AVALIAÇÃO DA AÇÃO ANTIOXIDANTE DA CURCUMINA DURANTE ESTOCAGEM DE BIODIESEL COMERCIAL PRODUZIDO COM ÓLEO DE SOJA E SEBO BOVINO

ASSESSMENT OF ANTIOXIDANT ACTION OF CURCUMIN DURING STORAGE OF COMMERCIAL BIODIESEL PRODUCED FROM SOYBEAN OIL AND BEEF TALLOW

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RESUMO

O biodiesel surgiu como uma fonte alternativa aos combustíveis fósseis. No Brasil, para se atribuir boa qualidade ao biodiesel, quanto à estabilidade à oxidação, é necessário que o mesmo apresente um mínimo de 8 h para o Período de Indução (PI), determinado à temperatura de 110 ^{0}C pelo método de Rancimat, de acordo com a resolução nº 45/2014 da ANP. Como, na maioria dos casos, o biodiesel produzido não atende a padrões estabelecidos de estabilidade oxidativa, é necessário adicionar antioxidantes, que retardam seu processo oxidativo. Dessa forma, esse trabalho propõe um estudo sobre a ação da curcumina, um antioxidante natural, em biodiesel comercial que foi produzido a partir da mistura de 80% óleo de soja e 20% sebo bovino. Neste estudo, as amostras ficaram estocadas durante 180 dias a 43 ^{0}C, de acordo com a norma ASTM D4625. Foi possível observar que a curcumina garantiu maior estabilidade oxidativa ao biodiesel e menores valores de índice de acidez, durante o período de estocagem. Estudos cinéticos indicaram que a amostra aditivada com curcumina apresentou maior valor de energia de ativação para o processo de degradação oxidativa, demonstrando que a adição deste antioxidante natural torna o biodiesel mais resistente à oxidação.

Palavras-chave: Rancimat, Estudo cinético, Índice de acidez.

ABSTRACT

Biodiesel has emerged as an alternative source to fossil fuels. In Brazil, to assign a good quality to biodiesel, regarding oxidation stability, it is necessary that the biodiesel shows a minimum of 8 h of induction period (IP), determined at a temperature of 110 ºC by the Rancimat method, in accordance with Resolution No. 45/2014 of ANP. As, in most cases, the biodiesel produced does not meet the established standards of oxidation stability, it is necessary to add antioxidants, which slow down the oxidative process. Thus, this paper proposes a study on the action of curcumin, a natural antioxidant, on commercial biodiesel produced from blending 80% soybean oil and 20% beef tallow. In this study, samples were stored for 180 days at 43 ºC, according to ASTM D4625 recommendations. It was possible to observe that curcumin ensured greater oxidation stability to biodiesel and lower acid number values during the period of storage. Kinetic studies showed that samples with the addition of curcumin showed the highest value of activation energy for the oxidative degradation process, demonstrating that adding this natural antioxidant makes biodiesel more resistant to oxidation.

Keywords: Rancimat, Kinetic study, Acid number.

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INTRODUCTION

Emerging as a sustainable alternative to fossil fuels, biodiesel has features such as being biodegradable, nontoxic, with a boiling point higher than diesel, free of sulfur and aromatics. In addition, it can be produced using low-cost raw materials, thus bringing economic and environmental benefits (Kumar *et al.*, 2018; Leonardo *et al.,* 2012).

Despite its advantages, biodiesel is more susceptible to oxidative degradation than petroleum diesel. Therefore, to ensure biodiesel quality, a minimum of 8 hours of Induction Period (IP) is fixed to the oxidation stability parameter at a temperature of 110 ºC, according to the Resolution No. 45 of 2014 of ANP - Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (Oliveira *et al.,* 2014).

In Brazil, the largest source of raw material for biodiesel production has been soybean oil; however, biodiesel can be produced from different sources of vegetable oils and animal fats. Nevertheless, few studies have been performed regarding biodiesel production using animal fats. Beef tallow is a waste generated in industries during the processing of animal meat that can be used in biodiesel production as a low-cost raw material, and its re-use contributes to sustainable development (Banković-Ilić *et al.*, 2014).

