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THERMAL AND KINETIC STUDY OF CORN BIODIESEL OBTAINED BY THE METHANOL AND ETHANOL ROUTES

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This work evaluates the thermal and kinetic behaviour of corn biodiesel obtained by the methanol and ethanol routes. As to the TG curves, in air three thermal decomposition steps are for the methanol biodiesel and two steps are for the ethanol biodiesel. These steps are related to the evaporization and/or combustion of the methyl and ethyl esters, respectively. The corn oil presented four thermal decomposition steps in air, and only one step in nitrogen. These steps were attributed to the evaporization and/or decomposition of triglycerides. The TG and DTA profiles of the biodiesel approach the mineral diesel oil ones.

Keywords: *ethanol biodiesel, methanol biodiesel, thermal stability*

Introduction

Currently, the main part of the energy-requirement of the World is covered by non-renewable sources such as petrochemicals, natural gas and coal. Since the demand and cost of petroleum based fuel is growing rapidly, these resources will be depleted in few years. It is also widely known that the combustion products derived from the fossil fuels lead to an increase in the atmospheric concentration of gases causing greenhouse effect, acid rain and depletion of the ozone layer [1–3]. Hence, efforts are being made to search alternative sources of energy. An alternative fuel must be technically feasible, economically competitive, readily available and environmentally acceptable [4, 5].

Thus, the total or partial substitutions of fossil fuels, in which diesel fuels are included, have always had an obvious environmental appeal. So, the biodiesel alternative has been studied on a worldwide scale and produced in several countries, e.g. Czech Republic, Austria, Slovak Republic, USA, Italy, Germany and France [5].

Biodiesel can be defined as the alkyl ester of fatty acids obtained by means of transesterification reaction. Such reaction, in the presence of an acidic, basic or enzymatic catalyst, takes place between any triglyceride and an alcohol, such as methanol and ethanol, yielding a methanol or ethanol biodiesel, respectively [6].

In Brazil, different vegetable oils as corn oil, castor oil, sunflower oil, soybean oil, cotton oil, palm oil, etc. are used. Corn contains 8–10% of oil in the grain [7]. The Brazilian corn production amounted to 34.9 million metric tons in 2005 [8]. OCDE has displayed a review on corn and corn oil, presenting the composition of corn oil, according to four different studies ranging from 1987 to 2001.

In these paper DTA-TG simultaneous method was used to study the thermal stability and decomposition of samples [10–13]. Besides, based on he thermal data, the present work aims to evaluate the kinetic behaviour too, of the corn biodiesel obtained by the methanol and ethanol routes.

Table 1 Mass percent composition of the fatty acids in refined corn oil [9]

Fatty acid	USDA01	And82	Codex99	Ort87
16:0 palmitic	11.4	8.6–16.5	11.5	11.0±0.5
18:0 stearic	1.9	0–3.3	2.0	1.8±0.3
18:1 incl. oleic	25.3	20.0–42.2	24.1	25.3±0.6
18:2 incl. linoleic	60.7	34.0–65.5	61.9	60.1±1.0
18:3 incl. linolenic	0.73	0–2.0	0.7	1.1±0.3

Sources: USDA, 2001; Anderson and Watson, 1982; Codex Alimentarius, 1999; Orthoefer and Sinram, 1987

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Experimental

TG and DTA curves were obtained using a simultaneous DTA/TG analyzer (SDT 2960, TA Instruments) in air and nitrogen (flow rate of 100 mL min^{-1}), in the 30–600°C temperature range at a heating rate of 10°C min^{-1}, using about 20 mg of initial sample masses in alumina crucibles.

The kinetic study was done according to the first of decomposition step of corn biodiesel oil obtained from both the methanol and ethanol routes. Dynamic heating was used to allow the determination of the reaction mechanism, the kinetic parameters and reaction order (n), apparent activation energy (E) and pre-exponential factor (A), using the decomposed fraction (α) in the 0.10–0.90 interval.

