


## The Catalytic Action of Copper Ions and the Rosemary Extract Antioxidant Effect in the Biodiesel Oxidation Reaction and the Implication in Arrhenius Behavior

Kelly R. Spacino,<sup>a</sup> Ana Carolina G. Mantovani,<sup>b</sup> Gustavo G. Marcheafave,<sup>b</sup> <sup>a</sup>  
Edmilson A. Canesin<sup>c</sup> and Dionisio Borsato <sup>\*,a</sup>

<sup>a</sup>Departamento de Química, Universidade Estadual de Londrina,  
Rod. Celso Garcia Cid, PR 445, km 380, 86057-970 Londrina-PR, Brazil

<sup>b</sup>Departamento de Física, Universidade Estadual de Londrina,  
Rod. Celso Garcia Cid, PR 445, km 380, 86057-970 Londrina-PR, Brazil

<sup>c</sup>Universidade Tecnológica Federal do Paraná,  
Rua Marçilio Dias, 635, 86812-460 Apucarana-PR, Brazil

Biodiesel contains esters in its composition which make it susceptible to oxidation. Among the factors that cause this reaction is the contamination with metal ions. In the present work, it was analyzed biodiesel samples obtained from a mixture containing 39.0% m/m soybean oil, 22.0% m/m beef tallow and 39.0% m/m poultry fat using a methyl route. Copper ions were added to the biodiesel to evaluate its catalytic action in the oxidation reaction, in the presence and absence of rosemary extract. During 192 h of assay, samples containing copper, without extract, showed shorter induction periods, higher rate constants and lower activation energy, when compared to samples containing extract, at the same assay temperature. Copper ions presented a strong catalytic action causing linearity deviations showing a super-Arrhenius behavior, while rosemary extract delayed the oxidative process and showed no linearity deviations.

**Keywords:** metal ions, super-Arrhenius behavior, kinetic parameters

### Introduction

Due to the large-scale use of fossil fuels as a source of energy the pollution in the world has increased. In order to minimize the environmental impact caused researches are targeting other forms of energy from renewable sources as biofuels.<sup>1</sup>

Biodiesel has therefore become a viable alternative because it has some benefits as the reduction of harmful gas emissions, carbon neutrality, lower engine oil consumption and thermal efficiency when comparable to pure diesel.<sup>2-6</sup>

However, biodiesel contains methyl esters of unsaturated fatty acids which makes it more susceptible to oxidation. This is a negative fact since when stored or even transported there is the possibility of formation of undesirable products as aldehydes, ketones, short-chain fatty acids, polymers and other products resulting from the oxidation.<sup>7,8</sup> The oxidation reaction may be caused by contact with air,

exposure to light, high temperatures and the presence of some transition metals.<sup>8</sup>

From the production period to the consumer, biodiesel can be contaminated with metal ions that can be derived from a variety of sources, such as the copper heat exchangers used in the biodiesel production,<sup>9</sup> the storage or transport containers where contamination occurs by direct contact with the container surface or by metallic sediment from the oxidation process.<sup>10,11</sup>

The presence of transition metal ions catalyzes the oxidation reaction decreasing the biodiesel induction period.<sup>2,12</sup> Furthermore, the transition metal ions capable of transferring only one electron as cobalt, iron, copper, manganese and vanadium are more active catalysts, and a very small concentration is sufficient to promote the oxidation reaction.<sup>13</sup>

In order to inhibit or slow the biodiesel degradation, additives should be used to improve the biofuel sustainability. The use of antioxidants has been the most efficient way to increase the stability of biodiesel thus prolonging its storage time.<sup>12</sup>

\*e-mail: dborsato@uel.br

Effective antioxidants are those capable of inhibiting or eliminating the free radicals formed in the oxidation reaction of the methyl esters from biodiesel.<sup>13,14</sup> Extracts from some plants has been used as natural antioxidants due to the phenolic compounds found in their compositions.<sup>14,15</sup> Hydroxyl groups present in antioxidant structures provide hydrogens inhibiting or stopping the propagation of free radicals.<sup>16</sup>

Rosemary extract has in its composition rosmanol, carnosic acid, carnosol, rosmarinic acid, among other phenolic compounds. These phenolic compounds contained in rosemary leaves are capable of stabilizing unsaturated methyl esters, acting as chelating agents of copper ions and thereby retarding the oxidative degradation of biodiesel.<sup>17,18</sup>

Studies<sup>15,16,19</sup> performed with rosemary extract in biodiesel show that it can decrease the rate constant ( $k$ ), consequently increasing the activation energy ( $E_a$ ), slowing the reaction and disfavoring the oxidation of biodiesel.

The aim of this study was to evaluate the catalytic action of copper and its implication in the Arrhenius linearity deviation during biodiesel oxidation reaction in the presence and absence of rosemary extract.

