Open Access

Journal of Energy and Power Technology

LIDSEN Publishing Inc.

Research Article

Evaluation of Oxidative Stability and Kinetic Parameters of the Cottonseed and Soybean Biodiesels by Rancimat and Differential Scanning Calorimetry Techniques

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Academic Editor: Islam Md Rizwanul Fattah

Special Issue: Biogas: From the Fuel Production Side to the Energy Generation

Journal of Energy and Power Technology
2022, volume 4, issue 4
doi:10.21926/jept.2204042

Received: September 26, 2022
Accepted: December 09, 2022
Published: December 22, 2022

Abstract

In this study, the oxidative stability of the cottonseed oil biodiesel (CB) and soybean oil biodiesel (SB) was investigated by two methodologies, Rancimat and Differential Scanning Calorimetry (DSC), using samples fresh and aged (mid-term storage condition (100 days)). The biodiesel samples were synthesized by transesterification and characterized by specific mass, kinematic viscosity, acidity value, ester content, viscosity index, and peroxide value. The activation energy (E_a), Arrhenius pre-exponential factor (Z), reaction order (n), and reaction rate at constant temperature (k(T)) were calculated by Borchardt and Daniels method. The

results showed that oxidation affected the physicochemical properties of the biodiesel samples, especially, acidity (mg KOH/g), peroxide value (meq/1000 g), and induction period, with a decrease of around 55% for CB and 29% for SB. For kinetic parameters, the k(T) of both aged samples presented the highest values, with an increase of around 314% for SB. It was also observed that the rate constants increased with decreasing values of the induction period, in agreement with the current literature. According to the evaluation, the Borchardt and Daniels method can be recommended for a quick assessment of the biodiesel oxidation kinetic parameters.

Keywords
Biodiesel storage; differential scanning calorimetry; Rancimat; kinetic parameters

1. Introduction

Biodiesel is a renewable fuel obtained by the transesterification of vegetable oils and animal fats and is mainly used in diesel cycle engines [1, 2]. Because it consists of a mixture of fatty acid esters that differs in the number of carbons and unsaturations, it is highly sensitive to oxidation [3, 4]. Thus, to be marketed, it needs to go through purification processes to meet its quality specifications [1, 5].

The evaluation of the oxidative stability of biodiesel is essential since the oxidation products such as aldehydes, ketones, and short-chain acids can accelerate the degradation process of fuel delivery materials [6, 7]. For example, high temperatures coupled with the presence of copper and nitrile rubber in the fuel delivery system can catalyze the oxidation process that accelerates fuel deterioration [6, 8, 9]. Thus, the stored fuel also can be contaminated by oxidized biodiesel that returns through the recirculation system [1].

Nowadays, biodiesel is only used in blends with fossil diesel at different proportions (20% vol (B20) in the United States and 30% vol (B30) in Indonesia, and 10% vol (B10) in Brazil) [10, 11]. However, because of the lower oxidative stability of biodiesel compared to fossil diesel, a greater proportion of metal corrosion and elastomer degradation could lead to early failure of fuel delivery materials [6, 7, 9]. Therefore, monitoring the oxidative stability of mid-term stored biodiesel samples and determining the kinetic parameters by different methods, including Differential Scanning Calorimetry (DSC), is important for the biofuel industry.

Several instrumental methods have been used to monitor the oxidative stability of biodiesel samples, such as Rancimat, Fourier Transform Infrared spectroscopy (FTIR), Ultraviolet-visible spectroscopy (UV-Vis), Two-channel and differential dielectric spectroscopy (TD-DES), Easy ambient sonic-spray ionization mass spectrometry (EASI-MS), Nuclear Magnetic Resonance spectroscopy (NMR), and Gas Chromatography-Mass Spectrometry (GC/MS) [12, 13]. However, most of these methodologies require many hours of experimentation and multiple tests, which makes their reproduction more complex and laborious. Thus, DSC appears as an alternative method to determine the thermal behavior of organic molecules and the kinetic parameters of exothermic reactions using a single scan at low heating rates and small specimen sizes, such as the method of Borchardt and Daniels, which is based on the relation between the degree of conversion (α) and

enthalpy changes obtained by dynamic DSC analysis and is one of the simplest for modeling exothermic reactions [14-18]. The great advantage of this method is the rapidity of performing the analysis [15].

