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Kinetic parameters of the oxidation reaction of commercial biodiesel with natural antioxidant additives

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ABSTRACT

Biodiesel in Brazil is obtained through the mixture of vegetable oils and animal fats. However, some of those raw material sources have characteristics that are more susceptible to oxidation. As an alternative to reduce the speed of the onset of the oxidation reaction, spices are added to biodiesel. The oxidative stability was analyzed through the period of induction using the Rancimat® method. This study evaluated the effects of antioxidant extracts from senna leaves, blackberry fruits and hibiscus flowers mixed to commercial biodiesel through the determination of kinetic parameters, as well as investigating possible linearity deviations from the Arrheneius equation. It was possible to verify that the rate constant values were smaller when compared to the control sample; lower values were observed for mixtures with higher proportions of hibiscus flower extract. The activation energy values did not present linear behavior, and some tests presented values above the control sample, showing that the addition of antioxidants can significantly alter this parameter. Sub-Arrhenius behavior was observed for the sample containing the binary mixture of senna leaves and hibiscus flowers and for the control; however, sample containing only senna leaf extract presented super-Arrhenius behavior.

1. Introduction

Commercial biodiesel is obtained through the mixture of vegetable oils – such as soybean, sunflower, palm oil - and animal fats - such as tallow, poultry fat and lard, depending on the production region and the sources of raw materials available (Orives et al., 2014; Chendynski et al., 2016). Since biodiesel is produced with unsaturated carbon chains, it may be less chemically stable than diesel (Angilelli et al., 2017).

Oxidation reaction in biodiesel occurs between esters of unsaturated fatty acids – molecules that are very reactive in the presence of oxygen from the environment, resulting in products such as aldehydes, ketones, polymers, acids, peroxides, among others. Therefore, oxidation can compromise the quality of the biodiesel and affect its performance as fuel, due to the changes that such molecules cause in its properties (Pullen and Saeed, 2012; Buosi et al., 2016). Currently, the most largely used substances to inhibit the oxidative degradation reactions are synthetic antioxidants, which are used in the food industry and other sectors. However, they present some negative factors such as their toxicity to humans and their low biodegradability (Carocho et al.,2014; Knothe et al., 2015; Spacino et al., 2015).

The use of natural antioxidant substances derived from plants and fruits can be a good alternative to synthetic antioxidants, since antioxidant substances such as tocopherols, phenolic compounds, flavonoids, terpenes, and carotenoids are extensively found in several plants in many different parts, from roots to leaves and even fruits. All natural antioxidants can be extremely useful in preventing biodiesel oxidation, especially phenolic compounds, since they present a hydroxyl group with more active electrons than those in fatty acid esters (which are a constituent of biodiesel). However, despite the potential advantages that natural antioxidants offer in enhancing the oxidation resistance of biodiesel, very few studies have sought to demonstrate their efficiency in inhibiting oxidation reaction, with little work on developing blends of natural antioxidants with commercially available biodiesel (Coppo et al., 2014; Spacino et al., 2015).

By using the Rancimat® method for determining the oxidative stability at different temperatures, several data can be obtained regarding electrical conductivity and the oxidation reaction induction period for biodiesel, showing the effects the antioxidant substances induce on the biofuel. From such data, the rate constant (k), and activation energy

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(AE) kinetic parameters can be estimated, with the application of the Arrhenius equation (Maia et al., 2011; Spacino et al., 2015). Those calculations can be used to evaluate the efficiency of adding antioxidants to biodiesel, as well as investigating how they can minimize or favor the oxidation reaction.

However, not all reactions can be explained by the mechanism proposed by Arrhenius, since it is known that more complex factors must be considered for some reaction processes, which may involve aspects of non-equilibrium distribution of reactants, geometry, tunneling effect, thermal factors, among others (Aquilanti et al., 2010, 2017; Silva et al., 2013). In order to explain the linearity deviations from the Arrhenius equation, new concepts were formulated covering all the influencing factors as complex system reactions, in response to the concept of Apparent Activation Energy (AAE) proposal (Aquilanti et al., 2010, 2017; Chendynski et al., 2017; Gregório et al., 2017).

AAE is generally understood as the energy system of complex reactions, in which the predominant mechanisms are the measurement of temperature changes. The AAE concept is also associated with case studies in which the programming energy is running and its graphs are curved either concave or convex (Silva et al., 2013; Carvalho-Silva et al., 2017).

Despite the advantages of natural antioxidants, there are still very few studies demonstrating their efficiency in inhibiting the oxidation reaction in biodiesel. Therefore, this study aimed at evaluating the performance of antioxidant extracts from senna leaves *(Cassia augustifólia)*, blackberry fruits (*Rubus* sp.), and hibiscus flowers (*Hibiscus rosa-sinensis* L.) in a mixture with commercial biodiesel, with the determination of the kinetic parameters of the oxidation reaction at different temperatures using a simplex-centroid mixture design. Possible linearity deviations from the Arrhenius equation in the respective assays will also be investigated.

