

## Artigo

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

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### Efeitos dos Íons $\text{Fe}^{3+}$ , $\text{Fe}^{2+}$ , $\text{Co}^{2+}$ e $\text{Cr}^{3+}$ na Estabilidade Oxidativa e Cinética da Reação de Oxidação do Biodiesel com e sem a Adição de Extrato de Alecrim

**Resumo:** O biodiesel por ter em sua composição ésteres insaturados, é susceptível a reação de oxidação. Estudos tem mostrado que pequenos traços de metais de transição são capazes de promover a sua oxidação. Amostras de biodiesel contendo  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$  e  $\text{Fe}^{3+}$ , na presença e ausência de extrato de alecrim, foram submetidas ao teste Rancimat, na temperatura de 110 °C, para verificar a sua estabilidade oxidativa frente a ação catalítica desses íons. Os resultados foram comparados com a amostra controle com e sem extrato de alecrim. A amostra controle apresentou período de indução de 8,29 horas e a amostra controle com extrato 11,42 horas. Quanto ao efeito catalítico dos íons metálicos no biodiesel, na ausência de extrato, a amostra contendo  $\text{Fe}^{3+}$  não apresentou período de indução nas 0,25 horas indicando total degradação do biocombustível. As amostras contendo os demais cátions, na ausência do extrato, o efeito catalítico seguiu a ordem  $\text{Fe}^{2+} > \text{Cr}^{3+} > \text{Co}^{2+}$ . Na presença de extrato a ordem apresentada foi  $\text{Fe}^{3+} > \text{Fe}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+}$ .

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

### 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  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  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  $\text{Fe}^{2+} > \text{Cr}^{3+} > \text{Co}^{2+}$ . In the presence of extract the order presented was  $\text{Fe}^{3+} > \text{Fe}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+}$ .

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

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# The Effect of Fe<sup>3+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup> e Cr<sup>3+</sup> Ions in the Oxidative Stability and Kinetics of biodiesel Oxidation Reaction With and Without the Addition of Rosemary Extract

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## 1. Introduction

## 2. Material and Methods

### 2.1. Biodiesel

### 2.2. Biodiesel chromatographic analysis

### 2.3. Alcoholic extract of Rosemary leaves

### 2.4. Determination of total phenolic compounds and antioxidant activity

### 2.5. Chromatographic analysis of the extract

### 2.6. Sample preparation

### 2.7. Determination of the induction period

### 2.8. Kinetic parameters

### 2.9. Flame Atomic Absorption Spectrometry (FAAS)

## 3. Results and Discussion

## 4. Conclusion

## 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.<sup>1-3</sup> Despite the reduction in emissions of harmful gases to the environment such as CO, SO<sub>2</sub> e SO<sub>3</sub>, nitrogen oxides may have their emissions increased during combustion in motor vehicles.<sup>4,5</sup>

Because is produced from various vegetable oils and animal fat, biodiesel contains unsaturated esters that are susceptible to the oxidation process, causing problems in its chemical stability, especially during storage.<sup>6-8</sup>

According to Fazal *et al.* (2017)<sup>9</sup> and Sui & Li (2019)<sup>10</sup> the chemical stability can be affected when the biodiesel is in contact with metals, particularly transition elements. According to Zuleta *et al.* (2012),<sup>11</sup> 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.<sup>12</sup>

Studies regarding catalysts activity in the biodiesel oxidation reaction have gained importance. Sui and Li (2019)<sup>10</sup> studied the effect of tetraethylenepentamine as an antioxidant in biodiesel with iron, nickel, manganese, copper and cobalt contamination. Fazal *et al.* (2018)<sup>13</sup> and Deyab (2016)<sup>14</sup> showed that 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.<sup>6,15-17</sup>

Rosemary (*Rosmarinus officinalis* L.) has some phenolic compounds, such as: rosmarinic acid, carnosol, rosmanol, etc, that are biologically active, having high antioxidant capacity.<sup>18</sup> 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.<sup>19</sup>

Messias *et al.* (2018)<sup>20</sup> 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)<sup>12</sup> 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<sup>3+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup> and Fe<sup>3+</sup> 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,<sup>21</sup> 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).<sup>22</sup> 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.<sup>22</sup>