With Borchardt and Daniels' method, some parameters such as activation energy (E_a), reaction order (n), and degree of conversion (α) can be evaluated, providing an overview of the kinetics behavior, which can be recommended when a quick assessment of the biodiesel oxidation kinetic parameters is needed since it requires only one DSC scan [15, 17, 18].

Other challenges to biodiesel quality are storage and long-distance transportation. Producers point out the need for actions to ensure the quality at all points of the biodiesel chain, from manufacturing to the final consumer, including the mixture with fossil diesel, storage, and transport in the various models [19]. The contact with air and water during storage can affect the quality of biodiesel, which is highly hygroscopic and, despite post-production provisions, degradation processes can occur during the transport and storage period, generating sludge and adhesive sediments [20, 21].

Under improper storage conditions, the moisture content can increase and consequently support bacteria colonization, since water is the main nutrient for microbial activity [19]. Thus, if biodiesel exceeds 30 days of certification and the difference to the specific mass at 20°C of the quality certificate is less than 3.0 kg m^{-3}, the water content, acidity index, and oxidative stability at 110°C must be determined again. If it is greater than 3.0 kg m^{-3}, biodiesel must be certificated again [5].

Researchers have also noted that the consumption of degraded fuel can lead the biomass formation at the oil-water interface, causing clogging of filters and pipes and wear in injector nozzles [20-23]. Because of this, the biodiesel evaluation in storage conditions is important to obtain more knowledge about the system (biodiesel and diesel-biodiesel) and indicate the necessary practices to ensure fuel quality at all points of the supply chain [1, 24].

For this reason, this study aimed to investigate the oxidative stability of the cottonseed oil biodiesel (CB) and soybean oil biodiesel (SB) by two methodologies, Rancimat and Differential Scanning Calorimetry using samples fresh and aged (mid-term storage condition (100 days)). The E_a, Arrhenius pre-exponential factor (Z), n, and reaction rate at constant temperature (k(T)) were calculated by Borchardt and Daniels method, and the efficiency was evaluated by the comparison with the induction period obtained by Rancimat. The biodiesel samples were synthesized by transesterification and characterized by specific mass at 20°C, kinematic viscosity at 40°C, acidity value, ester content, viscosity index, and peroxide value. The influence of oxidation on physicochemical properties was also shown. A comparison between the kinetics parameters obtained by the Borchardt and Daniels method and the influence of oxidation on physicochemical properties provides a preliminary result that can help indicate critical storage conditions for the biodiesel and diesel-biodiesel systems and propose a method for a rapid evaluation of the kinetic parameters of biodiesel oxidation.

2. Materials and Methods

2.1 Materials

Both cottonseed and soybean oils were acquired from a local market in Fortaleza (Brazil). Analytical grade methanol (99.8%), potassium hydroxide (85.0%), and sodium sulfate (99.0%) were purchased from Sigma Aldrich (United States).

2.2 Biodiesel Samples Production

The biodiesel samples were produced by alkaline transesterification using a three-neck round-bottom flask connected to a reflux condenser for each vegetable oil (cottonseed and soybean). The reaction was started after the addition of methanol, a molar ratio of 1:6 (oil/alcohol), and potassium hydroxide (1.0% wt. KOH/oil). The system was mixed using a magnetic stirrer and heated at 60°C for 1 hour. Afterward, the reaction mixtures were transferred to separating funnels for separate ester and glycerol phases. The ester phases were washed with distilled water to remove the excess methanol and catalyst. In the final step, ester phases were distilled in a rotatory evaporator and dried using anhydrous sodium sulfate to remove residual humidity.

