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Thermo-oxidative decomposition of biodiesel samples obtained from mixtures of beef tallow, soybean oil, and babassu oil

**G. A. A. Teixeira · A. S. Maia · R. Rosenhaim ·
I. M. G. Santos · A. L. Souza · A. G. Souza ·
N. Queiroz**

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Abstract Biodiesel can be obtained from various fatty acid sources. Each raw material has a different chemical composition that leads to different properties. Owing to these properties, the mixture of different proportions of raw materials can lead to biodiesels with best features in relation to physicochemical parameters such as viscosity, oxidative stability and flow properties, generating a fuel - whose characteristics meet the requirements of the current legislation of the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP). The objective of this study was to determine the physicochemical properties of biodiesel samples produced from mixtures of beef tallow, babassu oil, and soybean oil. The thermo-oxidative stability was evaluated using thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC). The results showed that all samples were in accordance to the ANP specifications. The biodiesel obtained from a mixture containing 50% of babassu oil had lower values of pour point, cold filter plugging point, and freezing point. This biodiesel also showed a higher thermo-oxidative stability in synthetic air and in oxygen atmospheres.

Keywords Biodiesel · TG · DSC · Blends

Introduction

Biodiesel is a monoalkyl ester obtained from transesterification reactions using lipids such as vegetable oils, animal fats, and waste cooking oil. It has attracted interest from researchers for presenting due to its properties similar to diesel oil [1–5]. Biofuels represent a great natural potential for fuel production especially in Brazil that already produces ethanol and biodiesel [6, 7].

Beef tallow is the second main source for biodiesel production in Brazil. It is considered as an excellent feedstock considering environmental reasons since it is a residue from the meat processing industry. Nowadays the main source for biodiesel preparation is the soybean oil due to its availability as Brazil owns a consolidated structure for its production [7]. In relation to biodiesel quality, transesterification reactions from soybean oil and beef tallow lead to a fuel out of the parameters established by the Brazilian National Agency of Petroleum, Natural Gas and Biofuel—ANP. For soybean oil, the high amount of unsaturated fatty acids leads to biodiesel with low oxidative stability [1, 8]. For beef tallow, fatty acids with long saturated chains have significantly higher melting points than unsaturated fatty compounds. In a mixture saturated fatty acids crystallize at higher temperatures than the unsaturated ones [9]. As a consequence it cannot be used in regions with cold weather. These drawbacks may be overcome by the mixture of these raw materials with babassu biodiesel which is characterized by saturated fatty acids with short chains and excellent oxidative stability [10].

Mixtures of different raw materials lead to biodiesels with different chemical compositions. As a consequence, a mixture of esters more adequate can be obtained in relation to physicochemical parameters such as oxidative stability and flow properties, avoiding the use of expensive additives. In spite of this, few studies were found reporting the production of biodiesel from a blend of animal fats and vegetable oils [11–13].

G. A. A. Teixeira · A. S. Maia · R. Rosenhaim ·
I. M. G. Santos · A. L. Souza · A. G. Souza · N. Queiroz (✉)
Universidade Federal da Paraíba, CCEN, DQ, Cidade
Universitária, Campus I, João Pessoa, PB 58059-900, Brazil
e-mail: neide@quimica.ufpb.br

This study aims at evaluating the physicochemical properties and thermo-oxidative stabilities of biodiesel samples obtained from mixtures of beef tallow, soybean oil, and babassu oil.

Experimental

Different proportions of beef tallow, babassu oil and soybean oil were used to produce the biodiesel, according to the following rate: 1:1:1 (MO-1), 2:1:1 (MO-2), 1:2:1 (MO-3), and 1:1:2 (MO-4). The transesterification reactions were performed using a ratio of 6:1 of methanol:oil/fat and 1.5% of catalyst (KOH) at 50 °C under constant stirring [14]. The reaction mixtures MO-1, MO-2, MO-3, and MO-4 produced the biodiesel samples named B1, B2, B3, and B4, respectively. The purification of the biodiesel samples was performed according to the literature [15].

