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Evaluation of the kinetic and thermodynamic parameters of oxidation reaction in biodiesel from a quaternary mixture of raw material

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ABSTRACT. A mixture of vegetable oil and animal fat as raw materials was optimized by simplex-centroid mixture design to produce a type of biodiesel with good oxidative stability, flow properties and reaction yield. Further, kinetic and thermodynamic parameters of oxidation reaction were determined by the accelerated method at different temperatures. Biodiesel produced with sodium methoxide as catalyst presented 6.5°C of cloud point, 2.0°C of pour point, and oxidative stability at 110°C equal to 8.98h, with a reaction yield of 96.04%. Activation energy of the oxidation reaction was 81.03 kJ mol^{-1} for biodiesel produced with sodium hydroxide and 90.51 kJ mol^{-1} for sodium methoxide. The positive values for $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ indicate that the oxidation process is endothermic and endergonic. The less negative $\Delta S^{\ddagger}$ for biodiesel produced with sodium methoxide (-28.87 JK^{-1} mol^{-1}) showed that the process of degradation of this biofuel was slower than that produced with NaOH. The mixture of raw materials proposed, transesterified with the methoxide catalyst, resulted in a biofuel that resisted oxidation for longer periods, making unnecessary the addition of antioxidant

Keywords: oxidative stability, animal fat, vegetable oil, catalyst.

Avaliação dos parâmetros cinéticos e termodinâmicos da reação de oxidação em biodiesel de uma mistura quaternária de matérias-primas

RESUMO. Com o objetivo de produzir um biodiesel com boas características de estabilidade oxidativa, propriedades de fluido e rendimento de reação, uma mistura de óleo vegetal e gordura animal de matérias-primas foi otimizada por delineamento de mistura simplex-centroide. Adicionalmente, os parâmetros cinéticos e termodinâmicos da reação de oxidação foram determinados pelo método acelerado em diferentes temperaturas. O biodiesel produzido com metóxido de sódio como catalisador apresentou ponto de névoa igual a 6,5°C, ponto de fluidez de 2,0°C, estabilidade oxidativa de 8,98h, com rendimento de reação de 96,04%. A energia de ativação da reação de oxidação foi de 81,03 kJ mol^{-1} para o biodiesel produzido com hidróxido de sódio e de 90,51 kJ mol^{-1} para o metóxido de sódio. Os valores positivos obtidos para o $\Delta H^{\ddagger}$ e $\Delta G^{\ddagger}$ indicam que a reação de oxidação é endotérmica e endergônica. O valor menos negativo de $\Delta S^{\ddagger}$ para o biodiesel produzido com metóxido de sódio (-28,87 $JK^{-1}mol^{-1}$) mostra que a degradação deste biocombustível é mais lenta que o daquele produzido com NaOH. A mistura de matérias-primas proposta, transesterificada com o catalisador metóxido, resulta em biocombustível que é resistente à oxidação por longos períodos, tornando a adição de antioxidante desnecessária.

Palavras-chave: estabilidade oxidativa, gordura animal, óleo vegetal, catalisador.

Introduction

The increasing demand for energy worldwide due to the reduction in fossil fuel sources has focused on biofuels as a sustainable substitute for diesel engines (Saxena, Jawale, & Joshipura, 2013).

The most common process for obtaining biodiesel comprises transesterification with short-chain alcohols, such as methanol and ethanol, triglycerides and catalyst. The methylic route is the most applied due to its high reaction yields. There is a wide variety of catalysts for this type of reaction, which may be acid or basic, and homogeneous or heterogeneous (Brito et al., 2012). Among the acid catalysts, studies have been performed with sulphuric, sulphonic, phosphoric and hydrochloric acid (Georgogianni, Katsoulidis, Pomonis, & Kontominas, 2009), while hydroxides and metal alkoxides are mainly used among the basic catalysts (Brito et al., 2012). For commercial ends, biodiesel is mainly produced with basic homogeneous catalyst since the process is less corrosive than the reaction with homogeneous acid catalysts. The catalysts are

also widely used since they present more favourable kinetics of transesterification reaction and enable the use of lower temperatures during the process (Xie & Li, 2006).