### 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)<sup>23</sup> 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<sup>-1</sup> 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 Cr<sup>3+</sup> (CrCl<sub>3</sub>·6H<sub>2</sub>O; Cinética Brand, 97.0% purity), Co<sup>2+</sup> (CoCl<sub>2</sub>·6H<sub>2</sub>O; Biotec Brand, 98.0% purity), Fe<sup>2+</sup> (FeCl<sub>2</sub>·4H<sub>2</sub>O; Synth Brand, 99.6% purity) at a concentration of 7.9 × 10<sup>-4</sup> mol cation in 200 mL of biodiesel, without and with 2%<sub>(w/w)</sub> of rosemary extract. Control samples were prepared using 200 mL of biodiesel (BC) and 200 mL of biodiesel containing 2%<sub>(w/w)</sub> of rosemary extract (BCE). All samples were stored for 6 days at room temperature and in the absence of light. Fe<sup>3+</sup> (FeCl<sub>2</sub>·6H<sub>2</sub>O; Synth Brand, 99.6% purity) content in samples without and with 2%<sub>(w/w)</sub> extract was 8.9×10<sup>-5</sup> mol in 150 mL. The concentration was lower than the other samples because preliminary assays with the 7.9 × 10<sup>-4</sup> 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.<sup>24</sup>

### 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 Cr<sup>3+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup> and Fe<sup>3+</sup> in biodiesel were determined by a Shimadzu VR 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%<sub>(w/w)</sub> being 42.02%<sub>(w/w)</sub> saturated methyl esters (miristic, palmitic and stearic) and 57.98%<sub>(w/w)</sub> 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.<sup>12</sup>

**Table 1.** Specifications of the biodiesel B100

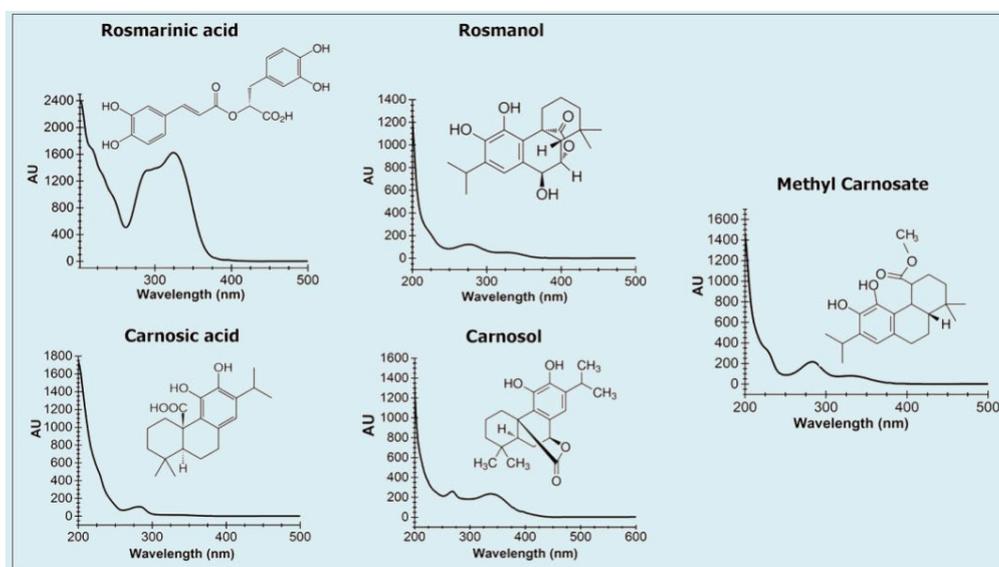
Parameter	Method	Specification	Unit	Result
Density (20°C)	ASTM D4052 <sup>25</sup>	850-900	kg m <sup>-3</sup>	879.6
Kinematic Viscosity (40°C)	ASTM D445 <sup>26</sup>	3.0-6.0	mm <sup>2</sup> s <sup>-1</sup>	4.46
Water content	ASTM D6304 <sup>27</sup>	Max 200	mg kg <sup>-1</sup>	180.1
Flash point	ASTM D93 <sup>28</sup>	Min 100	°C	142.1
Ester content	EN 14103 <sup>21</sup>	Min 96.5	% mass	98.71
Iodine Value	EN 14111 <sup>29</sup>	-	% mass	92
Induction Period	EN 14112 <sup>24</sup>	Min 8	hours	8.59
Acid number	ASTM D664 <sup>30</sup>	Max 0.5	mgKOH g <sup>-1</sup>	0.45
Free glycerin	ASTM D6584 <sup>31</sup>	Max 0.02	% mass	0.01
Total glycerin	ASTM D6584 <sup>31</sup>	Max 0.25	% mass	0.21
Monoglycerides	ASTM D6584 <sup>31</sup>	Max 0.70	% mass	0.68
Diglycerides	ASTM D6584 <sup>31</sup>	Max 0.20	% mass	0.11
Triglycerides	ASTM D6584 <sup>31</sup>	Max 0.20	% mass	0.07

