The Effect of Fe$^{3+}$, Fe$^{2+}$, Co$^{2+}$ and Cr$^{3+}$ Ions in the Oxidative Stability and Kinetics of biodiesel Oxidation Reaction With and Without the Addition of Rosemary Extract

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Rev. Virtual Quim., 2020, 12 (4), 1028-1037. Data de publicação na Web: 7 de Julho de 2020

http://rvq.sbq.org.br

Abstract

Biodiesel is susceptible to oxidation reaction since it has unsaturated esters in its composition. Studies have shown that small traces of transition metals are able to promote biodiesel oxidation. Biodiesel samples containing Cr$^{3+}$, Co$^{2+}$, Fe$^{2+}$ and Fe$^{3+}$ ions, in the presence and absence of rosemary extract, were submitted to the Rancimat test at 110 °C to verify the biodiesel oxidative stability against the catalytic action of these ions. The results were compared with control samples with and without rosemary extract. The control without extract presented induction period of 8.29 hours and the control with extract 11.42 hours. Regarding the catalytic effect of metal ions in biodiesel and in the absence of extract, the sample containing Fe$^{3+}$ showed induction period of 0.25 hours, indicating total degradation of the biofuel. For the samples containing the other cations, in the absence of the extract, the catalytic effect followed the order Fe$^{3+}$>Cr$^{3+}$>Co$^{2+}$. In the presence of extract the order presented was Fe$^{3+}$>Fe$^{2+}$>Co$^{2+}$>Cr$^{3+}$.

Keywords: Metallic ions; oxidation; rosemary extract; natural antioxidant.

Palavras-chave: Íons metálicos; oxidação; extrato de alecrim; antioxidante natural.
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1. Introduction

Biodiesel has become a good substitute for diesel presenting some advantages: can be obtained from raw materials of renewable sources, reduces the dependence on petroleum importation, causes less engine damages, has higher thermal efficiency, among others. Despite the reduction in emissions of harmful gases to the environment such as CO, SO$_2$, and SO$_3$, nitrogen oxides may have their emissions increased during combustion in motor vehicles.

According to Fazal et al. (2017) and Sui & Li (2019) the chemical stability can be affected when the biodiesel is in contact with metals, particularly transition elements. According to Zuleta et al. (2012), biodiesel has corrosive effect on metallic surfaces, promoting the release of ions into the medium. Small traces of them are enough to catalyze the oxidation reaction, decreasing its...
oxidative stability. Therefore, the mechanisms and kinetic parameters of the biodiesel oxidation reaction may be affected by the presence of transition metals. The increase of the reaction rate is determined by a complex mixture of factors: the metal and the type of complexes that form (inner or outer sphere), presence of chelating or complexing agent, the redox potential of the metal and its complexes, solvents and availability of oxygen or preformed hydroperoxides.

Studies regarding catalysts activity in the biodiesel oxidation reaction have gained importance. Sui and Li (2019) studied the effect of tetraethylenepentamine as an antioxidant in biodiesel with iron, nickel, manganese, copper and cobalt contamination. Fazal et al. (2018) and Deyab (2016) showed that it is important to evaluate the effect of biodiesel in automotive metal components due to its corrosive action. Many of the engine parts are composed of metals as aluminum, copper, stainless steel and alloys, which may contain iron, nickel, copper, cobalt, chromium, manganese and other metals.

To ensure the oxidative stability of biodiesel, synthetic antioxidants as TBHQ (tert-butylhydroquinone) and BHT (butylhydroxytoluene) are employed. However, recent researches have shown that plant extracts with the presence of phenolic compounds in their composition have been used as natural antioxidants, because besides effectively controlling the oxidation reaction of biodiesel, they also act as corrosion inhibitors.

Rosemary (Rosmarinus officinalis L.) has some phenolic compounds, such as: rosmarinic acid, carnosol, rosmanol, etc, that are biologically active, having high antioxidant capacity. Jin et al. (2019) stated that the carnosic acid present in rosemary is a strong antioxidant, capable of eliminating hydroxyl radicals by preventing the formation of singlet oxygen and perhydroxyl radicals that propagate the biodiesel oxidation reaction.

