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CHARACTERIZATION AND KINETIC COMPENSATION EFFECT OF CORN BIODIESEL

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This work presents the characterization and the kinetic compensation effect of corn biodiesel obtained by the methanol and ethanol routes. The biodiesel was characterized by physico-chemical analyses, gas chromatography, nuclear magnetic resonance and thermal analysis. The physico-chemical properties indicated that the biodiesel samples meet the specifications of the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) standards. The analyses by IR and ^{1}H NMR spectroscopy indicated the ester formation. Gas chromatography indicated that biodiesel was obtained with an ester content above 97%. The kinetic parameters were determined with three different heating rates, and it was observed that both the methanol and ethanol biodiesel obeyed the kinetic compensation effect.

Keywords: *corn biodiesel, kinetic compensation effect, thermogravimetry*

Introduction

Biodiesel can be defined as a mono alkyl ester of fatty acids derived from renewable sources, such as vegetable oils and animal fats, obtained by a transesterification process [1].

Transesterification is a chemical process that has the objective of modifying the structure of the vegetable oil, in order to make its physico-chemical properties close to those of petrodiesel [2]. On the other hand, it can be noticed that one great advantage of the transesterified vegetable oil is the possibility to substitute petrodiesel without any modification in the Diesel engine.

The overall process of the transesterification of vegetable oils and fats is a sequence of three reversible and consecutive reactions, in which the monoglycerides and the diglycerides are intermediary products. Glycerin is a coproduct of the transesterification process and its economical usage is another important feature for the feasibility of the biodiesel production process [3, 4].

In Brazil several oleaginous species are cultivated, such as the soybean, castor oil plant, sunflower and corn, which have the potential for their usage as raw materials for biodiesel production [4].

Corn (*Zea mays* L.) is a plant belonging to the gramineous family, and it is probably the oldest cultivated grain in the Americas. Its origin is probably from Central Mexico, where there are archaeological evidences of its usage dating from 5000 B.C. After the discovery of America, corn was introduced into Europe, Africa and Asia.

In relation to the alcohols, the most frequently employed are the short chain alcohols, such as methanol, ethanol, propanol and butanol. In Brazil, the use of ethanol is more advantageous, because it is produced in a wide scale and is used in vehicles, either pure or blended with gasoline. Moreover, it is a fuel obtained from biomass and, thus the whole process becomes totally independent of petroleum, promoting the production of a completely agricultural fuel. Ethanol production has already reached 7 billion liters a year, and the installed production capacity in Brazil is of the order of 16 billion dm^3/year [4].

As for the catalysts, transesterification can be undertaken either in an acid medium, or in a basic medium. However the reaction is faster in the presence of an alkaline catalyst than in the presence of the same amount of an acid catalyst, with higher yields and selectivity, besides showing smaller corrosion problems [4].

As a fuel, biodiesel has all the necessary characteristics to substitute petrodiesel, with the advantage of being virtually free from sulfur and organic compounds noxious to human beings. Moreover it is renewable and biodegradable [5, 6].

The literature has demonstrated that the activation energy depends on several experimental parameters, such as heating rate, particle size distribution of the sample, presence of impurities, atmosphere around the sam-

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ple, etc. Thus, it has been observed that for similar reactions or for a given reaction under different experimental conditions, a linear relationship was noticed between the logarithm of the pre-exponential factor and the activation energy. This relationship is known as kinetic compensation effect (KCE) or isokinetic effect, which states that for any variation in the activation energy, due to changes in the experimental conditions, there is a corresponding variation in the pre-exponential factor [1].

Therefore, the objective of the present work was to characterize the corn biodiesel obtained by the methanol and ethanol routes and to study the occurrence of kinetic compensation effect in the samples, using different heating rates of 10, 15 and 20°C min^{-1}.

Experimental

Physico-chemical analyses

The analyses of the pure biodiesel (B100) were performed in accordance with the standards of the American Society for Testing and Materials (ASTM) and Brazilian Association of Technical Standards (ABNT), as indicated by the Resolution 42 of ANP, the Brazilian National Agency of Petroleum, Natural Gas and Biofuels [7, 8].

Gas chromatography

The gas chromatography analyses were made in a CG-FID VARIAN 3800 gas chromatograph, with split/splitless injector.

Proton nuclear magnetic resonance (^1H NMR)

The ^1H NMR spectra were obtained in a GEMINI-300BB equipment in deuterated chloroform.