## Experimental

### Biodiesel

The biodiesel used was obtained in the Fuel Research and Analysis Laboratory of the State University of Londrina, Brazil, from a mixture containing 39.0% m/m of soybean oil, 22.0% m/m beef tallow and 39.0% m/m poultry fat, by methyl route according to da Costa *et al.*<sup>20</sup>

### Chromatographic analysis

The ester profile and quantification were performed following the standard EN 14103,<sup>21</sup> using a gas chromatograph (GC) with GC-2010 Plus (Shimadzu) equipment coupled to a Shimadzu MS-QP2010-Ultra mass spectrometer (MS). It was used a Restek model RT-2560 column of 100 m length with 0.25 mm of internal diameter and 0.25  $\mu\text{m}$  of film thickness. The injection was performed manually, with an injector temperature of 240 °C. Samples were prepared with 40 mg of biodiesel, 500  $\mu\text{L}$  of internal pattern C23 (Sigma-Aldrich, St. Louis, USA) and 500  $\mu\text{L}$  of heptane (Vetec, Rio de Janeiro, Brazil).

### Alcoholic extract of rosemary leaves

Ten grams of dried rosemary leaves at 60 °C were added to 250 mL of absolute ethyl alcohol. These mixtures

were kept in the absence of light for 48 h, then filtered and concentrated to approximately 50 mL using a heating plate at 50 °C. After cooling to the room temperature each extract was transferred to a 50 mL volumetric flask and completed with absolute ethyl alcohol (Anidrol, Diadema, Brazil).

### Determination of total phenolic and antioxidant activity

The total content of phenolic compounds in the extract was determined in triplicate via spectrophotometry (PerkinElmer, model UV-Vis LAMBDA 25) using 2 M Folin-Ciocalteu reagent (Sigma-Aldrich, St. Louis, USA) and the antioxidant activity was measured in triplicate by 2,2-diphenyl-1-picrylhydrazyl (DPPH, Sigma-Aldrich, St. Louis, USA) assay, according to the methodology described by Romagnoli *et al.*<sup>22</sup>

### Determination of the induction period (IP)

In each assay it was performed the accelerated heating method at 110, 115, 120 and 125 °C using the Rancimat equipment (Metrohm; model 873), according to the methodology described in the standard EN 14112.<sup>23</sup>

### Analysis of kinetic parameters

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, according to equation 1.<sup>24</sup>

$$\ln \Lambda = \ln \Lambda_0 - k(t_f - t_i) \quad (1)$$

where:  $\Lambda$  represents the conductivity at time  $t$  (h),  $\Lambda_0$  the initial conductivity, and  $t_i$  and  $t_f$  are the initial and final analysis time.

The activation energy ( $E_a$ ) was determined by the equation 2 with the data fitted as a linear model:

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

where:  $A$  is the pre-exponential factor;  $R$  is the gas constant;  $T$  is the temperature.

For deviations from the Arrhenius equation, the best data fit was the second-order polynomial model. The apparent activation energy calculations ( $E_{aa}$ ) were performed using equations 3 and 4:

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

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

where: the parameter C determines whether the curve is concave or convex, being negative for super-Arrhenius or positive for sub-Arrhenius; B is the parameter of quadratic approach. For that reason, the activation energy  $E_a$  is no longer a constant but depends linearly on  $1/T$ , as shown in equation 4.

#### Flame atomic absorption spectrometry (FAAS)

The copper concentration in biodiesel was 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 according to Messias *et al.*<sup>19</sup>

#### Samples preparation

The samples containing 200 mL of biodiesel (BC), 200 mL of biodiesel with 2% v/v of alcohol-free rosemary extract (BCE), 400 mL of biodiesel with  $2.4978 \times 10^{-3}$  g  $\text{Cu}^{2+}$  (BCu), corresponding to 6.2445 mg  $\text{L}^{-1}$ , and 400 mL of biodiesel with 2% v/v alcohol-free rosemary extract and containing  $2.4978 \times 10^{-3}$  g  $\text{Cu}^{2+}$  (BCuE) were stored for 8 days at room temperature and in the absence of light. The copper mass used as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Vetec, Rio de Janeiro, Brazil, 99.0% purity) was determined by preliminary tests in order to enable the monitoring of the biodiesel oxidation reaction kinetics.

## Results and Discussion

The antioxidant action of rosemary leaves extract is mainly caused by the presence of phenolic compounds such as carnosol, carnosic, gallic acid, etc., which are responsible for the biodiesel protection. Thus, the higher the activity of

the phenolic compounds, higher is the expected protective effect of the extract.<sup>25</sup>

The extract of dried rosemary leaves used were subjected to analysis of total phenols content and activity in order to verify the antioxidants efficiency. The content of total phenols, expressed as gallic acid equivalent (GAE), in the rosemary extract used was of 19.285 mg<sub>GAE</sub> g<sup>-1</sup><sub>dry mass</sub> and with activity of 54.2092 mg<sub>Trolox</sub> g<sup>-1</sup><sub>dry mass</sub>. In addition, according to Spacino *et al.*,<sup>14</sup> rosemary extract does not undergo thermal decomposition at the temperatures used to determine the induction period by the Rancimat method.

