PRODUCTION AND PHYSICOCHEMICAL CHARACTERIZATION OF METHYLIC AND ETHYLIC BIODIESEL FROM CANOLA OIL

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ABSTRACT

Nowadays, the fossil's fuel reserves have reduced, causing an increase on the oil's derivate prices. Thus, the biodiesel appears as an alternative, where the oil of canola is a source to this biofuel, which has from 40% to 46% of oil in grain and showed an excellent quality, due to be constituted of fat acids. This work presents physicochemical properties of canola's biodiesel produced from methylic and ethylic routes through the transesterification process. The results are in according to the established by National Agency of Petroleum, Natural Gas and Biofuels (ANP).

Keywords: canola; oil; biofuel.

OBTENÇÃO E CARACTERIZAÇÃO DO BIODIESEL DE CANOLA PELAS ROTAS METÍLICA E ETÍLICA

RESUMO

Atualmente as reservas de combustíveis fósseis têm diminuído, acarretando um aumento de preço dos derivados do petróleo. Desta forma o biodiesel surge como uma alternativa, sendo o óleo de canola uma opção para esse biocombustível, o qual possui de 40 a 46% de óleo no grão, e que é de excelente qualidade pela composição em ácidos graxos e já usado na Europa para produção de biodiesel. Este trabalho apresenta propriedades físico-químicas do biodiesel de canola nas rotas metílica e etílica através do processo de transesterificação e os resultados encontram-se dentro das normas estabelecidas pela Agência Nacional de Petróleo, Gás Natural e Biocombustíveis (ANP).

Palavras-chave: óleo de canola; biocombustível.

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INTRODUCTION

The fact that the world remains very dependent on oil still coming up as a big concern, based on current forecasts that, in the near future, the main oil reserves may become extinct [2, 3]. Furthermore, there are environmental and public health issues related to the combustion of fossil fuels. The combustion of fossil fuels leads to the emission of large quantities of CO_2, the main greenhouse gas [4]. Hoffman et al. showed an increase in the average concentration of CO_2 and other greenhouse gases in recent decades [5]. The concentration of CO_2 in the atmosphere has increased at a rate of 1.6 ppm.year^{-1}, from 1974 to 2004, as a result of human activities, such as fossil fuel consumption [4, 5]. In addition to greenhouse gases, the burning of fossil fuels leads to the emission of sulfur dioxide (SO_2) and particulate matters consisting of powder and ash suspended in the flue gas [6, 7]. Considering the changes in local biodiversity, these pollutants cause various ills to human health, such as respiratory disorders, allergies, degenerative lesions to nervous system and vital organs, cancer etc.

Currently, the demand for alternative fuels has been driven by economic and environmental factors. The world energy matrix is highly dependent on non-renewable energy resources, as reported by the latest edition of the BP Statistical Report Review of World Energy [1]. According to this, oil still dominates the world energy scene, reaching 33.1% of the global energy consumption in 2011, Figure 1 [1].

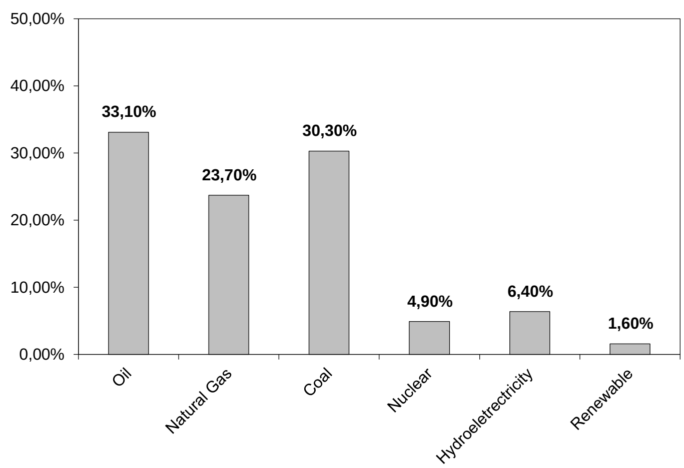


Figure 1. World energy consumption in 2011. Organized from [1]

In this scenario, a biofuel that has been proposed as an alternative to petroleum diesel is the biodiesel [8-13]. The American Society for Testing and Materials (ASTM) defines biodiesel as alkyl esters containing long chain carboxylic acids obtained from renewable sources, such as vegetable oils or animal fats [14, 15]. The Brazilian Biodiesel Program expands this definition by defining biodiesel as a fuel resulting of mixture in different proportions of mineral diesel and alkyl esters derived from vegetable oils [16]. “Bio” represents his renewable property, in contrast to traditional fuel-based oil, known as diesel [15].