To evaluate the physicochemical properties, oxidative stability and kinetic parameters were used in two groups: (1) fresh cottonseed biodiesel (FCB), fresh soybean biodiesel (FSB), and (2) aged cottonseed biodiesel (ACB), aged soybean biodiesel (ASB). Fresh samples were analyzed immediately after biodiesel production, while aged biodiesel samples were analyzed after a 100-day storage period at room temperature.

2.3 Physicochemical Properties and Compositional Analyses

The acidity value was determined following the American Oil Chemists Society (AOCS) method Cd 3d-63, and the kinematic viscosity at 40°C and specific mass at 20°C following ASTM D-7042, using a digital Viscometer Anton Paar SVM 3000, Stabinger (Austria). The peroxide value was carried out according to ISO 3960. The ester content of the fresh samples was determined by gas chromatography, according to ABNT (Portuguese acronym of Brazilian Association of Standard Techniques) 15764 standard, using a Varian (United States) Gas Chromatograph.

2.4 Accelerated Oxidative Stability Tests

The accelerated oxidative stability tests were carried out using the Rancimat method, according to EN (European Standards) 14112, by exposing 3.0 ± 0.1 g of the biodiesel sample to a temperature of 110 ± 0.9°C and an atmospheric air flux of 10 L/h and DSC analyses using a DSC 1 500 2624 Mettler Toledo (United States), following the American Society for Testing and Materials (ASTM) E537 standard [25]. In DSC analyses, a sample of (approximately) 5.0 mg was used, with a temperature range of 30-500°C, a heating rate of 5°C min^{-1}, and a synthetic air atmosphere at a flux of 50 mL min^{-1}.

2.5 Borchardt and Daniels Method

The kinetic parameters were estimated using the Borchardt and Daniels method (ASTM E2041) for the first exothermic peak of each sample, obtained by DSC analyses, which corresponds to the beginning of the thermo-oxidative degradation [14].

In the area of thermal analysis, many kinetic methods consider the rate to be a function of two variables, temperature (T) and the extent of conversion (α), Equation (1) [26, 27]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

The dependence of the process rate on temperature is represented by the rate constant ($k(T)$) and on the extent of conversion by the reaction model ($f(\alpha)$), while the nonisothermal program describes how the temperature changes linearly with time, as shown in Equation (2) [26]:

$$\beta = \frac{dT}{dt} = \text{const}ant \tag{2}$$

where β is the heating rate.

In the Borchardt and Daniels method, the rate equation is used to describe the dependence of the reaction rate on the amount of material present [14]:

$$\frac{d\alpha}{dt} = k(T)(1-\alpha)^n \tag{3}$$

where $f(\alpha) = (1-\alpha)^n$ and n is the reaction order (dimensionless).

Taking the natural logarithm of Equation (3), it obtains the form of a straight line, $y = mx + b$, with the plot of $\left(ln\left[\frac{d\alpha}{dt}\right]\right)$ *versus* $ln[1-\alpha]$, with the reaction order (n) as slope and $\ln[k(T)]$ as intercept [25, 26]. The method also uses the Arrhenius equation to parameterize the temperature dependence of the process rate, Equation (4) [14]:

$$k(T) = Zexp\left(\frac{-Ea}{RT}\right) \tag{4}$$

where *R* is the universal gas constant (= 8.314 J mol^{-1} K^{-1}).

As an alternative, one can combine the logarithmic form of Equations (3) and (4) resulting in Equation (5) [14]:

$$\ln\left[\frac{d\alpha}{dt}\right] = \ln[Z] + nln[1-\alpha] - \frac{Ea}{RT} \tag{5}$$

where $\frac{d\alpha}{dt}$ = reaction rate [min^{-1}], α = fraction reacted [dimensionless], Z = Arrhenius pre-exponential factor [min^{-1}], *n* = reaction order, *Ea* = activation energy [J mol^{-1}], and T = absolute temperature [K].