GC analyses were carried out in a (CG-FID) VARIAN 3800 Gas chromatograph with a split/splitless injector.

Results and discussion

The TG/DTG curves of corn oil in air (Fig. 1a) display four mass loss steps. All these steps are assigned to the volatilization and/or combustion of the triglycerides. The TG curve of the corn oil in nitrogen (Fig. 1b) presents only one step, ascribed to the evaporization and/or pyrolysis of the triglycerides.

The DTA curve of the corn oil, in air atmosphere (Fig. 2), presented four exothermic transitions. Conversely the DTA curve, in nitrogen atmosphere (Fig. 2), exhibited only one endothermic transition. The exothermic transitions were attributed to the combustion and the endothermic one to volatilization and/or pyrolysis of the triglycerides.

The TG/DTG curves of the biodiesel obtained using the methanol route in air (Fig. 3a), presented three steps. They are attributed to evaporization and/or combustion of the methyl esters, mainly of the methyl linoleate, the most abundant component in the methanol biodiesel, in agreement with the high concentration of linoleic acid in corn oil (Table 1).

On the other hand, the TG/DTG curves of the biodiesel obtained from the ethanol route (Fig. 3b) in air displayed two thermal steps which are also ascribed to the evaporization and/or combustion of the ethyl esters, whose main component is ethyl linoleate, as observed in the methanol route (Table 1).

The conversion of corn oil into methyl and ethyl esters was proved by the high concentrations of linoleates in the biodiesel samples. The gas chromatography results indicated high amounts of methyl linoleate (66%) and ethyl linoleate (77%) in the methanol and ethanol biodiesel samples, respectively.

The TG/DTG curves of the biodiesel produced by means of the methanol route (Fig. 4a) in nitrogen presented two thermal steps ascribed to the evaporization and/or pyrolysis of the methyl esters, mainly methyl linoleate. On the other hand, the TG/DTG curves of the ethanol biodiesel in nitrogen (Fig. 4b) show only one step related to the evaporization and/or pyrolysis of the esters, in this case ethyl esters, mainly ethyl linoleate.

Analyzing the DTA profile of the corn biodiesel obtained by the methanol route (Fig. 5a) in air, four exothermic transitions are observed. The first one displays a peak at 190°C and should be ascribed to the evaporization and/or combustion of methyl linoleate, whose boiling point is 192°C [14]. The remaining transitions are attributed to the combustion of the methyl esters. On the other hand, in the DTA curve of the same corn biodiesel in nitrogen (Fig. 5a), two endothermic transitions were observed. These transitions were attributed to the process of evaporation and/or pyrolysis of the methyl esters.

The DTA profile of corn biodiesel, obtained by the ethanol route (Fig. 5b) shows four exothermic transitions in air. The second peak is at 186°C and should be ascribed to the evaporization and/or combustion of ethyl linoleate, whose boiling point is 166°C [14].

The transitions were attributed to evaporization and/or combustion of the ethyl esters. Nevertheless, in