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)<sup>32</sup> 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.<sup>22</sup>

It was added 2%<sub>w/w</sub> alcohol free rosemary extract to the biodiesel containing metallic ions and the control sample, because according to Spacino *et al.* (2016)<sup>22</sup> and Chendynski *et al.* (2020),<sup>17</sup> 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 (Figure 1) shows the presence of rosmarinic acid, rosmanol, carnosic acid, carnosol and methyl carnosate, which are phenolic compounds present in rosemary that have antioxidant properties.<sup>33</sup>

The phenols identification in the extract was made based on the spectral profile of the PDA detector of the chromatographic separation by HPLC, comparing with characteristic profiles for secondary metabolites present in rosemary, according to the literature.<sup>23</sup>

**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  $19.285 \text{ mg}_{\text{GAE}} \text{ g}^{-1}_{\text{dry mass}}$  with activity of  $54.2092 \text{ mg}_{\text{Trolox}} \text{ g}^{-1}_{\text{dry mass}}$ . 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),<sup>22</sup> 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  $\text{Co}^{2+}$  (BCo and BCoE),  $\text{Cr}^{3+}$  (BCr and BCrE),  $\text{Fe}^{2+}$  (BFe<sup>2+</sup> and BFe<sup>2+</sup>E) and  $\text{Fe}^{3+}$  (BFe<sup>3+</sup>E) at the assay temperature. It was not possible to obtain Rancimat data for the BFe<sup>3+</sup> 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,<sup>34</sup> 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  $\text{Co}^{2+} > \text{Cr}^{3+} > \text{Fe}^{2+}$ , except for the test performed in

**Table 2.** Induction periods (IP) and rate constants (k) values for the controls (BC and BCE), and for  $\text{Co}^{2+}$  (BCr; BCrE),  $\text{Cr}^{3+}$  (BCr; BCrE),  $\text{Fe}^{2+}$  (BFe<sup>2+</sup>; BFe<sup>2+</sup>E) and  $\text{Fe}^{3+}$  (BFe<sup>3+</sup>E) samples at 110 °C

Induction periods (h) and rate constants (h <sup>-1</sup> )								
Control at the initial time				Control at the final time				
Time (h)	BC	BCE		Time (h)	BC	BCE		
0	8.29 (0.3375)	11.42 (0.2704)		120	7.36 (0.3462)	10.03 (0.2269)		
Time (h) Samples	0.25	8	24	32	48	56	72	
without extract	BCr	7.23 (0.3493)	6.4 (0.4097)	4.36 (0.5099)	4.05 (0.586)	2.43 -11.358	1.76 -14.827	1.2 -23.234
	BCo	6.59 (0.3700)	6.59 (0.3883)	5.84 (0.3951)	4.85 (0.5321)	3.85 (0.6725)	3.76 (0.7851)	1.89 -14.036
	BFe <sup>2+</sup>	5.13 (0.4015)	4.51 (0.5368)	3.37 (0.6799)	2.23 -11.716	2.06 -11.988	1.28 -13.689	
Time (h) Samples	24	48	72	96	120			
with extract	BCoE	10.3 (0.3445)	8.9 (0.4122)	7.36 (0.3594)	6.4 (0.4443)	5.78 (0.4948)		
	BCrE	9.79 (0.2346)	8.61 (0.2327)	8.55 (0.2453)	8.05 (0.2526)	7.66 (0.2611)		
	BFe <sup>2+</sup> E	7.6 (0.4028)	3.66 (0.705)	1.54 -18.321	1.18 -22.466			
	Time	0.25	8	24	32	56	72	
	BFe <sup>3+</sup> E	5.88 (0.4746)	5.35 (0.4105)	3.54 (0.7529)	3.23 (0.7754)	2.32 -12.041	2.06 -15.559	

the first 0.25 hours. The tests with longer induction period had lower rate constant, as expected, and the sample containing the  $\text{Co}^{2+}$  was the least influenced the oxidation reaction of biodiesel. The sample containing  $\text{Fe}^{2+}$  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<sup>2+</sup>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<sup>2+</sup>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  $\text{Cr}^{3+}$  has higher charge when compared to  $\text{Co}^{2+}$ . 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  $\text{Fe}^{2+}$ .

