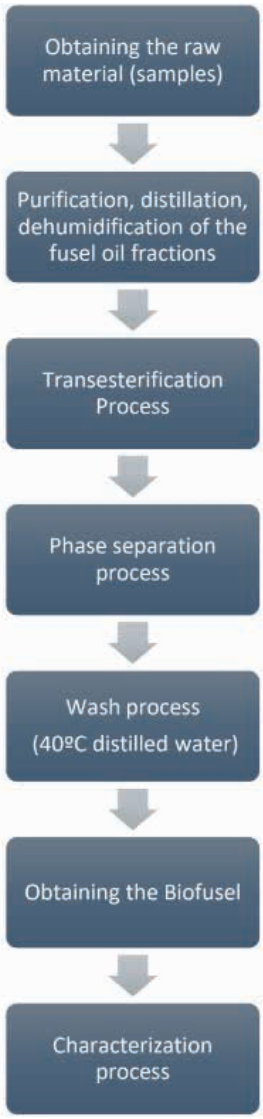

Figura 1 – Biofusel Flowchart

Source: Authors, 2022

Propanol fraction was chosen for making the fuel. Three samples were prepared with the second fraction taken from the fusel oil, with soybean oil, named from A1, A2 and A3, according to Table 1:

Sample	Catalyst	Catalyst (%)	Ratio fusel oil / soy oil (v/v)	Reaction Time (hours)
A1	NaOH	0,9	09:01	2
A2	NaOH	1,2	12:01	3
A3	NaOH	1,5	13:01	4

Table 1: Biofusel production specifications

To carry out all the samples, the temperature was set at 70 °C and agitation at 300 rpm. Then, the products were placed in separation funnels, remaining at rest for 24 hours, for the separation of the biodiesel/glycerol phases.

After separating the phases, the samples were washed with deionized water at warm (40ºC) for 5 minutes, and again placed in separation funnels, in order to remove the amount of washing water, as well as the remaining impurities. After the separation process in which the less dense phase is discarded, the collected samples were placed in a desiccator with silica gel for 10 days to remove moisture. The samples at rest can be seen in Figure 2.

Figure 2 - Biodiesel production (phase separation process)

SOURCE: Authors, 2022.

CHARACTERIZATION OF THE DISTILLATE FRACTION AND SAMPLE BIODIESEL PRODUCED

Once the biofuel was produced, their physico-chemical characterization was evaluated through American Standard Testing material (ASTM) and the National Petroleum Agency (ANP).

DETERMINATION OF DENSITY

Density acts as a characteristic property of a substance. 5ml each sample (biodiesel) were weighed. The cylinder with the biodiesel was weighed and recorded. The final weight was subtracted from the initial weight (mass). The Eq(1) was applied to get the density of the sample:

$$\rho = \frac{M}{V} \qquad (1)$$

DETERMINATION OF CLOUD POINT

5ml of each sample was poured into a test tube, ice was scooped into a beaker and the test tube containing the sample was placed in the beaker containing the ice. It was observed until wax crystals were noticed at the surface of the sample after which the temperature was recorded at this point.

DETERMINATION OF SPECIFIC GRAVITY

The engines are designed to operate with fuels in a certain density range, bearing in mind that the injection pump doses the injected volume. When there is a variation in density, the energy content of the injected portion and the air/fuel in the combustion chamber undergo changes (SHERIVE, 2002).

Density values above the adjustment ranges can lead to the rich mixture of air and fuel to vary its percentage, which can lead to increased emission of pollutants such as hydrocarbons, carbon monoxide and particulate matter. However, density with low values can favor the formation of lean mixtures, which causes loss of engine power and increased fuel consumption. The standards used for this test were ASTM – D1298 and NBR – 7148 (ANP).

The relative density was determined in relation to the specific mass of the standard liquid, that is, water.