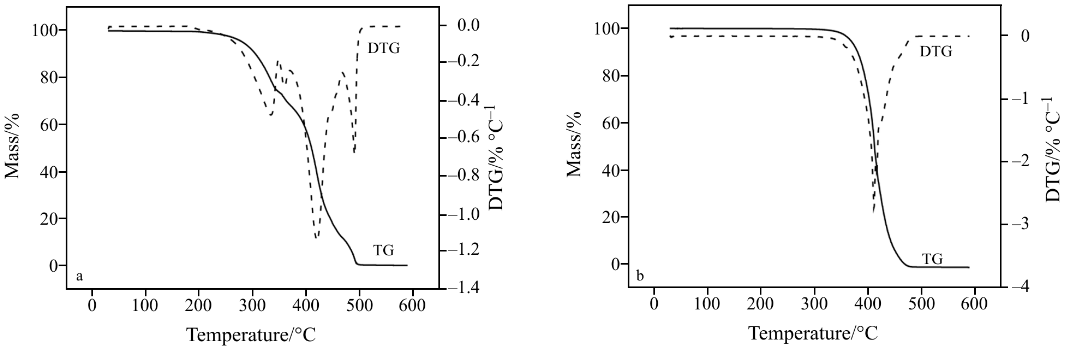

Fig. 1 TG/DTG curves of corn oil in a – air and b – N$_2$

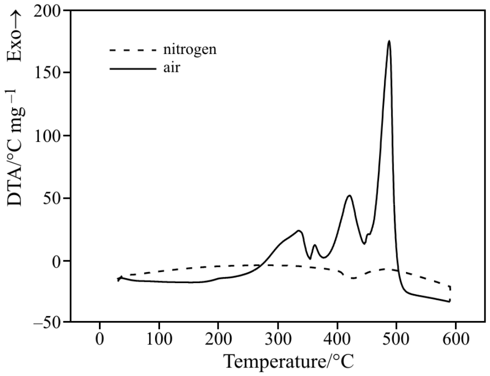

Fig. 2 DTA curves of the corn oil under different atmospheres

the DTA curve of the ethanol biodiesel in nitrogen (Fig. 5b) two endothermic transitions can be observed, where the first one is attributed to evaporization and the second one is representative to pyrolysis.

The representative data taken from the TG and DTA curves are summarized in Tables 2 and 3. These data allow to conclude that corn oil was thermally stable up to 225°C; the methanol biodiesel up to 139°C and the ethanol biodiesel is stable up to 159°C in air. In nitrogen corn oil was thermally stable up to 336°C; the methanol biodiesel up to 145°C and the ethanol biodiesel up to 169°C. In both atmospheres, the ethanol biodiesel was more stable than the methanol one.

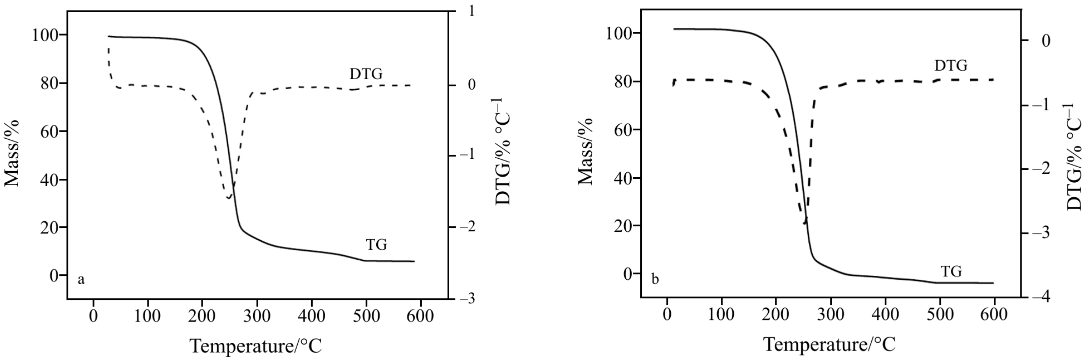

Fig. 3 TG/DTG curves of corn biodiesel obtained by the a – methanol and b – ethanol routes in air

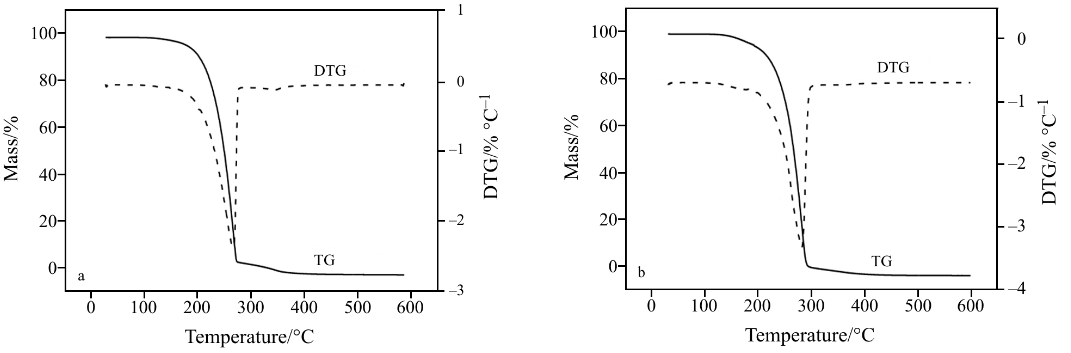

Fig. 4 TG/DTG curves of corn biodiesel obtained by the a – methanol and b – ethanol routes in nitrogen