The identification of fatty acid chains in the samples was accomplished by a gas chromatograph/mass spectrometer (GC–MS) from SHIMADZU, model CGMS-QP2010. The capillary column used was a Durabond DB-5HT (30 m long, 0.319 mm internal diameter and 0.10 μm film thickness). Column temperature was raised from 130 up to 170 °C with a heating rate of 2 °C/min, followed by a heating up to 187 °C (rate of 1 °C/min) and 250 °C (rate of 20 °C/min). Initial and final temperatures were held for 1 and 10 min, respectively. Injector temperature was set at 290 °C while the mass detector and interface temperatures were set at 250 °C. Fatty acid methyl esters (FAMEs) were identified by comparison of the mass spectra with existing standards in the software library (Mass Spectral Database NIST/EPA/NIH). The fatty acid composition was reported as a relative percentage of the total peak area.

Thermogravimetric (TG) and Differential Thermal Analysis (DTA) curves were obtained in a simultaneous thermal analyzer from Shimadzu, model DTG-60H, in oxygen and synthetic air atmospheres with a flow of 50 mL min^{-1}. A heating rate of 10 °C min^{-1} was used up to 700 °C. The DSC curves were obtained in an SDT 2960 thermal analyzer from TA-Instruments with a heating rate of 10 °C min^{-1} up to 600 °C in synthetic air atmosphere.

Results and discussion

The mixtures used as raw materials in the biodiesel synthesis were in accordance with the specifications of the SMADOF standards [16]. This quality control is important in the biodiesel production because factors such as moisture content and free fatty acids directly affect the synthesis efficiency and further purification of esters. The physicochemical properties of the biodiesel samples produced from mixtures of varying proportions of beef tallow, babassu oil, and soybean oil (Table 1) were in accordance with the ANP specifications [17]. Table 2 shows the fatty acid chromatographic profile from biodiesel samples.

The thermogravimetric curves of the mixtures of raw materials showed similar profiles in synthetic air and in oxygen, presenting three mass loss steps in both atmospheres. The two atmospheres were used to compare the influence of oxygen pressure in the oxidation reaction during the own analysis. All steps were assigned to the combustion of organic compounds (Fig. 1), as showed by the exothermic peaks in the DTA curves (Fig. 2).

The TG curves showed a temperature decrease at about 400 °C, especially when analysis was done in oxygen atmosphere (Fig. 1). Combustion reactions are characterized by a high amount of energy release, leading to a temperature increase. As DTA analysis is done by comparison with an inert reference the furnace is automatically turned off by the equipment software in order to decrease temperature difference between sample and reference, leading to a loop in the DTA curves (Fig. 2b). As TG/DTA

Table 1 Physicochemical properties of the biodiesel samples

Technical features	B1	B2	B3	B4	Limit	Method
Appearance	LII*	LII*	LII*	LII*	LII	–
Acidity index/mg KOHg^{-1}	0.25	0.26	0.25	0.26	0.50 (Máx.)	AOCS
Kinematic viscosity at 40 °C/mm^{2}s^{-1}	4.05	4.32	3.76	4.08	3.0–6.0	ASTM
Iodine index/g I_2/100 g	52.78	45.96	47.10	82.75	NS	AOCS
Specific weight at 20 °C/kgm^{-3}	874.9	874.1	875.8	876.6	850-900	ASTM
CFPP**/°C	7.0	11.0	4.0	5.0	19 (Máx.)	ASTM
Pour point/°C	3.0	7.0	1.0	2.0	NS	ASTM
Freezing point/°C	8.0	12.0	5.0	6.0	NS	ASTM

*LII** Clear and free from impurities, *CFPP*** Cold filter plugging point, *NS* Not stated

AOCS (American Oil Chemists Society), *ASTM* (American Society of Testing and Materials)

Table 2 Fatty acid chromatographic profile from biodiesel samples

Name/carbon number	Concentration/%			
	B1	B2	B3	B4
Caprylic (C 8:0)	1.78	0.69	2.04	0.90
Capric (C 10:0)	2.14	1.12	2.51	1.10
Lauric (C 12:0)	13.50	10.31	16.31	8.82
Myristic (C 14:0)	8.20	8.08	9.54	5.39
Pentadecatoic (C 15:0)	0.79	1.37	0.57	0.48
Palmitic (C 16:0)	15.19	6.11	14.31	14.37
Palmitoleic (C 16:1(9))	0.66	0.86	0.42	0.38
Margaric (C 17:0)	2.49	3.65	1.65	1.44
Stearic (C 18:0)	14.27	24.75	14.69	14.98
Oleic (C 18:1(9))	19.86	22.68	19.43	22.27
Linoleic (C 18:2(9, 12))	16.61	15.87	14.94	24.06
Linolenic (C 18:3(9, 12, 15))	3.27	3.05	2.53	4.22
Arachidic (C 20:0)	0.43	0.71	0.45	0.54
Behenic (C 22:0)	0.30	0.38	0.28	0.43
Others	0.51	0.37	0.33	0.62
Saturated chains	59. 09	57.17	62.35	48.45
Unsaturated chains	40.40	42.56	37.32	50.93

curves were obtained simultaneously, the differences in the profile of TG curves were observed.