Among the triacylglycerol used as raw material for biodiesel, vegetable oils stand out as most used, even though animal fat has been employed due to lower production costs and because it is environmentally advantageous to employ a material which is frequently discarded (Fadhil, 2013).The diversity of raw materials and production techniques results in variations in the physical and chemical properties of biodiesel and the mixture of fatty acids from several sources results in biofuels with different characteristics (Orives et al., 2014).

However, triacylglycerol from animals have high levels of saturation and affects the flow of biodiesel in regions with mild temperatures. Consequently it generates clogging problems in nozzles and filters and other engine problems (Cunha et al., 2009). Contrastingly, a lower degree of unsaturation leads to greater oxidation stability in biodiesel (Galvan et al., 2013).

The oxidative stability of biodiesel associated to the oxidation of fatty acid alkyl esters (FAAE) which comprise biofuel has been widely studied (Xin, Imahara, & Saka, 2009; Chen & Luo, 2011; Pullen & Saeed, 2012). However, no studies to date have evaluated the physical-chemical parameters in the oxidation reaction. Data of oxidative stability allow the determination of kinetic and thermodynamic parameters involved in the oxidation reaction mechanisms of biofuel. Parameters such as energy (E_a), enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$) and Gibbs free energy ($\Delta G^{\ddagger}$) activation evaluate the need for the addition of antioxidants and their efficiency, and estimate storage time, ensuring product quality in storage steps, distribution and use (Galvan et al., 2013).

Current investigation assesses the kinetic and thermodynamic parameters of oxidation reaction of biodiesel from a mixture of soybean oil, poultry fat, industrial tallow and pork lard, and also verifies the influence of transesterification catalysts in the final product.

Material and methods

Production of biodiesel

The reaction was carried out by the methylic route with PA methanol (Anidrol: 99.8%), with the catalyst, and slow agitation with heating at 65°C for 2h, under refluxing. Glycerol was then separated and the biodiesel was washed with acetic acid (0.01 mol L^{-1}) and distilled water until neutral pH. It was later dehumidified with anhydrous sodium sulphate (Anidrol: 99%) (Dias et al., 2014).

Raw material

Triacylglycerol sources used in transesterification comprised industrial tallow (Crystal Spironelli, Brazil), poultry fat (Big Frango, Rolândia Paraná State, Brazil), pork lard (Frimesa, Brazil) and soybean oil (Cooperative Imcopa, Cambé Paraná State, Brazil).

Catalysts

The catalysts tested were sodium hydroxide (F. Maia: 97.0%) and sodium methoxide (Sigma-Aldrich: 95%), both added to the mixture of raw material at a concentration of 15 mmol $100g^{-1}_{\text{raw material}}$

Yield

The yield (%) was determined according to the stoichiometry of the transesterification reaction (Equation 1), taking into account the weight of biodiesel obtained and the weight of raw materials used. Calculation was based on the molar weight of oleic acid:

$$\eta = \frac{m_1 W_1}{m_2 3 W_2}\, x\, 100 \qquad (1)$$

where:

η is the yield (%);

m_1 is the weight of biodiesel;

m_2 is the weight of raw material;

W_1 is the molecular weight of the triglyceride of oleic acid;

W_2 is the molecular weight of methyl oleate.

Cloud point and pour point

The cloud and pour point tests were conducted in accordance with ASTM D2500-05 (American Standard Test Method, 2005), wherein the cloud point is the starting temperature of solidification, and pour point indicates the temperature where the biodiesel stops flowing.

