

Artigo

Evaluation of the Behavior of the Kinetic Parameters of the Oxidation Reaction of Biodiesel in Contact With Metal Alloys During Storage

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Rev. Virtual Quim., 2020, 12 (3), 608-615. Data de publicação na Web: 14 de Maio de 2020

<http://rvq.sbq.org.br>

Avaliação do Comportamento dos Parâmetros Cinéticos da Reação de Oxidação do Biodiesel em Contato com Ligas Metálicas Durante o Armazenamento

Resumo: O biodiesel possui baixa estabilidade oxidativa devido ao alto teor de ésteres insaturados em sua composição, e sua degradação pode ocorrer devido à exposição ao ar, umidade, luz, calor, contaminação por microrganismos e presença de metais. Esta pesquisa tem como objetivo avaliar a influência de ligas de aço carbono, aço 1020 e amostra de tubulação industrial no armazenamento de biodiesel. A amostra de biodiesel em contato com a amostra de tubulação industrial apresentou menores valores do período de indução e, conseqüentemente, maiores constantes de velocidade, acelerando a degradação do biodiesel. O biodiesel em contato com o aço carbono e o aço 1020 apresentou menor degradação quando comparado à amostra de tubulação industrial. O biodiesel na presença da liga de aço carbono apresentou maior estabilidade oxidativa que a da amostra na presença de aço 1020. Algumas amostras apresentaram reações de oxidação complexas com desvios da linearidade descrita por Arrhenius.

Keywords: Ligas metálicas; estabilidade oxidativa; parâmetros cinéticos.

Abstract

Biodiesel has low oxidative stability due to the high content of unsaturated esters in its composition. Its degradation can occur due to exposure to air, humidity, light, heat, contaminants and in the presence of metals. This study aims to evaluate the influence of alloys of carbon steel, steel 1020 and sample of industrial pipe in biodiesel storage. The sample of biodiesel in contact with the pipe presented lower values of the induction period, and consequently higher rate constants, accelerating the biodiesel degradation. The biodiesel in contact with carbon steel and steel 1020 showed a lower degradation when compared to the industrial pipe sample. The biodiesel in the presence of the carbon steel alloy presented higher oxidative stability than the sample in the presence of steel 1020. Some samples presented more complex oxidation reactions with deviations of the linearity described by Arrhenius.

Palavras-chave: Metal alloys; oxidative stability; kinetic parameters.

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DOI: [10.21577/1984-6835.20200048](https://doi.org/10.21577/1984-6835.20200048)

Evaluation of the Behavior of the Kinetic Parameters of the Oxidation Reaction of Biodiesel in Contact With Metal Alloys During Storage

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Recebido em 28 de Março de 2019. Aceito para publicação em 22 de Abril de 2020.

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1. Introduction

Nowadays, the main source of energy used is derived from petroleum, although this resource is exhaustible and its frequent use have been causing many problems in the environment. Therefore, it has increased the number of researches about renewable energy, sources capable of replacing fossil components, especially diesel. Biodiesel has been revealed as an alternative fuel from renewable sources. It can be derived from oilseeds and animal fats. Some of the oil plants used have undesirable chemical characteristics, mainly unsaturated esters such as oleic acid, linoleic acid and linolenic acid, which are susceptible to oxidation reactions.¹⁻³

There are many competitive reactions for the hydroperoxides that propagate the formation of

free radicals with different kinetic behaviors and the generation of several products. There is the formation of decomposition products such as acids, aldehydes, esters, ketones, peroxides and alcohols, generated from factors as the presence of metallic ions, light incidence, humidity, high temperatures, oxygen, inorganic agents and microorganisms. Substances in which cause problems in the operation of the engine and shorten the storage period of the biofuel.⁴⁻⁶

Another factor that reduces oxidative stability is the presence of metallic alloys. The mechanisms and initiation rates of oxidation reactions catalyzed by metal alloys are determined by several factors as the type of metal, the complex formed, the chelating or complexing agent, the redox potential of the metal, and the presence of oxygen. Materials such as brass, iron, zinc, lead

and tin are among the catalysts of the biodiesel oxidation reaction, while carbon steel and aluminum are compatible to biodiesel.⁷

The biodiesel oxidation involves a series of complex chemical reactions with several stages, however it is known that the Arrhenius equation was originally proposed to explain elementary reactions where the activation energy remains constant during the reaction. This concept is simplified for the reactive processes that have a more complex description, depending on thermal factors, reagent unbalance distributions, tunneling effect, geometric configuration, among others.⁸⁻¹¹

The kinetics analysis of the biodiesel oxidation reaction provide data that support the understanding of how the degradation occurs, and also helps in the evaluation of the storage period. The values of the parameters of the Arrhenius equation cannot be directly measured, but it is possible to determine the activation energy from the experimental data of the rate constant as a function of temperature.¹² However, some published researches have shown deviations of linearity of the activation energy and its thermal dependence in some chemical reactions.^{10-11,13} The objective of the present study was to evaluate the oxidation reaction behavior of biodiesel in contact with metal alloys during storage.