Mass losses and temperature range of each step are showed in Table 3. All samples showed a meaningful increase in the mass loss of the third step when analysis was done in oxygen atmosphere. These results indicated that oxidation reactions probably occurred during analysis, leading to the formation of polymeric chains that decomposed at higher temperatures. This increase was smaller for sample obtained from the mixture with higher amount of babassu oil, indicating that it has a higher oxidative stability.

The DSC curves of the mixtures of raw materials (Fig. 3, Table 4) showed profiles similar to DTA curves, confirming that combustion reactions occurred in successive steps related to the heterogeneous composition of the samples.

Differences up to 10% are observed between the peak temperatures of DTA, DSC, and DTG curves. These differences can be due to the temperature decrease in TG curves associated to the loop in DTA curves. As a consequence of this behavior, a higher error is associated to the temperature values.

The TG/DTG curves of the biodiesel samples showed two mass loss steps as showed in Fig. 4, Table 5.

The first mass loss step was attributed to the volatilization of the shorter carbon chains identified by the endothermic transition in the DTA curves (Fig. 5a). This endothermic peak was easier to observe in the curves obtained in synthetic air, as oxygen atmosphere favored the combustion reactions hiding the endothermic transition. The second step was assigned to the ester combustion with an exothermic transition in the DTA curves (Fig. 5b).

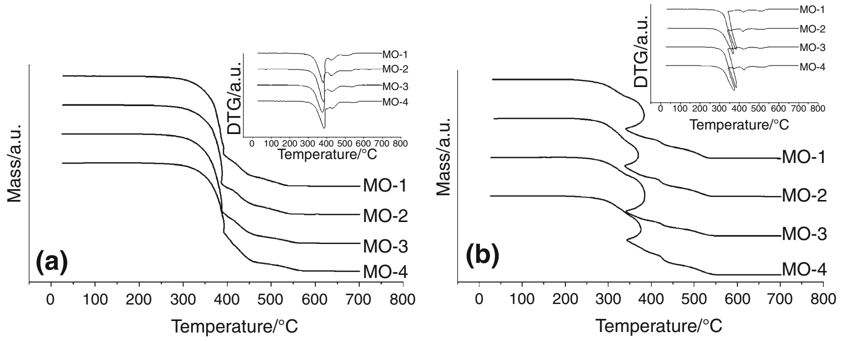


Fig. 1 TG and DTG curves of the mixtures of raw materials in synthetic air (**a**) and oxygen (**b**) atmospheres

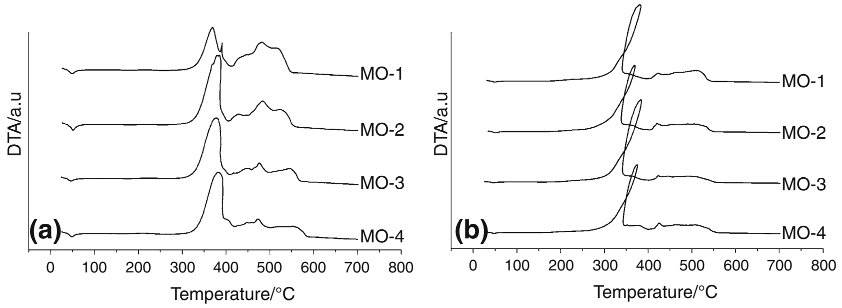


Fig. 2 DTA curves of the mixtures of raw materials in synthetic air (**a**) and oxygen (**b**) atmospheres

