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Biodiesel from soybean oil, castor oil and their blends

Oxidative stability by PDSC and rancimat

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Abstract Even not being described in the EN 14112 standard, PDSC has been used for the determination of the biodiesel oxidative stability, by OIT and OT measurements. In this study, biodiesel blends were obtained by mixing soybean (BES) and castor (BEM) ethyl esters and its induction periods were measured by Rancimat and PDSC. The blends (BSM_X) showed intermediate values of OSI, OT, and OIT, compared with BES and BEM. Although, the molar fraction of the components varied linearly in BSM_X, OSI, OT, and OIT values increased exponentially in relation to the castor biodiesel amount in the blends. Introduction of castor oil biodiesel increased the blend stability, so the BSM_{30} blend reached the OSI limit of 6 h. OSI, OIT, and OT showed a high-linear correlation, pointing out that PDSC can be used in the analysis of this kind of biodiesel, with a smaller sample and analysis time, as compared to Rancimat. The use of biodiesel blends was a good alternative in the correction of the oxidative stability of the final product without the need of antioxidant addition.

Keywords Biodiesel · Blends · Rancimat · PDSC

Introduction

The use of biodiesel as fuel has become attractive mainly by ecological benefits as it is produced from renewable fonts [1]. In Brazil, among the raw materials used in the biodiesel obtaining soybean oil [2] and castor oil [3] can be cited. The fatty chains of these oils differ significantly in relation to the amount of unsaturations, bis-allylic hydrogens and hydroxyls, leading to different physico-chemical characteristics among them.

One of the main problems associated with the use of biodiesel is its susceptibility to oxidative processes, like autoxidation. This is a radical process that involves chain reactions with three steps, initiation, propagation, and termination. The process begins with the removal of allylic and *bis*-allylic hydrogens with the formation of free radicals ($LH + I \rightarrow L^{\cdot} + IH$), where LH is the lipid and I is the autoxidation initiator (as heat, light, and others). In the propagation, the triplet oxygen ($^3\Sigma_g^- O_2$) is added to a fatty radical forming peroxides ($L^{\cdot} + O_2 \rightarrow LOO^{\cdot}$) that react removing hydrogens from other chains to form hydroperoxides ($LOO^{\cdot} + LH \rightarrow LOOH + L^{\cdot}$; $LOO^{\cdot} + IH \rightarrow LOOH + I^{\cdot}$). The process occurs indefinitely until termination when non-radical products are formed ($LOO^{\cdot} + LOO^{\cdot} \rightarrow LOOL + O_2$; $2L^{\cdot} \rightarrow L_2$). Besides the presence of oxygen, several other factors interfere in the biodiesel oxidation, including light, heat, and contaminations such as

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water, residual catalyst from the transesterification process and metals [4–7].

During the initial oxidative process, the concentration of LOOH remains low by a time interval named induction period (IP). After the IP, the concentration of LOOH increases indicating the beginning of the propagation process.

The oxidation state of oils and biodiesels can be monitored by several physico-chemical techniques, like iodine, peroxide, and acidity indexes and viscosity measurements. Spectroscopic analysis and chromatography can also reveal the formation of peroxides, hydroperoxides and secondary oxidation products. The great disadvantage of these methods is the punctual measurement of the oxidation state, being necessary days or months for the complete determination of the oxidative stability. Although accelerated methods use unattainable situations in natural conditions, its application causes a great economy of time and amount of sample.

Among the accelerated methods for determination of oxidative stability there are the Rancimat methods (EN 14112, 110 °C [8]) and AOCS (Cd 12b-92, [9]). The oxidative stability for fatty acid esters may also be accompanied successfully by pressure differential scanning calorimetry (PDSC) [3, 10].

In the Rancimat method the Oil stability index (OSI) is measured being related to the sudden increase in the deionized water conductivity, where the volatile oxidation products are collected. In PDSC, the oxidation temperature (OT) is determined in the dynamic measurement and the oxidative induction time (OIT) is obtained in the isothermal curve. Both are related to the onset of the exothermic peak characteristic of the oxidative process.

A recent work invested the relationship between the Rancimat technique and PDSC for pure Fatty acid methyl esters (FAME′s) [11]. A good correlation between OT and OSI (EN 14112) was found at 80 °C, but a low correlation was observed at 110 °C. The authors did not find works relating OSI with OIT at 110 °C for biodiesel and their blends.

This study aims at evaluating the thermal and oxidative stability of the ethylic biodiesel of soybean oil (BES), of castor oil (BEM) and their blends (BSM_X—where X is the percentage of BEM in the blend) using PDSC and Rancimat to determine the correlation among OT, OIT, and OSI.