2. Materials and methods

2.1. Biodiesel

Commercial Biodiesel (B100) provided by the company BS-BIOS (Marialva-PR) was used, within the specifications established by the ANP nº 3/2014.¹⁴ The biodiesel was produced using approximately 60.8% of unsaturated fatty acids and 39% of saturated fatty acids in a methyl route. The values of kinematic viscosity were 4.44 mm³/s, flash point was 151.5 °C, acid number was 0.44 mg/g, the iodine value was 107, cloud point was

5°C, pour point -1°C and density (20°C) were 879,9 kg/m³. The free and total glycerol were 0.015% (weight) and 0.217% (weight), respectively.

2.2. Preparation of the samples

The following assays were analyzed: pure biodiesel (control sample), biodiesel with carbon steel, biodiesel with steel 1020 and biodiesel with industrial pipe (*Londrina*- PR). The different metal alloys were previously cleaned with hexane (Synth, P.A.). In addition, it was submitted to a process of chemical stripping in acid solution HCl 8% (v/v) at 80 °C for the removal of oxides. The mixtures (Table 1) contained 400 mL of biodiesel and metal alloys with 100 cm² of superficial area, approximately, and were stored at room temperature in the absence of light. The analyzes occurred over a period of 163 days with intervals of 20 days, approximately.

2.3. Determination of the induction period

The biodiesel samples produced for each mixture were subjected to accelerated heating at 110 °C, 115 °C, 120 °C and 125 °C using the Rancimat equipment (Brand: Metrohm; Model: 873). According to the methodology described in the standard EN14112,¹⁵ for the analysis were weighed 3 g of each mixture presented in Table 1. These samples were taken to the accelerated heating with filtered and dehumidified air in molecular sieve of 0.3 nm (Brand: Metrohm) and bubbled with air at a rate of 10 L h⁻¹ for the determination of the oxidative stability. The samples were analyzed periodically as the samples degradation progressed.

2.4. Analyzes final samples

X-ray fluorescence (XRF) techniques were performed using a Shimadzu 7000 energy dispersive X-ray spectroscopy. Characteristic ray excitations and detections were performed

Table 1. Composition of mixtures containing metal alloys

Assay	Description
1	B100 (control sample)
2	B100 + Carbon steel
3	B100 + Steel 1020
4	B100 + Industrial pipe sample

under air and vacuum. A calibration curve with concentrations of Zn^{2+} ions ($Zn(NO_3)_2 \cdot 6H_2O$, Synth) of 2.0×10^{-4} , 4.0×10^{-4} , 6.0×10^{-4} , 8.0×10^{-4} mol L^{-1} was performed. All analyzes were realized in triplicate.

2.5. Analysis of the kinetic parameters

Reaction kinetics were investigated by subjecting samples to the accelerated oxidative stability test at temperatures of 110 °C, 115 °C, 120 °C and 125 °C. The conductivity data for each temperature up to the inflection point were calculated considering the first-order reaction and the value of the rate constants (k) were determined by the angular coefficient of the line, according to equation 1:

$$\ln \Lambda = \ln \Lambda_0 - k(t_f - t_i) \quad (\text{Eq.1})$$

Λ represents the conductivity at time t (h), Λ_0 represents the initial conductivity, and t_i and t_f initial and final analysis time, respectively.

The activation energy (Ea) was determined by equation 2 with the data fitted to the linear model:

$$\ln(k) = \ln A - \frac{E_a}{RT} \quad (\text{Eq.2})$$

For deviations from the Arrhenius equation, the data best fit was the second-order polynomial model and the apparent activation energy calculations (Eaa) were performed using equations 3 and 4:¹⁰⁻¹¹

$$\ln k(T) = \ln A + \frac{B}{RT} + \frac{C}{(RT)^2} \quad (\text{Eq.3})$$

$$E_{aa} = \frac{\delta \ln k}{\delta (\frac{1}{RT})} = -B - \frac{2C}{RT} \quad (\text{Eq.4})$$

3. Results and Discussion

Table 2 presents the results of the analysis of the biodiesel induction period at the four different temperatures, corresponding to the assays proposed in table 1. The sample containing carbon steel showed a decrease in the oxidative stability of biodiesel, when compared to control sample, but lower to the samples containing steel

1020 and to the metal used as industrial pipe in production and storage systems.

