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Análisis físicoquímico de biodiesel obtenido por mezclas de aceite de castor y aceite de freír

Physico-chemical analysis of biodiesel obtained from blends of virgin castor oil and waste frying oil

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Resumen

La producción de combustibles renovables ha tenido un gran impulso en los últimos años. Una alternativa es la producción de aceites vegetales con la capacidad de reemplazar todo o parte del diesel derivado del petróleo. El objetivo de este trabajo fue producir biodiesel a partir de mezclas de aceite de ricino virgen (VCO) y aceite de fritura (WFO) a partir de ruta etílica y catálisis alcalina y estudiar las propiedades físicas y químicas de los mismos. El biodiesel se obtuvo a partir de 5 diferentes materias primas: VCO (B1), WFO (B2) y tres mezclas diferentes (B3: 50% VCO; B4: 25% VCO; B5: 75% VCO). Las materias primas fueron evaluadas por el nivel de acidez, ácidos grasos libres, índice de saponificación y densidad. Para el biodiesel se determinó el índice de yodo, cetano, glicerina, ausencia de triglicéridos y reología. De acuerdo con los resultados, todas las muestras se encontraron dentro del estándar especificado para índice de yodo y densidad, pero el biodiesel de B1 presentó viscosidad y número de cetano no permitidos en la legislación. A pesar de que los resultados de B4 y B5 se ubicaron dentro de la legislación para biodiesel, B4 sería una mejor alternativa debido a una mayor cantidad de WFO.

Palabras clave: Biodiesel; Oleaginosas; Ricino; Transesterificación; Aceite de cocina usado.

Abstract

Renewable fuels production got a big boost in recent years. One alternative is the production of vegetable oils with the ability to replace all or partly the diesel fuel derived from oil. The objective of this work was to produce biodiesel from blends of virgin castor oil (VCO) and waste frying oil (WFO) from ethylic route and alkaline catalysis as well as to study the physical and chemical properties. Biodiesel was obtained from 5 different raw materials: VCO (B1), WFO (B2) and three different blends (B3: 50%VCO+50%WFO; B4:25%VCO+75%WFO; B5:75%VCO+25%WFO). The raw materials were evaluated by acidity level, free fatty acids, saponification index and density. For the biodiesel, the index of iodine, cetane, glycerin, absence of triglycerides and rheology was determined. According to the results, all samples were within the specified standard for iodine index and density, but B1 biodiesel showed viscosity and cetane number not allowed in the legislation. Despite the fact that B4 and B5 results were within the legislation for biodiesel, B4 would be a better alternative due to higher quantity of WFO.

Keywords: Biodiesel; Oilseeds; Castor beans; Transesterification, Waste cooking oil.

Introduction

Throughout the 20th century, petroleum refining products became the main form of energy generation and the main basis for the development of the chemical industry, generating a global dependence on this fossil fuel, making several countries susceptible to variations in the price of oil in the international market. However, the oil crisis, in the 70's and 80's, has given rise to several studies concerning the pyrolysis of triglycerides. With the risk of depletion

of some energy sources, especially fossil energy with no prospects of renewal, there is a motivation for the development of technologies that allow the use of renewable energy sources [1].

The burning of fossil fuels with the consequent release of greenhouse gases has intensified as society becomes more and more dependent on oil derivatives. This fuel, in addition to provoking innumerable and well-known environmental problems, is a finite resource, whose extraction process is becoming gradually more complex. This fuel

belongs to the category of non-biodegradable fuels. Moreover, pollutants, such as CO₂, are released into the atmosphere during their burn, besides the possibility of sulfur oxides emission. Once the planet cannot assimilate all CO₂ released in the long term, the accumulation of this and other gases cause the greenhouse effect increasing [2-5].

Biodiesel is a vegetable oils and fats derived fuel, commonly obtained by transesterification using a catalyst agent. It is classified as a renewable and biodegradable fuel, with low emission of polluting compounds into the atmosphere. Therefore, biodiesel has been seen as the fuel of the future. Indeed, biodiesel totally or partially replaces petroleum diesel fuel in stationary diesel engines (generators of electricity, heat, etc.) or within the automotive industry (trucks, tractors, vans, cars, etc.) and can be used pure or mixed with diesel in different proportions [6-8].