Experimental

The ethylic biodiesels of soybean (BES) and castor (BEM) oils were made by transesterification using KOH as catalyst [2, 3]. The blends (BSM_X) were prepared by addition of 25, 50, 75% (v/v) of BEM to BES, being denominated BSM25, BSM50, and BSM75, respectively.

The physicochemical analysis of acidity value (ASTM D-664), peroxide value (ASTM D-3703), iodine value (EN 14 111), kinematic viscosity, (ASTM D-445) and density (ASTM D-4052) were obtained for biodiesels and their blends, in order to determine the initial state of the samples and the influence of such parameters on oxidative stability [12–14].

The identification of fatty chains in the samples was made by a gas chromatograph mass spectrometer (GC–MS) SHIMADZU, model CGMS-QP2010. The used capillary column was a DB-23 (30 m; 0.25 mm; 0.25 μm), with helium as carrier gas, a flow of 96 mL min^{-1} and injection volume of sample of 1.0 μL.

The oxidative stability was determined according to the standard EN 14112 using Rancimat equipment (model 743 and 847, Metrohm). In this method, 3 g of sample were heated up to 110 °C, under constant air flow (10 L h^{-1}).

The dynamic and isothermal curves measured in the PDSC were obtained using a differential exploratory calorimeter (DSC 2920, TA Instruments) coupled to a pressure cell, using 10 mg of sample in a platinum crucible, oxygen atmosphere, and pressure of 1400 kPa. An isothermal measurement was done at the temperature of 110 °C. The OIT values were determined by the difference between the onset time and the initial time (time when the sample reached the isotherm temperature of 110 °C) [15]. In the dynamic measurement, sample was heated up to 600 °C with a heating rate of 10 °C min^{-1}.

Results and discussion

Table 1 shows the main components of BES, BEM, and BSM_X.

According to Table 1, 49.58% of polyunsaturated esters are present in BES while only 5.84% are present in BEM. As a consequence, the higher amount of BEM in the blend leads to a decrease in the concentration of polyunsaturated esters increasing the oxidative stability. It can also be observed that the composition percentage varied linearly for each blend, being observed a high increase in the

Table 1 Ethyl ester composition of biodiesels and their blends

Fatty chain	Biodiesels and blends/%				
	BES	BSM_{25}	BSM_{50}	BSM_{75}	BEM
Palmitic	13.64	10.46	7.14	4.36	1.44
Estearic	5.67	4.42	3.06	2.17	1.16
Oleic	25.27	19.74	13.99	9.10	3.99
Linoleic	42.45	33.21	24.00	14.63	5.29
Ricinoleic	0.00	22.32	45.49	65.23	85.83
Linolenic	7.13	5.40	3.58	2.11	0.55
Others	12.97	9.85	6.32	4.51	2.29

amount of ricinoleate and a great decrease of palmitate, oleate, and linoleate as the percentage of BEM in the blend increased.

The biodiesel blends were characterized by intermediate compositions of the original biodiesel's. This led to linear variations for some physico-chemical parameters, as showed in Table 2.

One of the parameters that varied linearly with the increasing amount of BEM in the blends was the acidity value. The increase of this parameter was directly related to an increase of the water amount in the biodiesel, favoring the process of hydrolysis and oxidation. In spite of the increase in the acidity, the values are still below the ASTM requirement [16].

The iodine value is a direct measurement of the unsaturation degree of the biodiesel, while the peroxide value measures the hydroperoxide amount, formed because of oxidation processes. As the oxidative stability is directly related to the unsaturation degree, the iodine value and the peroxide value varied in a decreasing way, except for the BSM_{75} that had an unexpected increase of the peroxide value. Owing to its low iodine and peroxide values the castor oil biodiesel tended to be more resistant to oxidation than the soybean biodiesel. This was because of the predominance of monounsaturated fatty esters in the castor oil biodiesel, that had ethyl ricinoleate (C18:1 OH) as main component. On the other hand, the highest oxidation tendency of the BES was caused by the highest amount of polyunsaturated fatty chains, around 50%. This way, a higher oxidative stability of BES may be reached after the blend preparation [16, 17].

The kinematic viscosity of the BEM (14.58 $mm^2\ s^{-1}$) was 3.3 times higher than BES one (4.50 $mm^2\ s^{-1}$). This result was already expected as BEM had hydrogen bonds among its chains due to the hydroxyl group in the ricinoleic fatty acid. This behavior was extended to the blends, whose viscosities increased with the concentration of castor oil biodiesel. The density results presented a tendency similar to the kinematic viscosity.

Isothermal and dynamic PDSC curves are shown in Fig. 1 and results are described in Table 3.

