Full Paper

Evaluating Antioxidant Eugenol on Oxidation Stability of Biodiesel Synthesized from Used Frying Oil

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Abstract: Due the environmental appeal, the demand of new processes and inputs has been increasing considerably in the last decade. Biodiesel is a biodegradable fuel obtained from vegetable oils or animal fats, including those discarded after use. The methyl and ethyl transesterification routes for biodiesel production were tested by using residual frying oil as raw material through the homogeneous basic catalyst, such as sodium hydroxide. In present work, it was evaluated the efficiency of the eugenol on the oxidation stability of the methyl and ethyl biodiesels synthesized from residual frying oil. The chromatographic analysis determined that the conversion of the yield to the methyl and ethylic esters (biodiesel) was 90.6% and 87.3% (m/m), respectively. For both biodiesel samples a rise of the eugenol concentration added resulted in an increase of the induction period (oxidation stability parameter evaluated by Rancimat method), with a consequent reduction of the acid number. Taking these results into account, it can be concluded that the samples obtained after eugenol addition can be used as biodiesel.

Keywords: biofuel; food waste; homogeneous catalysis; oxidative degradation

1. INTRODUCTION

Biodiesel is a recognized alternative fuel to the petroleum diesel due the potential to change the worldwide energy matrix and decrease the impact of fossil fuels on the environment. The most common composition includes mono-alkyl esters with long-chain of fatty acids originated from vegetable oils or animal fats [1]. The most currently employed conversion process of fatty acids in biodiesel is the transesterification with short chain alcohols catalyzed by strong basis, such sodium or potassium hydroxides [2-5].

At this moment, this fuel type only can be used in diesel engines mixed with diesel in volumetric proportion from 7 to up to 20% [6, 7]. The main problem is the increasing of oxidation rate caused by biodiesel because the unsaturated fatty acid chains, which affects the stability of the mixture. Thus, the addition of antioxidant agent can be attractive to decrease the degradation process of diesel-biodiesel blends [8-10].

In order to evaluate the oxidative stability of biodiesel, a recognized method is the Rancimat (EN 14112) [11-14], which is able to evaluate how much the stability oxidative can be increased by addition of different types of synthetic antioxidants, mainly monohydroxy or polyhydroxy phenol compounds, including ones with several ring substitutions, such as butylated hydroxytoluene, propyl gallate, tert-butylhydroquinone, among others. Nevertheless, tert-butylhydroquinone seems to be the most efficient antioxidant [2, 6, 11, 15].

Although there are numerous publications on the oxidative stability of biodiesel with antioxidants, little is available on biodiesel from used frying oil, and few researchers have used natural antioxidants in biodiesels. Natural antioxidants are renewable, safe, and less toxic than synthetic antioxidants and are widely used in food industry [2-5, 16]. Among natural antioxidants there is the phenylpropene eugenol, main constituent of the essential oil clove, has strong antioxidant action and can effectively scavenge free radicals in soybean oil during storage [17-19].

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Therefore, eugenol is a possible candidate to improve physical and chemical stabilities of biodiesels, but it was not found references to its use in biodiesel. It can promote the removal or inactivation of the free radicals that form during the initial or propagation of the chain reaction by donating hydrogen atoms to these molecules, thereby interrupting the chain reaction [8, 20]. This paper aims to evaluate the efficiency of eugenol antioxidant on the oxidation stability of biodiesel synthesized from residual frying oil.

2. MATERIAL AND METHODS

The biodiesel samples were synthesized starting from samples of residual frying oil through the methyl and ethyl transesterification routes catalyzed by sodium hydroxide (NaOH) [21, 22], where all of the reagents used in the synthesis were of analytical grade. Due the residual frying oil have elevated acid number, the free fatty acids were converted into respective esters via esterification reaction with the same alcohol of transesterification step. After that, the oil samples were transesterified with methanol and ethanol separately, under reflux conditions, by using 6:1 in molar ratio of alcohol to oil and 0.5% of NaOH catalyst (m/m of oil).

In both cases, the sequence steps include the precious mixture of alcohol to NaOH catalyst and vigorous stirring during 15 min before the addition of oil and subsequent heating up to temperature reaches 65 °C. After the reaction completion (after 1 h), the samples were transferred to separating funnel to provide phase separation. The less dense phase was distilled under reduced pressure and twice washed with the distilled water in order to remove glycerin residues, unreacted catalyst and eventual saponified byproducts. Then, the purified products were filtered through a Buchner funnel containing a layer of anhydrous sodium sulfate and lead to characterization stages.