Biodiesel production from beef tallow confers high oxidation stability, since esters that constitute this biodiesel feature less content of double bonds than biodiesel from vegetable oils such as soybean; however, has the disadvantage of forming crystals at lower temperatures. For this reason, blends have been used with different percentages of biodiesel of soybean oil and beef tallow, minimizing the disadvantages of these raw materials and leading to a biodiesel with improved oxidation stability-related properties (Oliveira *et al.,* 2012 and Cremonez *et al.,* 2016).

The oxidative process of biodiesel can be accelerated by several factors such as temperature, light, oxygen, contamination by metals, among others. As the temperature is one of the factors affecting oxidation stability, kinetic studies are performed regarding degradation in order to monitor the oxidative process at high temperatures. These studies can be performed by accelerated oxidation test by the Rancimat method. In this case, the IP is determined at different temperatures. From the IP values obtained by the Rancimat method, for each trial, graphs are constructed from the Arrhenius equation, which provides the value of activation energy (Ea) for the oxidative degradation process of biodiesel. The higher the value of Ea, the more resistant to oxidative process is the biodiesel (Spacino *et al.*, 2015; Gregório *et al.*, 2018).

To meet the quality standards required for oxidation stability, the addition of antioxidants to biodiesel is usually required. Antioxidants are substances that when added in small concentrations can slow down significantly the start of oxidative reactions by removing free radicals. These antioxidants can be natural or synthetic (Tang *et al.,* 2010; Pitaro *et al.,* 2012).

Several synthetic antioxidants are already being widely added to biodiesel. However, natural antioxidants have been increasingly studied. These substances can be extracted from roots, barks, leaves, fruits, and seeds; being biodegradable and less toxic, in addition, to ensure a sustainable character to biodiesel (Taghvaei & Jafari, 2015; Varatharajan & Pushparani, 2017).

Considering the relevance of the use of natural antioxidants in biodiesel conservation and increasing use of beef tallow as part of raw material, this paper proposes a study on the action of the natural antioxidant curcumin in commercial methyl biodiesel produced from a blend of soybean oil and beef tallow, at a rate of 80/20% (m/m), during storage at 43 ºC, in accordance with ASTM D4625 standard and by kinetic studies.

MATERIAL AND METHODS

A commercial sample of biodiesel produced via methyl route from a blend of 80% soybean oil and 20% beef tallow, acquired from an industry, without the addition of synthetic antioxidants was used for the experiments.

The natural antioxidant in the study is curcumin (Neon, 97%). Reagents used were of P.A. grade or higher. All analyses were performed in triplicate and the determined values expressed as a mean and standard deviation. Statistical analyses were performed by analysis of variance (ANOVA) and Tukey Test, using the software Bioestat 5.0, considering $p < 0.05$ (Biostat, 2008).

2.1. Determination by gas chromatography

The quantification of the major esters of fatty acids in commercial biodiesel (control) was

performed by gas chromatography with flame ionization detector (GC-FID), according to EN 14103 of 2003 recommendation, using a Shimadzu CG2014 equipment. For determination of the retention times of the esters, the standard Supelco 37 (FAME mix) was used.

2.2 Test in oven

Two conditions were used: pure biodiesel samples (control) and samples with the addition of curcumin (curcumin) at the concentration of 7500 mg kg^{-1}. Biodiesel samples were stored in amber bottles of 300 mL, totaling 15 bottles, filled to the brim, and covered with aluminum foil to prevent the influence of light on the oxidative process. Bottles were stored in an oven at 43 ± 1 ºC, in accordance with ASTM D4625 standard, a condition in which 1 week at 43 ºC represents 1 month of storage at room temperature (ASTM D4625, 2014). The storage period in the oven was 180 days, and analyses were performed immediately after preparation of samples (addition of an antioxidant to biodiesel) and after 30, 90, 120 and 180 days. In addition, a weekly rotation of the bottles was performed to ensure that every sample had the same influence of the conditions in the oven.