The chromatographic analysis showed that the biodiesel used consisted basically of the methyl meristic (3.19% m/m), methyl palmitic (22.68% m/m), methyl palmitoleic (1.90% m/m), methyl stearic (13.25% m/m), methyl oleate (26.72% m/m), methyl linoleate (25.30% m/m) and methyl linoleate (5.21% m/m) esters. The C20 methyl ester was not found, and the C22:0 content was 0.46% m/m of the biodiesel sample. Therefore, these esters together account for 98.71% m/m of the substances present in the B100 biodiesel used, being in accordance with the European Union specification where the ester content must be greater than 96.5% m/m. In addition, the content of mono-, di-, and triglycerides presented together 0.45% m/m and the free glycerin content observed was 0.015% m/m, lower than the Brazilian legislation which provides a maximum free glycerin content of 0.02% m/m.<sup>26</sup>

Before the oxidative stability analysis, the extract with antioxidant properties and alcohol-free was added to the B100 biodiesel in which the main parameters are presented in Table 1.

The samples of biodiesel control (BC), biodiesel containing the rosemary extract (BE), biodiesel containing copper ions (BCu) and biodiesel containing copper ions with rosemary extract (BCuE) were subjected to the accelerated oxidative stability test by the Rancimat method (EN 14112).<sup>23</sup> The values of the IP corresponding to the inflection point of curves of conductivity *versus* time were determined in each assay and control.

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

Parameter	Method	Specification	Result
Density (20 °C) / (kg m <sup>-3</sup> )	ASTM D4052 <sup>27</sup>	850-900	879.6
Kinematic viscosity (40 °C) / (mm <sup>2</sup> s <sup>-1</sup> )	ASTM D445 <sup>28</sup>	3.0 to 6.0	4.46
Water content / (mg kg <sup>-1</sup> )	ASTM D6304 <sup>29</sup>	max. 200	180.1
Flash point / °C	ASTM D93 <sup>30</sup>	min. 100	142.1
Ester content / (% mass)	EN 14103 <sup>21</sup>	96.5	98.71
Iodine value / (g I <sub>2</sub> 100 g <sup>-1</sup> biodiesel)	EN 14111 <sup>31</sup>	–	92
Induction period / h	EN 14112 <sup>23</sup>	min. 12	8.59
Acid number / (mg <sub>KOH</sub> g <sup>-1</sup> )	ASTM D664 <sup>32</sup>	max. 0.5	0.45

Table 2 shows the values of the analysis of the IP during the evaluated period. The lines separate the biodiesel containing or not rosemary extract at the beginning and end of the experiments. The analysis of the control and biodiesel samples with extract were performed at the beginning and at the end of the experiment, and according to the results (Table 2) presented a reduction of 12% in the induction period. This stability is due to the fact that the reaction of the oxygen with the double bonds present in the esters that compose the biodiesel are thermodynamically non-spontaneous, because the spins states are different. Oxygen is naturally in a triplet state while the double bonds of the biodiesel esters are in the singlet state.<sup>13</sup> The biodiesel samples containing copper ions suffered degradation faster than the control sample, and the sample containing the natural extract showed that the presence of these ions accelerates the oxidation reaction.

In the samples containing rosemary extract was observed a higher IP than in the samples without the extract. This

happens because the phenolic compounds present in the rosemary extract act as antioxidant retarding the oxidation process of the biodiesel. The phenols provide hydrogen to the free radical formed by restoring the ester molecule present in biodiesel. The free radical formed by the antioxidant molecule does not propagate the radical reaction, since the aromatic ring present in the phenolic compounds provides stability due to electronic delocalization.

Considering the oxidation reaction of biodiesel as a first order,<sup>14,33</sup> the rate constants were determined in all the assays using the angular coefficient, according to equation 1.

Table 3 shows the rate constants (k) at temperatures of 110, 115, 120 and 125 °C as well as the activation energy values obtained by applying equation 2 for the BC, BE, BCu and BCuE, during the storage period analyzed. The results in parentheses presented in the table refer to the samples containing rosemary extract.

**Table 2.** Samples induction period (IP) at 110, 115, 120 and 125 °C during the analyzed storage period

Sample	Storage period / h	Induction period / h			
		110 °C	115 °C	120 °C	125 °C
BC/BE	0	8.59/11.08	5.17/7.47	4.27/5.27	3.05/2.82
	0.25	8.43/10.69	5.80/7.49	4.16/5.28	3.04/3.72
	16.0	7.33/8.29	5.26/5.93	3.64/3.94	2.54/2.74
BCu/BCuE	40.0	5.73/7.63	3.94/4.97	2.81/3.65	1.89/2.54
	64.0	4.49/6.44	3.26/4.41	1.49/3.29	1.67/2.32
	88.0	3.11/5.24	2.38/3.93	1.74/2.63	1.31/2.01
	136.0	1.96/3.05	1.37/2.41	0.99/1.83	0.84/1.19
BC/BE	192.0	7.65/9.72	5.46/6.90	3.98/4.99	2.82/3.55

BC: biodiesel control; BE: biodiesel containing the rosemary extract; BCu: biodiesel containing copper ions; BCuE: biodiesel containing copper ions with rosemary extract.