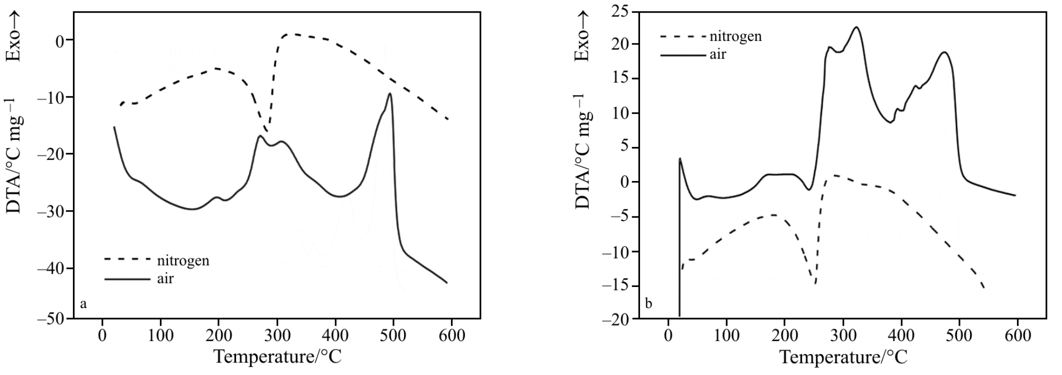

Fig. 5 DTA curves of corn biodiesel samples obtained by the a – methanol and b – ethanol routes in --- – nitrogen and — – air

Table 2 Representative TG data of corn oil, methanol corn biodiesel and ethanol corn biodiesel

Sample	Step	Temperature range/°C	T_{peak}/°C	Δm/%
Corn oil (air)	1st	225–350	332.78	25.6
	2nd	350–369	358.65	5.1
	3rd	369–468	420.33	56.2
	4th	468–524	489.23	11.6
Corn oil (N_2)	1st	336–476	412.83	100.0
Methanol corn biodiesel (air)	1st	139–286	249.09	89.9
	2nd	286–361	338.88	5.1
	3rd	416–494	488.31	4.2
Methanol corn biodiesel (N_2)	1st	145–281	268.08	94.1
	2nd	309–391	347.30	4.1
Ethanol corn biodiesel (air)	1st	159–376	275.08	95.1
	2nd	411–519	514.85	3.5
Ethanol corn biodiesel (N_2)	1st	169–407	277.92	98.6

Table 3 Representative DTA data of corn oil, methanol corn biodiesel and ethanol corn biodiesel

Sample	Transitions	$T_{initial}$/°C	T_{peak}/°C
Corn oil (air)	1st (exo)*	263	334
	2nd (exo)	355	362
	3rd (exo)	393	419
	4th (exo)	462	488
Corn oil (N_2)	1st (endo)**	402	418
Methanol corn biodiesel (air)	1st (exo)	168	190
	2nd (exo)	248	266
	3rd (exo)	292	313
	4th (exo)	441	492
Methanol corn biodiesel (N_2)	1st (endo)	39	58
	2nd (endo)	231	273
Ethanol corn biodiesel (air)	1st (exo)	57	71
	2nd (exo)	277	186
	3rd (exo)	312	333
	4th (exo)	455	517
Ethanol corn biodiesel (N_2)	1st (endo)	40	59
	2nd (endo)	240	283

*exo – exothermic; **endo – endothermic

The initial temperature of thermal decomposition of the biodiesel was lower than the oil itself, corroborating the decrease of viscosity due to the transesterification reaction. Such decrease influences the volatility. Thus the TG and DTA profiles of the biodiesel approach the mineral diesel ones.