Chromatographic analysis

Methyl esters contents were determined with gas chromatograph with flame ionization detector (GC-FID) system (Thermo - model Trace Ultra 3300) and CP - 7420 column (100% cyanopropyl/polysiloxane with 100 m length x 0.25 mm internal diameter x 0.25 µm film thickness: Select FAME) was employed. The temperature of split injector was 200°C and detector was maintained at 240°C. The oven heating initialized at 165°C for 7 min., and then, heated at a rate of 4°C $min.^{-1}$ until 185°C. It was maintained at

this temperature for 4.67 min. and, finally, heated at a rate of 6°C min.$^{-1}$ until it reached 235°C, where it was maintained for 5 minute. The flows of H_2 was 1.2 mL min.$^{-1}$, 30 mL min.$^{-1}$ of N_2 (make up) and 35 and 300 mL min.$^{-1}$, for H_2 and synthetic air, respectively. The injection volume was 2.0 µL. Data were retrieved and treated by Chromquest 5.0 software.

Oxidative stability

Samples of biodiesel were subjected to an accelerated method according to EN 14112 (European Committee for Standardization, 2003a), using Rancimat equipment (Metrohm, Switzerland, Model: 873); the induction period (IP), representing oxidative stability, was measured at 110, 115, 120, 125 and 130°C.

Determination of kinetic and thermodynamic parameters

Electrical conductivity (Λ) versus time (t) at each test temperature was adjusted considering first order kinetics; rate constants were determined according to Tan, Che Man, Selamat and Yusoff (2001) with Equation 2.

$$\ln \Lambda_0 = k(t_f - t_i) + \ln \Lambda \quad (2)$$

where:

Λ is the conductivity at time t;

Λ_0 is the initial conductivity,

t_i and t_f correspond to initial and final time, respectively.

The activation energy (E_a) was determined by Arrhenius equation (Equation 3):

$$\ln(k) = \ln A - E_a/RT \quad (3)$$

where:

k is rate constant (h^{-1});

A is the pre-exponential factor (h^{-1});

E_a is the activation energy (kJ mol^{-1});

R is the ideal gas constant (8.31447 JK^{-1} mol^{-1}),

T the absolute temperature (K).

On the other hand, enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation were determined by Eyring equation applied to activated complex theory (ACT) (Equation 4).

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

where:

k_B is the Boltzmann constant (1.38065×10^{-23} JK^{-1});

h is Planck's constant (6.62608×10^{-34} Js);

$\Delta H^{\ddagger}$ is the enthalpy of activation (kJmol^{-1});

$\Delta S^{\ddagger}$ is the entropy of activation (Jmol^{-1}K^{-1}).

Gibbs free energy of activation ($\Delta G^{\ddagger}$) for each temperature was obtained by Equation 5.

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad (5)$$

Experimental design

A simplex-centroid mixture design was applied for four components (soybean oil, industrial tallow, pork lard, poultry fat), with two repetitions at central point, with combinations of mixtures $2^{q}-1$, where q is the number of components equal to the sum 1 or 100% (Calado & Montgomery, 2003).

Results and discussion

Table 1 shows the responses of reaction yield, cloud and pour points, and oxidative stability (induction period) at 110°C for mixtures of the experimental design.

Table 1. Responses to reaction yield, cloud point (CP), pour point (PP) and induction period at 110°C (IP) of tests in the mixture design.

Assay	Mixture*	Yield / %	CP / °C	PP / °C	IP / h
1	(1,0,0,0)	98.63	3.0	-3.0	2.55
2	(0,1,0,0)	96.04	17.5	14.0	5.53
3	(0,0,1,0)	98.75	11.0	7.0	0.61
4	(0,0,0,1)	90.75	9.0	3.0	6.67
5	(½,½,0,0)	97.88	14.5	9.0	3.60
6	(½,0,½,0)	97.63	4.0	1.0	3.23
7	(½,0,0,½)	92.27	5.0	0.0	6.38
8	(0,½,½,0)	98.42	13.0	8.0	1.29
9	(0,½,0,½)	96.32	14.0	9.0	8.96
10	(0,0,½,½)	93.38	15.0	6.0	8.76
11	(⅓,⅓,⅓,0)	98.24	10.7	6.3	3.59
12	(⅓,⅓,0,⅓)	95.64	11.0	3.0	4.88
13	(⅓,0,⅓,⅓)	96.63	7.3	1.3	5.69
14	(0,⅓,⅓,⅓)	95.31	11.0	6.3	6.03
15	(¼,¼,¼,¼)**	95.06	9.3	4.0	6.00

*proportions of soybean oil, industrial tallow, pork lard, poultry fat.**average of triplicate at central point.