**Table 3.** Rate constants of biodiesel oxidation reaction and activation energies

Assay	Storage period / h	k / h <sup>-1</sup>				E <sub>a</sub> / (kJ mol <sup>-1</sup> )	R <sup>2</sup>
		110 °C	115 °C	120 °C	125 °C		
BC (BE)	0	0.3561 (0.2446)	0.5132 (0.3312)	0.6175 (0.5321)	0.8502 (0.8417)	70.89 (105.84)	0.9869 (0.9891)
	0.25	0.2813 (0.2109)	0.3828 (0.2696)	0.6233 (0.5094)	0.9499 (0.7174)	104.81 (109.15)	0.9913 (0.9717)
	16	0.3191 (0.2453)	0.3719 (0.3889)	0.7323 (0.7065)	1.1126 (0.9755)	111.96 (120.18)	0.9499 (0.9897)
	40	0.3526 (0.2674)	0.6351 (0.5641)	0.8542 (0.6093)	1.0963 (0.9164)	93.98 (95.83)	0.96 (0.904)
	64	0.5134 (0.3738)	0.5982 (0.4601)	1.8699 (0.7596)	1.3557 (1.0135)	103.02 (88.49)	0.7016 (0.9755)
	88	0.855 (0.4341)	1.1333 (0.5211)	1.4038 (0.9875)	1.1351 (1.5772)	27.29 (114.11)	0.467 (0.9588)
BCu (BCuE)	136	1.5323 (0.8642)	2.223 (1.1866)	3.1265 (1.4463)	2.0172 (2.4833)	30.07 (85.13)	0.2706 (0.9573)
	192	0.3604 (0.2954)	0.367 (0.3844)	0.6455 (0.4384)	0.8894 (0.7131)	82.79 (70.20)	0.9039 (0.9891)

k: rate constant; E<sub>a</sub>: activation energy; R<sup>2</sup>: determination coefficient; BC: biodiesel control; BE: biodiesel containing the rosemary extract; BCu: biodiesel containing copper ions; BCuE: biodiesel containing copper ions with rosemary extract. Results in parentheses refer to the samples containing rosemary extract.

The data from all the assays showed that the longer the storage period, the higher the rate constant ( $k$ ). The lower values were observed in the assays containing the rosemary extract and the higher values for the samples containing copper ions, indicating that the presence of these ions accelerates the oxidation reaction.

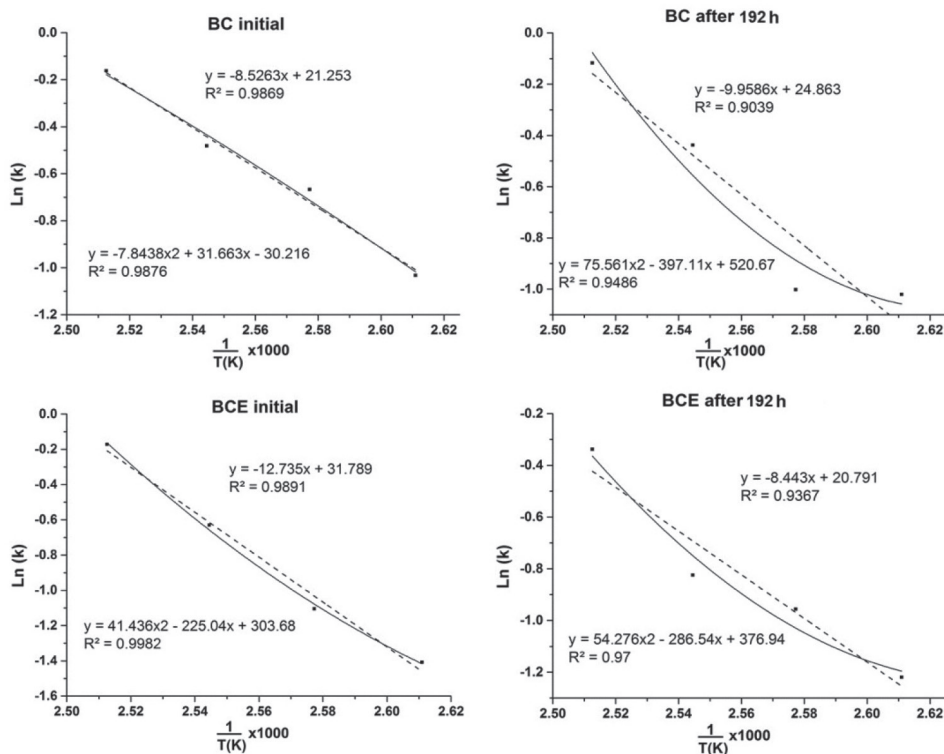
The activation energy for the samples containing or not the extract presented lower values at the end of the analysis period, as expected. The biodiesel samples containing only copper ions presented variation with a decrease in the activation energy in the assays performed after 64 and 136 h. We can observe that the samples containing copper ions and extract suffered smaller variations in the activation energy when compared to the samples with copper. The values of the determination coefficients ( $R^2$ ) for the biodiesel assays containing copper ions and without extract showed a decrease in the value indicating linearity deviations.