2.2.1 *Assessment of oxidation stability*

The oxidation stability was determined by the Induction Period (IP) using the equipment for analysis of Oxidation Stability Metrohm, model Professional Biodiesel Rancimat 893, according to the European standard EN 14112. In this method, 3.0 g of the sample is measured, using analytical, and placed in the reaction tubes that are placed in the heating block of the Rancimat equipment. Samples are analyzed under a constant air flow of 10 L h^{-1}, at a temperature of 110 ºC, and their respective volatile products are collected in containers containing 50 mL distilled and deionized water, and the conductivity was constantly monitored. The IP was determined by water conductivity versus time curve, by StabNet software, using the second derivative method.

The equipment tubes and connections were rigorously cleaned between each series of measurements, with Extran™ detergent, indicated for such analyses, and subsequently rinsed with ethyl alcohol and distilled water. Clean materials were dried in an oven at 55 ºC, according to manufacturer's guidelines (Methohm, 2014).

2.2.2 *Analyses of physicochemical indexes*

In these tests were performed analyses of Acid Number (AN) and Iodine Number (IN), following the ASTM D664 and EN 3961 methods, respectively, using a potentiometric titler Titrino Plus 848 (Metrohm).

For determination of Acid Number, 20 g of sample were used, since the acidity expected was between 0-1 mg kg^{-1}; dissolved in a mixture of solvents (toluene, isopropyl alcohol and water (50/49.5/0.5% v/v/v) and titrated with KOH solution 0.1 mol L^{-1} in isopropanol, standardized with benzoic acid (Sigma-Aldrich, ≥ 99.9%).

For the Iodine Number, 0.13 g of sample were used, since the expected value was between 100-150 g I_2/100g. The titration was performed with sodium thiosulphate solution (Synth) and standardized with potassium iodate (Dinâmica).

2.2.3 *Absorption spectroscopy in the UV-Vis*

The analyses were performed using a spectrophotometer Hitachi, model U-3000, with spectra scanning from 200 to 800 nm, in a quartz cuvette with 1 cm optical path. Samples were diluted in dichloromethane, in the proportion of 60 µL of the sample for 3000 µL of the solution.

2.3 *Kinetic study*

For the kinetic study, the IP was determined using the temperatures of 110 ºC, 120 ºC, and 130 ºC, for the control sample and for the sample with the addition of curcumin. From the IP values obtained by the Rancimat, graphs of ln(IP) versus the reciprocal of absolute temperature (1/T) were built for each test following the Arrhenius equation, which provides the value of activation energy (Ea) calculated by the angular coefficient of the straight line (Dunn, 2008). The Arrhenius equation was used in this study as described according to Dunn (2008) and Savi *et al.* (2017):

$$\ln(\mathrm{PI}) = B_0 + B_1 . T^{-1}$$

Where T is the absolute temperature in Kelvin and B_0 and B_1 are constants obtained by linear and angular coefficient, respectively, of the line obtained by linear regression of the curve of ln(IP) vs. 1/T; and the kinetic constant *k* is obtained for each temperature from the inverse of the IP(k = 1/ PI (h^{-1})).

The parameter B_0 relates to pre-

exponential factor, A (B_o = ln A), while the parameter B_1 relates to the activation energy of the equation, Ea (kJ/mol), where Ea = R.B_1, and R is the gas constant (Savi *et al.*, 2017).

RESULTS AND DISCUSSION

3.1. Characterization of commercial biodiesel by gas chromatography

Table 1 shows the data analyzed by gas chromatography of control sample of commercial biodiesel produced via methyl route from blending 80% soybean oil and 20% beef tallow. All quality parameters meet the quality parameters established.

The percentage of biodiesel conversion is the sum of the percentages of all esters. The results of this analysis indicated a 97.5% conversion for methyl biodiesel.

