

Use of different techniques in the evaluation of the oxidative stability of poultry fat biodiesel

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Abstract The poultry fat methyl (BMF) and ethyl (BEF) biodiesels were synthesized through transesterification by homogeneous basic catalysis. The chromatographic analyses showed the palmitic, stearic, oleic, and linoleic esters as majority components. Owing to its considerable amount of polyunsaturated fat acids, poultry fat usually leads to a biodiesel with low oxidative stability. In this study, the oxidation of their ethyl and methyl biodiesels was evaluated by Rancimat, PDSC, and PetroOxy. The OSI (Rancimat) was of 0.47 and 0.40 h for the ethyl and methyl biodiesel, respectively. In PDSC, both fuels presented an OT of about 120–123 °C. PetroOxy analysis indicated an OxyStab of 11 min for BEF and higher than 11 min for BMF. There was no correspondence among the oxidative stabilities of the employed techniques [OT(BEF) \approx OT(BMF), OSI(BEF) > OSI(BMF), and OxyStab(BEF) < OxyStab(BMF)]. The discussion of these results was based on the indicator measured by each technique: enthalpic events are observed by PDSC; conductivity of volatile secondary oxidation products is measured by Rancimat; reduction of the oxygen pressure is determined by PetroOxy. This discussion showed that these

different indicators do not reflect the same stage of the oxidative process as energy is released at the beginning of the propagation step, oxygen pressure decreases during the propagation step, and oxidation products are formed during the termination step.

Keywords Oxidative stability · Biodiesel · Poultry fat · PDSC · Rancimat · PetroOxy

Introduction

An important problem associated to commercial biodiesel acceptance is its low oxidative stability [1], which is determined by the nature of the fatty acid chains of oils or fats [2]. This fact can be evidenced by the relative values of the oxidation rate that have already been obtained for oleates (C18:1), linoleates (C18:2), and linolenates (C18:3), respectively, as 1: 41: 98 [3].

In relation to poultry fat, variations in fatty acid composition may be due to different factors as genetic origin, age, and sex of the poultries. The vitamin used in the poultry nutrition is another factor for the variation in fatty acid composition and in lipid deposit, especially in monogastric animals [4]. In general, poultry fat has a high tendency to unsaturated chains. Guzman et al. [5] compared the oxidative stability of biodiesels obtained from soybean oil and from poultry fat and showed that soybean biodiesel had a higher oxidative stability than poultry fat one.

The autoxidation is a radical process that involves basically three steps: (i) initiation ($LH + I \rightarrow L^\bullet + IH$), (ii) propagation ($L^\bullet + {}^3O_2 \rightarrow LOO^\bullet$; $LOO^\bullet + LH \rightarrow LOOH + L^\bullet$), and (iii) termination ($LOO^\bullet + LOO^\bullet \rightarrow LOOL + {}^3O_2$; $LOO^\bullet + I^\bullet \rightarrow LO + IO$), where LH is the

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lipid and I is the autoxidation initiator. Besides the presence of light and heat, several other factors interfere in biodiesel oxidation, including contaminations such as water, residual catalyst from the transesterification process and metals [6–9]. During the beginning of the oxidative process, the concentration of LOOH is low during a period known as induction period (IP). During the propagation step, hydroperoxide concentration increases abruptly, indicating the beginning of the global oxidative process. The process proceeds until the termination step, when the consumption of the radicals and formation of stable products occurs.

Accelerated tests have been used as experimental tools in the understanding of the lipid oxidative properties. The most used ones are Rancimat (EN 14112 method, [10]), PetroOxy (ASTM D 7545) and Pressurized differential scanning calorimetry (PDSC). Some works comparing the different techniques [11, 12] were used to evaluate the oxidative stability with reproducibility and reduction of time and amount of sample in relation to the Rancimat method, more commonly used in biodiesel monitoring. Unfortunately few works about oxidative stability of biodiesel derived from poultry fat were found in literature [5].

