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Evaluation of Biodiesel Oxidative Stability by Condutimetric Measurements

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ABSTRACT

The biodiesel stability is an issue of great interest in whole world. In the present study, the oxidative resistances of biodiesel samples, originating from three fatty raw materials, are compared. Biodiesel samples were obtained from ethylic and methylic transesterification, at 70ºC, using refined sunflower, soybean and rapeseed oils and KOH as the catalytic agent. These samples were subjected to an accelerated oxidation test at 110ºC, under air flow. The produced gases were collected in a container with an electrode immersed in distilled water for electric conductivity measurements. For all the samples, it was observed the electric conductivity increases with time as an indicative of the formation of oxidative products such as alcohols, formic acid or smaller fatty acids. The samples stability decreased with increasing air flow. Comparatively, ethylic biodiesel samples seemed to be a little more resistant to degradation process in comparison to methylic biodiesel. Among all the samples, biodiesel obtained from rapeseed oil was more resistant to oxidative degradation, which is in accordance with the least content of C18:2 fatty acids in the respective raw material structure.

Keywords: Biodiesel, Oxidative Stability, Rapeseed, Sunflower and Soybean

I. INTRODUCTION

The main constituents of biodiesel are the alkyl esters that can be obtained through transesterification of the triglycerides present in the vegetable oils. Biodiesel is a renewable fuel with excellent lubricity, biodegradability, and due to its higher flash point temperature, biodiesel fuel is inherently safer than many other fuels, such as petroleum diesel. However, its use may be compromised by factors that alter their specifications and that occur during production, transport and/or storage as a result of its lower oxidative stability compared to diesel oil. This lower stability is due to the content of unsaturated esters that can be easily oxidized, leading to the formation of degradation compounds such as acids, aldehydes, esters, ketones, alcohols and peroxides (1). These compounds affect the properties of the biodiesel and the vehicle performance.

Research has been done concerning the main factors that affect the stability of biodiesel (2-6). As oxidation time increases, parameters such as the kinematic viscosity, acid number, the ester content and peroxide number fail to fit biodiesel specifications. The negative effect of insaturation on the oxidative stability and viscosity has been reported in the literature (7-11).

Some methodologies have been developed or adapted to determine the factors associated with the stability of biodiesel. The aim of these methodologies is usually to evaluate both primary and secondary oxidation products, or to analyze changes in physical and chemical properties of biodiesel.

The objective of this study was to produce biodiesel by the transesterification reaction of vegetal oils (soybean, sunflower and rapeseed) with ethanol and methanol and to evaluate the oxidative stability of these samples by monitoring the electrical conductivity with respect to time degradation. Some biodiesel properties were also evaluated before and after oxidative treatment.

II. METHODS AND MATERIAL

A. Experimental

Transesterification Reaction

Biodiesel was obtained by transesterification reaction of rapeseed, sunflower and soybean refined oils, with methyl or ethyl alcohol using molar ethanol / oil ratio of 6/1 and KOH as catalyst (1% relative to the amount of oil). The reaction was performed in a reactor with a reflux system under constant stirring and heating at 70 °C. The product obtained after 1 h of reaction was purified by decantation and vacuum evaporation.

Stability Test

It consisted in a test to accelerate biodiesel degradation process in order to compare the oxidative resistance of the various samples.

A controlled air flow was fed to a tube containing the biodiesel sample, which was kept heated to a constant temperature of 110 °C. The gases produced by the oxidation were collected in a container with distilled and deionized water, and an electrode for measuring the electrical conductivity.

B. Characterization of Biodiesel

The acidity, viscosity and C18 esters content of biodiesel were determined before and after thermo-oxidative treatment.

Acidity index (AI)

The acid index provides indication of the presence of free fatty acids in biodiesel. A toluene - isopropanol solution (1: 1 V/V) was added at a given sample mass and titrated with a 0.1 M KOH in ethanolic solution. The acid index may increase over time due to degradation of biodiesel when in contact with air or water. Brazilian Agency of Petroleum, Natural Gas and Biodiesel (ANP) states that the acidity index shall not exceeds0.50 mg KOH per gram of sample (12).

Viscosity (VS)

The kinematic viscosity values were determined using a Cannon-Fenske viscometer immersed in a controlled bath at 40 °C. The viscosity can be used to evaluate the oxidation degree evolution as this reaction can generate compounds that increase the viscosity of the product. ANP determines that the value of the viscosity at 40°C lies between 3.0 and 6.0 $mm^2.s^{-1}$ (12).