Kinetic study

The kinetic study was based on the first TG step of the samples, using a dynamic heating. Once again the corn oil and corn biodiesel from the methanol and ethanol routes were studied. The reaction mechanism and important kinetic parameters, such as reaction order (n), apparent activation energy (E) and pre-exponential factor (A) was determined.

The selection of the mechanism that best describes the thermal decomposition reactions of the samples was done using the TG curves recorded applying dynamic heating. The $g(\alpha)$ functions of the different mechanisms were tested *vs*. the experimental data, using the Program of Thermal Decomposition Mechanisms by the Coats–Redfern dynamic method [13]. The chosen function is the one that leads to the highest linear correlation coefficient and the smallest standard deviation.

Corn oil and ethanol corn biodiesel displayed a R1 mechanism and methanol corn biodiesel a R3 one. Therefore, the samples presented reaction mechanisms based on geometric models of reaction orders 0 and 2/3, of limiting phase reactions with one dimension or three-dimension nuclear growth corresponding to the models R1 and R3, respectively.

The aforementioned kinetic parameters n, E_a and A were calculated by Coats–Redfern (CR), Madhusudanan (MD), Horowitz–Metzger (HM) and

Table 4 Kinetic parameters of the samples calculated from the first mass loss step

Sample	Parameters	CR	MD	HM	VK
Corn oil	n	0.15	0.00	0.29	0.16
	E/kJ mol^{-1}	73	70	96	82
	A/s^{-1}	$7.3\cdot 10^{3}$	$3.8\cdot 10^{3}$	$1.0\cdot 10^{6}$	$1.5\cdot 10^{10}$
	r	1	1	0.99995	0.993
Methanol corn biodiesel	n	0.63	0.62	0.81	0.63
	E/kJ mol^{-1}	88	88	108	94
	A/s^{-1}	$3.2\cdot 10^{6}$	$3.4\cdot 10^{6}$	$5.3\cdot 10^{8}$	$4.5\cdot 10^{12}$
	r	0.99984	0.9999	0.9998	0.9977
Ethanol corn biodiesel	n	0.04	0.04	0.30	0.28
	E/kJ mol^{-1}	82	82	107	98
	A/s^{-1}	$2.6\cdot 10^{5}$	$3.1\cdot 10^{5}$	$9.0\cdot 10^{7}$	$3.3\cdot 10^{12}$
	r	1	1	0.9999	1

Van Krevelen (VK) methods based on the first TG step of the samples (Table 4).

A good correlation between the kinetic parameters obtained by the Coats–Redfern and Madhusudanan integral methods was observed. This is due to the fact that they are based on similar mathematical operations. The same occurs with the approximation of Van Krevelen and Horowitz–Metzger methods.

Based on Coats–Redfern method, the following order in activation energy was observed: methanol biodiesel>ethanol biodiesel>corn oil.

Conclusions

Corn oil was thermally stable up to 225°C; the methanol biodiesel is stable up to 139°C and the ethanol biodiesel is up to 159°C in air. In nitrogen atmosphere the corn oil was thermally stable up to 336°C; the methanol biodiesel up to 145°C and the ethanol biodiesel up to 169°C. In both atmospheres, the ethanol biodiesel was more stable.

The initial temperature of thermal decomposition of the biodiesel was lower than the oil one, corroborating the decrease of the viscosity due to the transesterification reaction. Such decrease influences the volatility. Thus the TG and DTA profiles of the biodiesel approach the mineral diesel oil ones.

The model that best fits the experimental data of corn oil and ethanol biodiesel was the R1 one (zero order), whereas the best fit for methanol biodiesel was the R3 one (order 2/3). The following activation energy order was observed: methanol biodiesel>ethanol biodiesel>corn oil, according to Coats–Redfern method.

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