Comparing with the research of SANTOS et al. (2012)⁷, the results obtained are similar, since the carbon steel alloy in contact with the biodiesel causes a lower degradation of the sample, once it presented a higher IP than the steel 1020 and the industrial pipe samples.

According to SHARMA & JAIN (2012)¹⁶, which studied the oxidative reactions of *Jatropha curcas* biodiesel in the presence of metals during six months of storage, copper was the metal that most influenced the oxidation reaction, followed by other transition metals. According to that research, there is a greater compatibility of biodiesel with carbon steel, aluminum and stainless steel, although the alloys such as copper, lead, tin and zinc accelerate the oxidation reaction. It was observed that in this experiment carbon steel maintained the highest biodiesel oxidative stability and the sample of pipe presented the shortest induction period.¹³

The influence of several metals such as copper, iron and pure nickel was evaluated by Knothe & Dunn (2003)¹⁷ in the presence of methyl oleate by oxidative stability using the AOCS OSI Method Cd 12b-92. The analyzes were determined by a method based on the reading of the electrical conductivity of the volatile products of biodiesel degradation, in aqueous solution, similar to the Rancimat equipment. After the tests, it was verified that copper caused higher degradation, followed by iron and nickel. Although the mass of the metal did not influence the reaction, they observed that the smaller the particle size of the metal, the higher was the biodiesel degradation, being caused by the surface area increase.¹⁷

As shown in Table 2, it was possible to observe that the sample of industrial pipe accelerated the biodiesel oxidative process, and the sample with carbon steel was the one that provided higher oxidative stability, so this metal alloy is the most indicated among those studied to be used in biodiesel storage. According to Knothe and Dunn (2003)¹⁷ and Sarin et al. (2009)¹⁸, the surface area of the samples influences the oxidative stability of biodiesel, and they also observed that some types of metal alloys interact differently when in contact with biodiesel, leveraging the catalysis of the oxidation reaction.

The X-ray fluorescence (XRF) analysis can identifies substances or compounds present

Table 2. Induction period (IP) at temperatures of 110 °C, 115 °C, 120 °C and 125 °C during the analyzed storage period of control, carbon steel, steel 1020 and industrial pipe samples

Time (days)	IP (h)															
	Control sample				B100 + Carbon Steel				B100 + Steel 1020				B100 + Industrial pipe			
	110°	115°	120°	125°	110°	115°	120°	125°	110°	115°	120°	125°	110°	115°	120°	125°
23	6.89	4.95	3.48	2.22	6.16	4.57	3.23	1.82	6.21	4.49	2.98	2.44	4.68	3.51	2.45	1.75
57	6.14	4.25	2.98	2.09	5.40	3.86	2.76	1.93	4.61	3.40	2.45	1.69	3.81	2.70	1.90	1.44
79	5.52	3.79	2.63	1.90	4.85	3.42	2.36	1.65	4.02	2.84	2.02	1.44	3.31	1.93	1.70	1.20
100	4.86	3.40	2.40	1.63	4.25	2.96	2.09	1.49	3.72	2.59	1.77	1.34	2.75	2.00	1.43	1.03
120	4.35	3.04	2.12	1.49	3.87	2.56	1.82	1.35	3.11	2.12	1.53	1.10	2.36	1.70	1.25	0.73
142	3.90	2.62	1.84	1.31	3.23	2.25	1.56	1.13	2.61	1.90	1.31	0.91	2.09	1.42	0.94	0.59
163	3.48	2.40	1.66	1.17	3.00	2.03	1.45	1.00	2.58	1.71	1.21	0.79	1.62	1.13	0.79	0.53

in a solution. In this way, the XRF analysis was performed for the determination of metal ions present in the biodiesel samples at the end of the period evaluated. The control sample and the samples containing carbon steel and steel 1020 did not present any type of transition metal ions in the biodiesel. In the assay containing the pipe sample, zinc ions were detected with a concentration of $4.76 \times 10^{-4} \text{ mol L}^{-1}$. This fact indicates the transfer of ions to the biodiesel solution, resulting in a metallic catalysis in the oxidation reaction, confirmed by the lower oxidative stability in all analyzes by Rancimat, when compared to the other samples (Table 2).