The parameters assessed are important to ensure the good performance of biodiesel as a fuel. For instance, high contents of glycerol can cause engine clogging, as well as decrease biodiesel stability during storage (Munari *et al.,* 2009 and Oliveira *et al.,* 2018).

3.2 Test in oven

For the test in the oven, a control sample of pure commercial biodiesel and a sample with the addition of curcumin at the concentration of 7500 mg kg^{-1} were used. Some natural antioxidants were previously added to commercial biodiesel sample under study, and in the initial investigation, curcumin showed the highest antioxidant potential (SANTOS *et al.,* 2017).

3.2.1 *Assessment of oxidation stability*

Table 2 shows the values of IP of pure biodiesel (control) and with the addition of curcumin, depending on the time of storage at 43 ºC, according to ASTM D4625 recommendation. There was no significant difference in IP as a function of time, for none of the conditions; however, there were significant differences with the addition of curcumin in relation to the control sample. Both samples attended the standards required by Resolution No. 45 of 2014 of ANP (min 8 h of IP) showing initially an IP of 8.83 h for a control sample and 12.05 h for the sample with the addition of curcumin. Therefore, there was an increase in the oxidation stability of more than 3 h of IP with the addition of the natural antioxidant curcumin.

The samples remained with IP values, as required by Resolution No. 45 of ANP (2014), until the end of the 180 days and without significant changes. Figure 1 shows that samples with the addition of curcumin were more stable during the period up to 120 days since there was a lower variation of IP.

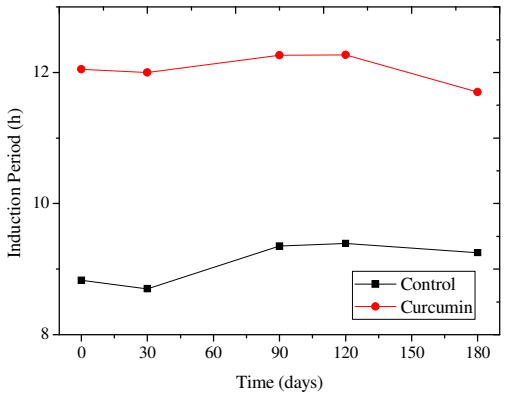

Figure 1. *Induction Period of samples in function of storage time*

Serqueira *et al.* (2015) also observed an increase in the IP of biodiesel from cotton oil with the addition of 1000 mg kg^{-1} of curcumin. This increase in the IP is assigned to the ability of curcumin to kidnap free radicals, inhibiting lipid peroxidation (Sun *et al.*, 2002; Marchi *et al.,* 2016).

It should be emphasized that the 180 days in the oven at 43 ºC correspond to approximately 2 years stored at room temperature. The control sample also showed good oxidation stability, probably due to the high presence of saturated esters derived from beef tallow (Oliveira *et al.,* 2012).

Pereira *et al.* (2017), analyzing the oxidation stability of different biodiesels without addition of antioxidants stored in steel tanks at room temperature for 250 days, observed greater stability in samples of biodiesel produced from blends of soybean oil (70-50%) with beef tallow (30-50%) when compared to biodiesel of pure soybean oil. In the same study, the authors observed that the addition of 50% beef tallow to soybean oil in biodiesel production increased oxidation stability (IP = 10.3 h) in approximately 4 h when compared to biodiesel produced only from soybean oil (IP = 6.4 h). This greater stability is probably because the beef tallow shows a higher amount of saturated fatty acids,

ensuring greater stability to biodiesel.

In study regarding the oxidation stability of biodiesel from soybean oil with addition of curcumin or beta-carotene stored at 25 ºC for 120 days, Sousa *et al.* (2014) observed that curcumin was more efficient when compared to beta-carotene, increasing oxidation stability in little more than 4 h with addition of curcumin at the concentration of 1500 mg kg^{-1}. The IP values determined were 4.97, 8.03 and 9.11 h for the pure soybean biodiesel (control) and with the addition of 1000 and 1500 mg/Kg of curcumin, respectively. The results obtained in the studies cited and in the present study indicate curcumin as an efficient natural antioxidant in improving the oxidation stability, both of biodiesel samples produced from soybean oil and blends of soybean oil and beef tallow, stored at different temperatures for long periods.

