Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 3, 945–949

THERMAL AND KINETIC EVALUATION OF COTTON OIL BIODIESEL

A. G. Souza[1*], *H. J. Danta*[2], *M. C. D. Silva*[3], *I. M. G. Santos*[1], *V. J. Fernandes Jr.*[2], *F. S. M. Sinfrônio*[3], *L. S. G. Teixeira*[4] *and Cs. Novák*[5]

[1]Departamento de Química, Universidade Federal da Paraíba, Campus I, João Pessoa, PB, Brazil
[2]Departamento de Química, Universidade Federal do Rio Grande do Norte, Natal, RN, Brazil
[3]Centro de Formação de Professores, Universidade Federal de Campina Grande, Cajazeiras, PB, Brazil
[4]Departamento de Engenharia Qímica e Arquitetura, Universidade Salvador, Salvador, BA, Brazil
[5]Research Group of Technical Analytical Chemistry of Hungarian Academy of Sciences, Budapest University of Technical and Economics, Szt. Gellert ter 4, 1111 Budapest, Hungary

The biodiesel obtained by transesterification by reaction between ester and an alcohol in the presence of catalyst. The purpose of this work is to evaluate the thermal and kinetic behavior of the methanol biodiesel derived from cotton oil. The quality analysis was done by gas chromatography and proton nuclear magnetic resonance spectrometry (^{1}H NMR) in order to examine if the product meets with the requirements of the European Standard EN 1403. The thermogravimetric profile of the cotton biodiesel indicated that the decomposition steps are associated to the volatilization and/or decomposition of the methyl esters. Kinetic data was also obtained by thermal analysis.

Keywords: *biodiesel, cotton oil, kinetics, methanol route*

Introduction

As the fossil sources are decrease, nowadays searching for new, mainly renewable energy sources has a great importance. In spite of being favorable from the energetic standpoint, the direct use of vegetable oils in Diesel engines is problematic. It is reported that various complication arise during the direct usage of vegetable oils in Diesel engines, such as carbonization of the injection camera, ejection resistance of the piston segments, dilution of the crankcase oil contamination of the lubricating oil and poor atomization of the fuel, which are mostly attributable to the low volatility and the high viscosity[1]. These problems are efficiently solved by the transesterification reaction that decreases the molecular mass of the oils increasing the volatility and decreasing the viscosity [1–3].

The biodiesel can be obtained by the transesterification process resulted by the reaction between an ester (lipid) and an alcohol in the presence of a catalyst (acid, basic or enzymatic), producing an ester (biodiesel) and glycerin as a coproduct. The molecular mass close to petrodiesel and similar physico-chemical properties make biodiesel a much better petrodiesel substitute than vegetable oils 'innatura' [4].

Therefore, the purpose of this work was to evaluate the thermal and kinetic behavior of the cotton oil biodiesel obtained by the methanol route.

Experimental

Materials

The biodiesel was synthesized using cotton oil obtained from Brazilian industries. Transestherification with methanol (methanol route) was carried out as described by Parente (2003) [5].

Methods

The biodiesel was analyzed by gas chromatography (GC) to determine the conversion of triacylglyceride to methyl esters of the corresponding fatty acids upon the transesterification reaction. A Varian 3800 GC-FID gas chromatograph was used. The column was a mixture of 5% phenyl and 95% polydimethylsiloxane, with dimensions of 30.0·0.25·0.25mm. The injector temperature was of 290°C and the detector of 300°C, with 1:50 split factor [6].

The ^{1}H NMR spectra were obtained in a GEMINI-300BB equipment, using deuterated chloroform as a solvent.

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

Thermogravimetric (TG) and calorimetric (DSC) curves were simultaneously obtained by using a SDT2960 Thermal Analyzer from TA Instruments.

---

* Author for correspondence: agouveia@quimica.ufbp.br

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

The non-isothermal dynamic analysis method at a heating rate of 10°C min^{-1} was used. The runs were performed at air and nitrogen, in the 28–600°C temperature range, using 110 mL min^{-1} flow rate. The initial (T_i) and final (T_f) decomposition temperatures were obtained from the TG curves.

Results and discussion

The cotton biodiesel was obtained by alkaline transesterification using the methanol route. The good quality of the product was confirmed by means of the infrared spectroscopy, gas chromatography and ^{1}H NMR techniques.