Table 3 Thermogravimetric results of the mixtures of raw materials

Sample	Atmosphere	Step	T_{initial}/°C	T_{final}/°C	Mass loss/%	T_{peak}/°C DTG	T_{peak}/°C DTA
MO-1	Synthetic air	1	139	404	76.1	378	366, 391 (exo)
		2	404	476	17.7	424	477 (exo)
		3	476	567	7.3	514	520 (exo)
	O_2	1	191	389	74.5	375	380 (exo)
		2	389	462	12.9	418	422 (exo)
		3	462	599	12.9	513	516 (exo)
MO-2	Synthetic air	1	190	399	75.6	371	383 (exo)
		2	399	488	18.9	424	483 (exo)
		3	488	615	6.1	527	524 (exo)
	O_2	1	97	388	74.3	374	367 (exo)
		2	388	461	13.9	416	421 (exo)
		3	461	562	11.8	516	510 (exo)
MO-3	Synthetic air	1	207	403	76.3	373	374 (exo)
		2	403	486	18.4	430	476 (exo)
		3	486	599	5.9	536	547 (exo)
	O_2	1	212	392	80.3	375	383 (exo)
		2	391	462	10.3	423	423 (exo)
		3	462	567	9.8	510	502 (exo)
MO-4	Synthetic air	1	201	408	71.7	385	381 (exo)
		2	408	485	21.4	405, 431	474 (exo)
		3	485	600	6.9	549	552 (exo)
	O_2	1	170	395	71.5	375	374 (exo)
		2	395	466	16.3	424	425 (exo)
		3	466	588	12.6	513	514 (exo)

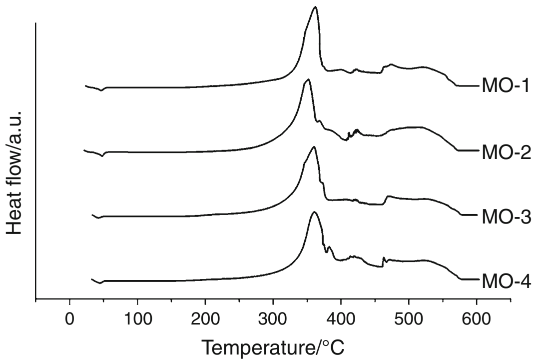


Fig. 3 DSC curves of the mixtures of raw materials in synthetic air atmosphere

Table 4 Calorimetric data of the mixtures of raw materials

Samples	Transition	T_{peak}/°C	Energy/J g^{-1}
MO-1	exo	362	2409
MO-2	exo	349	2038
MO-3	exo	360	2830
MO-4	exo	351	1973

The B3 biodiesel presented a higher thermal stability in relation to the others in the two studied atmospheres. This result was in agreement with the lowest unsaturation degree of the fatty acids (Table 2). In relation to the short carbon chains present in B3, it seems that longer esters led to a higher interaction among them avoiding volatilization at low temperatures.

Comparing TG and DTA curves of biodiesels (Figs. 4, 5) with the mixtures ones (Figs. 1, 2), a different behavior was obtained being observed that the DTA curves did not present the loop while TG curves did not present the temperature decrease. This difference can be explained by the chain size as biodiesel samples contain shorter molecules in relation to the mixtures, making volatilization easier and leading to the release of less amount of energy during combustion reactions.

DSC results of biodiesel samples are presented in Fig. 6, Table 6. The difference among the curves was related to the endothermic peak of the first step, relative to the ester volatilization. For B1 and B3, one endothermic peak was observed. For B2, two superposed endothermic peaks were found. For B4 sample, the endothermic peak was not observed, probably due to the higher amount of C18 esters as longer chains lead to

Fig. 4 TG and DTG curves of the biodiesel samples in synthetic air (**a**) and oxygen (**b**) atmospheres