3.2.2 *Assessments of physicochemical indexes*

The Acid Number relates to the concentration of free fatty acids formed during the oxidative process in biodiesel, therefore the higher its acidity, the greater the level of degradation of the sample (Oliveira *et al.*, 2018). It is defined as the mass (mg) of potassium hydroxide required to neutralize the free fatty acids of 1 g of sample. Table 3 shows the values of AN of pure biodiesel (control) and with the addition of curcumin, throughout the period of storage at 43 ºC, according to ASTM D4625 recommendation.

The samples remained within the limit established (max 0.50 mg KOH/g). However, we can observe there was a significant increase in the AN for all samples, depending on the time of storage. Nevertheless, there was a significant difference with the addition of curcumin when compared to the control sample, with lower AN values throughout the storage period.

It is worth mentioning that Pereira *et al.* (2017) observed an increase in AN of biodiesel with the increase in the proportion of beef tallow in the blend with soybean oil used as raw material, reaching 0.30 mg KOH/g at a rate of 30/70%. In this study, blending 20% beef tallow and 80% soybean oil, we observed an AN of 0.26 mg KOH/g, and with the addition of curcumin, this index decreased to 0.21 mg KOH/g. Therefore, the addition of curcumin minimized the increased acidity caused by the higher proportion of beef tallow in the blend used as raw material in biodiesel production.

The lower AN in the sample with the addition of curcumin is related to the lower content of free fatty acids, showing lower oxidative degradation for this biodiesel sample. This result shows the efficiency of curcumin in controlling the acidity of biodiesel samples, in addition to ensuring excellent oxidation stability.

Schober & Mittelbach (2004) observed an increase in the AN of waste cooking oil biodiesel and rapeseed biodiesel with the addition of 1000 mg kg^{-1} of synthetic antioxidants Ionox 220, Vulkanox BKF, Vulkanox ZKF and DTBHQ. Considering that the AN tends to increase during storage and the maximum value established by RAMP 45 of ANP (2014) is 0.50 mg KOH/g, the results observed indicate curcumin as a more efficient antioxidant for application in biodiesel, because it decreases the AN even at higher concentration and maintains low values of AN during long periods of storage.

For the Iodine Number, the European Standard EN 14111 establishes a maximum value of 120 g I_2/100g, used as a reference in this study. Throughout the period of storage, the IN values for the pure biodiesel (control) and with addition of curcumin remained below the threshold established by the standard, without significant difference between them (Table 4).

The IN corresponds to the measure of the total number of double bonds present in biodiesel, the higher the index, the greater the number of double bonds. There was a decrease in the IN of biodiesel samples with and without the addition of curcumin at the period of 90 days (Figure 2); this might have happened due to the decrease of unsaturations in the biodiesel and formation of free radicals, which happens during the oxidative process (Ínanç & Maskan, 2014).

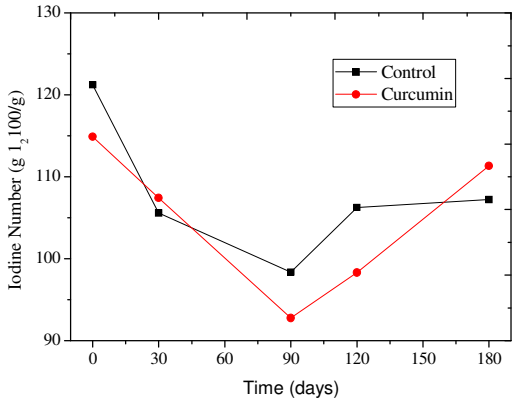

Figure 2. *Iodine Number of samples in function of storage time*

There was a decrease in the value of IN in all samples immediately after the beginning of the

storage period. Similar behavior was observed by Ayoola *et al.* (2016) and Kovács *et al.* (2011), which indicates a decrease in the number of double bonds and the beginning of the degradation process of samples.