Infrared spectroscopy

In Fig. 1a it can be noticed that the infrared spectrum of cotton oil agrees with the literature [7, 8]. Absorption bands at about of 3000 cm^{-1} are ascribed to the H–C= group and between 2930 and 2855 cm^{-1} for the –CH2– group, about 1745 cm^{-1} for the carbonyl group, about of 1160 cm^{-1} for C–O–C from the ester functional group and at 716 cm^{-1} attributed to the $-(CH_2)_n-$ sequence of aliphatic chains of fatty acids.

Figure 1b displays the infrared spectrum of the cotton biodiesel, obtained by the methanol route. The spectrum presents a strong band at 1735 cm^{-1} ascribed to the ester C=O axial deformation and two medium bands at 1170 and 1190 cm^{-1} related to the C–O bond.

Gas chromatography

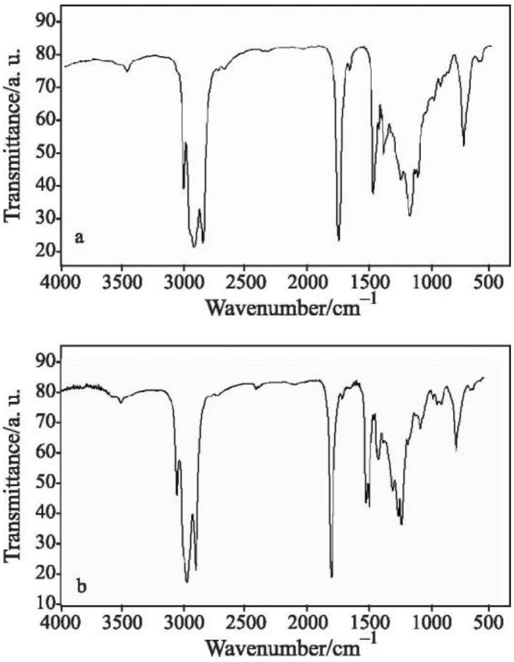

Fig. 1 Infrared spectra of a – cotton oil and b – cotton biodiesel by the metanol

Table 1 presents the fatty acid composition of cotton oil obtained in the present work by gas chromatography and the composition of the methyl esters of the cotton biodiesel obtained by the methanol route. For the sake of comparison it also includes the fatty acid composition of cotton oil reported in [9]. The methyl ester composition in the cotton oil biodiesel obtained by the methanol route is quite close to the original cotton oil composition. The analysis of the present work practically lies within the limits listed in [9].

The overall amount of methyl esters in the cotton biodiesel was of 96.80%. This value is better than the value of 96.5%, required by the European standard EN 1403. The main constituent in the biodiesel is methyl linoleate.

Proton nuclear magnetic resonance

In the Proton NMR spectrum of cotton oil the presence of the triacylglycerides can be observed by the multiplets noticed in the range of 4–4.5 ppm (Fig. 2).

Table 1 Fatty acid composition of cotton oil and methyl ester composition of the cotton oil biodiesel obtained by methanol route

Numerical symbol	IUPAC name	Common name	Cotton oil fatty acid comp./%		Biodiesel methyl ester comp./%
			present work	reference [8]	
C 14:0	tetradecanoic acid	myristic acid	1.5	<1	1.4
C 16:0	hexadecanoic acid	palmitic acid	25.0	17–31	25.0
C 16:1	9-hexadecenoic acid	palmitoleic acid	–	<1	–
C 18:0	octadecanoic acid	stearic acid	1.72	1–3	1.60
C 18:1(9)	9-octadecenoic acid	oleic acid	28.0	13–21	26.0
C 18:2(9,12)	9,12-octadecadienoic acid	linoleic acid	40.0	34–60	39.02
C 18:3(9,12,15)	9,12,15-octadecatrienoic acid	linolenic acid	0.52	<1	0.50
Others			3.26		3.26
			100.0		96.8