Messias et al. (2018) used rosemary extract to prevent biodiesel oxidation and found that even after 6 months of storage, biodiesel still had an induction period longer than 8 hours. Chendynski et al. (2019) studied the effect of iron ions in the biodiesel oxidative stability and found that samples containing rosemary extract presented higher induction period value and lower rate constants.

The aim of this work was to study the effect of metallic Cr$^{3+}$, Co$^{2+}$, Fe$^{2+}$ and Fe$^{3+}$ ions in the oxidative stability and kinetics of the biodiesel oxidation reaction with and without the addition of rosemary extract.

2. Material and Methods

2.1. Biodiesel

The biodiesel used was obtained in the Fuel Research and Analysis Laboratory of the State University of Londrina, Brazil, from a mixture of raw material containing soybean oil, beef tallow and poultry fat, by methyl route, using NaOH as a catalyst.

2.2. Biodiesel chromatographic analysis

The biodiesel methyl ester profile and quantification were performed following the standard EN 14103, using a gas chromatograph with CG-Shimadzu-GC2010-plus equipment coupled to a Shimadzu MS-QP2010-Ultra mass spectrometer. A Restek model RT-2560 column of 100 m length, 0.25 mm internal diameter and 0.25 mm film thickness was used. The injection was performed manually, with an injector temperature of 240 °C. The samples were prepared with 40 mg of biodiesel, 500 µL of internal pattern C23 (Sigma-Aldrich) and 500 µL of heptanes (Vetec).

2.3. Alcoholic extract of Rosemary leaves

The rosemary used was grown on a land next to the Fuel Research and Analysis Laboratory of the State University of Londrina, Brazil. The leaves were collected, washed, dried at 40 °C in an oven and then crushed and vacuum packed in polyethylene packages until being used.

The alcoholic extract with antioxidant properties was produced with dried rosemary leaves (Rosmarinus sp.), according to Spacino et al. (2016). Before being added to biodiesel, rosemary extract was heated at 40 °C until the alcohol was evaporated.

2.4. Determination of total phenolic compounds and antioxidant activity

The total content of phenolic compounds in the extract was determined in triplicate by the spectrophotometry (PerkinElmer, model UV–vis
LAMBDA 25) using 2 N Folin–Ciocalteu reagent (Sigma–Aldrich). The antioxidant activity was obtained in triplicate by DPPH (Sigma–Aldrich) assay.22

2.5. Chromatographic analysis of the extract

Chromatographic analysis was performed by Thermo Scientific® Finnigan Surveyor system coupled with a Plus Photodiode Array detector (PDA) (San Jose, USA). Chromatographic conditions used in this study were previously obtained by Zabot et al. (2014)23 with some modifications. The phenolic compounds were separated by an ACE 5 C18 column (250×4.6 mm, with 5 μm particle size). The flow rate was 1 mL min⁻¹ with 20 °C controlled temperature and monitored at 200–800 nm. For HPLC analysis, crude extract was diluted in 10.0 mL of initial mobile phase (1:100, v/v), and filtered through a 0.2 μm hydrophilic polypropylene membrane (Chromafil, Duren, Germany). The data were processed using the ChromQuest 4.2 program.

2.6. Sample preparation

Biodiesel samples were prepared individually by adding Cr³⁺ (CrCl₃.6H₂O; Cinética Brand, 97.0% purity), Co²⁺ (CoCl₂.6H₂O; Biotec Brand, 98.0% purity), Fe²⁺ (FeCl₂.4H₂O; Synth Brand, 99.6% purity) at a concentration of 7.9 x 10⁻⁴ mol cation in 200 mL of biodiesel, without and with 2% (w/w) of rosemary extract. Control samples were prepared using 200 mL of biodiesel (BC) and 200 mL of biodiesel containing 2% (w/w) of rosemary extract (BCE). All samples were stored for 6 days at room temperature and in the absence of light. Fe³⁺ (FeCl₂.6H₂O; Synth Brand, 99.6% purity) content in samples without and with 2% (w/w) extract was 8.9x10⁻⁵ mol in 150 mL. The concentration was lower than the other samples because preliminary assays with the 7.9 x 10⁻⁴ mol concentration caused an IP variation from 8.29 h to 0.07 h in 0.25 h of assay.