Equation (5) has the form *z = a + bx + cy*, where z ≡ $ln\left[\frac{d\alpha}{dt}\right]$, a ≡ $ln[Z]$, b ≡ *n*, x ≡ $ln[1-\alpha]$, c ≡ $\frac{Ea}{R}$, and y ≡ $\frac{1}{T}$. To solve Equation (5), a multiple linear regression analysis was applied following the ASTM E1970 standard [28].

The method of Borchardt and Daniels was chosen for the kinetic parameters determination of exothermic reaction because of its simplicity and ease of use, which allows the determination of the reaction order, the frequency factor, and the activation energy in a single rapid measurement [15, 17, 18]. The results obtained by Borchardt and Daniels's method have been compatible with data obtained by conventional methods [29, 30]. Spacino et al. (2015) determined the kinetic and thermodynamic parameters of soybean oil biodiesel containing natural herbal extracts using a Rancimat model 873 at temperatures of 110, 115, 120, and 125°C with a rate of air 10 L h^{-1} [29]. According to the results of Spacino et al. (2015) [29], the rate constants increased with decreasing values of the induction period at different temperatures. Ong et al. (2013) [30] reported the catalyst-free transesterification of leather tanning waste with high free fatty acid (FFA) content at super-critical conditions and the kinetic parameters determined by nonlinear regression fitting. The

authors observed that the variation of activation energy was strongly related to the rate constant and that higher activation energy corresponds to a slower reaction rate. They also presented the slope of the regressed lines of Arrhenius plots, indicating the temperature sensitivity of the rate constants [30]. The same trend was observed in our study once aged samples (ACB and ASB) showed the highest rate constants.

3. Results and Discussion

3.1 Physicochemical Properties of Biodiesel Samples

The physicochemical properties of fresh and aged biodiesel samples are shown in Table 1. The ASTM D6751 was used as standard.

Table 1 Physicochemical properties of fresh cottonseed biodiesel (FCB), fresh soybean biodiesel (FSB), aged cottonseed biodiesel (ACB), and aged soybean biodiesel (ASB).

Physicochemical properties	ASTM D6571	FCB	ACB	FSB	ASB
Ester content, %	-	94.9	-	96.5	-
Acidity, mg KOH/g	Max. 0.5	0.08	0.15	0.10	0.14
Density at 20°C, kg/m^3	860–900	882.3	882.3	883.2	883.7
Kinematic viscosity at 40°C, mm^2/s	1.9–6.0	4.21	4.30	4.12	4.18
Peroxide value, meq/1000 g	-	15.94	53.29	12.95	51.24

According to the results, the acidity (mg KOH g^{-1}) and peroxide value (meq/1000g) presented a significant difference between fresh and aged biodiesel samples. For CB, the acid value increased by 87.5%, while the peroxide value increased by 234.3%, considering fresh and aged samples. For SB, the acid value increased by 40.0%, and the peroxide value increased by 295.7%. However, density at 20°C (kg m^{-3}) and kinematic viscosity at 40°C (mm^2 s^{-1}) did not show significant alteration in the two samples.

These differences may be justified by the mechanism of oxidation, which occurs in multi-steps, including initiation, propagation, and termination [31]. In initiation, free radicals are formed, especially in the presence of prooxidants such as light, heat, and metal. After that, the unsaturations of the fatty acid methyl esters are attacked. In propagation, the free radicals react with atmospheric oxygen to produce peroxides and hydroperoxides. Then, in the termination step, a combination occurs between peroxides radicals and other non-radical products generating stable products such as peroxides, aliphatic alcohols, carboxylic acids, aldehydes, ketones, and shorter fatty acids. The oxidation products may alter the quality of biodiesel, affecting its physicochemical properties and increasing its acidity and peroxide value [3, 24, 31, 32].

3.2 Oxidative Stability Tests

Rancimat results are presented in Figure 1, including the change in the Induction Period (IP) of the fresh and aged biodiesel samples. Neither sample attended the minimum limit (3 hours) specified by the ASTM D6751 standard. Thus, it was indicated that antioxidant application can increase the oxidative stability of the samples [3, 4, 32, 33].

