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Original article

Kinetic and thermodynamic parameters in biodiesel oxidation reaction in the presence of coffee leaves and sage extracts

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ABSTRACT

The biodiesel obtained from soybean oil consists mainly of esters of unsaturated fatty acids which gives it low oxidative stability. In order to inhibit the oxidative reactions, extracts of arabica coffee leaves and sage were added to the biodiesel. The induction period, the kinetic and thermodynamic parameters were determined using the Rancimat method at temperatures 110, 115, 120 and 125 °C. The results of induction periods containing sage extract and coffee leaves were 7.30 and 6.86 h, respectively, higher values than that obtained for biodiesel without addition of antioxidant species. Among the thermodynamic parameters it was observed that the activation entropy was negative ($\Delta S^{\ddagger} < 0$) for all the tests indicating the formation of activated complexes. The values of free energy of Gibbs indicated the increase of the energy necessary for the biodiesel to oxidize when in the presence of extracts of sage and coffee leaves, isolated or in mixture, which proves its efficiency as antioxidant agents.

Introduction

The large demand of energy and environmental problems shows the necessity to search sources of clean and renewable energy to replace the fossil fuels and contribute to sustainable development [1]. Among the most promising renewable fuels stands out biodiesel, constituted by a mixture of alkyl esters of fatty acids produced by transesterification from vegetable oil and/or animal fats with short-chain alcohols in the presence of catalyst, usually sodium or potassium hydroxide, or a strong acid [2,3].

Biodiesel can be obtained from a wide variety of oil, such as sunflower, palm, cottonseed, soybean and other species and also animal fats, as well as waste oil used for frying [4,5]. However, some oilseeds have undesirable chemical characteristics, which are incorporated into the biodiesel during the obtaining process. The presence of unsaturations in chemical composition of the biodiesel raw material, makes it susceptible to accelerated oxidation by the presence of metal ions, light, temperature, ionizing radiation, and other oxidizing agents, forming peroxides and oxidative products, that can reduce their storage period and cause problems in the operation of the engine [6,7].

To reduce biodiesel oxidation, substances known as antioxidants are added to the biofuel, which may be natural or synthetic [2]. The effect of antioxidant on biodiesel oxidation rate depends on many factors, among them, the structural formula, storage conditions and the chemical composition of the sample [8]. In biodiesel, the action of antioxidants is to inhibit free radicals formed during the oxidative processes, interrupting the chain reaction of fuel degradation.

The sage (*Salvia officinalis* L.) is recognized for its antioxidant capacity related to polyphenolic compounds (phenolic acids, polyphenols, flavonoids, phenolic terpenes) [9]. Cuvelier et al. [10] identified the antioxidant constituents of sage as carnosol, rosmadial, carnosine acid, rosmarinic acid and epirosmanol, compounds known for their antioxidant properties. The leaves of arabic coffee is little known about the chemical compounds present in its leaves, and the majority of studies concerning the chemical composition of the coffee is related to the grain. However, Silva [11] reports that it was possible to identify in the leaves of *Coffea Arabica,* phenolic compounds that have an important role in the neutralization of free radicals such as chlorogenic acid, caffeic acid, gallic acid, vanillin and p-coumaric acid.

The study of oxidative stability by the Rancimat method at different temperatures provides the determination of kinetic parameters, such as rate constant (k) and activation energy (Ea) and thermodynamic parameters as enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$) and Gibbs free energy ($\Delta G^{\ddagger}$) in the activated state of biodiesel oxidation reaction [12]. Therefore, this research aimed to present an analysis of the efficiency of natural antioxidant extracts, isolated and in mixture, comparing the thermodynamic and kinetic parameters of biodiesel oxidation reaction.

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Experimental

Biodiesel B100

The transesterification reaction of tricylglycerides of 100 g of soybean oil without synthetic antioxidants was performed using sodium methoxide as a catalyst in 50 mL of absolute methanol, analytical grade (concentration: 0.8% w/w) under reflux and slow stirring for 2 h at 60 °C according to Borsato et al. [2]. The phases were separated in a 250 mL funnel to promote the separation of glycerol, triglycerides and alcohols present [2]. The esters obtained were washed with an aqueous solution of 1.5% hydrochloric acid, at 80 °C and with distilled water up to neutral pH and dehumidified with anhydrous sodium sulfate [3].

Natural antioxidants extracts

Samples were collected and left in the stove at 60 °C for drying until the constant weight. For the preparation of natural antioxidants alcoholic extracts, 10 g of dehydrated arabica coffee leaves (*Coffea* sp.) and sage (*Salvia officinalis* L.) were weighed and mixed with 250 mL of absolute ethanol. This mixture was kept for 48 h at rest and the extracts were filtered, evaporated with the aid of a heating plate at 60 °C to obtain approximately 50 mL which were transferred to 50 mL volumetric flasks and completed with absolute ethanol.

Determination of total phenolics compounds

The determination of phenolic compounds content, present in the ethanolic extracts of the species, were performed by spectroscopy (Spectrophotometer Perkin Elmer model UV/VIS Lambda 25) at 760 nm using the Folin-Ciocalteu method using the methodology adapted by Kumazawa et al. [13]. The results are expressed as total polyphenols content in mg equivalent of Gallic Acid (EAG) g^{-1} dry mass.