5 ml of water was poured into a cylinder of a known weight; the cylinder with the water was then weighed and recorded. The final weight was subtracted from the initial weight (mass). The same procedure was repeated for the samples and readings taken after which Eq(2) was applied.

$$\rho = \frac{\rho_{sample}}{\rho_{water}} \quad (2)$$

DETERMINATION OF KINEMATIC VISCOSITY

10 ml of each sample (biodiesel) was poured into a beaker, viscometer spindle suitable for the quantity of biodiesel poured, was dipped into the sample until it covered a considerable amount of the spindle. The rotational rate was set at 30 rpm for 5 mins, and the reading was taken. The viscosity was determined according to Eq(3).

$$\nu = c \, . \, t \quad (3)$$

DETERMINATION OF FLASH POINT

Flash points are determined experimentally by heating the liquid in a container (cup) and then introducing a small flame just above the liquid surface. The temperature at which there is a flash/ignition is recorded as the flash point.

DETERMINATION OF ACID VALUE

The acid value of an oil is determined by titrating a solution of the oil in diethyl ether with an alcoholic solution of sodium or potassium hydroxide. It is expressed as the amount of KOH (in mg) to neutralize 1 g of oil. For each sample, 2.0 g of biodiesel were weighed, 25 ml of ether/ethanol solution (2:1) and phenolphthalein were added after the solution was homogenized, the sample was titrated until the appearance of a pink color. The acidity calculation (AV) is determined according to Eq(4).

$$AV = \frac{(5{,}6 * V_{KOH} * f_{KOH})}{M_{amostra}}$$

DETERMINATION OF SAPONIFICATION VALUE

Saponification value is a measure of the content of ester linkages. It is determined by back titration of potassium oxide in the presence of phenolphthalein indicator with 0.5 N sulfuric or hydrochloric acid. The method

consists of weighing 2.0 g of biodiesel, adding after weighing, the alcoholic solution of KOH at 4% and heated for 30 minutes. After cooling, phenolphthalein was added to the solution and titrated with 0.5 M Hydrochloric Acid (HCl) until the pink color disappeared. The difference between the amount in mL of HCl spent in the titration is equivalent to the amount of KOH spent in saponification, whose index is given by Eq(5).

$$SV = \frac{(V * f * 28)}{M}$$

DETERMINATION OF PEROXIDE VALUE

This method describes the determination of peroxide values for animal oils and fats, vegetable oils and fats, as well as for flavour and fragrance materials. The peroxide value is a parameter specifying the content of oxygen as peroxide, especially hydroperoxides in a substance. The peroxide value is a measure of the oxidation present. 5.0 g of each sample is weighed and 30 mL of Acetic Acid and Chloroform solution (3:2) are added and homogenized. After the solution has been homogenized, 0.5 mL of KI (Potassium Iodide) is added, it rests for 1 minute and 30 ml of distilled water is added, the indicator used in the analysis is the 1% starch solution. The peroxide value is determined by Eq(6).

$$PV(\text{mEq Peroxide}/1000\ \text{g}) = \frac{A * N * 1000}{M}$$

BIOFUEL YIELD VALUE

The biodiesel yield was calculated using Eq(7).

$$R(\%) = \frac{V_{obtained\ biofusel}}{V_{prepared\ biofusel}} x\ 100 \qquad (7)$$

NUCLEAR MAGNETIC RESONANCE OF FUSEL OIL DISTILLATION FRACTIONS

The study of carbon nuclei by Nuclear Magnetic Resonance (NMR) spectroscopy is a very important technique for determining the structure of organic molecules. The fractions obtained from the fractional distillation of fusel oil were determined from Nuclear Magnetic Resonance experiments, 1H and 13C NMR, and later compared with the data obtained in the literature.

RESULTS AND DISCUSSION

According to the Nuclear Magnetic Resonance of Fusel Oil Distillation Fractions, the second fraction collected by the temperature of was due mostly to the presence of propanol, even though the presence of other alcohols, such as ethanol and isoamyl were detected. This leads to a conclusion that a high level of purification.

Different results were obtained as several tests of the characteristics of oil were carried out on them. Most of them were within limits when compared with ANP and ASTM. Results in Table 2 show the characterization carried out on the biofusel samples A1, A2 and A3, produced according Table 1.

	Unity	A1	A2	A3	ANP (limit)	ASTM
SV	mgKOH/g	187,1	186,3	184,2	170 - 190	
AV	mgKOH/g	0,23	0,23	0,25	0,3	
ρ	kg/m³	936	860	901	701 - 806	850 - 900
SG	-	0.93	0.91	0.88	0.87 - 0.90	0.86 - 0.90
PV	meq/kg	0.73	0.80	0.79	0,5	
v	mm²/s	3.6	4.8	3.9	3.0 - 6.0	1.9 - 6.0
Cloud Point	ºC	14	14	11	-	-

Flash Point	°C	110	126	114	100	130

Table 2: Results of analysis of Biofusel samples

Regarding Table 2, it appears that the fraction of fusel oil is a good substitute for the production of Biodiesel.