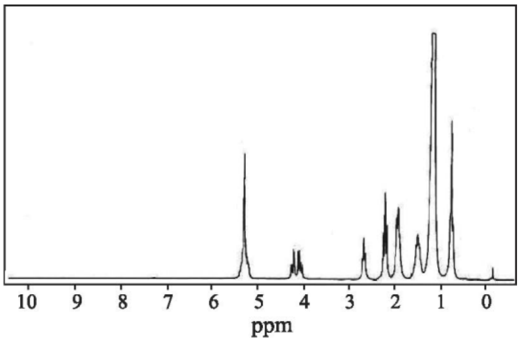

Fig. 2 ^{1}H NMR spectrum of cotton oil

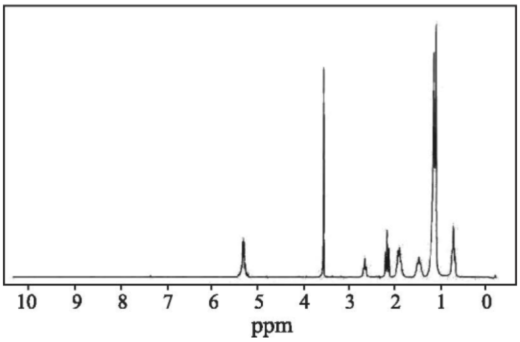

Fig. 3 ^{1}H NMR spectrum of cotton biodiesel, methanol route

In the ^{1}H NMR spectrum of cotton biodiesel obtained by the methanol route (Fig. 3) in the 4–4.5 ppm range the absence of peaks was observed. In the methanol biodiesel a strong singlet was identified at 3.5 ppm, ascribed to the methyl esters.

Thermal analyses

The TG curve of cotton oil in synthetic air presented three mass loss steps between 188–538°C attributed to the volatilization and combustion process of the triacylglycerides which are approximately 96% of the total amount of samples. The first step occurs between 188 and 370°C with a mass loss of 36%. In the second step in the 370–470°C range 52% mass loss can be observed. The third step from 470 to 538°C was accompanied by 12% of mass loss. Thus, in air cotton oil was thermally stable up to 188°C and the methanol biodiesel was stable up to 127°C. The TG/DTG curve of the cotton oil in nitrogen presented only one mass loss step between 314–488°C which is related to the volatilization and/or pyrolysis of the triacylglycerides.

The TG/DTG curves presented in Fig. 4 illustrate the thermal behavior of the cotton biodiesel, methanol route, in synthetic air and nitrogen. The TG/DTG curves of the cotton biodiesel, methanol route, in a synthetic air atmosphere (Fig. 4a) presented two mass loss steps, between 127–414°C without residue. The steps are ascribed to the volatilization and/or combustion of the methyl esters, with the prevalence of methyl linoleate. The TG/DTG curves of the methanol biodiesel in a nitrogen (Fig. 4b) presented only one mass loss step, attributed to the volatilization and/or pyrolysis of the methyl esters (Table 2).

According to Table 2, it was observed that the cotton oil biodiesel, methanol route, presents a lower onset decomposition temperature both in air and in nitrogen than cotton oil does. This indicate that the biodiesel presents a higher volatility approaching the petrodiesel characteristics and improving the fuel properties.

The calorimetric data of cotton oil and cotton biodiesel, methanol route are listed in Table 3. In a synthetic air cotton oil displayed exothermic transitions ascribed to the combustion of the triacylglycerides and in nitrogen the endothermic transitions are attributed to its volatilization and/or pyrolysis. The DSC curve of the methanol biodiesel in air presented three exothermic transitions attributed to the volatilization and/or combustion of the methyl esters, whereas in nitrogen two endothermic transitions were noticed, also attributed to volatilization and/or pyrolysis. The enthalpy values related to the synthetic air atmosphere are higher than the ones for the nitrogen atmosphere.

Kinetic study

The kinetic study [10–12] of the thermal decomposition process of cotton oil and methanol biodiesel comprises the determination of the reaction mechanism and the kinetic parameters. The dynamic heating method at a heating rate of 10°C min^{-1} was

Table 2 Main thermogravimetric data of the samples in different atmospheres

Sample	Step	T_i/°C	T_f/°C	Δmass/%
Cotton oil (air)	1st	188	370	36.0
	2nd	370	470	52.0
	3rd	470	538	12.0
Cotton oil (N_2)	1st	314	488	99.8
Cotton oil biodiesel, methanol route (air)	1st	127	295	91.8
	2nd	295	414	8.2
Cotton oil biodiesel, methanol route (N_2)	1st	114	305	100.0