Although assays 1, 2, 3, 5, 6, 8, 11 and 13 had high reaction yields, they also revealed induction periods below 6 hours, minimum value established by the EN14214 (European Committee for Standardization, 2003b). Assay 4 had suitable cloud point, pour point and induction period, but constituted the mixture with the lowest reaction yield. Assays 9 and 10 presented induction periods higher than 6 hours determined in the legislation, although they had undesirable cloud and pour points. The formulation with the best performance characteristics was that in assay 7, with yield 92.27%, cloud point at 5°C, pour point at 0°C and IP in 6.38h.

Optimization with simplex-centroid mixture design aimed at formulating a mixture of raw materials that would lead to the production of biodiesel which provided high reaction yield, induction period in accordance with EN 14214 (European Committee for Standardization, 2003b) without compromising the values of cloud and pour points. The ratio between saturated and unsaturated portions of these sources of triacylglycerol influences oxidative stability and flowing properties.

Figure 1 shows optimal formulation with 32% soybean oil, 12% tallow, 6% pork lard and 50% poultry fat. The formulation with the four raw materials provided the best results for the evaluated parameters when compared to test 7, coupled to lower costs due to animal fats at low market price.

The formulation optimized by the experimental design was transesterified with sodium methoxide and sodium hydroxide to evaluate whether the reaction mechanism by different catalysts affected the characteristics of biodiesel.

Table 2 shows the responses presented for biodiesels produced, in triplicate, with each catalyst. In the case of biodiesel obtained with sodium methoxide, t-Test for Single Means showed no significant difference between optimal values estimated and mean obtained experimentally for the four parameters evaluated, with p rates at $0.34 \leq p \leq 0.46$.

Yield values are relevant to substitute soybean oil as raw material because the reaction yield is related to the process´s economic viability.

Table 2. Data of biodiesel obtained by each catalyst.

	NaOH	$NaOCH_3$
Yield / %	90.68	96.04
Cloud Point / ºC	8.0	6.5
Pour Point / ºC	0.5	2.0
IP at 110ºC / h	6.10	8.98