C18 Esters Composition

It is an important characterization in order to quantify the ethyl esters in C18:0-C18:2 range which are the main constituents present in the biodiesel (Cx: y, where x = number of carbon atoms in the molecule; y = number of instaurations in the molecule). If degradation of the sample occurs, these values can be changed. The analyses were conducted with a CP-3800 gas chromatograph (Varian model) equipped with a flame ionization detector (FID) and a CP WAX 52 CB column. The furnace temperature was maintained at 200°C and H_2 was used as carrier gas.

III. RESULTS AND DISCUSSION

Figures 1 to 3 show the curves with the electric conductivity values measured during the stability tests for the rapeseed, sunflower and soybean ethylic biodiesel samples, respectively. It can be observed by the graphs that the three samples showed biodiesel conductivity curves with the same pattern: an initial period in which the conductivity remained constant with time (initiation period) and then a continued growth of conductivity (propagation period) up to a maximum level (termination). This behaviour is consistent with the chain peroxidation mechanism outlined below:

Initiation Period:

$$RH + I \rightarrow R^* + IH$$

Propagation Period:

$$R^* + O_2 \rightarrow ROO^*$$

$$ROO^* + RH \rightarrow ROOH + R^*$$

Termination Period:

$$R^* + R^* \rightarrow R\text{-}R$$

$$ROO^* + ROO^* \rightarrow \text{stable products}$$

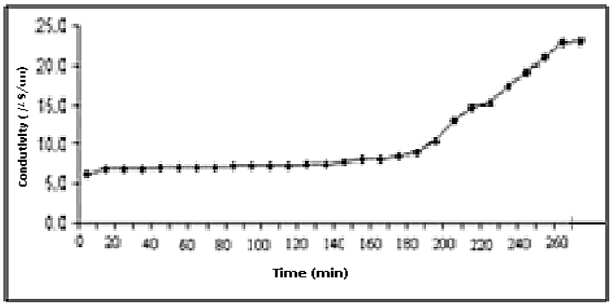

Figure 1: Conductivity of rapeseed ethylic biodiesel with oxidation time

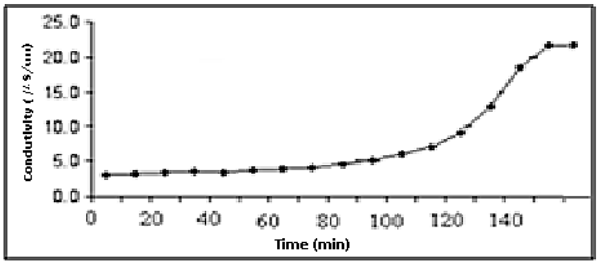

Figure 2: Conductivity of sunflower ethylic biodiesel with oxidation time

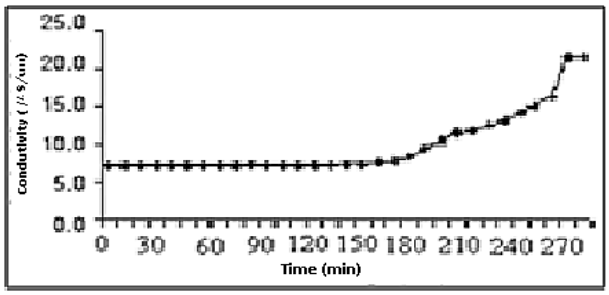

Figure 3: Conductivity of soybean ethylic biodiesel with oxidation time

At the initiation period, there is the formation of carbonic free radical (R *) stimulated by the presence of light and heat. At the propagation period, the free radical reacts with oxygen from the air, effectively triggering oxidative process. At this stage there is the formation of primary oxidation products, peroxide radicals (ROO *) and hydro peroxide (ROOH). In the last step, the termination, free radicals originate secondary oxidation products such as epoxies, volatile and non-volatile compounds obtained by scission and rearrangement of hydro peroxides, mainly aldehydes, alcohols, formic acid and smaller fatty acids (9).

At first, the concentration of hydroperoxide is very low and remains so until a certain period of time has elapsed. After this period, the peroxidation reactions intensify, initiating a global oxidation process that leads to the rapid increase in hydroperoxide concentration.