With longer storage periods, the IN values increase, probably due to conjugated dienes that are also formed during oxidation of samples (Suota *et al.*, 2018). Significant differences were not observed between the two conditions (with and without the addition of curcumin) regarding this parameter.

3.2.3 *Absorption spectroscopy in the UV-Vis*

The characterization of samples by absorption spectroscopy in the UV-Vis spectra was performed during the entire period of storage in order to monitor the formation of by-products, generated from the oxidative process of biodiesel.

During the degrading process of biodiesel, there is oxidation of esters of polyunsaturated fatty acids, causing the formation of hydroperoxides and displacement of double bonds, with consequent formation of conjugated dienes, which absorb at 232 nm (Tolentino *et al.,* 2014). By the analysis of absorption spectroscopy in the UV-Vis region, it was possible to observe intense absorption in the region near 232 nm for biodiesel with and without the addition of curcumin, characteristic of formation of conjugated dienes (Figure 3).

The sample with the addition of the natural antioxidant curcumin showed lower values of absorption of conjugated dienes throughout the storage period, being more stable when compared to the control sample, as demonstrated in Figure 1 for the sample with curcumin for the IP parameter.

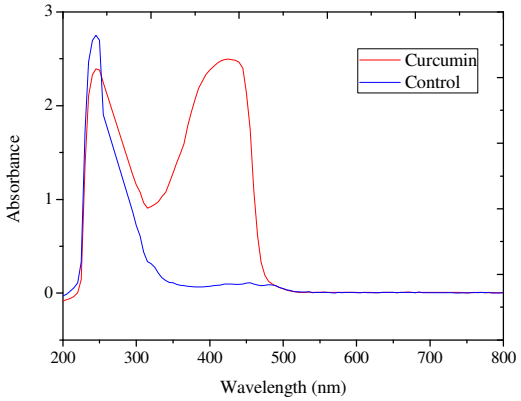

Figure 3. *Absorption spectra in the UV-VIS of samples at 180 days of storage*

The maximum absorption wavelength (λ_{max}) of curcumin is at 425 nm (Erpina *et al.*, 2017). Figure 3 shows there is absorption at this wavelength, confirming the presence of curcumin at the end of the storage period.

3.3 Kinetic Study

Figure 4 shows the results of the study at different temperatures performed by the Rancimat method for a control sample and with the addition of curcumin at the concentration of 7500 mg kg^{-1}.

From the graphs of ln(IP) vs. 1/T and using the modified Arrhenius equation, the values of Ea were obtained, corresponding to 87.74 kJ mol^{-1} for a control sample and 99.14 kJ mol^{-1} for the sample with the addition of curcumin. The highest value of activation energy for the sample with curcumin confirms that the addition of this natural antioxidant in biodiesel makes it even more resistant to the oxidative process. This indicates curcumin as an effective antioxidant even when biodiesel was stored at high temperatures.

Dunn (2008) obtained the value of Ea = 90 kJ mol^{-1} for methyl biodiesel from soybean oil. Angilelli *et al.* (2017) obtained the value of Ea = 81.03 kJ mol^{-1} for biodiesel produced with sodium hydroxide as raw material 32% soybean oil and 68% of different animal fats (beef, pork, and chicken). While Rogmanoli *et al.* (2018) found a value of Ea = 86.25 kJ mol^{-1} for commercial biodiesel from soybean oil. These values are similar to that found in this study for the control sample of biodiesel produced blending 80% soybean oil and 20% beef tallow (Ea = 87.74 kJ mol^{-1}).