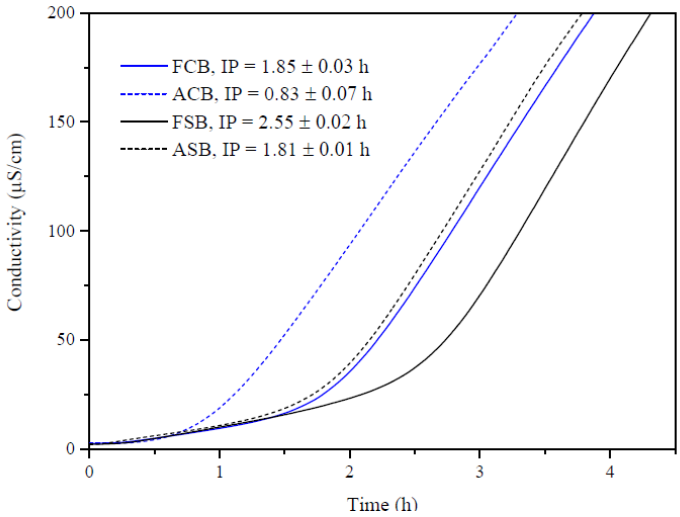

Figure 1 Rancimat curves of fresh and aged biodiesel samples, including their IP values, in hours. Solid blue line: fresh cottonseed biodiesel (FCB); dashed blue line: aged cottonseed biodiesel (ACB); solid black line: fresh soybean biodiesel (FSB); and dashed black line: aged soybean biodiesel (ASB).

Some characteristics may explain the low IP values of the biodiesel samples, such as the high content of unsaturated fatty acid methyl esters (methyl linoleate (18:2), and methyl oleate (18:1)) [34-36], and the natural antioxidants (tocopherols and carotenoids) remotion due to the oil treatment (refining, bleaching, and deodorizing), transesterification, and biodiesel treatment.

In addition to the Rancimat tests, DSC analyses of the biodiesel samples were carried out, as shown in Figure 2. Fresh and aged samples showed three exothermic peaks. However, only the first peak was considered to assess the oxidation reaction of the biodiesel, as it indicated the formation of hydroperoxide [37].

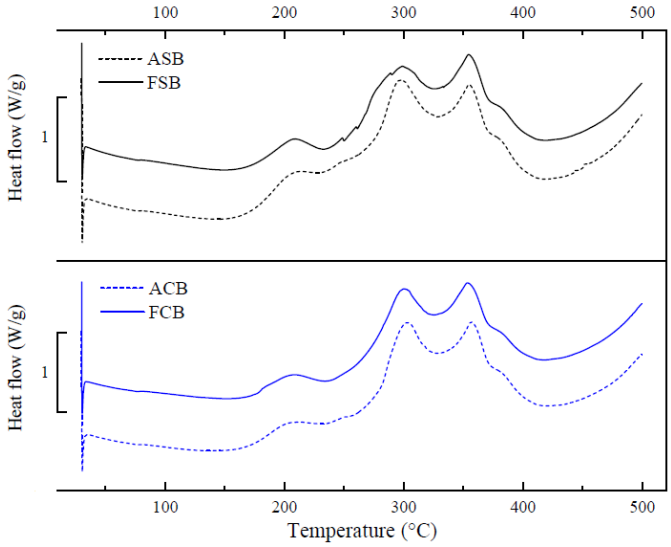

Figure 2 Differential Scanning Calorimetry (DSC) curves of fresh and aged samples. Solid blue line: fresh cottonseed biodiesel (FCB); dashed blue line: aged cottonseed biodiesel (ACB); solid black line: fresh soybean biodiesel (FSB); and dashed black line: aged soybean biodiesel (ASB).