Infrared spectroscopy

The absorption spectra in the infrared region were obtained in a model MB-102 BOMEM spectrometer, using KBr tablets at the 4000–400 cm^{-1} range.

Thermogravimetry

The thermogravimetric (TG) curves were obtained in a model SDT 2960 Thermal Analyzer from TA Instruments, using a synthetic air atmosphere, flow rate of 100 mL min^{-1}, alumina crucibles and mass sample of about 20 mg, at the temperature range from 30 to 600°C [9–11].

Results and discussion

Physico-chemical analyses

As can be observed from the results of the physico-chemical analyses, displayed in Table 1, the biodiesel samples, obtained by the two studied routes, fit the specifications established by ANP in its Resolution 42 [7]. It can be seen that the biodiesel sulfur content is negligible; this confers a great advantage to biodiesel, in that no sulfur bearing compounds are produced upon its combustion in Diesel engines. Besides, the low content of free glycerin in the biodiesel is also observed. This indicates that the purification stage was adequate in the successful removal of glycerine.

It is observed that the flash point of biodiesel, obtained either by the methanol or the ethanol route, meets the ANP specification limit. This higher flash point is translated into greater safety in the biodiesel transportation, handling and storage.

Gas chromatography

The samples of the obtained biodiesel were analyzed by gas chromatography, in order to assess the conversion of the triglycerides into their methyl and ethyl esters. Table 2 presents these results, as well as theoretical compositions based on fatty acid compositions of corn oil available in the literature [12]. The results, as expected by the corn oil composition, indicated the prevalence of the methyl and ethyl linoleates, respectively.

The conversion of above 97% of corn oil into methyl and ethyl esters in the biodiesel samples confirms the efficiency of the conversion of the fatty ac-

Table 1 Physico-chemical tests of corn biodiesel obtained by the methanol and ethanol routes

Test	Methanol biodiesel	Ethanol biodiesel	ANP limit according to Resolution 42
Acid number/mg KOH g^{-1}	0.28	0.80	max. 0.80
Free glycerin/%	0.007	0.015	max. 0.02
Total glycerin/%	0.25	0.27	max. 0.38
Moisture/%	0.042	0.044	max. 0.05
Sulfur/%	0.000	0.0003	note
Flash point/°C	168	169	min. 100°C
Density at 20°C/kg dm^{-3}	0.8804	0.8761	note
Copper corrosion	1	1	1

Table 2 Composition of the methyl and ethyl esters of the corn biodiesel

Esters	Experimental composition		Theoretical composition[a]			
	methyl/%	ethyl/%	USDA 01	And 82	Codex 99	Ort 87
Caprylate	0.1290	0.0550	n.a.[b]	n.a.[b]	n.a.[b]	n.a.[b]
Caprate	0.0943	0.0026	n.a.[b]	n.a.[b]	n.a.[b]	n.a.[b]
Laureate	0.0089	0.0054	n.a.[b]	n.a.[b]	n.a.[b]	n.a.[b]
Myristate	0.0934	0.0449	n.a.[b]	n.a.[b]	n.a.[b]	n.a.[b]
Stearate+oleate	19.799	14.662	27.2	20–45.5	26.1	26.2–28.0
Linoleate	66.048	77.179	60.7	34.0–65.5	61.9	60.1±1.0
Palmitate	1.562	2.583	11.4	8.6–16.5	11.5	11.0±0.5
Linolenate	0.790	0.664	0.73	0–2.0	0.7	1.1±0.3
Others	8.905	2.511	n.a.[b]	n.a.[b]	n.a.[b]	n.a.[b]
Total	97.4338	97.7193				

[a]Based on corn oil fatty acid compositions from the literature [13]. Sources: USDA, 2001; Codex Alimentarius, 1999; Anderson and Watson, 1982; Orthoefer and Sinram, 1987. [b]Not available

ids into esters by the adopted procedure. It is considered that gas chromatography is an efficient technique to evaluate if the conversion into esters was complete and, consequently, if the biodiesel production was complete. It is thus observed that biodiesel obtained by both routes fits the European standard prEN 1403 that requires an ester content above 96.5%.

Proton nuclear magnetic resonance (^1H NMR)

Figure 1 presents the ^1H NMR spectrum of corn biodiesel, produced by the methanol route. The complete absence of triglycerides can be observed (4 to 4.5 ppm), due to their conversion into methyl esters, as can be noticed in the spectrum at 3.58 ppm.