Regarding the economic importance of biodiesel production, it can cooperate with the economic development of several regions of the world, since biodiesel can be produced from any source of fatty acids, however not all of them make the process industrially feasible. The use of waste oils and fats (frying oil, refining lees, sewage grease, vegetable oils or animal fats), which are out of legislation standards and useless for another ends, is promising since it avoids improper disposal [9]. The recycling of waste oils and fats for biodiesel obtaining can cooperate with the economic development of several regions of Brazil and other countries. Moreover, the consumption of biodiesel and its blends can reduce petrol dependence, as well as generate alternative jobs in less favorable geographic areas to other economic activities [10, 11].

Nowadays, issues associated with the environment have worsened significantly, in view of the disorderly increase in population and the subsequent generation of large amounts of recycling complex waste. At present, to ensure survival on the planet, every effort should be made in order to recycle most of the generated waste, including the oil used in frying. This material can be transformed in biodiesel by transesterification and reused as fuel. Considering that after successive re-use in frying the oil has its fatty acid composition and physico-chemical characteristics altered, therefore it becomes inadequate for food processing even when subjected to purification [12, 13].

In an attempt to contribute to the reduction of atmospheric pollution, the objective of this work was to produce biodiesel from blends of virgin castor oil (VCO) and waste frying oil (WFO) from ethylic route and alkaline catalysis as well as to study the physical and chemical properties.

Materials and Methodology

Raw material to obtaining the biodiesel

The biodiesel was obtained by the transesterification

reaction, from virgin castor oil (VCO), waste frying oil (WFO), and blends of VCO and WFO in different proportions as: B1 (100% VCO), B2 (100% WFO), B3 (50% VCO+50% WFO), B4 (25%VCO+75% WFO) and B5 (75% VCO + 25% WFO). The WFO samples, provided by an event company (which prepares snacks by immersion in heated soybean oil), were filtered in two stages: (i). larger particles and food residues were removed by a steel wool pad attached to a nylon sieve; (ii) smaller particles were vacuum-filtered with Whatman filter paper nº 2. The resulting filtrate was vacuum-dried for 90 min at 100° C, according to Zhang *et al.* [14].

Transesterification reaction to obtaining the biodiesel from the blends

Transesterification was carried out in a magnetic stirrer with heating (Model 753A, FISATOM), where 100 mL of each blend was heated to 55°C. After that, 33 mL ethyl alcohol and 1 g KOH (catalyst) were added to the reactional mixture with stirring in order to keep system uniform temperature (55°C) and homogeneity for 80 minutes. After that, the mixture was cooled down at room temperature and distilled under reduced pressure in order to remove ethyl alcohol excess. The resulting ester/glycerin mixture was transferred to a separating funnel and kept standing for 24 h, yielding two phases: biodiesel (upper phase) and glycerin (lower phase). After glycerin removal, biodiesel was washed and heated at 100°C for 15 min for water and residual ethyl alcohol removal [15, 16].

The yield of each biodiesel sample was calculated according to equation (1):

$$\% \text{ of yield} = \left(\frac{\text{Volume of biodiesel}}{\text{Volume of reactional mixture}} \right) \cdot 100$$

Where the volume of reactional mixture is the sum (oil blend + ethyl alcohol).

Physico-chemical parameters

The initial blend was characterized according to acidity level by Potentiometric Titration with NaOH 0,1N (ASTM D664 - 11a) [17], saponification index (ASTM D1387 - 89) [18], density (through a glass densimeter Anton Paar, model DMA 35N) (ASTM D1298 - 12b) [19] and free fatty acid composition (A.O.A.C., 2004) [20]. The free fatty acid composition was obtained with a gas chromatograph (Varian CG3800), using CP-WAX58 capillary column equipped with flame ionization detector, according Machado & Druzian [21].

The resulting biodiesel was characterized with respect to the acidity level [17], iodine value (ASTM D1959-97) [22], cetane number (ASTM D4737-10) [23], density (ASTM D1298 - 12b) [19] and glycerin by UV Spectroscopy [24]. The absence of triglycerides was

Table 1: Blend composition used as raw material for biodiesel obtaining and physical and chemical parameters.