The parameters of the first peak are presented in Table 2, following the ASTM E537 standard. To evaluate the oxidative stability of the biodiesel samples, the extrapolated onset temperature (Ts) was used as the main criterion, as reported by the literature [3, 38, 39]. Fresh and aged biodiesel samples showed similar Ts values. Oxidation started at 173.77°C and 173.55°C for FCB and ACB, respectively, and at 175.77°C and 175.14°C for FSB and ASB, respectively. Figueredo et al. (2020) [3] reported an extrapolated onset temperature of 181.30°C for babassu biodiesel under the same experimental DSC conditions, a value consistent with the results found in our study, as babassu oil consists of 90% wt. of saturated molecules, thus, it shows more stable.

Table 2 Differential Scanning Calorimetry (DSC) parameters for the first peak of fresh cottonseed biodiesel (FCB), fresh soybean biodiesel (FSB), aged cottonseed biodiesel (ACB), and aged soybean biodiesel (ASB).

DSC parameters	FCB	ACB	FSB	ASB
Onset Temperature (To), °C	168.48	164.01	163.20	168.66
Extrapolated Onset Temperature (Ts), °C	173.77	173.55	175.77	175.14
Peak Temperature (Tp), °C	205.12	202.29	206.80	205.35
Enthalpy (Δh), J/g	34.91	29.82	38.65	36.16

Comparing the results of the DSC analysis and the Rancimat method, the same trend was observed for the susceptibility to oxidation of the samples. The FCB presented a lower Ts compared to FSB, implying that FCB was more susceptible to oxidation. For the Rancimat method, FCB also showed a lower IP when compared to FSB, with values of 1.85 and 2.55 hours, respectively. This may occur probably due to the higher polyunsaturated fatty acid methyl ester (FAME) content of the CB (C18:2 + C18:3 = 58.4 ± 0.3 wt.%) compared to that of SB (57.6 ± 0.1 wt.%) [35, 40].

3.3 Estimation of Kinetic Parameters

The kinetic parameters were estimated by Borchardt and Daniels method, including Activation Energy (*Ea*), Arrhenius pre-exponential factor (*Z*), reaction order (*n*), and reaction rate at constant temperature *k*(T). The results are shown in Table 3.

Table 3 Kinetic parameters of fresh cottonseed biodiesel (FCB), fresh soybean biodiesel (FSB), aged cottonseed biodiesel (ACB), and aged soybean biodiesel (ASB), according to Borchardt and Daniels' method.

Kinetic parameters	FCB	ACB	FSB	ASB
Activation Energy (Ea), kJ/mol	118.19 ± 0.51	116.92 ± 2.33	143.09 ± 1.18	133.59 ± 2.32
The logarithm of the Arrhenius pre-exponential factor [ln(Z)], min^{-1}	25.14 ± 0.13	24.82 ± 0.59	31.40 ± 0.30	28.98 ± 0.58
Reaction rate at 25°C [k(T)], min^{-1}	1.62×10^{-10}	1.97×10^{-10}	3.68×10^{-12}	1.52×10^{-11}
Reaction order (n)	1	1	1	1
Reproducibility factor (R^2)	0.999	0.992	0.998	0.994

The main kinetic parameter used to evaluate the oxidative stability of the biodiesel samples is the *Ea*. Thus, a higher *Ea* indicates that biodiesel is more resistant to oxidation processes. According to the results, the *Ea* of FSB (143.09 kJ mol^{-1}) was higher than that of FCB (118.19 kJ mol^{-1}), which was consistent with the trend observed in the Rancimat method and DSC analyses. Nogueira et al. (2020) reported an *Ea* of 137.27 ± 2.57 kJ mol^{-1} for the oxidation of the soybean biodiesel, which was consistent with the result reported in this study [33]. For the aged samples, the trend was sustained, the ASB presented a higher *Ea* (133.59 kJ mol^{-1}) than the ACB (116.92 kJ mol^{-1}).

Finally, to prove the efficiency of the Borchardt and Daniels method for the evaluation of oxidative stability biodiesel, the relationship between *ln*[*k*(T)] and 1/T of the fresh and aged biodiesel samples was plotted, see Figure 3.