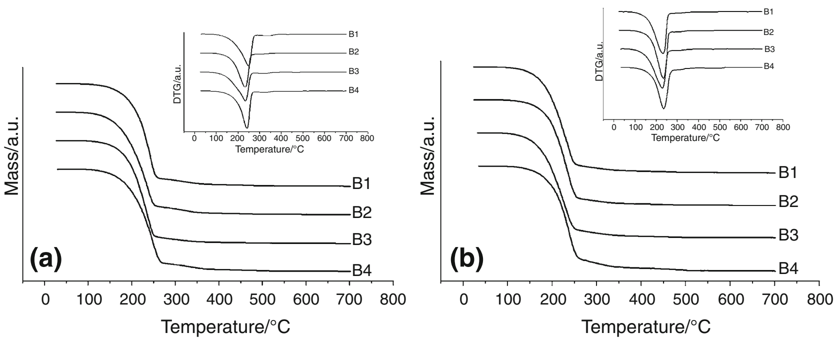
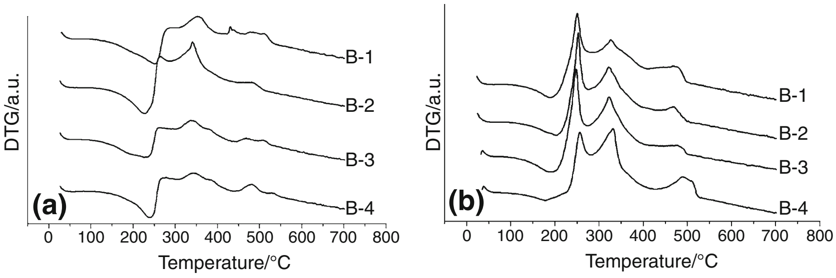


Table 5 Thermogravimetric results of the biodiesel samples

Sample	Atmosphere	Step	T $_{\text{initial}}$/°C	T $_{\text{final}}$/°C	Mass loss/%	T$_{\text{peak}}$/ºC DTG	T$_{\text{peak}}$/ºC DTA
B1	Synthetic air	1	62	295	94.5	248	253 (endo)
		2	295	413	5.5	348	358 (exo)
		3	–	–	–	–	429 (exo)
	O_2	1	71	291	95.9	232	250 (exo)
		2	291	518	4.1	314	327,477 (exo)
B2	Synthetic air	1	74	282	96.0	233	229 (endo)
		2	282	504	4.0	319	341, 481 (exo)
	O_2	1	83	285	95.5	234	253 (exo)
		2	285	486	4.5	314	322, 469 (exo)
B3	Synthetic air	1	79	285	94.0	235	236(endo)
		2	285	537	6.0	323	340, 465 (exo)
	O_2	1	89	279	94.0	229	247 (exo)
		2	279	507	6.0	311	322, 476 (exo)
B4	Synthetic air	1	76	289	94.4	242	241(endo)
		2	289	540	5.6	327	343, 484 (exo)
	O_2	1	88	287	94.5	236	256 (exo)
		2	287	532	5.5	325	333, 489 (exo)

Fig. 5 DTA curves of the biodiesel samples in synthetic air (**a**) and oxygen (**b**) atmospheres



higher London forces among molecules, making volatilization more difficult. In the others steps exothermic peaks were observed associated to the ester combustion. As in the mixture of raw materials, successive peaks were observed due to the heterogeneous characteristic of the samples.

In relation to the peak temperatures from DTA, DTG, and DSC curves, much lower values were obtained using DSC. This behavior is associated with the different configurations of each equipment and with the highest sensitivity of DSC technique making it possible to detect events at lower temperatures.

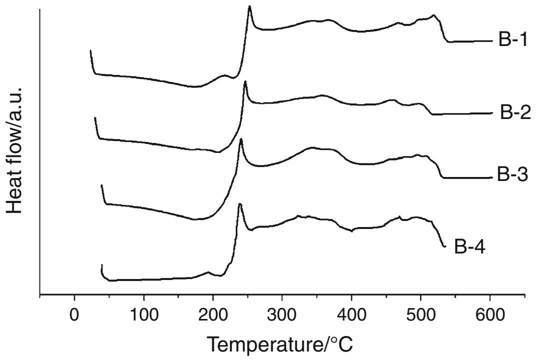


Fig. 6 DSC curves of the biodiesel samples in synthetic air atmosphere

Table 6 Calorimetric data of the biodiesel samples

Samples	Transition	T_{peak}/°C	Energy/J g^{-1}
B1	endo	174	99.8
	exo	252	59.3
B2	endo	176	3.6
	endo	205	8.8
	exo	246	26.6
B3	endo	170	4.3
	exo	240	59.8
B4	exo	195	57.4
	exo	240	55.8

Conclusions

The profile of mixtures of raw materials for biodiesel production and of the own biodiesel samples was evaluated using TG, DTA, and DSC techniques. The mixtures of raw materials presented combustion reactions and polymerization during analysis, as indicated by the increase in the mass loss of the third step when analysis was done in oxygen atmosphere. This polymerization was not observed in the biodiesel samples. On the other hand, volatilization was observed at different temperatures according to the chemical composition of the esters.

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