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Production and Characterization of Biodiesel from Cotton Oil as an Alternative Energy in Substitution of Soybean Oil

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Abstract

Biodiesel production has currently used virgin raw materials that have a direct use for mainly food uses, as in the case of vegetable oils, mainly soybean, and may in some cases affect food safety. Raw materials such as cotton oils that are obtained from seeds, which are the residual products of productive chains, can help food security, energy and the exploration of new sources of energy of less environmental impact. The present work investigated the chemical and physical characteristics of biodiesel produced from cotton oil in comparison to soybean oil (BOA). The results show that the acidity and viscosity of the BOA are within the permissible values of ANP 03/2014, and the viscosity of the BOA product of the transesterification of soybean oil has values of 4.41 ± 0.20 mm^2s^{-1}. Finally, it can be concluded that cotton oil may be an alternative to replace soybean oil; however, the availability of raw material may play an important role.

Keywords: Biodiesel, cotton oil, soybean oil, transesterification.

1. Introduction

The indiscriminate use of fossil fuels and their resulting environmental problems has stimulated the search for and development of new, renewable sources for energy production [1, 2]. Biodiesel can be considered as a renewable source, even if its combustion can cause the emission of carbon dioxide (CO2), this can be converted again into biomass through photosynthesis, this means that the CO2 produced should not in principle contribute to the imbalance of the chemical composition of the atmosphere that could aggravate global warming [3, 4]. However, this may depend on the inherent characteristics of the inputs used to produce biodiesel, and may not have a completely neutral balance sheet when some of the inputs are not from renewable sources [5].

Biodiesel refers to a form of vegetable oil or animal fat-based diesel fuel and as a very promising alternative to replace the diesel oil [6, 7]. One of the renewable fuels widely investigated in the last decade is the alkyl ester derived from long chain fatty acids, better known as biodiesel [1, 8, 9], which can be produced from vegetable oils and animal fats [10, 11]. Vegetable oils and animal fats can not be used directly in diesel engines because of their high viscosity, high density, high glow point and low calorific power. The use of biodiesel as a substitute for diesel oil is mainly due to their similar physical and chemical characteristics [9, 12, 13]. However, the use of raw materials, alcohols, and catalysts can directly shave the properties of biodiesel [14, 15].

The most used raw materials for biodiesel production in the US and Europe are soybean (Glycine max) and rapeseed (Brassica napus), respectively. In Brazil the main raw materials used for biodiesel production are and soybean oil (70%) and bovine tallow (16%) [16]. However, in Brazil, cotton oil is also having an important share in the oil mix to produce biodiesel [17], with the amount of oil of cotton used was increased from 1,904 m3 of the year 2007 to 78,840 m3 to the year 2015 being the third most used oleaginous input (2%) [17].

The properties of biofuels, specifically biodiesel (B100), are governed by technical specifications that depend on the geographical scope in the place where they are, and for the European Union are based on the EN-14214 standards, for the US with the ASTM D-6751 [14], and for the Brazilian territory the ANP standard 03/2014 [18]. Table 1 shows the permissible limits of the European, North American and Brazilian specifications for biodiesel B100, and these have some variations that depend mainly on the inputs used for their production.

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Table 1.Biodiesel technical specifications for B100: Brazilian (ANP), European (EN) and North American standards (ASTM)

Specification/Properties	Units	ANP 03/2014	EN-14214	ASTM-D6751
Specific mass at 20°C	g/cm^3	0,85-0,90	0,86–0,90	-
Kinematic viscosity at 40°C	mm^2/s	3,0-6,0	3,50–5,00	1,9–6,0
Flash point	°C	100 min	120 min	130 min
Cetane number	-	-	51 min	47 min
Sulphur	mg/kg	5,0 max	10,0 max	15,0 max
Phosphorus	mg/kg	10,0 max	10,0 max	10,0 max
Water content	mg/kg	200 max	500 max	500 max
Acid value	mg KOH/g	0,50 max	0,50 max	0,80 max
Free glycerol	% weight	0,02 max	0,02 max	0,02 max
Total glycerol	% weight	0,25 max	0,25 max	0,24 max
Sulphated ashes	% weight	0,020 max	0,020 max	0,020 max
Methanol	% weight	0,20 max	0,20 max	-
Monoacilglycerol	% weight	0,70 max	0,80 max	-
Diacilglycerol	% weight	0,20 max	0,20 max	-
Triacilglycerol	% weight	0,20 max	0,20 max	-
Esters content	% weight	96,5 min	96,5 min	-
Iodine value	-	-	120 max	-
Oxidation stability at 110°C	h	6 min	6 min	-
Corrosiveness by the copper (NBR14359) , 3h a 50°C	-	No. 1	No. 1	No. 3