The main method used for the biodiesel production is the transesterification reaction, which consists in a reaction of triglycerides with an alcohol, in presence of a catalyst, Figure 2 [10, 11, 16]. The catalytic via most used for this process is the alkaline homogeneous catalysis, which highlights the use of the following catalysts: sodium or potassium hydroxide and sodium or potassium alkoxide [10, 11, 16]. Regarding the type of alcohol employed, the most widely used is methanol, because it is more reactive. However, in the case of Brazil, for example, the biodiesel production using ethanol becomes more attractive because the country has extensive experience in the production of this alcohol. Besides the environmental factors, the methanol being derived from non-renewable source and toxic, fact that is in contrast with ethanol, which is renewable and nontoxic [16].

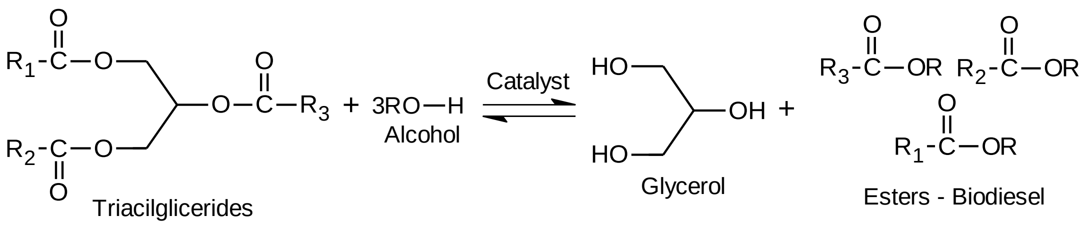


Figure 2. General equation of transesterification reaction.

Regarding the raw material to be used in biodiesel production, there are several studies that have developed the synthesis of biodiesel, starting up of various types of raw materials, including vegetable oils, animal fats, waste frying oils and lipids extracted from microalgae [17, 18]. Canola oil has been widely used in Europe for biodiesel production in large scale, due to the good performance of the biodiesel produced at lower temperatures. This property is justified by the fact of canola oil being rich in unsaturated fatty acids, Table 1. This oil has been used in several studies to test transesterification reactions conducted under adverse conditions, such as heterogeneous catalysts [19-21], in situ reactions [22], use of ultrasound [23] and alcohol in supercritical state [24], etc. In most studies, the type of alcohol employed was the methanol.

In this context, the present study aimed to promote the production and physicochemical characterization of methylic and ethylic biodiesel produced from canola oil, emphasizing the importance of ethylic route for the Brazilian scenario.

Table 1. Fatty acid composition of canola oil [25].

Fatty acid	Percentage
Palmitic C16:0	3.90 %
Stearic C18:0	1.10 %
Oleic C18:1 (9)	64.40 %
Linoleic C18:2 (9, 12)	20.40 %
Linolenic C18:3 (9, 12, 15)	9.60 %

MATERIAL AND METHODS

Canola oil (Liza) was purchased in the local market and used without any modifications. Potassium hydroxide (KOH), ethanol (EtOH) and methanol (MeOH) of analytical grade were purchased from Synth, São Paulo, Brazil and used without any pretreatment. All other solvents used were analytical grade.

For obtaining biodiesel by methylic route initially was prepared the potassium methoxide from stirring of a mixture of methanol and KOH. The effect of the alcohol volume was investigated, maintaining a fixed percentage of catalyst (2%). The following volumes of methanol were used: 20, 30, 40 and 50 mL. Then, the potassium methoxide was added to 100 g of canola oil, and transesterification reaction carried out for 40 minutes under stirring, at room temperature. After the reaction has been completed, the mixture was transferred to a decantation funnel, leaving it for 30 minutes to obtain phase separation biodiesel / glycerin. Removal the glycerin phase and the biodiesel crude was subjected to a washing process with HCl 0.1 M. Then, the methylic esters were washed with distilled water and pure biodiesel was obtained by separating water by decantation, and traces of moisture and alcohol removed by distillation. The procedure for obtaining biodiesel by ethylic route was identical to the methylic route.

The following physicochemical analysis were performed: acid number, color, viscosity, density at 15ºC, flash point, saponification number and oxidative stability, following standard methods established by ANP and ASTM. The oxidative stability was obtained following the European standard method EN 14112, using the equipment 873 Biodiesel Rancimat, Methrom.

RESULTS AND DISCUSSION

The canola oil used in this study had an acid number of 0.40 mg KOH/g (Table 2). Prior knowledge of the acid number of the oil for use in biodiesel production has a great importance: depending of the results obtained, you can select the most appropriate catalytic via. Oils with high values of acid number, which means having a high level of free fatty acids (FFAs), are not recommended for the transesterification reaction via alkaline homogeneous catalysis, due to parallel neutralization reaction. This situation may take place between the alkaline catalyst and the FFAs, leading to the formation of emulsions and reduced process yield, Figure 3 [10, 26]. In general, vegetable oils with acid number of up to 6 mgKOH/g are susceptible to alkaline transesterification [27]. The canola oil used in this study had an acid number lower than the threshold value that has been adopted (6 mgKOH/g) and, thus, the transesterification reaction via alkaline homogeneous catalysis was chosen as synthetic pathway for the production of methylic and ethylic biodiesel.