Moser [11] determined the oxidative stability of fatty acid ethyl esters by Rancimat and dynamic PDSC. An OSI value higher than 40 h was found for stearate ethyl ester, while values of 3.5, 1.1, and 0.2 h were found for ethyl esters of oleate, linoleate, and linolenate, respectively. OT values of 195.9, 176.8, 142.2, and 129.2 °C, were found for the ethyl esters of stearate, oleate, linoleate, and linolenate, respectively. In relation to ricinoleates, OSI and OT values were only found for the methylic ester [11]. The author showed that the hydroxyl group in the C18:1 fatty chain reduces the oxidative stability, in relation to the methyl oleate, but has a higher stability than polyunsaturated methylic esters. This result indicates that the hydroxyl group does not lead to an oxidation site as reactive as the allylic and bis-allylic hydrogens, in the fatty chains.

In this case, the BEM had 86% of ethyl ricinoleate, 7% of saturated esters and only 6% of polyunsaturated esters, being quite stable, with OSI of 48 h. This result is in agreement to the low value of peroxide index in relation to BES, which was more susceptible to the formation of peroxides in accelerated tests and in natura, with an induction period (OSI) of 2.55 h (below the inferior limit of 6 h established by the standard EN 14112).

BES presented a smaller OIT, while the BEM presented an OIT 18.5 times higher. Values of OIT for the fatty acid ethyl esters were not found in the literature, but as in the OT, the polyunsaturated chains led to less stable biodiesels.

The blends showed intermediate values of OSI, OT, and OIT, compared with BES and BEM. Although the molar fraction of the components varied linearly in BSM_X, OSI, OT, and OIT values, increase exponentially in relation to the percentage of castor oil biodiesel in the blends, Fig. 2. This result shows that the desired oxidative stability can be achieved in the blends without the need for antioxidants.

Through the exponential adjustment, it was possible to verify that the BSM_{30} blend reached the inferior limit of the standard EN 14112, indicating that at least 30% of BEM should be added to BES to attain the desired oxidative stability.

OT values showed a small increase for BSM_{50}. This value cannot be compared to OIT or OSI, as different properties are evaluated. While OT is related to the temperature necessary for oxidation, OIT and OSI are related to the time, being assigned to kinetic aspects. Moreover, in spite of this increase, Fig. 3 showed an excellent linear

Table 2 Physicochemical properties of biodiesels and their blends

Physical-chemical analyses	BES	BSM_{25}	BSM_{50}	BSM_{75}	BEM	Requirements [16]
Acidity value/mg KOH g^{-1}	0.25	0.27	0.33	0.36	0.42	≤0.80
Peroxide value/mEq kg^{-1}	39.25	30.80	29.85	35.92	14.78	–
Iodine value/mg I_2 100 g^{-1}	143.95	130.35	119.72	104.16	91.14	≤120
Kinematic viscosity 40 °C/$mm^2\ s^{-1}$	4.50	5.81	7.73	10.77	14.89	1.9–6.0
Density 20 °C/kg m^{-3}	876.3	888.1	896.9	905.8	915.7	–

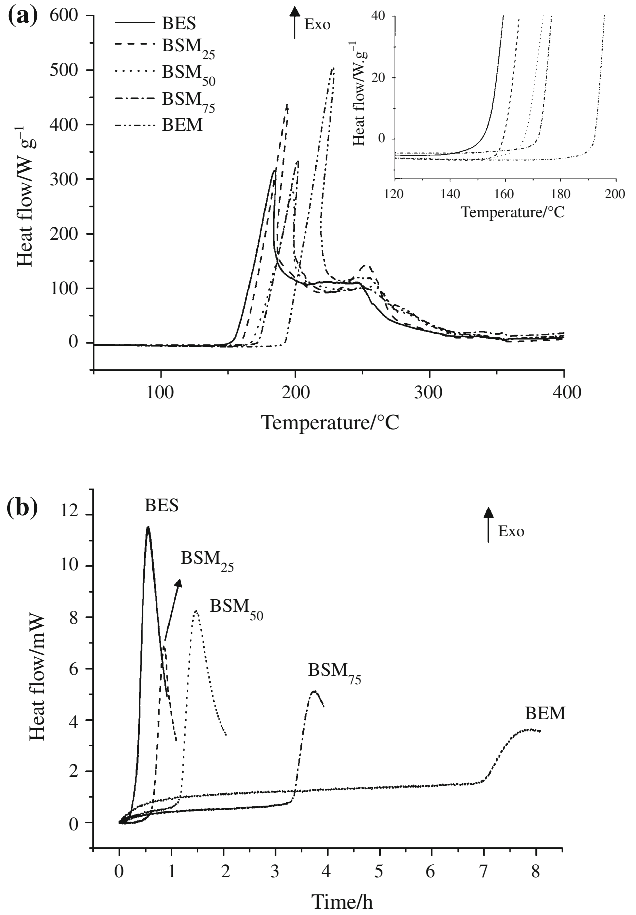

Fig. 1 PDSC dynamic curves (**a**) and isothermal curves (**b**) for the biodiesels and blends