Source: adapted from [14, 18, 19, 20]

2. Methodology

A. Biodiesel synthesis

The biodiesel produced was through the methyl route by means of basic transesterification of refined soybean oil (SO) and cotton oil (CO). The catalyst used for the reaction was KOH. The reaction conditions were performed taking into account the methodology described by [21]. The molar ratio of methanol and oil was 6:1, excess methanol would help complete the reaction by consuming all long chain fatty acids. The amount of catalyst to be used was 0.6% with respect to the mass of the oil. The reaction temperature was 55°C kept constant for 60 minutes, the oil had to be preheated to 50°C before adding the catalyst and methanol (monoxide) mixture. The stirring has to be kept constant and at low speed allowing the mixture of the oil with the methoxide, a stirring speed near 300 rpm is recommended.

Figure 1 shows the details of the experimental apparatus installed to perform biodiesel synthesis, the system must be assembled taking into account that it is completely closed so that the methanol can react with the oil. The condensation system will allow recovery of methanol.

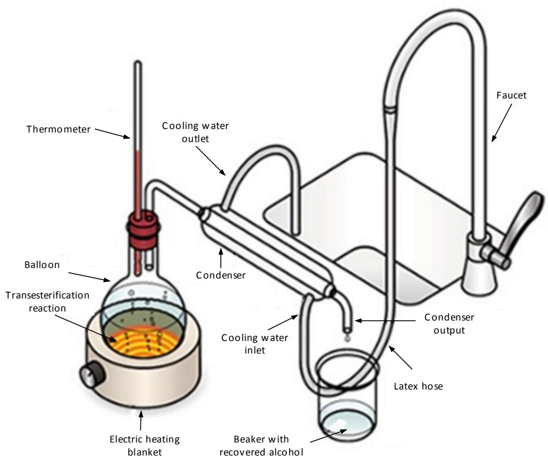

Fig. 1. Scheme of the system for the synthesis of biodiesel.

The obtained biodiesel (raw biodiesel) of both soybean (BSO) and cotton (BCO), after the reaction was separated by decanting in a funnel for phase separation for 12 hours, after which the biodiesel yield was quantified according to equation 1 described by [21, 22, 23]. Subsequently the raw biodiesel after decantation was washed with distilled water at 50 ° C for 5 sequential times, during this process the pH of the wash water decreased from 11 to 6.5, close to neutral value.

$$Yield_{biodiesel}(\%) = \frac{weight\ of\ raw\ biodiesel}{weight\ of\ oil\ used} \times 100 \qquad (1)$$

B. Characterization analysis

a. Ester content

The ester content was determined by the analysis of gas chromatography, following the standard EN 14103 (2001). A gaseous chromatograph Shimadzu-GC with flame ionization detector, RTX-Wax capillary column (Restek, 30 m, 0.32 mm id, 0.25 µm df), split injection (1:50) and injector temperature at 250 ºC was used. The volume injected was 1 µL, column temperature: 210°C and the entrainment gas was helium, with a flow rate of 30 mL/min. Calculation of the ester content is performed using equation 2.

$$Esteres\ (\%) = \left(\frac{\sum A - API}{API} \times \frac{CPI}{C_{sample}}\right) \times 100 \qquad (2)$$

At where; $\sum A$ is the sum of the areas corresponding to the peaks of the esters (C14:0 to C24:0); API is the area of the internal standard (C17:0 - methyl heptadecanoate); CPI is the concentration of the internal standard in the sample injected (mg/L) and C_{sample} is the concentration of the sample injected (mg/L).

b. Acidity Index (AI) and Free Fatty Acids (FFA)

The analyzes of acidity index and the percentage of free fatty acids were carried out on the samples of vegetable oil, as well as on the biodiesel obtained. The procedure for the analysis is to know the amount of KOH in concentration of 0.1 M required for the neutralization of one gram of sample which is previously dissolved in 25 ml of a neutral solvent mixture consisting of diethyl ether and absolute ethanol in 1:1 ratio to which 3 phenolphthalein drops are added as indicator and titrated until the coloration of the solution turns pink. The acidity can be calculated according to equation 3. The percentage of free fatty acids is calculated using equation 4, which expresses the percentage in terms of oleic acid.

$$AI\ (mg\ KOH/g) = \frac{5{,}61 \times M \times V}{W} \times 100 \quad (3)$$

$$FFA\ (\%) = \frac{28{,}2 \times M \times V}{W} \times 100 \quad (4)$$

At where; M is the molarity of KOH; V is the volume of KOH consumed in titration in mL; W is the mass in grams of the sample to holder; 5.61 is the molecular mass of potassium hydroxide; and 28.2 is a constant (mass of oleic acid neutralized by 1 mg of KOH).