The direct initiation of the oxidation reaction in the presence of  $\text{Cu}^{2+}$  ions involves the removal of an electron from the double bond of the ester molecule to the metal ion reducing it.<sup>13</sup> However, in the presence of oxygen and reduced copper ion, it acts as a conduit to transfer an electron to the oxygen to form the superoxide anion ( $\text{O}_2^-$ ) or its conjugate acid, the perhydroxyl radical ( $\text{HO}_2^-$ ). This chemical species would serve as a source of singlet oxygen that react 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 esters.<sup>13,34</sup> The rate and selectivity of the direct electronic transfer of reactions are influenced by the type of metallic complex formed. Although we added  $6.2445 \text{ mg L}^{-1}$  of copper ions, the analysis by the FAAS showed that the concentration of copper ions dissolved in biodiesel was  $0.07 \text{ mg L}^{-1}$ . According to Schaich,<sup>13</sup> in the presence of organic substrates the formation of complexes with the metal ion occurs, causing the transfer of electrons in a quick and selective way.

The Arrhenius activation energy was initially proposed for simple reactions in which the activation energy remains constant. According to Silva *et al.*<sup>35</sup> and Gregório *et al.*,<sup>24</sup> the oxidation of biodiesel presents several complex chemical reactions depending on thermal factors, non-equilibrium distributions of reagents, tunneling, geometric configuration, among others, that directly influence the response obtained and the behavior of the activation energy. Therefore, the apparent activation energy ( $E_{aa}$ ), also obtained through experimental data, becomes the most viable alternative because is temperature dependent, being obtained applying equations 3 and 4.<sup>24,36,37</sup>

Figure 1 shows the graphics of  $\ln k$  versus  $1/T$  for the assays of the biodiesel and biodiesel samples containing rosemary extract for the first (time zero) and the last day. At zero time, the determination coefficients obtained were equal to 0.99 for the control sample. The extract sample



**Figure 1.** Graphs of  $\ln k$  versus  $1/T$  for the assays of control biodiesel (BC) and biodiesel samples containing rosemary extract (BCE).

showed a linear behavior and the Arrhenius equation (equation 1) can be used to determine the activation energy. After 192 h of assays the  $R^2$  values decreased, showing a tendency for a non-linear behavior. This fact was caused due to the time that the biodiesel was stored and not because of the presence of metals in the sample used, since FAAS analysis did not detect any trace of copper, iron, cobalt, chromium or manganese ions.

Figure 2 shows the graphs of  $\ln k$  versus  $1/T$  for the copper ion sample assays. In the interval of 0.25-40 h we can observe a linear behavior with a slight concave change when using the polynomial fit. As storage time increases, the non-Arrhenius behavior is observed, where the linearity deviations of the Arrhenius equation increase considerably, showing the need for a second-degree polynomial fit (equation 3). This deviation depends on the value of  $C$  (equation 4) which can be sub-Arrhenius when the value is positive resulting in a concave curve or

super-Arrhenius when  $C$  is negative resulting in a convex curve.<sup>37,38</sup>

The biodiesel in the presence of copper ions until the first 40 h of assay presented a linear behavior following the Arrhenius law. From the 40 h of storage the fits are no longer linear with low  $R^2$  values,  $0.27 \leq R^2 \leq 0.70$ , for the longest and shortest storage time, respectively. The curves are now convex with Arrhenius deviations needing a polynomial fit. Therefore, from the 40 h of storage the apparent activation energy decreases with the increase of the temperature, showing a super-Arrhenius behavior, where the transport phenomena are considered important because they accelerate the oxidation process as the temperature increases. According to Aquilanti *et al.*,<sup>37,38</sup> for sub-Arrhenius behavior, the activation energy increases with increasing temperature, and in the case of super-Arrhenius, decreases with increasing temperature. Several studies<sup>24,39-42</sup> with different reactions and matrices also reported deviations in the activation energy