Table 3 Calorimetric data of the samples in different atmospheres

Sample	Transition	T_{peak}/°C	Enthalpy/J g^{-1}
Cotton oil (air)	1st	351	1263 (exo)
	2nd	416	634 (exo)
	3rd	497	2520 (exo)
Cotton oil (N_2)	1st	48	21.2 (endo)
	2nd	423	240 (endo)
Cotton oil biodiesel, methanol route (air)	1st	201	30.8 (exo)
	2nd	263	121 (exo)
	3rd	365	57.0 (exo)
Cotton oil biodiesel, methanol route (N_2)	1st	60	2.23 (endo)
	2nd	262	132 (endo)

Table 4 Mechanisms of the first thermal decomposition step of the samples

Sample	Atmosphere	Model
Cotton oil	synthetic air	R1
	N_2	F1
Cotton oil biodiesel, methanol route	synthetic air	R1
	N_2	R1

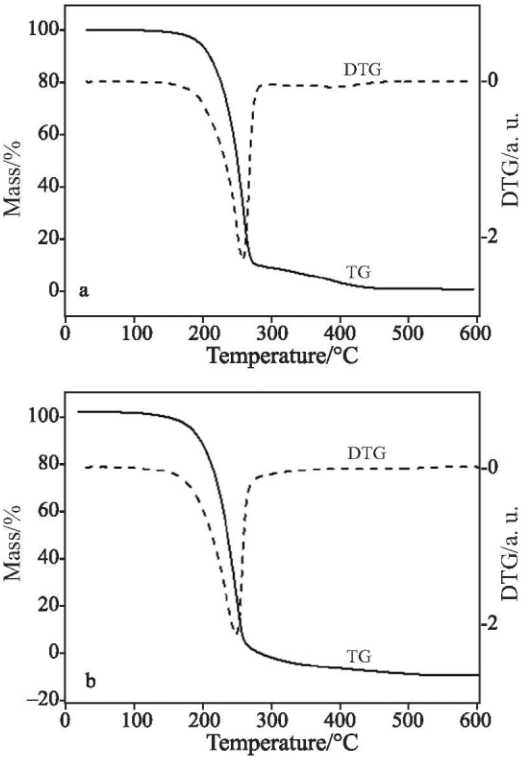

Fig. 4 TG/DTG curves of the methanol biodisel from cotton oil in a – synthetis air and b – nitrogen

Table 5 Kinetic parameters of the samples in different atmospheres

Atm.	Method	Parameters	Cotton oil	Methanol biodiesel
Air	CR	n	0.00	0.25
		E/kJmol^{-1}	87.3	71.7
		A/s^{-1}	$6.5\cdot10^{9}$	$7.3\cdot10^{4}$
		r	1.0000	1.0000
	MD	n	0.00	0.31
		E/kJmol^{-1}	87.6	73.3
		A/s^{-1}	$7.6\cdot10^{11}$	$1.2\cdot10^{5}$
		r	1.0000	1.0000
	VK	n	0.02	0.34
		E/kJmol^{-1}	96.2	81.7
		A/s^{-1}	$1.5\cdot10^{11}$	$2.4\cdot10^{11}$
		r	1.0000	1.0000
	HM	n	0.09	0.44
		E/kJmol^{-1}	106.9	91.1
		A/s^{-1}	$5.7\cdot10^{6}$	$1.2\cdot10^{6}$
		r	0.9998	0.9999
N_2	CR	n	1.43	0.04
		E/kJmol^{-1}	219.8	76.6
		A/s^{-1}	$3.7\cdot10^{14}$	$1.46\cdot10^{5}$
		r	0.9990	1.0000
	MD	n	1.58	0.05
		E/kJmol^{-1}	231.9	77.1
		A/s^{-1}	$3.7\cdot10^{15}$	$1.8\cdot10^{5}$
		r	0.9989	1.0000
	VK	n	1.64	0.15
		E/kJmol^{-1}	250.2	87.6
		A/s^{-1}	$4.5\cdot10^{22}$	$6.0\cdot10^{11}$
		r	1.0000	1.0000
	HM	n	1.71	0.23
		E/kJmol^{-1}	255.6	96.2
		A/s^{-1}	$2.9\cdot10^{17}$	$2.5\cdot10^{7}$
		r	0.9991	0.9998

employed taking into account the $0.10<\alpha<0.90$ decomposed fraction range. The $g(\alpha)$ equations were tested using the Coats–Redfern dynamic method with the support of the thermal Decomposition Mechanism Program [13]. Table 4 presents the mechanisms determined for the first thermal decomposition step of the samples.