c. Dynamic and kinematic viscosity

Viscosity is the resistance that the fluid presents to the flow. The rheological behavior of the samples, both oil and biodiesel, were evaluated by means of the absolute (dynamic) viscosity using the Brookfield viscometer model DVIII ultra. Absolute or dynamic viscosity measures the force required to move a unit of area to a unit distance and the result is given in cP or mPa.se and can be calculated by equation 5. The kinematic viscosity determines the relationship between the dynamic viscosity and a density of the fluid through equation 6, in which case it can use standard values of the different fluids of table 2.

$$\tau_{yx} = \mu \frac{dv}{dy} \quad (5)$$

At where; τ_{yx} is the shear stress (mPa); μ is the dynamic viscosity (mPa.s); and $dv/_{dy}$ is the shear rate (s-1)

$$\upsilon = \frac{\mu}{\rho} \quad (6)$$

At where; υ is the kinematic viscosity (mm2 / s); μ is the dynamic viscosity (mPa.s); and ρ is the fluid density (kg / m3).

Table 2. Densities in g/ml oil and biodiesel of cotton and soybean.

Fluid Density	Sample	Value	Reference
Cotton oil density (25 °C)	CO	0,9170	[17]
Soybean oil density (25 °C)	SO	0,9175	[17]
Cotton biodiesel density (15 °C)	BCO	0,8828	[10]
Soybean biodiesel density (15 °C)	BSO	0,8840	[10]

Source: adapted from [14, 24, 25, 26]

3. Results and discussion

The yield obtained in the transesterification reaction was higher than 100%, yielding 103% for biodiesel of soybean oil and 108% for biodiesel of cotton oil. According to [20], yields above 98% can be reached for transesterification reactions with homogeneous alkaline catalysts, and, for supercritical processes where the catalyst is not used [27, 28], yields between 85-90% can be obtained [6]. According to [21], it is possible to reach yields in excess of 100% by mass, but the molar yields can not exceed 100%, this may depend on the type of alcohol used, higher alcohols may lead to higher yields [29, 30]; the higher or fusel alcohols have more than 2 carbons, thus have higher molecular weight and higher boiling point [29]. However, the chromatography values used to determine the percentage of esters present in biodiesel suggest that there may still be monoglycerides, diglycerides and triglycerides, as well as present glycerol may have increased yield, considering that the percentage of methyl esters for biodiesel from cotton and soy were 68.87% and 69.06% respectively.

The oils used in both cotton and soybean have the best characteristics for the production of biodiesel, which have a low acidity because they are refined oils, with an acid value of 0.04 ± 0.001 for cotton oil and 0 , 13 ± 0.02 for soybean oil. In addition, vegetable oils by their inherent characteristics have a high kinematic viscosity, as shown in table 3, which is decreased by the transesterification process.

Table 3. Physicochemical properties of cotton oil (CO) and soybean (SO).

Property	Unit	CO	SO
Acid value	mg KOH/g	0,04 ± 0,001	0,13 ± 0,02
Free Fat Acids	%AGL	0,19 ± 0,01	0,66 ± 0,08
Dynamic viscosity	mPa.s	36,45 ± 1,13	35,83 ± 1,32
Kinematic viscosity	$mm^2.s^{-1}$	39,75 ± 1,28	39,05 ± 1,50

Table 4 shows the characteristics of the biodiesel obtained from the basic transesterification of soybean and cotton oils. Characteristics such as acidity presented values of 0.02 ± 0.0001 for cotton biodiesel and 0.03 ± 0.0003 for soybean biodiesel. The viscosity of the obtained biodiesel corresponds to the viscosity of the Newtonian fluids, which can be confirmed by Figure 2, which shows the shear rate (s -1) versus shear stress (mPa) and the shear rate (s -1) versus Dynamic viscosity (mPa.s), with Newtonian fluids having a linearity in the graphs shown, different from non-Newtonian fluids. The kinematic viscosity values for biodiesel obtained from cotton oil were 4.46 ± 0.20 and for soybean biodiesel was 4.41 ± 0.20.

The obtained values of acidity and viscosity are within the permissible limits of the Brazilian standard that regulates the quality of biodiesel produced. However the ester content of the biodiesel produced does not exceed the minimum value of 96.5% allowed, mainly due to the fact that the reaction may not have been completed.

Table 4. Chemical physical properties of cotton biodiesel (BCO) and soybean biodiesel (BSO).