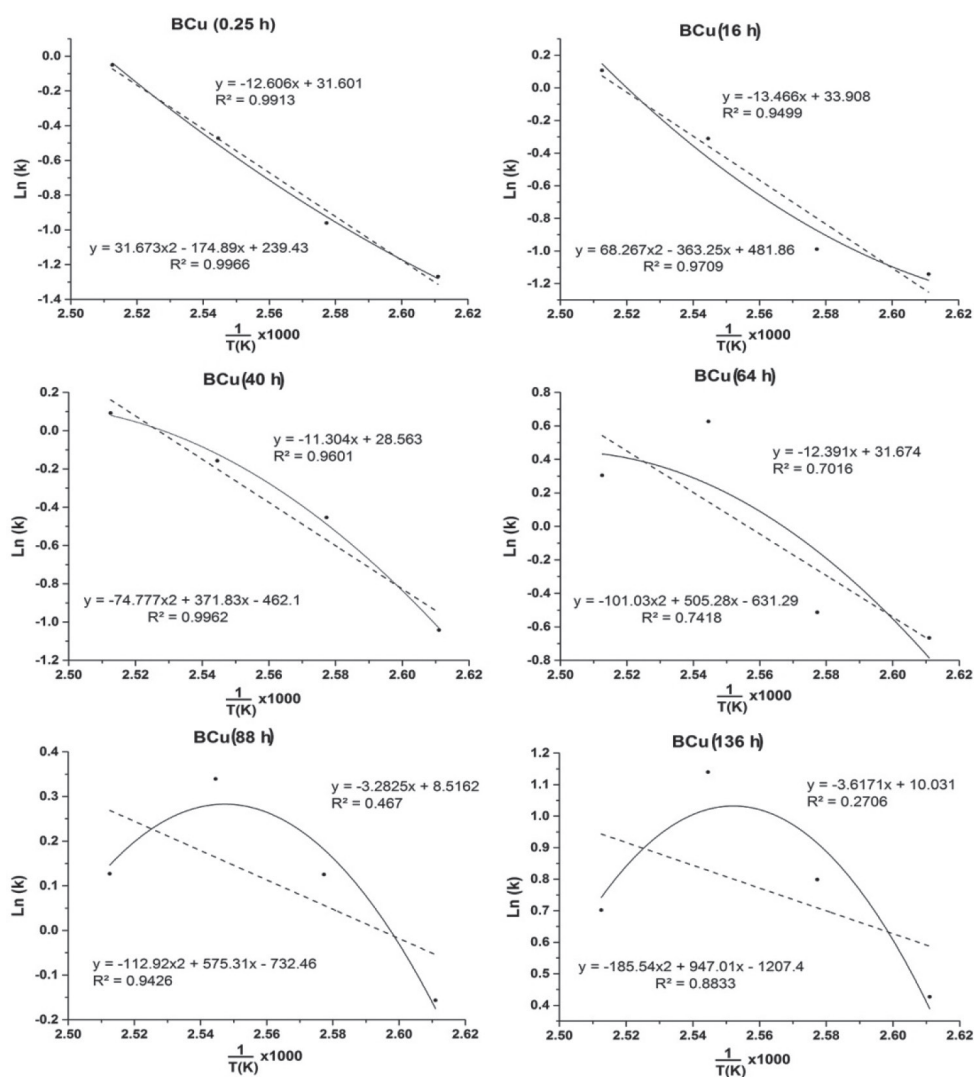
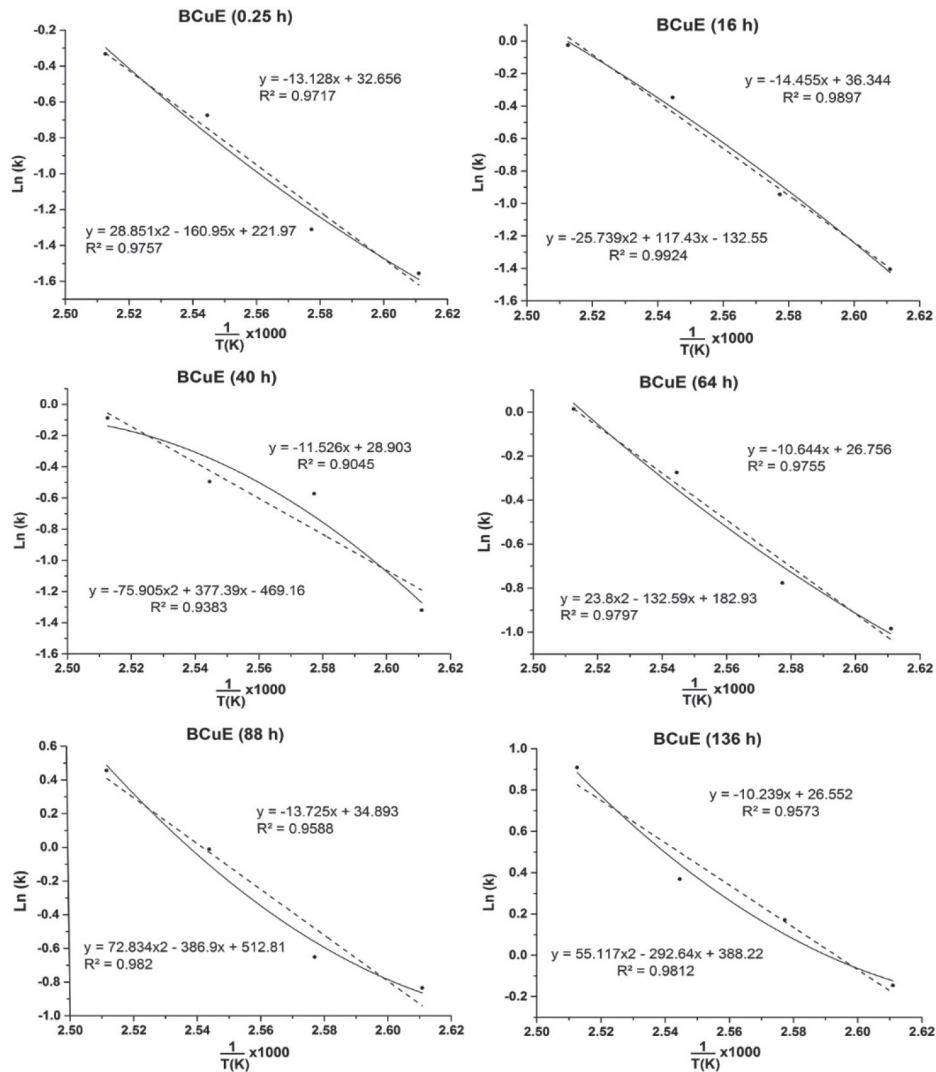