Xiong *et al.* (2016), analyzing biodiesel produced from waste frying oil by the PetroOXY method, obtained the value of Ea = 94.04 kJ mol^{-1} for the control sample, reaching Ea = 97.30 kJ mol^{-1} with the addition of synthetic antioxidant pyrogallol. This suggests that the addition of antioxidants both synthetic, such as the one used in the study of Xiong *et al.* (2016), and natural, such as curcumin used in this study, increase the values of activation energy, providing biodiesel as a final product with greater oxidation stability.

Moreover, using the IP data obtained from the Rancimat equipment at different temperatures, it was performed an extrapolation of the storage time using the StabNet software for the control sample and with the addition of curcumin at two different temperatures (Table 5).

The sample with the addition of curcumin showed greater extrapolated time of storage at both temperatures, 25 ºC, and 43 ºC, therefore it can be stored for approximately 10 years at room temperature without change in quality regarding oxidation stability. According to ASTM D4625, storage for 180 days at 43 ºC corresponds to approximately 2 years at room temperature, coinciding with the values found for the control sample on the extrapolation at 25 ºC. It is worth mentioning that the extrapolation considers only oxidative degradation and does not take into account the hydrolytic and by the action of microorganisms' degradations of the biofuel under study.

CONCLUSIONS

Curcumin was effective in slowing down the formation of free fatty acids, leading to lower values of Acid Number and lower variation in Induction Period values during storage of biodiesel. The values found during the storage period remained within the standard required by Resolution No. 45 of 2014 of ANP.

The method used for the storage test, ASTM D4625, describes that a sample stored at the temperature of 43 ºC for 1 week, is equivalent to 1 month stored at room temperature; therefore, the samples would maintain good oxidation stability for at least 2 years, if stored at room temperature.

In kinetic studies, the sample with addition of curcumin showed the greatest value of activation energy (Ea = 99.14 kJ mol^{-1}), demonstrating that, with the addition of this natural antioxidant biodiesel has become much more resistant to oxidative degradation, increasing in 4.7 times the estimated storage time at 25 ºC using the extrapolation by the Arrhenius equation.

Moreover, the blend of soybean oil with beef tallow can be considered a good raw material for biodiesel production, since soybean oil is produced on large scale in the country, while beef tallow is considered a raw material of low added value; and the commercial biodiesel studied produced by blending soybean oil/beef tallow at a rate of 80/20% showed properties in accordance with the quality parameters established by Resolution No. 45/2014 of ANP for oxidation stability and acid number.

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Table 1. *Quality parameters determined by gas chromatography for a sample of commercial biodiesel*

Parameters	Unit	Test Method	Thresholds	Results
Specific mass at 20 0C	kg/m3	ASTM D 4052	850 –900	882
Kinematic Viscosity a 40 0C	mm2/s	ASTM D 445	3,0 – 6,0	4,6
Water content, max	mg/kg	ASTM D 6304	200	175,4
Ester content, min.	% mass	EN 14103	96,5	97,5
Free glycerol, máx.	% mass	ASTM D6584	0,02	<0,001
Total glycerol, máx.	% mass	ASTM D6584	0,25	0,12
Monoacylglycerol, máx.	% mass	ASTM D6584	0,70	0,44
Diacylglycerol, máx.	% mass	ASTM D6584	0,20	<0,092
Triacylglycerol, máx.	% mass	ASTM D6584	0,20	0,01

Table 2. Induction Period values for samples in function of storage time

Time (days)	IP (h)	
	Control	Curcumin
0	$8,83 \pm 0,06^{aA}$	$12,05 \pm 0,16^{bB}$
30	$8,70 \pm 0,04^{aA}$	$12,00 \pm 0,13^{bB}$
90	$9,35 \pm 0,04^{aA}$	$12,26 \pm 0,14^{bB}$
120	$9,39 \pm 0,21^{aA}$	$12,27 \pm 0,09^{bB}$
180	$9,25 \pm 0,02^{aA}$	$11,70 \pm 0,02^{bB}$

Same lowercase letters in the same column or same uppercase letters in the same row are not significantly different ($p < 0.05$).