2.7. Determination of the induction period

The assays were performed at 110 °C using the Rancimat equipment (Brand: Metrohm; Model: 873), according to the methodology described in the standard EN14112.24

2.8. Kinetic parameters

Reaction kinetics were investigated by subjecting samples to the accelerated oxidative stability test at 110 °C. The conductivity data for each temperature up to the inflection point were calculated considering the first-order reaction and the values of the rate constants (k) were determined by the linear fit angular coefficient of the ln of conductivity vs time in hours.

2.9. Flame Atomic Absorption Spectrometry (FAAS)

The ions concentration of Cr³⁺, Co²⁺, Fe²⁺ and Fe³⁺ in biodiesel were determined by a ShimadzuVR AA-6601F Flame Atomic Absorption Spectrometer (Kyoto, Japan) equipped with a specific cathode lamp as the radiation source and a deuterium lamp for background correction. The analysis and the calibration curve were performed in triplicate.

3. Results and Discussion

For a biodiesel to be used pure or in combination with diesel is necessary to present some quality standards to ensure the safety of emissions from its burning, as its performance, engine integrity, transportation safety and handling. Products of biodiesel degradation should also be monitored during storage, being the induction period and ester content important parameters to be determined. The reference values for these determinations are well established and the biodiesel B100 used in this work is in accordance with the international standards (Table 1).

Chromatographic analysis showed that the biodiesel used in the experiment had ester content of 98.71% (w/w) being 42.02% (w/w) saturated methyl esters (miristic, palmitic and stearic) and 57.98% (w/w) unsaturated methyl esters (palmitoleic, oleate, linoleic and linolenic), which justifies the high induction period of 8.59 hours, although not containing antioxidants in its composition. Since biodiesel has unsaturated methyl esters in its composition, it is exposed to the oxidation process that can be accelerated in the presence of some transition metallic cations.12
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Analysis by FAAS shows that in the control biodiesel (BC) was not detected the presence of iron, copper, cobalt and chromium metallic cations, which according to Schaich (2005) act as catalysts of the oxidation reaction. However, to ensure preservation of oxidative stability and thus a longer storage period, biodiesel needs the addition of antioxidants.

It was added 2% w/w alcohol free rosemary extract to the biodiesel containing metallic ions and the control sample, because according to Spacino et al. (2016) and Chendynski et al. (2020), rosemary leaf extract is a viable alternative to retard the oxidative degradation of B100 biodiesel since the compounds present in extract do not cause damage to the environment, are easily obtained and offers an effective protection in biodiesel storage. Chromatographic analysis of the extract shows the presence of rosmarinic acid, rosmanol, carnosic acid, carnosol and methyl carnosate, which are phenolic compounds present in rosemary that have antioxidant properties.

| Parameter               | Method          | Specification | Unit    | Result |
|-------------------------|-----------------|---------------|---------|--------|
| Density (20°C)          | ASTM D4052     | 850-900       | kg m⁻³  | 879.6  |
| Kinematic Viscosity (40°C) | ASTM D445   | 3.0-6.0       | mm² s⁻¹ | 4.46   |
| Water content           | ASTM D6304     | Max 200       | mg kg⁻¹ | 180.1  |
| Flash point             | ASTM D93       | Min 100       | °C      | 142.1  |
| Ester content           | EN 14103       | Min 96.5      | % mass  | 98.71  |
| Iodine Value            | EN 14111       | -             | % mass  | 92     |
| Induction Period        | EN 14112       | Min 8         | hours   | 8.59   |
| Acid number             | ASTM D664      | Max 0.5       | mgKOH g⁻¹ | 0.45 |
| Free glycerin           | ASTM D6584     | Max 0.02      | % mass  | 0.01   |
| Total glycerin          | ASTM D6584     | Max 0.25      | % mass  | 0.21   |
| Monoglycerides          | ASTM D6584     | Max 0.70      | % mass  | 0.68   |
| Diglycerides            | ASTM D6584     | Max 0.20      | % mass  | 0.11   |
| Triglycerides           | ASTM D6584     | Max 0.20      | % mass  | 0.07   |