Table 3 Parameters of oxidative stability

Parameters of oxidative stability	Biodiesels and blends				
	BES	BSM$_{25}$	BSM$_{50}$	BSM$_{75}$	BEM
OT/°C	161.43	161.53	169.47	173.37	192.85
OIT/h	0.38	0.71	1.23	3.35	7.01
OSI/h	2.55	4.07	9.30	22.17	48.00

correlation between OSI and OIT and between OSI and OT, although the measurements done by Rancimat and PDSC are related to different stages of the oxidation mechanism. That correlation can not be guaranteed for other biodiesels and blends, once methyl esters that contained less than ten carbons in the fatty acid chain can not be analyzed at 110 °C (EN 14112) because of excessive sample evaporation.

Once guaranteed the correlation among those techniques for biodiesels of soybean, castor oil and their blends, it was determined that the OT (°C) and OIT (h) that corresponded to the inferior limit of the standard EN 14112 (OSI = 6 h, 110 °C) was 164.2 °C and 1.99 h, respectively.

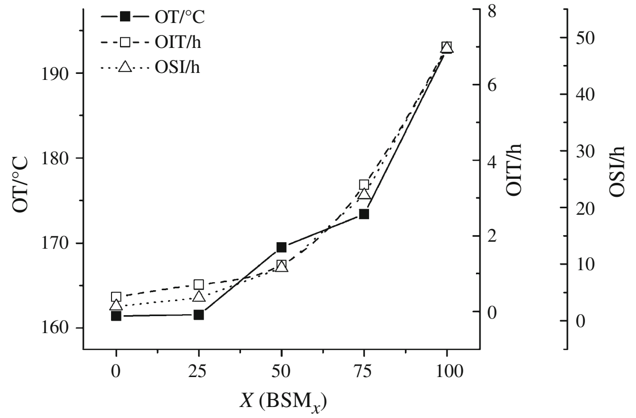

Fig. 2 OT, OIT, and OSI values as a function of castor oil biodiesel amount in BSM$_x$ blends

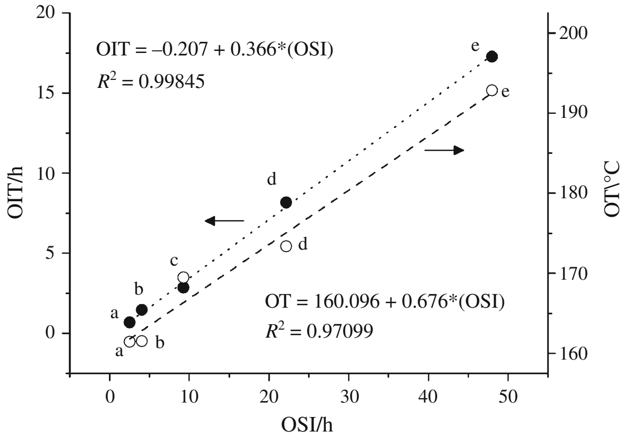

Fig. 3 Correlation between Rancimat and PDSC according to °C isothermal analyses at 110 (**a** BES. **b** BSM$_{25}$. **c** BSM$_{50}$. **d** BSM$_{75}$. **e** BEM)

Comparing the two techniques used in determination of oxidative stability, PDSC had the advantage of increasing the total number of oxygen moles present in the cell avoiding the loss of volatile components of biodiesel, besides the acceleration of the oxidative reaction at low temperatures [18]. Another advantage is the possibility of kinetic parameters determination using dynamic and isothermic measurements.

Conclusions

According to the characterization techniques used in this study, the addition of BEM to BES increased the BSM$_X$ blends oxidative stability. A direct correlation was observed between the PDSC and Rancimat techniques (standard method EN 14112). An excellent linear correlation was observed among the values of OSI, OT and OIT.

Through the exponential adjustment of the graph showing OT, OIT, OSI values as a function of the blend composition, it was shown that the BSM_{30} blend reached the inferior limit for the value of 6 h of OSI, corresponding to about 2 h of OIT and 164.2 °C of OT. It could also be concluded that the use of biodiesel blends was a good alternative in the correction of the oxidative stability of the final product without the need of antioxidant addition.

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