Figure 2. Linear behavior and Arrhenius deviations from the biodiesel oxidation in the presence of copper ions.



**Figure 3.** Graphs of  $\ln k$  versus  $1/T$  for the assays of biodiesel samples containing copper ions and rosemary extract (BCuE).

behavior, and the greater the reactional complexity, the greater the probability of the deviations occur.

Figure 3 shows the graphs of  $\ln k$  versus  $1/T$  for the assays of samples containing copper ions and rosemary extract (BCuE). We can observe that the linear behavior predominates in the assays even in the presence of copper ions. It is reported in the literature<sup>18</sup> that flavonoid compounds can complex transition metals, which are catalysts of processes that give rise to and propagate oxidation reactions. According to Moreno *et al.*,<sup>18</sup> the phenolic compounds present in the rosemary extract act as chelators of metals and superoxides which serve as singlet oxygen source reducing or eliminating its catalytic active form, as previously described.

## Conclusions

Biodiesel samples containing copper ions had lower

oxidative stabilities and higher rate constants when compared to the samples of biodiesel and biodiesel containing rosemary extract, showing that copper is a strong catalyst for the oxidation reaction of the biodiesel, causing deviations of the Arrhenius linearity.

The extract of rosemary used as natural antioxidant changed the kinetic parameters of the oxidation reaction with the decrease of the rate constant and increase of the activation energy, retarding the oxidation process and avoiding deviations of linearity even in the presence of copper ions.

## Acknowledgments

The authors thank the State University of Londrina (UEL) and Fuel Analysis and Research Laboratory (LAPC) for the technical support.