Figure 2 presents the ^1H NMR spectrum of the ethyl route biodiesel, in which the triglycerides were converted into ethyl esters, observed in the spectrum as a quartet at about 4.0 ppm. These spectra provide evidence for the transesterification reaction of the corn biodiesel, thus indicating that it was complete.

Figure 3a displays the infrared spectrum of the corn biodiesel, methanol route. It presents a strong band related to the carbonyl group at 1744 cm^{-1}, medium bands related to the ester C–O axial deformation at 1171 and 1207 cm^{-1} and the presence of the group $(CH_2)_n$ at 723.3 cm^{-1}. The absence of a wide band at the 2500–3300 cm^{-1} region confirms the low moisture content of the sample.

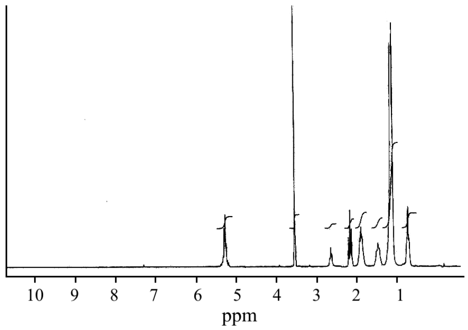

Fig. 1 ^1H NMR spectrum of corn biodiesel, methanol route

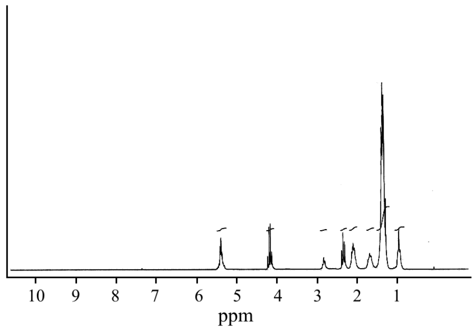

Fig. 2 ^1H NMR spectrum of corn biodiesel, ethanol route

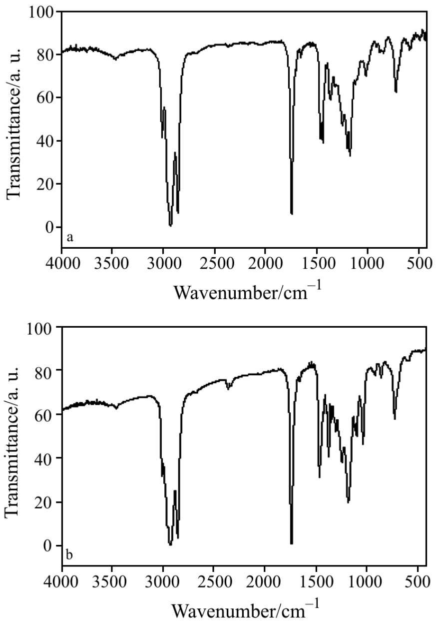

Fig. 3 Infrared spectrum of corn biodiesel, a – methanol route and b – ethanol route

Figure 3b illustrates the infrared spectrum of the corn biodiesel, ethyl route. The ester C=O axial deformation is observed at 1740 cm^{-1}, as well as two medium bands related to the ester C–O axial deformation at 1180 and 1200 cm^{-1}. The presence of a band ascribed to the group $(CH_2)_n$ is observed at 723.3 cm^{-1}. The low moisture content can be observed by the absence of a wide band at the 2500–3300 cm^{-1} region.

Influence of the heating rate on the thermogravimetric profile

In order to study the influence of the heating rate on the thermogravimetric profile of the biodiesel, the TG curves were obtained with heating rates of 10, 15 and 20°C min^{-1} (Fig. 4).

The increase of the heating rate leads to a less uniform heat distribution, a higher temperature gradient, shifting the thermogravimetric curves toward higher temperatures.

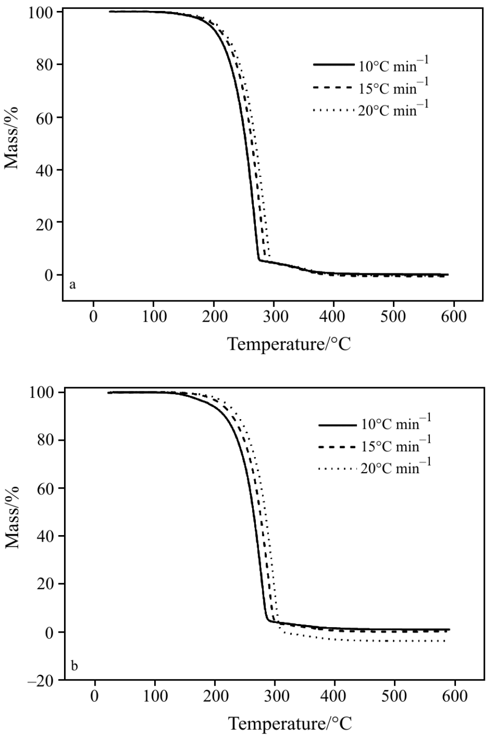

Fig. 4 TG curves of the biodiesel obtained from the a – methanol and b – ethanol routes at different heating rates