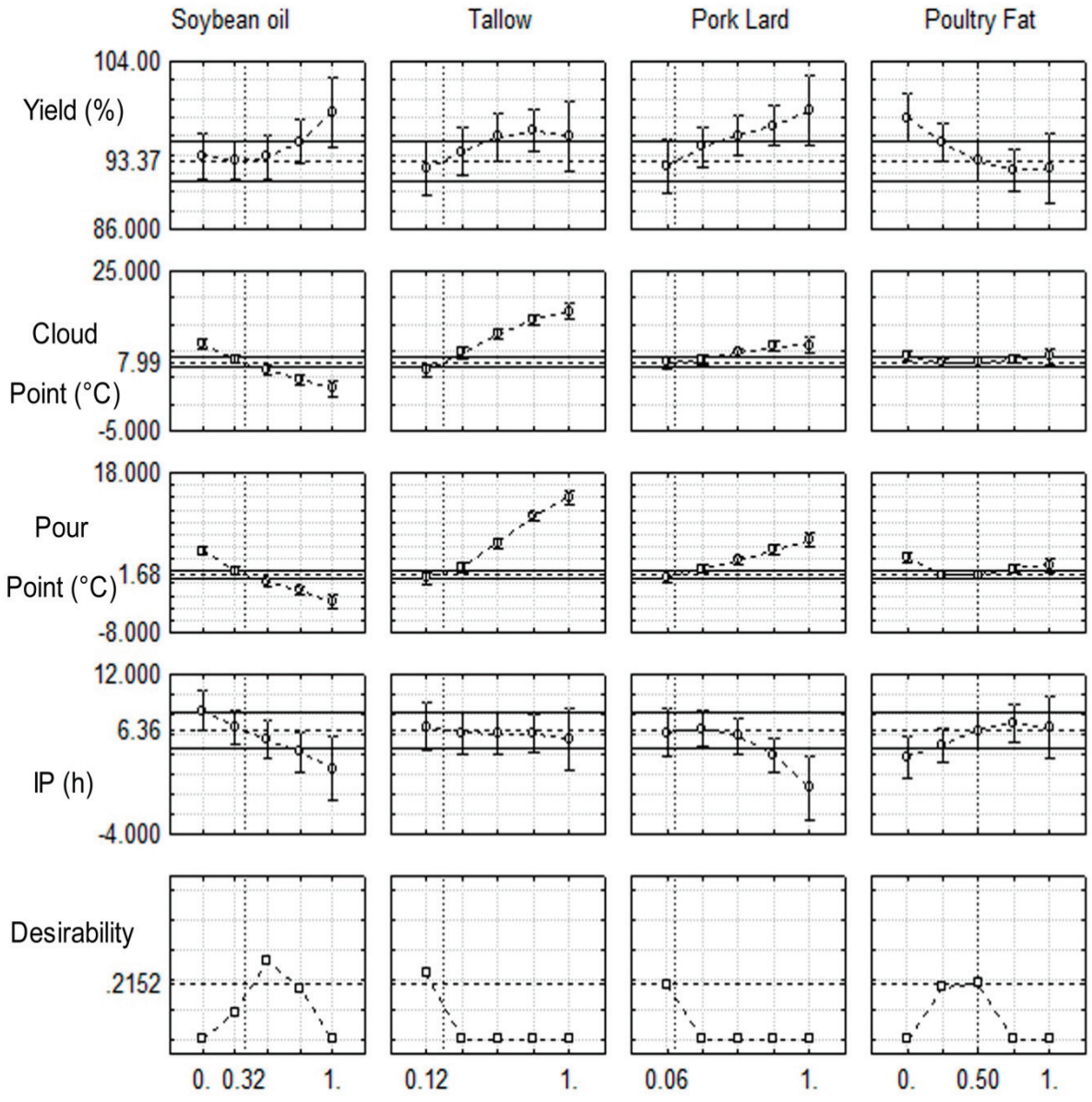


Figure 1. Multi-response optimization for the four parameters evaluated.

Sodium hydroxide showed lower yield, complying with the literature. The catalyst is frequently used in industry due to its lower sensitivity to water (Lobo & Ferreira, 2009).

Values for oxidative stability, 6.10 and 8.98h for the hydroxide and sodium methoxide, respectively, are of great interest. The biodiesel sample produced with sodium methoxide showed oxidative stability, considerably higher than 6h established by legislation (Brasil, 2014) and indicated that the biofuel did not require the addition of antioxidants to maintain quality during distribution, storage and use in vehicles.

Induction period values of 1.42 h (Borsato et al., 2014) and 1.36 h (Ryu, 2010), for biodiesel from soybean oil, have been reported in the literature. The higher value obtained in current study may be attributed to the types of fatty acids in the raw materials. The saturated and unsaturated levels in biodiesel from each raw material and from the mixtures with each catalyst are given in Figure 2, matching those reported in the literature (Imahara, Minami, & Saka, 2006; Pupa, 2004; Ramalho, Santos, Maia, Souza, & Souza, 2011).

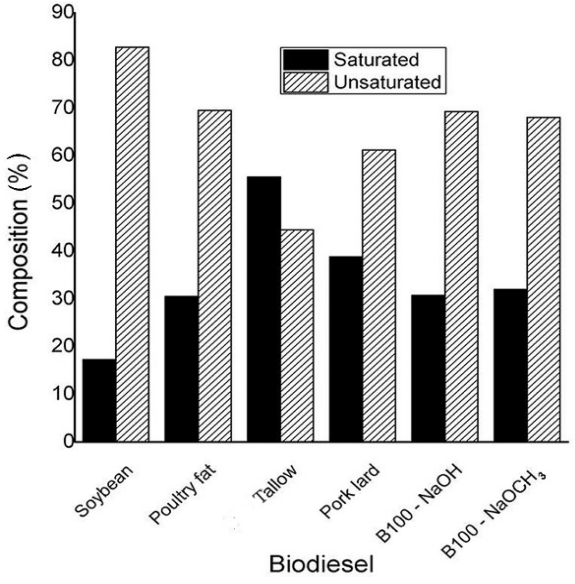


Figure 2. Percentages of saturated and unsaturated components in the biodiesel produced with the two catalysts.