The objective of this study was to investigate the oxidative stability of ethyl and methyl biodiesels derived from poultry fat using Rancimat, PDSC, and PetroOxy methods.

Experimental

For the obtainment of the biodiesel derived from the poultry fat, the transesterification reaction was used with KOH as homogeneous catalyst. Methanol and ethanol routes were used with a molar ratio of 1:6 (poultry fat/alcohol) [13–16]. The analytic indexes of acidity (ASTM D-664), iodine (EN 14111), free glycerin (ASTM D-6584), total glycerin (ASTM D-6584), kinematic viscosity (ASTM D-445), free fatty acids [17], and specific mass (EN ISO 3675/EN ISO 12185) were obtained for the two biodiesels.

The esters composition was determined using Shimadzu CGMS-QP2010 gas chromatography–mass spectrometry (GC–MS) with a Durabond capillary column (DB-SHT), helium as carrier gas with a flow of 3 mL min⁻¹ and a detector temperature of 250 °C.

The values of oil stability index (OSI) were obtained from the Rancimat curves according to the method EN 14112 [10], using the Metrohm Rancimat 743 equipment. In this method, 3 g of sample were heated at 110 °C under constant air flow (20 L min⁻¹). The formed volatile gases were collected in deionized water whose conductivity was monitored.

Samples were analyzed in a pressure differential scanning calorimeter, model DSC 2920 from TA Instruments. The analyses were done using 10 mg of sample in a platinum crucible, oxygen atmosphere, pressure of 1400 kPa and heating rate of 10 °C min⁻¹. The oxidation temperature (OT) was obtained by the intersection between the extrapolation of the baseline and the tangent of the first exothermic peak. Isothermal analyses were done in the same conditions of pressure and atmosphere at temperatures of 80, 90, and 95 °C to determine the oxidative induction time (OIT). The OIT values were determined by the difference between the onset time and the initial time when the sample reached the isotherm temperature [17].

The PetroOxy curves were obtained in the Petrotest PetroOxy 13-3000 equipment, based on the ASTM D525 Standard, with the following analysis conditions: 5 mL of sample, oxygen pressure of 650 kPa, and isothermal temperature of 140 °C. The oxidative stability (OxyStab) was measured as the time necessary to attain 10% of reduction from the maximum pressure obtained.

Results and discussion

Table 1 shows composition of the poultry fat, the methyl (BMF), and ethyl (BEF) biodiesels and the oxidative stability indexes of each pure component, according to Moser (2009) [12], obtained by PDSC and Rancimat. The composition of the poultry fat presented great proportion of palmitic, oleic, and linoleic acid chains. The biodiesels composition was maintained similar to the oil, with significant reduction of the linoleic acid fat chain after the transesterification reaction, mainly in the ethyl biodiesel. This reduction is probably inherent to process of the purification. This behavior was already observed in soybean biodiesel by Candeia et al. [16] and indicated that other reactions besides transesterification occurred during biodiesel synthesis.

Table 2 shows the physicochemical properties and the oxidative stabilities of the ethylic and methyl biodiesels. Similar values of acidity values, free glycerin, total glycerin, kinematic viscosity, and specific mass were found for the biodiesels. The iodine value was higher for BMF due to the highest amount of polyunsaturated fatty acids, as showed in Table 1. The free fatty acid value was also higher for BMF, although both values were low. In that way, all the verified physicochemical parameters were in accordance with the ASTM D6751-02 [18] requirements and EN 14214 standard specifications [19], indicating the good quality and the similarity among BMF and BEF biodiesels.