The analyzes of specific gravity returned values close to those obtained in the literature, but higher to the limits of ANP and ASTM, between 0.91 and 0.98. The specific gravity of biodiesel is usually lower than that of water and since the fatty acid content always determines the specific gravity; the denser the vegetable oil, the denser the biodiesel. Additionally, as denser as the biodiesel the higher is its energy, and increased strength.

Specific gravity is important for fuel injection systems, because optimal air/fuel ratios (Younis et al., 2009).

For the relative density, all the samples showed to be close to the values established, having as a value between 860 and 936 kg/m^3, showing that fusel oil can be a great substitute for ethyl or methyl alcohol.

The flash point is the lowest temperature at which fuel produces enough vapor to cause an ignition which leads to flame. Biodiesel with higher flash points is less flammable or hazardous than biodiesel with lower flash points. The flash points for all samples were up to 130 °C, which is the minimum ASTM recommended to avoid risk of fire in case of accidents. The flash point values may also be connected with its viscosity, as products with low viscosity tend to have lower flash points (Rusidianasari et al. 2020).

ASTM and ANP did not specify the required cloud point for biodiesel probably due to the variance in climate conditions worldwide, but requires that the cloud point be reported to the customer. If a customer is not careful to select an appropriate biodiesel feedstock, the fuel may get cloudy unexpectedly in cold weather and can block the fuel filters. The cloud point is usually used to test the performance of the biodiesel during unusual low temperatures. Olusegun et al. (2019) and Younis et al. (2009) in their respective studies got a cloud point of 7.30C and -20 °C respectively which is quite different from samples results obtained in this study, and that is a very important parameter to analyse, as the lower is the cloud point, the better the biodiesel (Younis et al, 2019).

The kinematic viscosity is usually done to know the flow property of the biodiesel. The samples showed out to be among the limits of the ASTM and ANP, fitting into the international values. It was reported by Rusidianasari *et al.* (2020) that the viscosity of the biodiesel yield will increase with a higher temperature.

With an increase in temperature, there is an increase in the conversion of triglycerides thereby increasing the flow property of the product. Also, the higher the viscosity, the thicker and more difficult for the biodiesel to flow. It also results in an improper atomization of the fuel injector, contributing to air air pollution and several air causative diseases.

For the acid value results, all samples are within the limits established by the ANP of 0.3 mgKOH/g samples standard. Regarding those results, samples within the standard, the acid value represents the necessary mass of an alkaline hydroxide to neutralize free fatty acids. It is shown as well that the ratio of alcohol and oil was fine, as the concentration of catalyst influences the reaction.

Comparing the results of Rossi et al., (2018) who produced biodiesel from soybean oil and obtained the saponification index between 171.17 to 189.4 mgKOH/g, with those obtained in the work, it is possible to infer that the samples are within the values obtained by the study by Rossi et al., (2018). Values above 200 mgKOH/g, may be related to the low molecular weight of fatty acids, impurities in the raw material, among others, and low values are

related to the high molecular weight of fatty acids.

The results obtained regarding the peroxide value showed that the results are above the limit established by the ANP, (0.5 kg KOH/g). This may be related to the processing and the chemical composition of the fusel oil.

The average yield of the biofuel samples was calculated, obtaining of around 84.1%, is below what is expected range of 95%.

CONCLUSION

In the present work, it can be concluded that it is possible to carry out the biodiesel synthesis process from fusel oil, and that it is a new attractive alternative for the reuse of this residue within the sugar and alcohol industry.

The physical-chemical analysis of the biofuel samples made from the distillation of fusel oil, showed that fusel oil can be a great substitute for ethyl or methyl alcohol, since the values are, for the most part, within those established by the ANP and ASTM.

The team believes that biodiesel obtained from fusel oil has enormous potential to be used commercially, and is an abundant product in the sugar and alcohol sector, which will add value to this sector.

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