For the BFe<sup>3+</sup>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,  $\text{Fe}^{3+}$  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  $\text{H}\cdot$ .<sup>32</sup> 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),<sup>35</sup> 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  $\text{Cr}^{3+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Fe}^{3+}$ .

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 decrease.<sup>36</sup> This explains the low catalytic power of  $\text{Cr}^{3+}$  for the oxidation reaction of biodiesel in relation to other metallic ions. In the case of  $\text{Fe}^{3+}$ , it forms complexes more unstable than other metallic ions in the same oxidation state, due to its electronic configuration  $d^5$ , that does not generate additional stability with the complex formation, leaving the ion more available to catalyze the biodiesel oxidation reactions.

Tagliabue *et al.* (2005)<sup>37</sup> reported that  $\text{Fe}^{3+}$  was more effective as a catalyst in the oxidation

reaction of biodiesel when compared to  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{4+}$ . Knothe and Steidley (2018)<sup>38</sup> state that trace amounts of  $\text{Fe}^{3+}$  are capable of promoting lipid oxidation. According to Schaich (2005)<sup>32</sup> 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,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions complex with the medium. In these complexes the electrons quickly transfer to oxygen, forming the superoxide anion ( $\text{O}_2^-$ ) or its conjugate acid, the perhydroxyl radical ( $\text{HO}_2^-$ ), which are singlet oxygen sources reacting with the unsaturated ester, forming the free peroxide radical, and then the hydroperoxide that forms the alkoxy and hydroxy radical, rapidly propagating the oxidation reaction of the biodiesel esters.<sup>32,39</sup>

When comparing the reduced ions, we observed that  $\text{Fe}^{2+}$  was more efficient in oxidizing biodiesel than  $\text{Co}^{2+}$ . Both ions catalyze the reaction through an auto-oxidation mechanism that generates radical oxygen.<sup>32</sup> The electronic configurations of  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  are, respectively,  $d^6$  and  $d^7$ , and an oxidation to the +3 state leads to a decrease in the electronic repulsion effect by generating states with fewer paired electrons. However, in iron, the resulting state +3 has a  $d^5$  configuration, without paired electrons, which makes oxidation more favorable as it leads to a more stable electronic configuration of the metal. For the cobalt, the auto-oxidation from state +2 to state +3 leads from an electronic configuration  $d^7$  to  $d^6$ , in which there is a decrease in the repulsive effect, but less pronounced than in the case of iron.

In samples containing cobalt and chromium ions, the IP decreases slowly because these metallic ions form complexes of inner sphere in the biodiesel, slowing down the flow of electrons and consequently delaying the oxidation reaction.<sup>32</sup>

#### 4. Conclusion

The transition metallic ions  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  showed catalytic effect in biodiesel oxidation reaction. When evaluating IP and k, the greatest catalytic effect was observed with  $\text{Fe}^{3+}$  and the smallest with  $\text{Co}^{2+}$ .  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+} > \text{Fe}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+}$ . 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.