Antioxidant activity analysis

The quantitative evaluation of antioxidant activity was carried out by monitoring the consumption of free radical DPPH (2,2-diphenil-1-picrilhydrazil) by measuring the decrease of absorbance using a UV-Vis spectrophotometer at 517 nm, with the standard Trolox (6-hydroxy-2,5,7,8-tetrametilcromo-2-carboxylic acid) was performed according to Casagrande et al. [14] and Georgetti et al. [15] methodology with modifications.

The antioxidant activity results were expressed as total antioxidant Trolox equivalent and also expressed as a percentage calculated by the Eq. (1):

$$AA(\%) = \frac{Ac-(Aa-Ab)}{Ac\times 100} \tag{1}$$

where Ac: absorbance of the control without antioxidants addition; Aa: sample absorbance; Ab: blank absorbance and AA: antioxidant activity.

Oxidative stability determination and induction period

In each biodiesel sample was added different volumes of extract so as to contained the total concentration of phenols in the samples was 2.56 mg of each extract isolated or mixture in 100 g of biodiesel after total evaporation of ethyl alcohol and before the evaluation of oxidative stability. This concentration was determined by preliminary tests of oxidative stability at 110 °C in order to achieve the induction period (IP) value not less than 6 h following the methodology reported by Coppo et al. [16] and Spacino et al. [17].

Three grams of biodiesel samples, containing the established amounts of natural antioxidants extracts without ethanol, as well as the control samples, were taken in the accelerated heating equipment Rancimat model 873 (Metrohm® – Herisau/Switzerland) in triplicate at a air supply rate of $10\,L\,h^{-1}$, at temperatures of 110, 115, 120 and 125 °C, in accordance with the official standard EN 14112 [18]. In high temperature conditions, under a constant air flow, there is the formation of volatile compounds, biodiesel degradation products, that cause an increase in electrical conductivity, it is possible to detect the IP corresponding to inflection point of the electrical conductivity of the graph curves ($\mu S\,cm^{-1}$) *versus* time (s) recorded automatically by the device [12].

Kinetic parameters of biodiesel oxidation reaction

With the adjusted data of the natural logarithm (ln) of the electrical conductivity (Λ) *versus* time, provided by Rancimat test, the rate constants (k) were determined, considering the first-order reaction due to the high concentration of oxygen compared to the amount of oil in the sample [19]. According to Eq. (2), the slope corresponds to the rate constant (k) of biodiesel oxidation reaction [20].

$$\ln \Lambda_0 = k(t_f - t_i) + \ln \Lambda \tag{2}$$

where Λ is the conductivity at time t; Λ_0 is the initial conductivity, and t_i and t_f correspond to the initial and final time, respectively.

For the activation energy of biodiesel oxidation reaction, the Arrhenius equation was used [12], establishing a direct relationship between temperature and rate constant (Eq. (3)).

$$\ln(k) = \ln A - Ea/RT \tag{3}$$

where k is the rate constant (h^{-1}), A is the pre-exponential factor (h^{-1}), Ea the activation energy ($kJ\,mol^{-1}$), R is the universal constant of ideal gases ($8.31447\,J\,K^{-1}\,mol^{-1}$) and T the absolute temperature (K). A plot of ln k *versus* T^{-1} gives a straight line, where the linear coefficient corresponds to the pre-exponential factor and the angular to $-Ea/RT$.

Thermodynamic parameters of biodiesel oxidation reaction

Thermodynamic parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) were estimated by activated complex theory (ACT) developed by Eyring in 1935. The effect of temperature on the reaction rate was interpreted using the ACT as described by Eq. (4) [21,22].

$$\ln(k/T) = [(\ln k_B/h + (\Delta S^{\ddagger}/R)] - (\Delta H^{\ddagger}/R)(1/T) \tag{4}$$

where k_B is Boltzmann's constant ($1.38065 \times 10^{-23}\,J\,K^{-1}$), h the Planck constant ($6.62608 \times 10^{-34}\,J\,s$), $\Delta H^{\ddagger}$ the activation enthalpy ($kJ\,mol^{-1}$), $\Delta S^{\ddagger}$ the activation entropy ($J\,K^{-1}\,mol^{-1}$) and the notation ‡ refers to the state of activated complex.

According to the Eyring equation, the regression of ln k/T *versus* 1/T (K^{-1}) derived from the ACT, gives a straight line with the slope ($-\Delta H^{\ddagger}/R$) and the interception [ln (k_B/h) + ($\Delta S^{\ddagger}$/R)], which allows the determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively. The Gibbs free energy of activation ($\Delta G^{\ddagger}$) was determined for each temperature using fundamental thermodynamic equation dictated by Eq. (5) [23].

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{5}$$

Results and discussion

To evaluate the antioxidant effect was determined the total phenolic content and antioxidant activity in extracts of arabica coffee leaves and sage. The values obtained were respectively, 12.472 and 10.367 $mg_{EAG}\,g^{-1}$ dry mass, with antioxidant activity of 11.246 and 8.243 $mg_{Trolox}\,g^{-1}$ dry mass, obtaining a linear relationship between phenolic content and antioxidant activity with a determination coefficient (R2) equal to 0.997.

Samples of biodiesel B100 in mixture with dry extracts in different proportions, and the control, were subjected to accelerated test for oxidative stability by the Rancimat method for determining the values of electrical conductivity and the IP values. Fig. 1 presents the electrical