*Results are expressed as the mean ± standard deviation of triplicate experiments.

Table 3. *Acid Number of samples, depending on the time of storage*

Time (days)	AN (mg KOH/g)	
	Control	Curcumin
0	$0,2652 \pm 0,0017^{aA}$	$0,2168 \pm 0,0133^{gG}$
30	$0,2433 \pm 0,0011^{bB}$	$0,2463 \pm 0,0229^{hH}$
90	$0,2544 \pm 0,0038^{dD}$	$0,2542 \pm 0,0081^{jJ}$
120	$0,2713 \pm 0,0017^{eE}$	$0,2497 \pm 0,0070^{kK}$
180	$0,2827 \pm 0,0057^{fF}$	$0,2650 \pm 0,0075^{lL}$

Same lowercase letters in the same column or same uppercase letters in the same row are not significantly different ($p < 0.05$).

*Results are expressed as the mean ± standard deviation of triplicate experiments.

Table 4. *Iodine Number of samples in function of storage time*

Time (days)	IO (g I_2/100g)	
	Control	Curcumin
0	121,2 ± 1,3^{aA}	114,8 ± 3,6^{aA}
30	105,5 ± 1,0^{bB}	107,4 ± 5,5^{bB}
90	98,3 ± 5,7^{dD}	92,7 ± 10,0^{dD}
120	106,2 ± 9,8^{eE}	98,3 ± 5,9^{eE}
180	107,2 ± 3,1^{fF}	111,3 ± 2,2^{fF}

Same lowercase letters in the same column or same uppercase letters in the same row are not significantly different ($p < 0.05$).

*Results are expressed as the mean ± standard deviation of triplicate experiment

Table 5. *Extrapolation of storage time of samples*

Sample	Temperature	
	25 ^{0}C	43 ^{0}C
Control	2.30 years	0.30 years
Curcumin	10.8 years	1.11 years

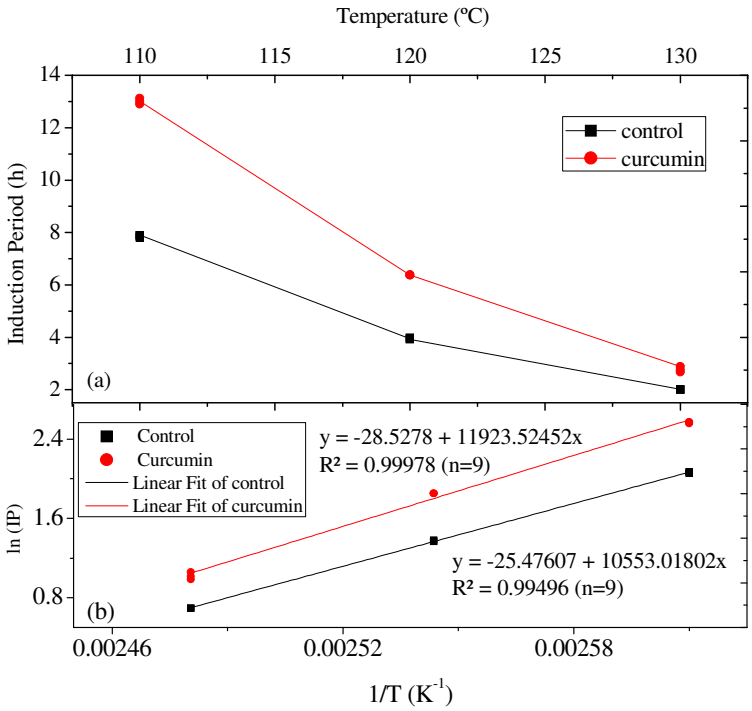

Figure 4. *Oxidation stability for a control sample and with the addition of curcumin at different temperatures: (a) IP obtained by the Rancimat method in function of temperature; (b) linear relationship of the neperian logarithm of IP and the reciprocal of the absolute temperature*