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#### References

- Mishra, V. K.; Goswami, R. A review of production, properties and advantages of biodiesel. *Biofuels* **2018**, *9*, 273. [CrossRef]
- Dabdoub, M. J.; Bronzel, J. L.; Rampin, M. A. Biodiesel: a critical overview on the current status and perspectives at the academy and industry. *Química Nova* **2009**, *32*, 776. [CrossRef]
- Atabani, A. E.; Silitonga, A. S.; Badruddin, I. A.; Mahlia, T. M. I.; Masjuki, H. H.; Mekhilef, S. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews* **2012**, *16*, 2070. [CrossRef]
- Mota, C. J. A.; Pestana, C. F. M. Co-products from Biodiesel Production. *Revista Virtual de Química* **2011**, *3*, 416. [CrossRef]
- Ferreira, S. L.; Santos, A. M. dos; Souza, G. R. de; Polito, W. L.; Módolo, D. L. Análise por cromatografia gasosa de BTEX nas emissões de motor de combustão interna alimentado com diesel e mistura diesel-biodiesel (B10). *Química Nova* **2008**, *31*, 539. [CrossRef]
- Kovács, A.; Tóth, J.; Isaák, G.; Keresztényi, I. Aspects of storage and corrosion characteristics of biodiesel. *Fuel Processing Technology* **2015**, *134*, 59. [CrossRef]
- Ramos, L. P.; Kothe, V.; César-Oliveira, M. A. F.; Muniz-Wypych, A. S.; Nakagaki, S.; Krieger, N.; Wypych, F.; Cordeiro, C. S. Biodiesel: Matérias-Primas, Tecnologias de Produção e Propriedades Combustíveis. *Revista Virtual de Química* **2017**, *9*, 317. [CrossRef]
- Pinho, D. M. M.; Suarez, P. A. Z. Pinho. Do Óleo de Amendoim ao Biodiesel- Histórico e Política Brasileira para o Uso Energético de Óleos e Gorduras. *Revista Virtual de Química* **2017**, *9*, 39. [CrossRef]

- <sup>9</sup>Fazal, M. A.; Jakeria, M. R.; Haseeb, A.; Rubaiee, S. Effect of antioxidants on the stability and corrosiveness of palm biodiesel upon exposure of different metals. *Energy* **2017**, *135*, 220. [CrossRef]
- <sup>10</sup>Sui, M.; Li, F. Effect of TEPA on oxidation stability and metal ion content of biodiesel. *Renewable Energy* **2019**, *143*, 352. [CrossRef]
- <sup>11</sup>Zuleta, E. C.; Baena, L.; Rios, L. A.; Calderón, J. A. The Oxidative Stability of Biodiesel and its Impact on the Deterioration of Metallic and Polymeric Materials: a Review. *Journal of the Brazilian Chemical Society* **2012**, *23*, 2159. [CrossRef]
- <sup>12</sup>Chendynski, L. T.; Romagnoli, É. S.; Mantovani, A. C. G.; Kimura, M.; Marquesa, L. C.; Borsato, D. Influence of Copper and Metallic Alloys on the Oxidation Reaction of Commercial Biodiesel in Mixture with Natural Antioxidant. *Journal of the Brazilian Chemical Society* **2019**, *30*, 90. [CrossRef]
- <sup>13</sup>Fazal, M. A.; Suhaila, N. R.; Haseeb, A.; Rubaiee, S.; Al-Zahrani, A. Influence of copper on the instability and corrosiveness of palm biodiesel and its blends: An assessment on biodiesel sustainability. *Journal of Cleaner Production* **2018**, *171*, 1407. [CrossRef]
- <sup>14</sup>Deyab, M. A. Corrosion inhibition of aluminum in biodiesel by ethanol extracts of Rosemary leaves. *Journal of the Taiwan Institute of Chemical Engineers* **2016**, *58*, 536. [CrossRef]
- <sup>15</sup>Baştürk, A.; Ceylan, M. M.; Çavuş, M.; Boran, G.; Javidipour, I. Effects of some herbal extracts on oxidative stability of corn oil under accelerated oxidation conditions in comparison with some commonly used antioxidants. *LWT- Food Science and Technology* **2018**, *89*, 358. [CrossRef]
- <sup>16</sup>Romagnoli, É. S.; Borsato, D.; Silva, L. R. C.; Tashima, D. L. M.; Canesin, E. A. Influence of the extracts of senna leaves, blackberries and hibiscus flowers in the oxidation reaction of commercial biodiesel. *Biofuels* **2017**, *1*. [CrossRef]
- <sup>17</sup>Chendynski, L. T.; Cordeiro, T.; Messias, G. B.; Mantovani, A. C. G.; Spacino, K. R.; Zeraik, M. L.; Borsato, D. Evaluation and application of extracts of rosemary leaves, araçá pulp and peel of bacuri in the inhibition of the oxidation reaction of biodiesel. *Fuel* **2020**, *261*, 116379. [CrossRef]
- <sup>18</sup>Jancikova, S.; Jamróz, E.; Kulawik, P.; Tkaczewska, J.; Dordevic, D. Furcellaran/gelatin hydrolysate/rosemary extract composite films as active and intelligent packaging materials. *International Journal of Biological Macromolecules* **2019**, *131*, 19. [CrossRef] [PubMed]
- <sup>19</sup>Jin, Y.; Liu, Z.; Liu, D.; Shi, G.; Liu, D.; Yang, Y.; Gu, H.; Yang, L.; Zhou, Z. Natural antioxidant of rosemary extract used as an additive in the ultrasound-assisted extraction of anthocyanins from lingonberry (*Vaccinium vitis-idaea* L.) pomace. *Industrial Crops and Products* **2019**, *138*, 111425. [CrossRef]
- <sup>20</sup>Messias, G. B.; Chendynski, L. T.; Gomes Mantovani, A. C.; Suquila, F. A. C.; Tarley, C. R. T.; Moreira, I.; Borsato, D. Physical-chemical investigation of the oxidation reaction of biodiesel during storage in contact with carbon steel and 1020 steel in the presence of natural rosemary extract. *Biofuels* **2019**, *1*. [CrossRef]
- <sup>21</sup>EN 14103: Fat and Oil Derivatives. Fatty Acid Methyl Esters (FAME). Determination of Ester and Linolenic Acid Methyl Ester Contents. **2003**.
- <sup>22</sup>Spacino, K. R.; da Silva, E. T.; Angilelli, K. G.; Moreira, I.; Galão, O. F.; Borsato, D. Relative protection factor optimisation of natural antioxidants in biodiesel B100. *Industrial Crops and Products* **2016**, *80*, 109. [CrossRef]
- <sup>23</sup>Zabot, G. L.; Moraes, M. N.; Rostagno, M. A.; Meireles, M. A. A. Fast analysis of phenolic terpenes by high-performance liquid chromatography using a fused-core column. *Analytical Methods* **2014**, *6*, 7457. [CrossRef]
- <sup>24</sup>EN 14112, Determination of oxidation stability (accelerated oxidation test), Berlin, 2003.
- <sup>25</sup>ASTM D4052, Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter. *ASTM International* 2002.
- <sup>26</sup>ASTM D445, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity). *ASTM International* 2007.
- <sup>27</sup>ASTM D6304, Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration (Withdrawn 2016). *ASTM International* 2004.
- <sup>28</sup>ASTM D93, Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester. *ASTM International* 2001.
- <sup>29</sup>EN 14111, Fat and oil derivatives. Fatty acid methyl esters (FAME). Determination of iodine value, 2003.
- <sup>30</sup>ASTM D664, Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration. *ASTM International* 2011.
- <sup>31</sup>ASTM D6584-17, Standard Test Method for Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography. *ASTM International* 2017.