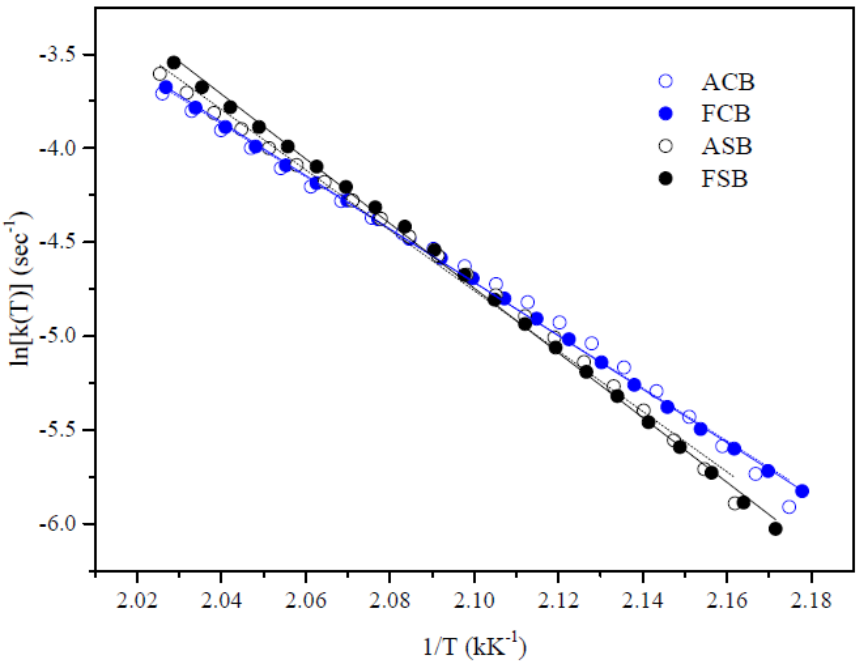

Figure 3 Plot of 1/T versus ln[k(T)] of fresh and aged samples. Filled blue circle: fresh cottonseed biodiesel (FCB); non-filled blue circle: aged cottonseed biodiesel (ACB); filled black circle: fresh soybean biodiesel (FSB); and non-filled black circle: aged soybean biodiesel (ASB).

All samples showed a linear relationship between the *ln*[*k*(T)] and the 1/T. The straight lines represented reproducibility coefficients (R^2) higher than 0.9925. Thus, the oxidation of biodiesel followed the Arrhenius equation being possible to apply the Borchardt and Daniels method.

4. Conclusions

Cottonseed and soybean oils were converted to biodiesel by transesterification and then stored for 100 days at room temperature to evaluate the oxidative stability by the Rancimat method and DSC. The kinetic parameters were obtained by Borchardt and Daniels method, and physicochemical properties followed the ASTM D6751 standard. Results for fresh and aged biodiesel samples were in accordance with standard limits, except for oxidative stability. For the induction period, a decrease of around 55% and 29% occurred for CB and SB, respectively. The acidity and peroxide

value also showed significant changes, increasing by 87.5% and 243.3% for CB and by 40.0% and 295.7% for SB. For kinetic parameters, k(25°C) presented an increase of 313% to the SB: $3.68 \cdot 10^{-12}$ (fresh) and $1.52 \cdot 10^{-11}$ (aged), and activation energy showed a 6.6% decrease for the same biodiesel. The difference between results obtained from the Rancimat method, DSC curves, and kinetic parameters for fresh and aged biodiesel samples indicate the efficiency of these techniques for the evaluation of oxidative stability of biodiesel samples from different sources and oxidative stages.

Author Contributions

The authors contributed equally to this work.

Funding

This study was supported by CNPq (308280/2017-2, 313647/2020-8), FUNCAP (PS1-00186-00255.01.00/21), FINEP, and CAPES (Finance Code 001).

Competing Interests

The authors have declared that no competing interests exist.

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