Table 2. Physicochemical properties of the samples of canola oil, methylic biodiesel and ethylic biodiesel.

Property	CO	MB*	EB**	Brazil - ANP 07/2008	USA – ASTM D6751	EU - EN 14214
Acid number (mgKOH/g)	0.40	0.59	0.80	0.50	0.50	0.50
Oxidative stability (h)	6.32	4.37	4.73	6	3	6
Color	0.50	0.50	0.50	---	---	---
Kinematic viscosity at 40ºC ($mm^2. s^{-1}$)	46.00	6.00	7.00	3.0-6.0	1.9-6.0	3.5-5.0
Cetane number (min)	---	48.9	47.4	---	47	51
Density at 15ºC (g/cm^3)	0.89	0.75	0.85	---	0.86-0.90	---
Flash point (ºC)	316.00	185	184	100 min	130 min	120 min
Saponification number (mg KOH/g)	56.32	57.3	54.2	---	---	---

*methylic Biodiesel; **Ethylic Biodiesel

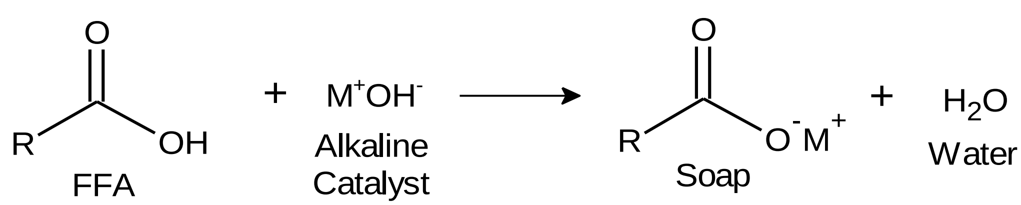


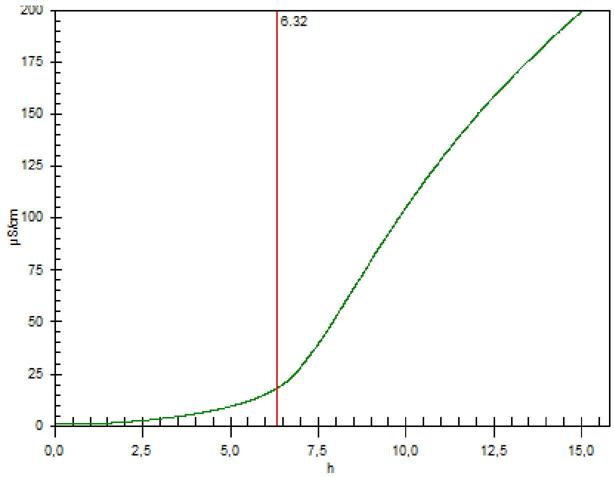
Figure 3. Neutralization reaction between a basic catalyst and FFA

In this study, we investigated the biodiesel production from canola oil using methanol and ethanol as alcohols, and different quantities of these alcohols. The transesterification reaction consisting of reaction equilibrium and, therefore, a molar ratio alcohol: oil above the stoichiometric ratio (3:1) is required for shifting the reaction towards the products and guarantee good yields [28-30]. Furthermore, a greater quantity of alcohol provides better solubility between triacylglycerides and alcohol [30]. Due to the important influence of the proportion of alcohol used during the biodiesel synthesis, several works have taken this issue into account in studies of process optimization. Freedman et al. [31] studied the variables affecting the alkaline methanolysis of cottonseed, peanut, sunflower and soybean oils. Regarding the effect of the molar ratio methanol:oil, experiments was conducted by varying the molar ratio between 1:1 and 6:1. For methanolysis of sunflower oil, it was obtained a yield of 98% using a molar ratio of 6:1. The same result was observed for the remaining oils, with yields in the range of 93-98%. Chen et al. [32] has studied the reaction parameters for the biodiesel production from Tung oil (*Vernicia montana*). Using methanol as alcohol, the effect of the molar ratio alcohol:oil (a:o) was studied in the range 3 to 28. When the ratio a:o was increased from 3 to 6, the yield increased significantly, from 80.4% to 97.6%. Alamu et al. [33] conducted studies on the influence of the molar ratio ethanol:palm kernel oil (e:PKO). Experiments were conducted for the e:PKO rations 0.100, 0.125, 0.150, 0.175, 0.200, 0.225 and 0.250, under the following reaction conditions: temperature 60ºC, 120 min of reaction time and 1.0% concentration of catalyst KOH. The yields of biodiesel obtained for this rations e:PKO were: 29.5%, 54%, 75%, 89%, 96%, 93.5% and 87.2%. Thus, it was demonstrated that the yield of biodiesel increased when the molar ratio of e:PKO raised, until the value of 0.200. The results of analysis of biodiesel quality from palm kernel oil showed that biodiesel produced has their properties according to the relevant specifications. Ramezani et al. [34] optimized the reaction conditions for the production of methylic biodiesel from castor oil. Using a molar ratio methanol:castor oil equal to 8:1 the highest yields were obtained.