GC-MS analyses were performed through an SHIMADZU QP 2010 Plus-CG-MS equipment with flame ionization detector (FID). The injection volume was 1,0 μL carried by 1.5 mL min^{-1} of helium gas with split ratio of 1:45 in Stabilwax column (30 m; 25 mm; 0.25 μm). The temperature was increased by 5 °C min^{-1} from 60 °C for 2 min, 200 °C for 10 min, and ending at 250 °C. Fatty acids esters were identified by their mass spectra and by the retention time compared with reference standards and the quantitative calculation was taken with methyl heptadecanoate internal standard.

Oxidative stability measurements were carried out using Rancimat equipment model 893 (Metrohm) in accordance with EN 14112 standard method [23]. In this method, the oxidation of biodiesel was induced by passing air at a flow rate of 10 L h^{-1} through the sample (3.000 g ± 0.001 mg) and then through a cell with water (deionized water). At the same time, the sample flask was kept at 110 °C. Volatile oxidation products (mainly formaldehyde and short-chain acids) were absorbed by the water, causing an increase in conductivity. Water conductivity was monitored to determine the onset of oxidation and to determine an induction period (IP). The IP is the break point of the conductivity vs time curve registered by the Rancimat equipment. The second derivative of the measured curve was used for the automatic determination of induction period.

Acid number is defined as the number of milligrams of potassium hydroxide (KOH) necessary to neutralize one gram of biodiesel in order to provide the quantity of free fatty acids and acids originating from degradation reactions of biodiesel during the production process and its storage [25]. The acid number determinations follow the ABNT-NBR 14448 method, rigorously weighed 20.00 g followed by pouring 126 mL of toluene: isopropanol: water mixture (1.00: 0.95: 0.05). The mixture was potentiometrically titrated with glass electrode pHmeter Tec-3MP using isopropanol solution of KOH at 0.09283 mol L^{-1} previously standardized with primary standard potassium hydrogen phthalate. The acid number was calculated according the Tubino and Aricetti formula (2011).

The B100 methyl and ethyl biodiesel samples were prepared in triplicate containing antioxidant agents TBHQ at 0.025% (m/m), following literature specification [6,8] and eugenol at 1.50% (m/m). Thus, this parameter was determinate by the Rancimat method with a minimum induction period (approximately 6h) in accordance with the European norm EN 14214 [26]. It was also evaluated several concentrations of eugenol in order to get an efficient profile: 0.00, 0.05, 0.10, 0.15, 0.20, 0.50, 1.00 e 2.00% (m/m).

The results were analyzed in the BioEstat5.3® program. For the tests, ANOVA analysis of variance was performed with a significance level of 95% and Tukey's test a *posteriori*.

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3. RESULTS AND DISCUSSION

The previous esterification of used frying oil was able to reduce the acid number from 1.77 to 1.00 mg$_{(KOH)}$ g^{-1}. After transesterification, the volume of biodiesel product was measured and yield percentages (%, v/v) for the methylic and ethylic transesterification were 87.3% and 87.0%, respectively. Table 1 shows the fatty acid percentages determined through CG-MS characterization for biodiesel samples and the soy oil parameter. It is possible to observe the esters composition is very similar to the soy oil in nature, which is an important compositional aspect, taking in account the absence of parallel reactions or thermal degradations in carbon chain during the transesterification process [8, 28].

Table 1. Fatty acid amounts for methylic and ethylic biodiesel sample compared to soy oil.

Fatty acid	Symbol[a]	methylic BD (%m/m)	ethylic BD (%m/m)	Soy oil / % (m/m)[b]
Linoleic	(C18:2)	40.60	34.55	44.0 – 62.0
Oleic	(C18:1)	22.30	17.99	19.0 – 30.0
Palmitic	(C16:0)	6.80	9.60	7.0 – 14.0

[a]Cx:y, where: x = number of carbon: y = number of carbon double bonds. [b] Souce: Singh, 2010 [27].

In Table 2 is presented the physicochemical parameters determined for biodiesel samples. It is possible to observe the synthesis process and the purification steps were relatively efficient, once the values for residuals components are lower than ANP reference. Nevertheless, diglycerides still persist in ethylic biodiesel samples, which can affect the oxidative stability [29]. The induction period also presented lower value, but is acceptable when the raw fatty acid is originated from residual frying oil, which present higher thermal degradation [4, 5]. Thus, the addition of antioxidant agents is required for this sample types, as discussed in previous works [3, 8].

Table 2. Physicochemical parameters founded for methylic and ethylic biodiesels samples compared to ANP resolution references.

Property	Unit	Method	Methylic BD	Ethylic BD	[a]ANP
Free glycerin	% (m/m)	CG- FID	0.00	0.00	0.02
Total glycerin	% (m/m)	CG- FID	0.04	0.28	0.25
Monoglycerides	% (m/m)	CG- FID	0.10	0.44	0.70
Diglycerides	% (m/m)	CG- FID	0.08	0.70	0.20
Triglycerides	% (m/m)	CG- FID	0.00	0.06	0.20
Ester content	% (m/m)	CG-MS/ EN 14103	90.6	87.3	96.5
Induction period (IP)	h	Rancimat/EN 14112	4.19 ± 0.18	4.40 ± 0.07	8.00
Acid number (AN)	mg$_{(KOH)}$ g^{-1}	ABNT-NBR 14448	0.27 ± 0.01	0.40 ± 0.01	0.50

[a] Values established by ANP resolution 45(2014) [28].