Considering that the biodiesel oxidation reaction is of the first order ^{4,19}, all the rate constants (Eq.1) were determined. Table 3 show the rate constants (k) at the four temperatures analyzed for each metal alloy during the storage period. According to the storage period, the rate constant (k) increased due to the propagation of free radicals formed, modifying the kinetic

parameters.¹³ The highest rate constants were found in biodiesel in contact with the sample of industrial pipe, which contains zinc ions. These ions accelerate the formation of large amounts of free radicals in stored biodiesel.

Table 4 presents the values of the activation energy of the samples in each analysis period. It can be noted that was not the same behavior observed in elementary reactions, ⁸ suggesting changes in the equation proposed by Arrhenius and the need for a polynomial adjustment of the second order (Eq. 3 e Eq. 4).¹⁰⁻¹¹

Figure 1 shows the graphics of some tests with linearity deviations in the Arrhenius equation. The behavior of the curve may be convex, named super-Arrhenius, in which the activation energy decreases with increasing temperature or concave, the sub-Arrhenius, in which the activation energy increases with increasing temperature¹⁰⁻¹¹.

Coutinho et al. (2015)²⁰ verified that the reactions that presented convex curves (super-Arrhenius) are contributions of classic phenomena.

Table 3. Rate constants (k) of the oxidation reaction of the control, carbon steel, steel 1020 and industrial pipe samples

Time (days)	k															
	Control Sample				B100 + Carbon Steel				B100 + Steel 1020				B100 + Industrial Pipe			
	110°	115°	120°	125°	110°	115°	120°	125°	110°	115°	120°	125°	110°	115°	120°	125°
23	0.34	0.51	0.75	1.15	0.40	0.60	0.75	1.61	0.42	0.56	0.91	1.16	0.59	0.84	1.26	1.74
57	0.50	0.72	0.97	1.30	0.55	0.76	1.03	1.39	0.64	0.88	1.09	1.63	0.75	1.08	1.48	1.84
79	0.57	0.81	1.18	1.58	0.60	0.84	1.29	1.77	0.67	1.04	1.49	2.09	0.92	1.65	1.95	2.70
100	0.62	0.91	1.36	1.83	0.69	0.92	1.51	2.06	0.78	1.08	1.82	2.30	1.10	1.49	2.35	3.20
120	0.68	1.02	1.38	2.20	0.81	0.71	1.51	2.54	0.96	1.41	1.98	3.03	1.23	1.82	2.27	4.36
142	0.74	1.04	1.73	1.99	0.85	1.11	1.99	2.37	1.04	1.56	2.43	2.84	1.48	2.13	3.41	4.24
163	0.81	1.11	1.75	2.25	0.94	1.42	2.04	3.10	1.11	1.74	2.63	4.03	1.82	2.59	3.97	5.96

Table 4. Samples values of activation energy in several periods

Assays	Ea (kJ mol ⁻¹)						
	Days						
	23	57	79	100	120	143	163
B100 (Control)	102.04	80.59	87.30	92.66	96.60	88.23	93.81
B100 + Carbon Steel	110.66	78.41	93.03	95.80	105.8	92.39	99.68
B100 + Steel 1020	89.23	77.07	95.25	96.09	96.06	87.48	108.49
B100 + Industrial Pipe	92.62	76.18	86.81	92.87	101.29	92.11	101.00