## References

1. Li, F.; Liu, Z.; Ni, Z.; Wang, H.; *J. Mater. Res. Technol.* **2019**, *8*, 3681.
2. Fazal, M. A.; Suhaila, N. R.; Haseeb, A.; Rubaiee, S.; *J. Cleaner Prod.* **2018**, *181*, 508.
3. Rajkumar, S.; Thangaraja, J.; *Fuel* **2019**, *240*, 101.
4. Rocabruno-Valdés, C. I.; González-Rodríguez, J. G.; Díaz-Blanco, Y.; Juantorena, A. U.; Muñoz-Ledo, J. A.; El-Hamzaoui, Y.; Hernández, J. A.; *Renewable Energy* **2019**, *140*, 592.
5. Xu, C.; Nasrollahzadeh, M.; Sajjadi, M.; Maham, M.; Luque, R.; Puente-Santiago, A. R.; *Renewable Sustainable Energy Rev.* **2019**, *112*, 195.
6. Rodríguez-Padrón, D.; Puente-Santiago, A. R.; Balu, A. M.; Muñoz-Batista, M. J.; Luque, R.; *ChemCatChem* **2019**, *11*, 18.
7. Liu, Z.-W.; Li, F.-S.; Wang, W.; Wang, B.; *J. Energy Inst.* **2019**, *92*, 861.
8. Bussler, L.; Izida, T.; Lima, S. M.; Andrade, L. H. C.; *Spectrochim. Acta, Part A* **2019**, *217*, 190.
9. Mohammed, H. A.; Bhaskaran, G.; Shuaib, N. H.; Saidur, R.; *Renewable Sustainable Energy Rev.* **2011**, *15*, 1502.
10. Comin, M.; de Souza, A. C. D.; Roveda, A. C.; Yahagi, S. S.; de Oliveira, L. H.; Amaral, M. S.; Silva, C. A. A.; Fiorucci, A. R.; Gomes, R. S.; Caires, A. R. L.; *Fuel* **2017**, *191*, 275.
11. Obadih, A.; Kannan, R.; Ramasubbu, A.; Kumar, S. V.; *Fuel Process. Technol.* **2012**, *99*, 56.
12. Sui, M.; Li, F.; *Renewable Energy* **2019**, *143*, 352.
13. Schaich, K. M. In *Bailey's Industrial Oil and Fat Products*; Shahidi, F., ed.; John Wiley & Sons, Inc.: New Jersey, 2005, Part 1, ch. 7.
14. Spacino, K. R.; da Silva, E. T.; Angilelli, K. G.; Moreira, I.; Galão, O. F.; Borsato, D.; *Ind. Crops Prod.* **2016**, *80*, 109.
15. Spacino, K. R.; Borsato, D.; Buosi, G. M.; Chendynski, L. T.; *Fuel Process. Technol.* **2015**, *137*, 366.
16. Coppo, R. L.; Pereira, J. L.; da Silva, H. C.; Angilelli, K. G.; Rodrigues, P. R. P.; Galvan, D.; Borsato, D.; *J. Biobased Mater. Bioenergy* **2014**, *8*, 545.
17. Lee, K. H.; Lee, J.-S.; Kim, E. S.; Lee, H. G.; *LWT--Food Sci. Technol.* **2019**, *101*, 138.
18. Moreno, S.; Scheyer, T.; Romano, C. S.; Vojnov, A. A.; *Free Radical Res.* **2006**, *40*, 223.
19. Messias, G. B.; Chendynski, L. T.; Mantovani, A. C. G.; Suquila, F. A. C.; Tarley, C. R. T.; Moreira, I.; Borsato, D.; *Biofuels* **2019**, DOI 10.1080/17597269.2019.1629523.
20. da Costa, J. K. T.; Angilelli, K. G.; Spacino, K. R.; da Silva, E. T.; Silva, L. R. C.; Borsato, D.; *Semina: Cienc. Exatas Tecnol.* **2016**, *37*, 107.
21. EN 14103: *Fat and Oil Derivatives - Fatty Acid Methyl Esters (FAME) - Determination of Ester and Linolenic Acid Methyl Ester Contents*; European Committee for Standardization, Brussels, 2003.
22. Romagnoli, É. S.; Borsato, D.; Silva, L. R. C.; Tashima, D. L. M.; Canesin, E. A.; *Biofuels* **2018**, DOI 10.1080/17597269.2017.1418569.
23. EN 14112: *Fat and Oil Derivatives - Fatty Acid Methyl Esters (FAME) - Determination of Oxidation Stability (Accelerated Oxidation Test)*; European Committee for Standardization, Brussels, 2003.
24. Gregório, A. P. H.; Romagnoli, É. S.; Borsato, D.; Galvan, D.; Spacino, K. R.; *Sustainable Energy Technol. Assess.* **2018**, *28*, 60.
25. Zobot, G. L.; Moraes, M. N.; Rostagno, M. A.; Meireles, M. A. A.; *Anal. Methods* **2014**, *6*, 7457.
26. Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP); Resolution No. 14, of May 11, 2012; DOU, 05/18/2012, No. 96, Section 1, p. 79. Available at <http://pesquisa.in.gov.br/imprensa/jsp/visualiza/index.jsp?data=18/05/2012&jornal=1&pagina=79&totalArquivos=304>, accessed in January 2020.
27. ASTM D4052: *Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter*; ASTM International, West Conshohocken, PA, 2002.
28. ASTM D445: *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)*; ASTM International, West Conshohocken, PA, 2007.
29. 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, West Conshohocken, PA, 2004.
30. ASTM D93: *Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester*; ASTM International, West Conshohocken, PA, 2001.
31. EN 14111: *Fat and Oil Derivatives - Fatty Acid Methyl Esters (FAME) - Determination of Iodine Value*; European Committee for Standardization, Brussels, 2003.
32. ASTM D664: *Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration*; ASTM International, West Conshohocken, PA, 2011.
33. Borsato, D.; Cini, J. R. M.; da Silva, H. C.; Coppo, R. L.; Angilelli, K. G.; Moreira, I.; Maia, E. C. R.; *Fuel Process. Technol.* **2014**, *127*, 111.
34. Aurand, L. W.; Boone, N. H.; Giddings, G. G.; *J. Dairy Sci.* **1977**, *60*, 363.
35. Silva, V. H. C.; Aquilanti, V.; de Oliveira, H. C. B.; Mundim, K. C.; *Chem. Phys. Lett.* **2013**, *590*, 201.
36. Nishiyama, M.; Kleijn, S.; Aquilanti, V.; Kasai, T.; *Chem. Phys. Lett.* **2009**, *470*, 332.
37. Aquilanti, V.; Mundim, K. C.; Elango, M.; Kleijn, S.; Kasai, T.; *Chem. Phys. Lett.* **2010**, *498*, 209.
38. Aquilanti, V.; Coutinho, N. D.; Carvalho-Silva, V. H.; *Philos. Trans. R. Soc., A* **2017**, *375*, 20160201.
39. Coutinho, N. D.; Silva, V. H. C.; de Oliveira, H. C. B.; Camargo, A. J.; Mundim, K. C.; Aquilanti, V.; *J. Phys. Chem. Lett.* **2015**, *6*, 1553.



40. Peleg, M.; Engel, R.; Gonzalez-Martinez, C.; Corradini, M. G.; *J. Sci. Food Agric.* **2002**, *82*, 1346.
41. Peleg, M.; Normand, M. D.; Corradini, M. G.; *Crit. Rev. Food Sci. Nutr.* **2012**, *52*, 830.
42. Li, N.; Taylor, L. S.; Mauer, L. J.; *J. Agric. Food Chem.* **2011**, *59*, 6082.

*Submitted: October 4, 2019*

*Published online: January 27, 2020*