Kinetic compensation effect

The kinetic compensation effect was evaluated in the biodiesel obtained by both the methanol and ethanol routes. The first thermal decomposition step, ascribed to the volatilization and/or decomposition of the esters was investigated. With this purpose, the kinetic data were obtained using the heating rates of 10, 15 and 20°C min^{-1} and decomposed fraction (α) values varying from 0.10 to 0.90. The kinetic calculations were performed by the Coats–Redfern method. The best fit corresponded to reaction mechanisms based on geometric models of reactions taking place at the boundary layer. Ethanol corn oil biodiesel displayed a mechanism R1 and methanol corn oil biodiesel a mechanism R3, reaction orders 0 and 2/3, respectively.

Table 3 Kinetic parameters for the first stage of biodiesel decomposition

Kinetic parameter	Heating rate/°C min^{-1}		
	10	15	20
		methanol	
E/kJ mol^{-1}	87.6	81.6	76.7
A/s^{-1}	$3.2\cdot10^6$	$5.5\cdot10^5$	$1.9\cdot10^5$
r	0.99984	1	1
		ethanol	
E/kJ mol^{-1}	82.0	77.3	73.9
A/s^{-1}	$2.6\cdot10^5$	$3.6\cdot10^4$	$8.8\cdot10^4$
r	1	0.9999	1

It was thus verified that, with the increase of the heating rate, the activation energy decreases; this was attributed to a faster heat transfer (Table 3).

In order to validate the dynamic kinetic data, the kinetic compensation effect was evaluated. This is done by noticing that, with the variation of the heating rate, exists a linear relationship between the logarithm of the pre-exponential factor (ln$A$) and the apparent activation energy (E_a). For all the analyzed samples, such a linear relationship was observed (Fig. 5). The methanol corn oil biodiesel was more stable.

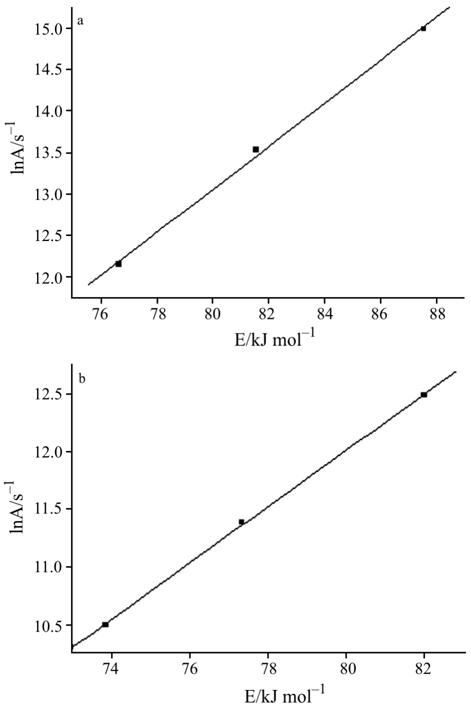

Fig. 5 Kinetic compensation effect for the biodiesel obtained by the a – methanol and b – ethanol routes

Conclusions

Corn biodiesel was characterized by several techniques, for example, infrared spectroscopy, nuclear magnetic resonance and gas chromatography. The results obtained by such techniques confirmed that a good quality biodiesel was obtained, using both the methanol and ethanol routes. The biodiesel production process adopted led to a conversion into methyl and ethyl esters above 97%.

In relation to the physical-chemical parameters, the biodiesel obtained by both routes fits the standards established by ANP.

With increase of heating rate, a decrease in the activation energy was observed, ascribed to a faster heat transfer. The samples of methanol and ethanol biodiesel were shown to obey the kinetic compensation effect. With varying heating rates of 10, 15 and 20°C min^{-1}, a linear relationship was observed between the kinetic parameters of biodiesel, activation energy and pre-exponential factor.

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