Figure 1. PDA spectra of phenolic compounds obtained by chromatographic separation
Rosemary dried leaves extract was subjected to analysis of total phenols content and activity, in order to verify the antioxidants efficiency. The content of total phenols in rosemary extracts, expressed as gallic acid equivalent, was $19.285 \text{ mg GAE g}^{-1} \text{ dry mass}$ with activity of $54.2092 \text{ mg Trolox g}^{-1} \text{ dry mass}$. In addition, rosemary extract does not undergo thermal decomposition at the temperature used to determine the induction period by the Rancimat method. According to Spacino et al. (2016), the thermogravimetric analysis (TGA) of lyophilized rosemary extract showed that the thermal decomposition in the first event occurred at 121.26 °C.

The control samples as well as those containing the metallic ions, with and without extract, were submitted to the Rancimat test at 110 °C to study the influence of the cations used in the biodiesel oxidation reaction. For all samples containing the ions, the same biodiesel with and without rosemary extract was used.

Table 2 shows the values of induction period (IP) and rate constant (k) for the controls without and with rosemary extract (BC and BCE), at the beginning and the end of experiments, as well as biodiesel samples containing salts of Co$^{2+}$ (BCo and BCoE), Cr$^{3+}$ (BCr and BCrE), Fe$^{2+}$ (BFe$^{2+}$ and BFe$^{2+}$E) and Fe$^{3+}$ (BFe$^{3+}$E) at the assay temperature. It was not possible to obtain Rancimat data for the BFe$^{3+}$ sample since between the sample preparation time and the first sampling time (0.25 h) the biodiesel was already completely oxidized, presenting an IP of 0.07 h at 110 °C.

According to Table 2, the control sample (BC) at time zero presented IP of 8.29 h and the control with extract (ECB) presented IP above the stipulated by the EN 14214, which establishes a minimum time of 8 hours. After 120 hours of storage, samples showed a reduction in the IP of 11% and 12% for the BC and BCE samples, respectively. The rate constant of the oxidation reaction for the BCE sample was lower when compared to that observed for the BC sample, indicating that the rosemary extract delayed the biodiesel oxidation process.

The biodiesel samples containing metallic ions and without extract, presented IP ranging from Co$^{2+}$ > Cr$^{3+}$ > Fe$^{2+}$ except for the test performed in Table 2.