Property	Unit	BCO	BSO	ANP 03/2014
Acid value	mg KOH/g	0,02 ± 0,0001	0,03 ± 0,0003	0,50 max
Free Fat Acids	%AGL	0,10 ± 0,0005	0,15 ± 0,001	-
Dynamic viscosity	mPa.s	3,89 ± 0,18	3,94 ± 0,18	-
Kinematic viscosity	$mm^2.s^{-1}$	4,41 ± 0,20	4,46 ± 0,20	3,0-6,0
Ester content	%	68,87	69,06	96,5 min

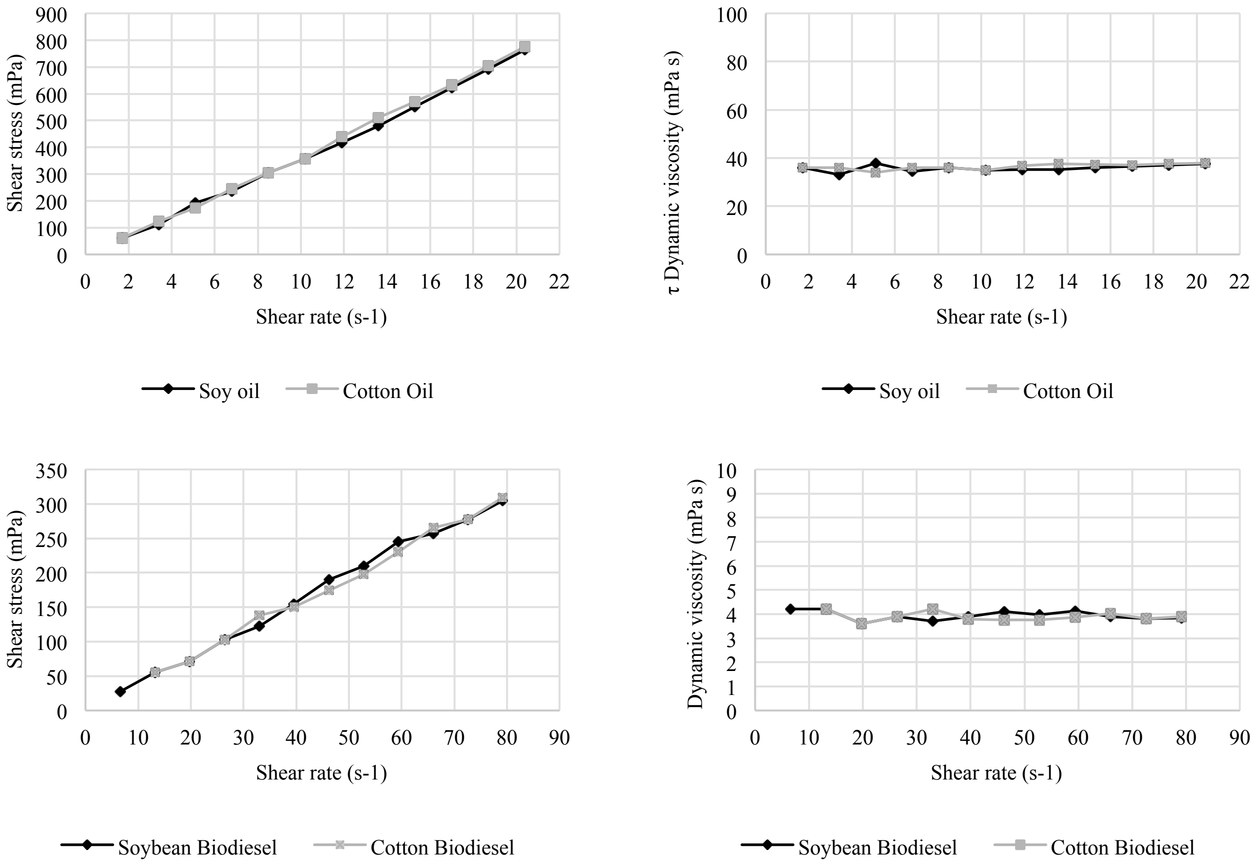

Fig. 2. Characteristic graph of Newtonian fluids made for soybean and cotton oils and soybean and cotton biodiesel.

4. Conclusions

Soybean oil biodiesel has a higher yield than cotton oil biodiesel due mainly to the lower acidity that soybean oil has, considering that the raw materials used were refined oils of both cotton and soya.

Transesterification of vegetable oils by the methyl route reduces oil viscosity to values similar to petroleum diesel so that biodiesel can be used instead of fossil fuels, having kinematic viscosity values for the cotton oil biodiesel of 4.46 $\pm$ 0.20 and for soybean biodiesel of 4.41 $\pm$ 0.20.

The oil of cotton has similar characteristics than the oil of soybean, being able to be used for the production of biodiesel in industrial scale; however, production on a scale that allows for profitability may depend on the quantity of raw material available, for which an assessment is still indispensable to know some characteristics in this sense.

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