- <sup>32</sup> Schaich, K. M. Lipid oxidation: theoretical aspects. *Bailey's industrial oil and fat products* **2005**. [[CrossRef](#)]
- <sup>33</sup> Madsen, H. L.; Bertelsen, G. Spices as antioxidants. *Trends in Food Science & technology* **1995**, *6*, 271. [[CrossRef](#)]
- <sup>34</sup> EN 14214, Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines-Requirements and test methods, 2019.
- <sup>35</sup> Moreno, S.; Scheyer, T.; Romano, C. S.; Vojnov, A. A. Antioxidant and antimicrobial activities of rosemary extracts linked to their polyphenol composition. *Free Radical Research* **2006**, *40*, 223. [[CrossRef](#)] [[PubMed](#)]
- <sup>36</sup> Housecroft, C. E.; Sharpe, A. G.; *Inorganic Chemistry*, 4th Ed, Pearson Education Ltd: Harlow, 2012.
- <sup>37</sup> Tagliabue, S.; Gasparoli, A.; Bella, L. della; Bondioli, P. Influence of metal contamination on biodiesel thermo-oxidation stability. *Rivista Italiana delle Sostanze Grasse* **2005**, *82*, 93. [[Link](#)]
- <sup>38</sup> Knothe, G.; Steidley, K. R. The effect of metals and metal oxides on biodiesel oxidative stability from promotion to inhibition. *Fuel Processing Technology* **2018**, *177*, 75. [[CrossRef](#)]
- <sup>39</sup> Aurand, L. W.; Boone, N. H.; Giddings, G. G. Superoxide and singlet oxygen in milk lipid peroxidation. *Journal of Dairy Science* **1977**, *60*, 363. [[CrossRef](#)]