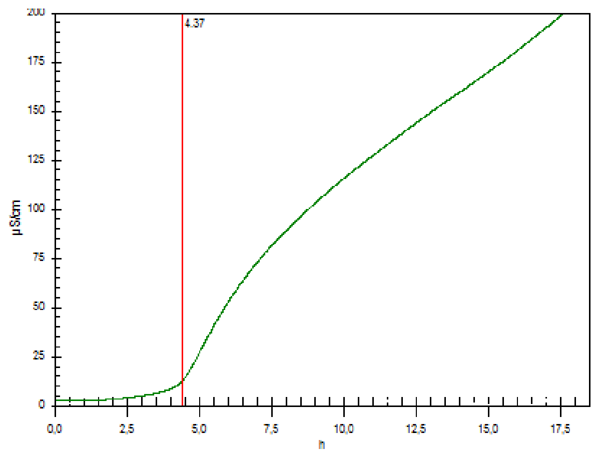
In the present study, the highest yields were obtained using 30mL of methanol (yield = 87.7%) and 50 mL of ethanol (yield = 93.7%). Considering the average molar mass of canola oil equal to 876.6339 g/mol, and the density of ethanol (0.7893 g/cm^3) and methanol (0.7914 g/cm^3), the volume values can be converted for molar ratio alcohol:oil:methanol, 4.3:1 and ethanol, in a ratio 7.5:1. The results of this study are consistent with the literature briefly reviewed above, where the molar ratios alcohol:oil were between 3:1 and 8:1. The higher molar ratio alcohol: oil of ethanol can be explained by the fact that methanol is more reactive than ethanol. However, the yield of the ethylic route was higher than methylic route, which may compensate the greater expense with alcohol.

The results obtained for physicochemical characterization of the samples of canola oil and biodiesel as well as standard values according to the American, European and Brazilian specifications are organized in Table 2. The graphics with the oxidative stability for the oil and biodiesel samples are shown in Figure 4. Both samples of biodiesel, methylic and ethylic showed satisfactory physicochemical properties, with a few exceptions. The acid number obtained for both biodiesel samples was slightly higher than the limit of the national and international specification (0.5 mgKOH/g). The results were very slightly above 0.5, meaning that the acidity of the samples can be easily corrected, for example, by optimizing the purification process. Even the local humidity may have affected the acidity of the samples, so the results can still be considered satisfactory.

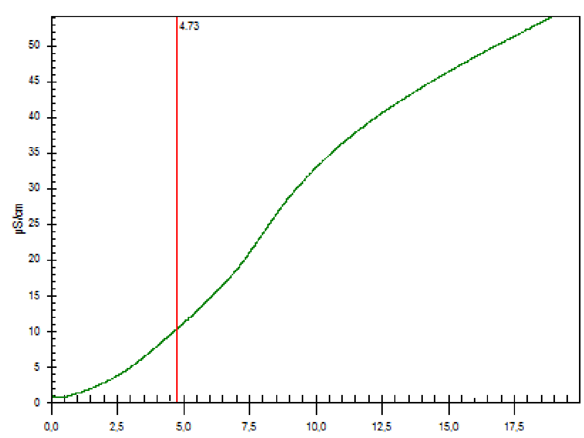
Regarding the oxidative stability, the national and international specifications set the minimum value of 6 h for the oxidative stability. The biodiesel samples did not reach this value stability. However, the values obtained were satisfactory, being superior to other types of biodiesel found in the literature [35]. The oxidative stability of biodiesel sample can be corrected in future studies by the use of antioxidants [27].



(a)



(b)



(c)

Figure 4. Oxidative stability of (a) canola oil (b) methylic biodiesel and (c) ethylic biodiesel

CONCLUSIONS

The transesterification of canola oil by the methylic and ethylic routes in room temperature was noted to be a viable process for biodiesel production, and the physicochemical properties of both products were compatible with national and international standards. It emphasizes the fact that ethylic biodiesel has presented satisfactory physicochemical properties, and have been obtained with a high yield, configuring itself as a good alternative for Brazil, which would result in reduced imports of methanol. Tests with pretreatment of canola oil will be made in order to improve the oxidative stability of the biodiesel obtained.

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