Blend	Acidity (mgKOH/goil)	Free Fatty Acid (%)	Saponification Index (mgKOH / g oil)	Density (g/cm3)	Fatty acid composition (wt%)					
					C16:0	C18:0	C18:1	C18:2	C18:3	C22:0
B1	0.24 ± 0.01	1.52 ± 0.42	215.03 ± 0.56	0.96 ± 0.02	1.50±0.01	2.00±0.03	92.50±0.04	2.70±0.04	0.25±0.02	1.05±0.04
B2	1.82 ± 0.02	6.44 ± 0.77	328.99 ± 0.23	0.92 ± 0.01	11.40±0.02	3.28±0.00	22.18±0.00	56.24±0.01	6.90±0.01	0.00±0.00
B3	1.11 ± 0.40	4.46 ± 0.39	298.32 ± 0.14	0.94 ± 0.01	6.45±0.01	2.64±0.03	57.34±0.02	29.47±0.04	3.58±0.02	0.52±0.04
B4	1.70 ± 0.20	4.76 ± 0.40	311.92 ± 0.21	0.93 ± 0.01	8.93±0.01	2.96±0.00	39.76±0.03	42.86±0.00	5.24±0.02	0.26±0.04
B5	1.02 ± 0.01	3.90 ± 1.19	296.15 ± 0.16	0.95 ± 0.01	3.98±0.00	2.32±0.01	74.92±0.02	16.09±0.01	1.91±0.03	0.79±0.01

VCO: virgin castor oil;
WFO: waste frying oil;
C16:0: palmitic acid;
C18:0: stearic + dihydroxystearic acids;
C18:1: oleic + ricinoleic acids; C18:2: linoleic acid; C18:3: linolenic acid;
C22:0: behenic acid.

verified through proton nuclear magnetic resonance ($^1\text{H-NMR}$). The conversion rate was calculated as the percentage of oil transformed into biodiesel (ethyl esters), based on the data generated through Nuclear Magnetic Resonance (NMR in the infrared region), where the biodiesel samples were dissolved in chloroform and the spectra obtained in a Varian spectrometer (Mercury – 300MHz).

The rheological behavior of the biodiesel was analyzed in a rotating rheometer (Brookfield, LV - DVII), with the samples at 40°C. The rheograms were adjusted Casson and Power Law (Ostwald-de-Waele) models, and the rheological parameters obtained were: consistency coefficient (K), n : behavior index (n), Casson yield stress (K_{0C}) and Casson viscosity (K_C).

Results and Discussion

The results presented in Table 1, regarding the composition in fatty acids (by chromatographic analysis), show differences between the degree of unsaturation of the oils analyzed. That is, the blends with high VCO content (above 50%, that is, B1, B3 and B5) presented as the majority unsaturated fatty acid the oleic acid, presenting excellent quality characteristics; however, the blends containing the highest concentration of linoleic acid are those with frying oil in the highest proportions. These results are in agreement with those obtained by Silva [25], who analyzed the physical-chemical properties and profile of fatty acids in andiroba oil.

All blends present acidity values within the standards recommended by legislation, since all of them had an acidity level below than 3% [26]. The higher WFO acidity level can be explained by the break down and release of the triglycerides chains, considering that free fatty acids are produced by oxidation reactions that are intensified during the frying process [27].

The higher saponification index can be explained by the fact that the blends are not refined, which saponification index ranges from 177 to 187 $\text{mg}_{\text{KOH}}/\text{g}$, for top quality oils [28].

The density values of the blends corroborate with those found in the literature [29, 30]. According to the Brazilian standards recommended [31], the density specification for use in engines lies between the 0.85-0.90 g/cm^3 range. Valente et al [30] observed this density specification in blends with 70% biodiesel from waste cooking oil or from castor oil in diesel fuel N° 2.

Regarding to the biodiesel yield, presented in Table 2, except for B1, yields higher than 50% of transesterification were observed ($B4 > B2 > B5 > B3$) and the lower reaction yield, observed in B1, can be attributed to the alkaline catalyst reaction with VCO free fatty acids, which resulted in soap.

As shown in Table 2, B1, B4 and B5 are in accordance with the legislation [32], which affirms that the maximum acidity level for biodiesel is 0.50 $\text{mg}_{\text{KOH}}/\text{g}_{\text{oil}}$. All the samples showed iodine index within the specified standard in a maximum value of 120 $\text{g}_{\text{I}_2}/\text{g}_{\text{oil}}$ [29, 30] and the density is within the specified standard as well of 900 K/m [33].

A high amount of free glycerin was observed in the blends with high ricinoleic acid content (B1, B3 and B5). According with Vieira et al. [34], a reaction between the hydroxyl group of this fatty acid and the carboxyl group results dimers, which are detected as diglycerides, resulting in values that exceed the process expectation.

Respecting to cetane number, except for B1, the cetane number of biodiesel is in the allowed range (30-45). According with Lôbo, Ferreira and Cruz [29], the cetane number increases with the length of the non-branched carbon chain. As showed in Table 1, Ricinoleic acid is the predominant fatty acid in VOC, therefore a low cetane number for B1 was expected.