According to Orives et al. (2014), the relation between saturated and unsaturated components remains in the biofuel produced. Consequently, it is expected that the biodiesel from the mixture of fatty acids presents an intermediate composition of saturated and unsaturated to that observed in the individual components.

Consequently, animal fats replacing vegetable oil in biodiesel production are advantageous for storage time since the unsaturation degree is directly related to the susceptibility to oxidation of the material that has been produced. Mixtures of vegetable oils and animal fats in biodiesel have a higher oxidative stability than those merely produced with vegetable raw materials.

Cloud and pour points are factors that impair the use of animal fats in raw materials for biodiesel since they are associated with a higher degree of saturation in FAAE (Lopes et al., 2008). Research by Wang, Thompson and Van Gerpen (2011) showed a cloud point equal to 18.3°C for biodiesel from beef tallow and 2.5°C for biodiesel from soybean oil. Since the biodiesel in this research was produced from a mixture with 68% animal fat, 6.5°C complies with what has been expected. When evaluating the pour point, or rather, the temperature at which the biodiesel stops flowing, 0.5°C was reported. Dunn (2009) demonstrated values between -1.6 and 1.0°C for soybean oil biodiesel and between 10.2 and 15.7°C for beef tallow biodiesel. The substitution of more than 50% animal fat by vegetable oil caused no significant losses in flowing properties at low temperatures. Moderate values are the result of poultry fat as the mixture´s major constituent. As mentioned above, animal fats have lower levels of saturation among raw materials and therefore a lower trend to solidify at lower temperatures.

The study of induction periods at each temperature determines kinetic parameters, such as rate constant and activation energy, and thermodynamic parameters, such as enthalpy, entropy and activation of Gibbs free energy. The Rancimat method provides conductivity data as an indication of the occurrence of oxidation of the material analysed as a function of time. Thus, it is possible to determine the reaction rate constant, *k,* by conductivity variation and Equation 2. Table 3 shows the induction period, rate constants determined by Equation 2, and the corresponding correlation coefficients. By raising the temperature of the test, there is also an increase in *k*, indicating that the oxidation process is temperature-dependent. The correlation coefficients indicate the suitability of data in the model represented by Equation 2.

Table 3. Induction periods, rate constants and correlation coefficients for oxidation reaction.

	NaOH			$NaOCH_3$		
Temperature °C	IP / h	k / h^{-1}	R^2	IP / h	k / h^{-1}	R^2
110	6.10	0.4856	0.9866	8.98	0.3681	0.9953
115	4.41	0.6185	0.9871	6.44	0.5077	0.9927
120	3.00	0.9844	0.9857	4.38	0.6952	0.9821
125	1.99	1.2245	0.9467	3.03	0.9817	0.9445
130	1.59	1.6723	0.9902	2.03	1.5953	0.9808

Rate constants were determined for the two different catalysts. The higher values were obtained

when sodium hydroxide was used, in accordance with the lower induction period at 110°C given above. These higher *k* values indicate that oxidation of the biofuel was faster than that of the other sample evaluated.

In both cases reaction rate constants were lower than those reported by Borsato et al. (2014) at 110, 115, 120 and 125°C for biodiesel from a mixture of 90 % soybean oil and 10 % pork lard, and sodium methoxide as catalyst. In the test conducted at 110 °C, the biodiesel produced with sodium methoxide presented a rate constant 5 times lower than that obtained by Borsato and associates when using the same catalyst. Since the structure of unsaturation of the fatty acids remained in the transesterification product, more saturated materials would also produce more saturated biodiesel, or rather, more resistant to oxidation reaction biodiesel and lower rate constants (Tan et al., 2001).