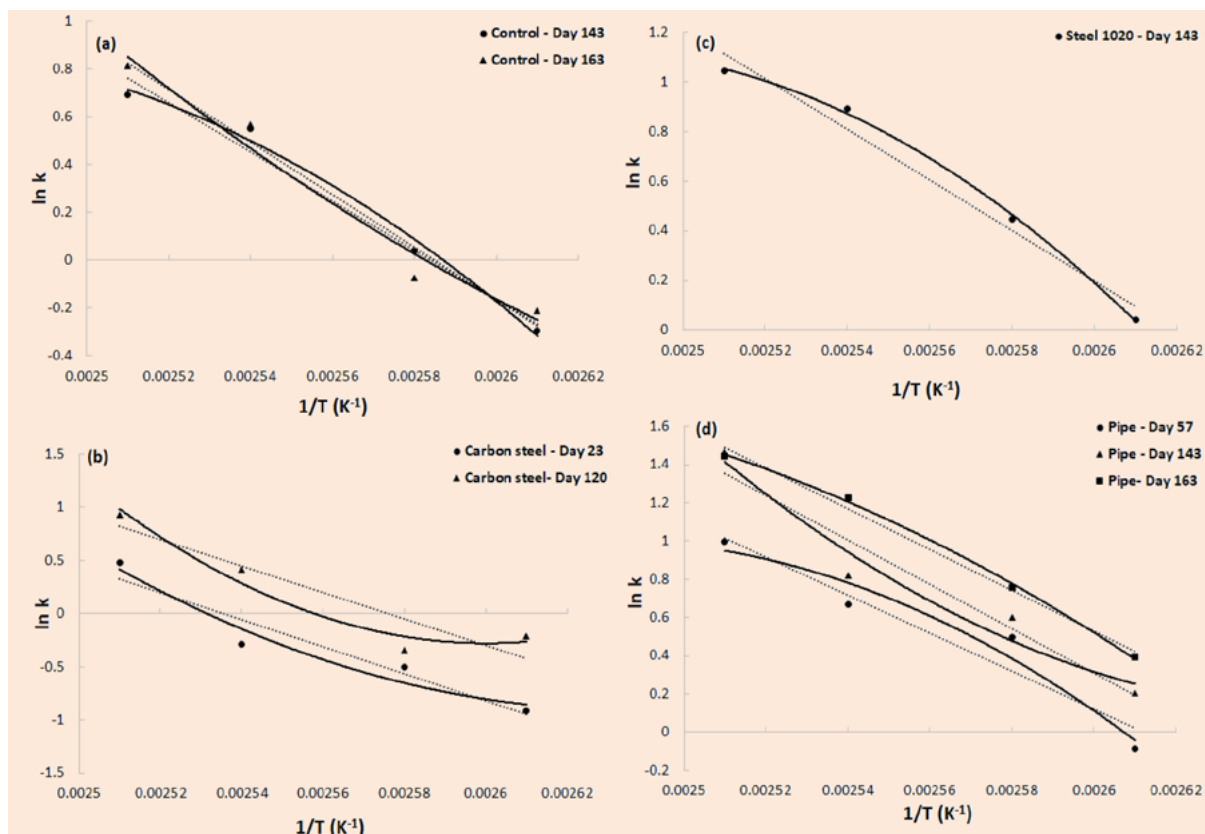


Figure 1. Deviations of the linearity of the samples in the respective days of analysis: (a) Control, (b) Carbon Steel, (c) Steel 1020 and (d) Industrial Pipe

This behavior is manifested by the phenomena treated by Tsallis non-extensive thermodynamics.¹¹ The concave curves (sub-Arrhenius) are related to the behavior of tunneling of quantum-mechanical effect. In tunneling, a particle or a system of particles crosses a region in space (barrier) in which its total energy is lower than the potential energy of the barrier. Tunneling can be significant in chemical phenomena, in which wave functions describing the particle tunneling have significant amplitude across the barrier region.²¹

It can be observed that the tests of the control sample on day 163, and the samples of biodiesel in

contact with carbon steel on day 23, carbon steel on day 143 and industrial pipe on day 120 had convex curvature, the super-Arrhenius deviation. The assays of the control sample analyzed on day 143, containing steel 1020 on day 143, and industrial pipe on day 79 and 143, presented concave curvature, the sub-Arrhenius deviation.

Note that adjusting the second-order polynomial curve gives an improvement in the coefficient of determination ($0.95 \leq R^2 \leq 0.98$), in relation to the linear fit ($0.86 \leq R^2 \leq 0.99$), showing that there is a dependence of the activation energy with the temperature.

4. Conclusion

The oxidative and kinetic stability parameters were used to evaluate the biodiesel oxidative behavior in contact with metallic alloys. The biodiesel containing the industrial pipe sample had the highest rate constants and the lowest induction periods at all temperatures. The XRF analysis confirmed the presence of zinc ions in the biodiesel in contact with the pipe sample. The ions of this metal accelerated the oxidative process, so metal alloys containing the zinc are not indicated for storage.

The samples of carbon steel and steel 1020 are the metal alloys that have least accelerated the degradation of biodiesel. Carbon steel presented the highest compatibility with biodiesel, while steel 1020 accelerated the biodiesel oxidative process. The carbon steel proved to be a suitable metal alloy for the biodiesel storage, since in its kinetic parameters it presented smaller rate constants (k).

Acknowledgements

UEL, Fuel research and analysis laboratory, IFPR, CNPq and CAPES.

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