2. Experimental Section

2.1. Biodiesel

The Laboratory of Fuel Research and Analysis at the State University of Londrina provided the commercial biodiesel. The biodiesel oxidative stability was analyzed according to the standard method EN 14214 (2008), and the chromatographic analysis according to EN 14103 (2003).

According to the chromatographic analysis, the biodiesel used showed a composition of C14 to C22 methyl esters, with total ester content of 97.28% (m/m). This biodiesel is in compliance with the specifications established by the European Union (EN 14214, 2008) and the National Petroleum, Natural Gas and Biofuel Agency (BRASIL, 2014), whose minimum percentage is 96.5%. The sample presented saturated ester content of 27.18%, with 70.10% (m/m) unsaturated esters.

2.2. Antioxidant extracts

The extracts of senna leaves, blackberry fruits and hibiscus flowers were prepared with 10 g from each dried sample added to 250 mL of absolute ethyl alcohol. This mixture was kept in the dark and at rest for 48 h, then filtered and concentrated to approximately 50 mL with heating plate at 60 °C. After cooling to room temperature, the extract was transferred to a 50-mL volumetric flask, completing with approximately 1 mL of absolute ethyl alcohol. The amount of phenolic compounds present in each of the extracts was determined by the Folin-Ciocalteu method adapted by Kumazawa et al. (2004). The values of the phenolic compounds obtained for senna leaves, blackberry fruits and hibiscus flowers were 4.060; 16.452; 4.618, respectively, expressed in gram of gallic acid equivalent (GAE).

Table 1
Rate constants at the different temperatures and AE mean for the assays following the experimental design.

Assays	Proportions [a]	k (h^{-1})				AE
		110 °C	115 °C	120 °C	125 °C	kJ mol^{-1}
1	(1. 0. 0)	0.4858	0.6734	0.8623	1.4605	89.85
2	(0. 1. 0)	0.3184	0.4753	0.6257	0.9172	87.47
3	(0. 0. 1)	0.2585	0.3921	0.6547	0.7676	91.65
4	(½.½.0)	0.3536	0.4532	0.6604	0.8564	76.79
5	(½.0.½)	0.2786	0.403	0.5602	0.7011	78.61
6	(0.½.½)	0.3014	0.4541	0.5465	0.8373	82.37
7	(⅓.⅓.⅓)	0.3103	0.4305	0.6009	0.8642	86.31
8	(⅓.⅓.⅓)	0.3081	0.4186	0.5428	0.8719	85.57
9	(⅓.⅓.⅓)	0.3015	0.4208	0.6377	0.7921	84.06
Control	–	0.6122	1.0274	1.2804	1.7658	86.25

[a] Proportion of senna leaf, blackberry fruit and hibiscus flower extracts.

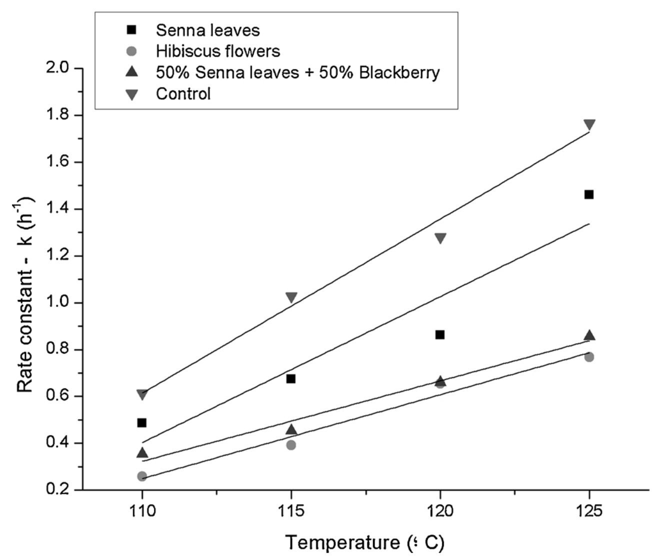

Fig. 1. Relation of the values of k for the temperatures of 110, 115, 120 and 125 °C of the assays that presented more accentuated behavior.

2.3. Preparation of biodiesel/antioxidant mixtures

In order to carry out the oxidative stability test of the biodiesel/antioxidant mixtures, a fixed amount of phenolic compounds was defined. In this study, the set amount of 5.6 mg GAE was added to 100 g of biodiesel.

The assays containing the senna leaf, blackberry fruit and hibiscus flower extracts were prepared following a simplex-centroid experimental design. Initially, the volumes used in the extracts were calculated to correspond to the set phenolic amounts. Then, the volume of the alcoholic extracts were transferred to beakers and heated in the kiln at 50 °C in order to evaporate the alcohol.

The dry extracts were removed from the kiln and, after cooling, 100 g of biodiesel were added to each one. These mixtures were agitated for approximately 10 min and stored in the dark for 12 h. Finally, the samples were analyzed using the Rancimat® equipment. Approximately 3 g of each mixture and the control sample were weighed for each analysis at the temperature of 110, 115, 120 and 125 °C.

2.4. Determination of the induction period

The B100 biodiesel samples in mixtures in the isolated, binary and ternary with senna leaf, blackberry fruit and hibiscus flower extracts were heated in the Rancimat® equipment (Metrohm, model: 873), at