Rate constant of different temperatures applied to equations 3, 4 and 5 determined the kinetic and thermodynamic parameters for biodiesel oxidation reaction shown in Table 4.

Table 4. Influence of each catalyst in kinetic and thermodynamic parameters of biodiesel oxidation reactions.

	NaOH	$NaOCH_3$
E_a / kJ mol^{-1}	81.03	90.51
$\Delta H^{\ddagger}$ / kJ mol^{-1}	77.77	87.24
$\Delta S^{\ddagger}$ / JK^{-1} mol^{-1}	-50.11	-28.87
$\Delta G^{\ddagger}$*/ kJ mol^{-1}	97.46	98.59

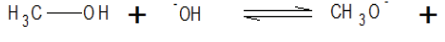
*Average of $\Delta G^{\ddagger}$ for each evaluated temperatures.

$\Delta H^{\ddagger}$ values were higher than those by Galvan et al. (2013), 68.75 kJ mol^{-1}, which involved a mixture of soybean oil, beef tallow and poultry fat. $\Delta S^{\ddagger}$ obtained by Galvan et al. (2013) and by Borsato et al. (2014) for control samples were -72.05 and -190.25 J K^{-1}mol^{-1}, respectively. According to Ong et al. (2013), the negative values for $\Delta S^{\ddagger}$ may be associated with the formation of activated species in the state in which the reactants combine to form complexes, thereby reducing the number of free species. Thus, the more negative the activation entropy, the more activated complexes species are formed and, finally, the higher the reactivity (Choi, Kim, Jeong, Kim, & Yoo, 2011). Lower negative values of $\Delta S^{\ddagger}$ for both catalyst are in accordance to higher oxidative stability, mainly for the methoxide case.

Activation energy represent the minimum energy required for the reaction to occur; the higher the activation energy is for biodiesel oxidation, the lower will be the oxidizing susceptibility of biofuel during storage (Atkins & Paula, 2006). Biodiesels showed E_a approximately 3.5 times higher than that obtained by Borsato et al. (2014) in a sample of biodiesel produced from soybean oil and pork lard with no addition of antioxidants. These activation energy were higher than those obtained in tests with antioxidants 3-tert-butyl-4-hydroxyanisole (BHA) and 3,5-di-tert-butyl hydroxytoluene (BHT), isolated or in mixtures. This proved that the biofuel produced dispenses the addition of radical suppressors to inhibit degradation reactions during storage.

The biodiesel oxidation reaction showed higher activation energy, higher enthalpy of activated complex formation, and less negative entropy, or rather, it is a more endergonic process than that reported in literature for similar biodiesel samples (Borsato et al., 2014; Maia et al., 2011).

However, even though the unsaturation content of the product was not affected by the catalyst employed, there was a difference between the oxidative stability of biodiesels produced with sodium hydroxide and sodium methoxide. The transesterification with sodium methoxide had only one active nucleophile, ion $(OCH_3)^-$, and sodium hydroxide in the presence of methanol provides more nucleophilic species (Schuchardt, Sercheli, & Matheus, 1998), as shown in the following balance (Equation 6):



(6)

where as methoxide only leads to the formation of fatty acids methyl esters (FAME), the mechanism with sodium hydroxide may form FAME, coupled to free fatty acids and soap due to OH^-.

Conclusion

The quaternary mixture containing soybean oil, poultry fat, pork lard and industrial tallow produced biodiesel with good oxidative stability results, indicating that the addition of antioxidants is unnecessary. Sodium methoxide among the tested catalysts causes the production of biofuels with improved characteristics for all the evaluated aspects. The kinetic and thermodynamic parameters indicate that the biodiesel oxidation reaction produced with sodium methoxide as catalyst occurred more slowly, albeit with a more stable biofuel, less susceptible to oxidative degradation.

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