There was no significant difference between the results for proton nuclear magnetic resonance for B1 and B5 conversion rate (Table 2). However, increased amounts of WFO in the blend led to lower conversion rates. The conversion was greater when B3 was used as raw material for biodiesel production. A possible explanation for this would be the fact that the NMR methodology was unable to separate and quantify the individual sterols [28], since the methodology consists of the identification of the mo-

Table 2: Volumetric yield of the transesterification reaction and biodiesel physico-chemical parameters.

Blend	Composition	Transesterification Yield (%)	Acidity level (mgKOH/goil)	Iodine Index (gI ₂ /goil)	Density (g/cm ³)	Free glycerin (%)	Cetane number	Conversion rate* (%)
B1	100% VCO	28.46	0.27 ± 0.01	110.86 ± 2.32	0.95 ± 0.01	0.64 ± 0.01	24.46	40.08
B2	100% WFO	56.15	0.56 ± 0.01	99.05 ± 0.98	0.92 ± 0.01	0.02 ± 0.01	33.39	23.82
B3	50% VCO + 50% WFO	52.31	0.55 ± 0.02	77.99 ± 0.13	0.92 ± 0.01	0.28 ± 0.04	31.90	61.49
B4	25% VCO + 75% WFO	59.21	0.48 ± 0.01	93.01 ± 4.81	0.92 ± 0.01	0.03 ± 0.03	30.99	32.68
B5	75% VCO + 25% WFO	53.08	0.27 ± 0.01	76.30 ± 3.49	0.94 ± 0.09	0.33 ± 0.01	31.19	40.53

* obtained from spectrum analysis (NMR).

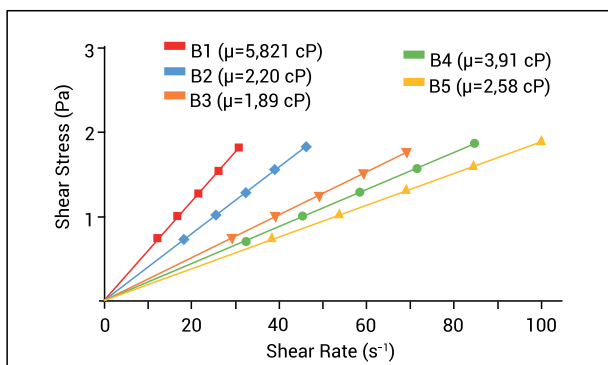
lecules present, in the region of 4.05-4.35 ppm, during a transesterification reaction by ¹H-NMR and certification by NMR 13C. That is, in the quartet generated by protons of ethoxy group (-OCH₂CH₃), the unfolding at lower chemical displacement (4.09) is the only resonance peak that does not overlap with any other mono-, di- or triglyceride.

Table 3 shows that all biodiesel samples presented the rheological behavior of a Newtonian fluid, since the values for behavior index (n) and Casson yield stress (K_{oc}) are close to 1 and 0, respectively and, thus, the rheogram can be represented by a straight line through the origin, as shown in Fig.1. For this case, the parameter K equals the absolute viscosity of the Newtonian model, directly related to the internal friction of the biodiesel, that is, to the resistance to the flow.

Table 3: Rheological parameters of different biodiesel formulations.

Biodiesel samples	Power			Casson		
	K	n	r ²	K _{oc}	K	r ²
B1	0.95 ± 0.13	0.98 ± 0.01	0.99	0.03 ± 0.00	0.76 ± 0.07	0.99
B2	0.22 ± 0.11	0.99 ± 0.02	0.99	0.02 ± 0.00	0.47 ± 0.12	0.99
B3	0.21 ± 0.19	0.97 ± 0.03	0.99	0.09 ± 0.00	0.43 ± 0.05	0.99
B4	0.39 ± 0.12	1.01 ± 0.03	0.99	0.02 ± 0.00	0.63 ± 0.14	0.99
B5	0.28 ± 0.15	0.98 ± 0.04	0.99	0.06 ± 0.00	0.50 ± 0.18	0.99

K: consistency coefficient, n: behavior index, r²: correlation coefficient, K_{oc}: Casson yield stress.

Figure 2: Rheograms of biodiesel formulations.

Conclusion

The blend composed by 25% VOC + 75% WFO (B4) showed up attractive with respect to oil reuse, cheapening the overall process and avoiding inappropriate waste disposal along with environmental pollution, besides all parameters are within the legislation.

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