| Table 2. Induction periods (IP) and rate constants (k) values for the controls (BC and BCE), and for Co$^{2+}$ (BCr; BCrE), Cr$^{3+}$ (BCr; BCrE), Fe$^{2+}$ (BFe$^{2+}$; BFe$^{2+}$E) and Fe$^{3+}$ (BFe$^{3+}$E) samples at 110 °C |
|---|---|---|---|
| **Time (h)** | **Samples** | **Control at the initial time** | **Control at the final time** |
| | | BC | BCE | BC | BCE |
| | 0 | 8.29 (0.3375) | 11.42 (0.2704) | 120 | 7.36 (0.3462) | 10.03 (0.2269) |
| 0.25 | 7.23 (0.3493) | 6.4 (0.4097) | 4.36 (0.5099) | 4.05 (0.586) | 2.43 (1.76) | 1.76 (1.23) |
| 8 | 6.59 (0.3700) | 6.59 (0.3883) | 5.84 (0.3951) | 4.85 (0.5321) | 3.85 (0.76) | 3.76 (1.89) |
| 24 | 5.13 (0.4015) | 4.51 (0.5368) | 3.37 (0.6799) | 2.23 (0.6725) | 2.06 (1.28) |
| 32 | 6.59 (0.3700) | 6.59 (0.3883) | 5.84 (0.3951) | 4.85 (0.5321) | 3.85 (0.76) | 3.76 (1.89) |
| 48 | 5.13 (0.4015) | 4.51 (0.5368) | 3.37 (0.6799) | 2.23 (0.6725) | 2.06 (1.28) |
| 56 | 6.59 (0.3700) | 6.59 (0.3883) | 5.84 (0.3951) | 4.85 (0.5321) | 3.85 (0.76) | 3.76 (1.89) |
| 72 | 5.13 (0.4015) | 4.51 (0.5368) | 3.37 (0.6799) | 2.23 (0.6725) | 2.06 (1.28) |
| **Time (h)** | **Samples** | **Control at the final time** |
| | | BC | BCE |
| 24 | 10.3 (0.3445) | 8.9 (0.4122) | 7.36 (0.3594) | 6.4 (0.4443) | 5.78 (0.4948) |
| 48 | 9.79 (0.2346) | 8.61 (0.2327) | 8.55 (0.2453) | 8.05 (0.2526) | 7.66 (0.2611) |
| 72 | 7.6 (0.4028) | 3.66 (0.705) | 1.54 (0.7529) | 1.18 (0.7754) | 2.32 (1.2) |
| 96 | 5.88 (0.4746) | 5.35 (0.4105) | 3.54 (0.7529) | 3.23 (0.7754) | 2.32 (1.20) |
| 120 | 5.88 (0.4746) | 5.35 (0.4105) | 3.54 (0.7529) | 3.23 (0.7754) | 2.32 (1.20) | 2.06 (1.05) |
the first 0.25 hours. The tests with longer induction period had lower rate constant, as expected, and the sample containing the Co$^{2+}$ was the least influenced the oxidation reaction of biodiesel. The sample containing Fe$^{3+}$ ions without extract presented lower IP and higher k in all assays. After 72 hours it showed no IP, indicating that the oxidation reaction was in its final phase and that the sample was already completely degraded.

Analyzing the biodiesel samples containing rosemary extract and cations, with reference to the control sample (BC), that presented an IP of 7.36 hours at the end of the experiment, we verified that the BCoE sample took 72 hours to reach the same value. The BCrE sample, presented IP equal to 7.66 hours at the end of the experiment, which is higher than that observed in the same period for the BC sample. The sample BFe$^{2+}$E presented an IP of 7.6 hours in the first 24 hours of the experiment, indicating a greater catalytic effect in the oxidation reaction even with the extract addition. The samples rate constants followed the order BFe$^{2+}$E > BCoE > BCrE at all sampling times.

The BCr sample presented lower IP when compared to BCo. However, when rosemary extract is added the IP value is inverted, being higher for the BCrE sample than for BCoE. When comparing the biodiesel samples containing the metallic ions and in the presence of the extract, we found that after 72 hours of experiment the BCrE sample presented higher IP than the BCoE sample. This possibly happens because the Cr$^{3+}$ has higher charge when compared to Co$^{2+}$. Thus, it forms more inert complexes with the phenolic compounds present in rosemary extract, reducing its catalytic effect in the oxidation reaction.

Table 2 also shows that even cobalt and chromium ions acting as catalysts in the biodiesel oxidation reaction, the addition of rosemary extract was able to delay the oxidation reaction during the 120 hours of experiment. The protective effect was more effective in the biodiesel containing chrome ions with 33% IP reduction, while in biodiesel containing cobalt ions the reduction was 49% at the end of the experiment. In addition, the oxidation reaction rate constant of the cobalt ion-containing sample was 1.8 times higher at the end of the experiment compared to the initial BCE sample.

Although the rate constant values are very close for the BCrE and BCoE samples, they did not remain stable during the storage time, because applying the t test for a simple sample, we verified that there is a significant difference between the averages of the observed values and the value obtained after 120 hours of experiment with $p = 0.02$. The same analysis showed no significant difference ($p = 0.1$) when this test was applied to a sample containing Fe$^{2+}$.

For the BFe$^{3+}$E sample in the first 0.25 hours of experiment there was a decrease of the IP value of 48.51% when compared to the initial value of the sample BCE. In relation to the other metallic ions, Fe$^{3+}$ was the one that most reduced the value of IP and presented the highest rate constant.

For the phenolic compounds present in rosemary extract to retard the oxidation reaction, they must eliminate free radicals formed at the initiation and propagation stages by donating H•. However, the property of phenolic compounds in retarding the oxidation reaction of biodiesel is sacrificial and happens until every antioxidant is consumed.