In Table 3, the induction period is showed for pure and added antioxidant agents TBHQ and eugenol. In spite of the TBHQ to be more efficient, the eugenol antioxidant shows an important increasing in that parameter. The induction period for TBHQ addition is according to ANP and European EN 14214 requirements, but the eugenol addition is according to European EN 14214 only. However, an important result is provided by a study of the dependence of eugenol concentration on induction period, as is shown in Figure 1.

As shown in Figure 1, the induction period for ethylic biodiesel shows higher values than for methylic ones, despite the several oscillations values during the increasing in eugenol concentration. It is important to reveal the biodiesel were stocked by 6 months before this study, because aids to understand the reduction of induction period values founded when compared to those ones presented in Table 3.

In Figure 2 it is shown the evolution of acid number for biodiesel samples as a function of eugenol concentration. There is a noticed reduction of acid number up to 0.2% of eugenol concentration and no significant enhancement for higher values. Thus, it is not important the increasing of eugenol concentration in order to improve the biodiesel quality, concerning the antioxidant agent.

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Table 3. Comparative induction period (average) for biodiesel samples as a function of antioxidant agent.

Sample	Ethylic BD (h)	Methylic BD (h)
BD-Pure	4.40 ± 0.07 [aBB]	4.19 ± 0.18 [bBB]
BD-TBHQ (0.05 % m/m)	12.26 ± 0.04 [aA]	7.26 ± 0.08 [bA]
BD-Eugenol (1.50 % m/m)	6.03 ± 0.03 [aA]	5.09 ± 0.01 [bA]

[A] Comparison between treatments, antioxidant additions (columns). [a] comparison of two types of biodiesels (lines). Same letter means the differences is not significant for those samples according Tukey tests ($p < 0.05$).
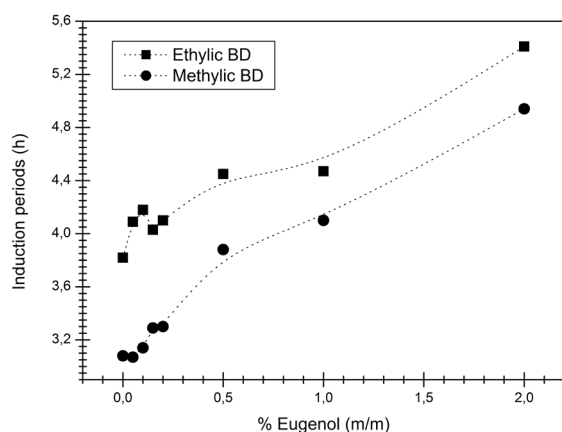

Figure 1. Evolution of induction period (triplicate average) for biodiesel samples as a function of eugenol concentration.
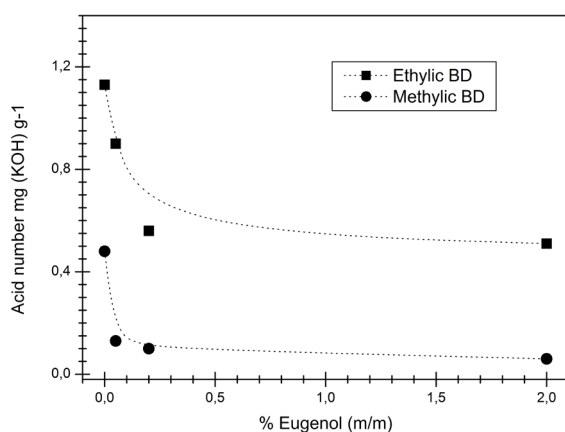

Figure 2. Evolution of acid number (triplicate average) for biodiesel samples as a function of eugenol concentration.

4. CONCLUSION

In that work, several biodiesel samples were prepared from residual frying oil through homogenous catalysis with NaOH catalyst. Two transesterification alcohols were used in order to compare physicochemical parameters, acid number and period of induction for oxidative reaction. Several parameters showed in according to ANP requirement,

which is an important result, concerning the low quality of the thermally degraded residual frying oils. In addition, an accurate study about the use of eugenol as antioxidant agent was also performed, which showed that acid number and period induction can be improved with low amount of antioxidant agent. Some parameters remain inadequate, such as diglycerides amount and insufficient conversion rate, but new investigation can be carried out in order to make better these parameters.

5. ACKNOWLEDGMENTS

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