Most of the samples presented a reaction mechanism based on a boundary layer reaction with a one dimension nuclear growth, corresponding to the R1 model (zero order). The only exception was the case of cotton oil in nitrogen, which presented F1 mechanism, based on a first order reaction.

The kinetic parameters [13–16] were calculated for the first thermal decomposition step of the samples (Table 5). Four different methods were used: Coats–Redfern (CR), Madhusudanan (MD), Van Krevelen (VK) and Horowitz–Metzger (HM).

Comparing the calculated activation energies by all the methods in the two atmospheres it was noticed that the activation energy for the cotton oil was higher than the one for the methanol biodiesel. In nitrogen higher activation energy values were obtained. Similarities between the kinetic parameters obtained by Coats–Redfern and Madhusudanan integral methods were observed. It can be possible attributed to the similar mathematical data treatments. The same is valid, although somewhat lower extent with the Van Krevelen and Horowitz–Metzger approximation methods.

Conclusions

Cotton biodiesel was characterized by infrared spectroscopy, gas chromatography, proton nuclear magnetic resonance and thermal analyses. According to the results 96.8% conversion of the triacylglycerides to methyl esters was achieved. Furthermore, the degree of conversion was higher than the one required by the European standard EN 1403. The thermogravimetric and calorimetric profiles of the cotton biodiesel obtained by the methanol route indicated that the mass loss steps are associated to the volatilization and/or decomposition (by combustion or pyrolysis) of the methyl esters, with the prevalence of methyl linoleate. At air, cotton oil was thermally stable up to 188°C and the methanol biodiesel up to 127°C.

According to Table 2 cotton oil biodiesel (methanol route) presents a lower onset decomposition temperature both in air and in nitrogen compared to cotton oil. This indicates that the biodiesel presents a higher volatility approaching the petrodiesel characteristics and improving the fuel properties.

The activation energy values for cotton oil are higher than the ones for the methanol biodiesel. This was noticed with the usage of all the methods and in both atmospheres.

Acknowledgements

The authors acknowledge the CAPES and CNPq Brazilian agencies.

References

1 G. Knothe, Fuel, 84 (2005) 1059.
2 M. M. Conceição, R. A. Candeia, F. C. Silva, A. F. Bezerra, V. J. Fernandes Jr. and A. G. Souza, Ren. Sustain. Energ. Rev., In press.
3 M. M. Conceição, R. A. Candeia, H. J. Dantas, L. E. B. Soledade, V. J. Fernandes and A. G. Souza, Energy Fuels, 19 (2005) 2185.
4 L. P. Ramos, Quim. Nova, 23 (2000) 120.
5 E. J. S. Parente, Biodiesel: Uma aventura tecnológica num país engraçado. Fortaleza, Ceará: Tecbio, 2003.
6 C. H. Collins, Introdução a métodos cromatográficos, Editora da Unicamp, Campinas, 2000.
7 A. Blayo, A. Gandini and J. L. Nest, Ind. Crops Prod., 14 (2005) 155.
8 R. M. Silverstain, Identificação espectrométrica de compostos orgânicos, LTC Editora, Rio de Janeiro, 2000.
9 CyberlipidCenter, site , accessed at July 12, 2006.
10 M. M. Conceição, A. M. L. Melo, N. Narain, I. M. G. Santos and A. G. Souza, J. Therm. Anal. Cal., 67 (2002) 373.
11 M. M. Conceição, V. J. Fernandes Jr., F. S. M. Sinfrônio, J. C. O. Santos, M. C. D. Silva, V. M Fonseca and A. G. Souza, J. Therm. Anal. Cal., 79 (2005) 461.
12 M. M. Conceição, A. G. Souza, M. F. S.Trindade, T. G. Nascimento, C. F. S. Aragão and R. O. Macedo, Thermochim. Acta, 433 (2005) 163.
13 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
14 P. M. Madhusudanan and C. G. R. R. Nair, Thermochim. Acta, 12 (1975) 97.
15 H. H. Horowitz and R. Metzger, Anal. Chim., 35 (1963) 1964.
16 W.C. Van Krevelen, Van Herden and Hutjens, Fuel, 30 (1951) 253.

Received: September 19, 2006
Accepted: August 17, 2007

DOI: 10.1007/s10973-006-8199-5