Furthermore, according to Moreno et al. (2006), phenolic compounds present in rosemary leaf extract act as chelating agents of metallic ions, forming superoxides in biodiesel that serve as a source of singlet oxygen, accelerating the oxidation. Therefore, by reducing or eliminating the catalytic active form of the metallic ion, rosemary extract confers greater protective action against the biodiesel oxidation reaction.

Comparing the action of transition metallic ions in biodiesel with extract, we see that the order in which metals catalyze the oxidation reaction from the slowest to the fastest is Cr$^{3+}$ < Co$^{2+}$ < Fe$^{2+}$ < Fe$^{3+}$. The compounds present in rosemary extract have immobilizing effect in these ions due to their complexation, making them less available to catalyze oxidation reactions. In general, transition metallic ions at higher oxidation states form more inert coordinating compounds than those with lower oxidation states, and their catalytic effect decreases. This explains the low catalytic power of Cr$^{3+}$ for the oxidation reaction of biodiesel in relation to other metallic ions. In the case of Fe$^{3+}$, it forms complexes more unstable than other metallic ions in the same oxidation state, due to its electronic configuration $d^3$, that does not generate additional stability with the complex formation, leaving the ion more available to catalyze the biodiesel oxidation reactions.

Tagliafu et al. (2005) reported that Fe$^{3+}$ was more effective as a catalyst in the oxidation
reaction of biodiesel when compared to Cu\textsuperscript{2+}, Zn\textsuperscript{2+} and Mn\textsuperscript{4+}. Knothe and Steidley (2018)\textsuperscript{38} state that trace amounts of Fe\textsuperscript{3+} are capable of promoting lipid oxidation. According to Schaich (2005)\textsuperscript{32} the mechanisms and the rate of the metal-catalyzed initiation reactions are determined by several factors, including the medium, the metal and the type of complex formed, inner or outer sphere, and that only metals that transfer an electron can be active catalysts. In lipids, and similarly in biodiesel, Fe\textsuperscript{2+} and Fe\textsuperscript{3+} ions complex with the medium. In these complexes the electrons quickly transfer to oxygen, forming the superoxide anion (O\textsubscript{2}\textsuperscript{−}) or its conjugate acid, the perhydroxyl radical (HO\textsubscript{2})\textsuperscript{−}, which are singlet oxygen sources reacting with the unsaturated ester, forming the free radical oxygen. Consequently delaying the oxidation reaction. Biodiesel, slowing down the flow of electrons and metallic ions form complexes of inner sphere in the medium. In these complexes the electrons quickly transfer to oxygen, forming the superoxide anion (O\textsubscript{2}\textsuperscript{−}) or its conjugate acid, the perhydroxyl radical (HO\textsubscript{2})\textsuperscript{−}, which are singlet oxygen sources reacting with the unsaturated ester, forming the free radical oxygen. Consequently delaying the oxidation reaction.

4. Conclusion

The transition metallic ions Cr\textsuperscript{3+}, Co\textsuperscript{3+}, Fe\textsuperscript{2+} and Fe\textsuperscript{3+} showed catalytic effect in biodiesel oxidation reaction. When evaluating IP and k, the greatest catalytic effect was observed with Fe\textsuperscript{3+} and the smallest with Co\textsuperscript{3+}. Fe\textsuperscript{3+} was the strongest oxidizing agent when compared to other ions, because even reducing its concentration, it showed no induction period in the first 0.25 hours of experiment, indicating the total biodiesel degradation in this short period. By analyzing the ions with the addition of rosemary extract, was observed that the order of velocity in which the oxidation reaction proceeds, from the fastest to the slowest was Fe\textsuperscript{3+} > Fe\textsuperscript{2+} > Co\textsuperscript{3+} > Cr\textsuperscript{3+}. Rosemary extract besides restoring the free radicals formed has an inhibitory effect in the catalytic action of metallic cations that may be present in biodiesel.

Acknowledgements

The State University of Londrina (UEL) for the technical support and CAPES for granting the scholarship.

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