The hydroperoxides formed in the propagation step decomposes generating secondary oxidation products. The presence of these compounds leads to a increase in the electrical conductivity of biodiesel, as can be seen in the Figures.

Table 1 shows the results of the characterizations of ethylic biodiesel samples from different oils before and after the oxidative treatment.

TABLE 1
RESULTS OF THE CHARACTERIZATION OF ETHYL BIODIESEL SAMPLES OBTAINED FROM DIFFERENT OILS BEFORE AND AFTER THE OXIDATIVE TREATMENT

Characterization	Rapeseed	Sunflower	Soybean
AI before (mg/g)	0.15	0.29	0.16
AI after(mg/g)	2.14	2.63	2.37
VS before (mm^2/s)	4.0	3.9	4.2
VS after (mm^2/s)	4.2	4.1	4.3
C18:0 before	0.7	2.7	2.4
C18:0 after	1.0	2.9	2.7
C18:1 before	65.7	17.7	22.6
C18:1 after	60.5	12.5	19.2
C18:2 before	18.2	58.1	72.9
C18:2 after	10.8	50.9	60.1

By analysing Table 1, it is observed an increase of the acid value with the oxidation time. This increased acidity must be due to a partial hydrolytic degradation of biodiesel caused by water or moisture, with the formation of carboxylic acids as shown in the following reaction:

$$\underset{\text{ester}}{RCOOR'} + H_2O \rightarrow \underset{\text{carboxylic acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH}$$

At the end of the oxidative treatment (termination period), the acidity of all the samples don't meet the standards values required by ANP (maximum = 0.5 mg KOH / g) (12).

Concerning the viscosity, it is observed that its value remained virtually constant, indicating no formation of more viscous products, such as those resulting from the

polymerization. Also from Table 1, we can observe the decrease in the percentage of unsaturated esters, particularly the C18: 2 content, which refers to a chain having 18 carbon atoms and 2 unsaturations. The unsaturation tends to be preferentially oxidized over other carbon- carbon bond, and so the result is consistent with what would be expected. The effects of air flow and the type of alcohol used in the transesterification were also evaluated in the biodiesel degradation process and results are summarized in Table 2.

TABLE 2
EFFECTS OF AIR FLOW AND METHYL (MetOH) AND ETHYL (EtOH) ALCOHOLS ON DEGRADATION TIME OF BIODIESEL SAMPLES

Oil / Alcohol	**Degradation time (min)**	
	Air flow (150 mL/min)	**Air flow (600 mL/min)**
Rapeseed / EtOH	250	240
Rapeseed / MetOH	200	160
Sunflower / EtOH	170	90
Sunflower / MetOH	150	70
Soybean / EtOH	220	130
Soybean / MetOH	150	110

From Table 2, it can be seen a decrease in degradation time with increasing air flow rate, consistent with the greater amount of oxygen present. Regardless of the raw material, samples of ethylic biodiesel proved to be slightly more resistant to degradation than the respective methylic biodiesel samples. This result seems to indicate that increasing the size of the alcohol group causes increased oxidative stability of biodiesel. A similar result was obtained by Waynick (13) which found that the ethyl esters are more resistant to primary oxidation reactions.

The degree of oxidation of fatty compounds is dependent on the unsaturation content of the molecule and can be predicted using the formula below (14):

$$\text{Degree of oxidation} = \frac{(0.02\%\,C18{:}0 + C18{:}1 + 2\%\,C18{:}2)}{100}$$

Using the previous formula, the tendency to oxidation would be as follows: soybean > sunflower > rapeseed. However, the results obtained in this study indicate that the soybean biodiesel was more resistant to degradation than the sunflower biodiesel. The higher initial acidity of sunflower oil should have negatively impacted this result. Among the samples obtained, rapeseed biodiesel was more resistant to thermal oxidation process, including in a higher air flow. This improved stability appears to be related not only to the structural characteristic of the raw material which has lower ester content in the range C18:2 as well as the low initial acidity of the starting oil.

IV.CONCLUSION

The oxidization process alters the acidity of biodiesel. However, the lubricity characteristics are unaffected by the degradation process. It was not possible to establish a direct correlation between the structural characteristics of the fatty raw material and the degree of oxidation of the samples. The oxidation resistance appears to depend not only on the amount of polyunsaturated fatty acids in the molecule but also the initial acidity of the grease starting materials.

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