The OSI values of the BEF and BMF biodiesels were of 0.47 and 0.40 h, respectively, below the minimum limit of

Table 1 Fatty acid chromatographic profile of the poultry fat, the ethylic and the methylic biodiesels, and the oxidative stability parameters of the methylic and ethylic (in *parenthesis*) fatty acids [12]

Fatty acid	Composition/%			Oxidative stability [12]	
	Poultry fat	BEF	BMF	OSI/h	OT/°C
Miristic C _{14:0}	0.70	0.94	1.07	>40	198.5
Palmitic C _{16:0}	25.57	29.74	29.05	>40	198.4
Palmitoleic C _{16:1}	3.62	4.16	4.23	2.1	172.9
Stearic C _{18:0}	7.75	11.21	10.49	>40 (>40)	197.2 (195.9)
Oleic C _{18:1}	36.64	40.53	39.56	2.5 (3.5)	174.9 (176.8)
Linoleic C _{18:2}	24.69	7.40	14.13	1.0 (1.1)	142.6 (142.2)
Linolenic C _{18:3}	1.02	–	–	0.2 (0.2)	129.8 (129.2)
Others	–	6.02	1.47	–	–

Table 2 Physicochemical characteristics from ethylic and methylic biodiesel

Analysis	Units	BEF	BMF	Limits [19]
Acidity value	mg KOH/g	0.28	0.27	≤0.80
Iodine value	g I ₂ /100 g	100.0	106.0	≤120
Free glycerin	% mass	0.010	0.010	≤0.020
Total glycerin	% mass	0.180	0.170	≤0.240
Free fatty acids	% mass	0.14	0.28	–
Cinematic viscosity at 40 °C	mm ² /s	4.75	4.71	1.9–6.0
Specific mass at 15 °C	kg/m ³	877	877	860–900
PDSC (OT)	°C	120	123	–
Rancimat at 110 °C (OSI)	h	0.47	0.40	≥6.0
PetroOxy (OxyStab)	min	11	>11	–

6.0 h determined by the EN 14214 standard. According to literature [12], the saturated fatty acid chains are responsible for the high OSI values (>40 h), while the unsaturated chains present values among 3.5–1.0 h. As the OSI values obtained in this study were smaller than the majority component ones, the authors believe that the biodiesels already presented hydroperoxides, metals, or other substances responsible for the oxidative stability decrease. No preliminary tests were done in the biodiesel.

The oxidative stability was also evaluated by PDSC dynamic curves as showed in Fig. 1a, b.

Both biodiesels presented an OT around 120–123 °C (insert in Fig. 1a), smaller than the OT values of their majority components, showed in the Table 1. As well as in Rancimat, these results indicated that a previous oxidation reaction occurred. This reaction could be due to the process of fat extraction from poultry that is done under heating. The free radicals, peroxides, and hydroperoxides formed in this raw material could be extended to the biodiesels.

In spite of this drawback, the process of fat extraction applied in this study was chosen because it is the conventional one adopted by food industry, due to its low cost and to the absence of solvent, the so called green chemistry.

Even in a chemical method, the use of hexane as solvent would be necessary besides heat to guarantee its separation from the fat, which could also lead to pre-oxidation.

Another indication of this behavior is the isothermal curves presented in Fig. 1c. In the 95 °C isothermal curve a small exothermic peak was observed, but it was not possible to determine the OIT value because this peak started before the temperature stabilization. At lower temperatures, the exothermic peak got broader, making evaluation more difficult.

The behaviors observed in the isothermal curves were probably related to the profile of the dynamic curves. Comparing the present PDSC curves (Fig. 1a) with the profile of the FAME and FAEE pattern curves [20, 21], an atypical behavior could be observed—two superposed exothermic peaks were present at the beginning of the oxidation process. This behavior was clearly observed in Fig. 1b that shows the first derivative for this region with two well-defined peaks. The first step occurred in the same temperature range for BEF and BMF, while the second one was observed at lower temperatures for BEF.

The evaluation of the induction period by the PetroOxy method is illustrated in the Fig. 2. For the OxyStab

Fig. 1 **a** PDSC dynamic curves of BEF and BMF; the determination of OT is shown for BMF; **b** application of the first derivative for the first exothermic events; **c** isothermal curves of the BEF

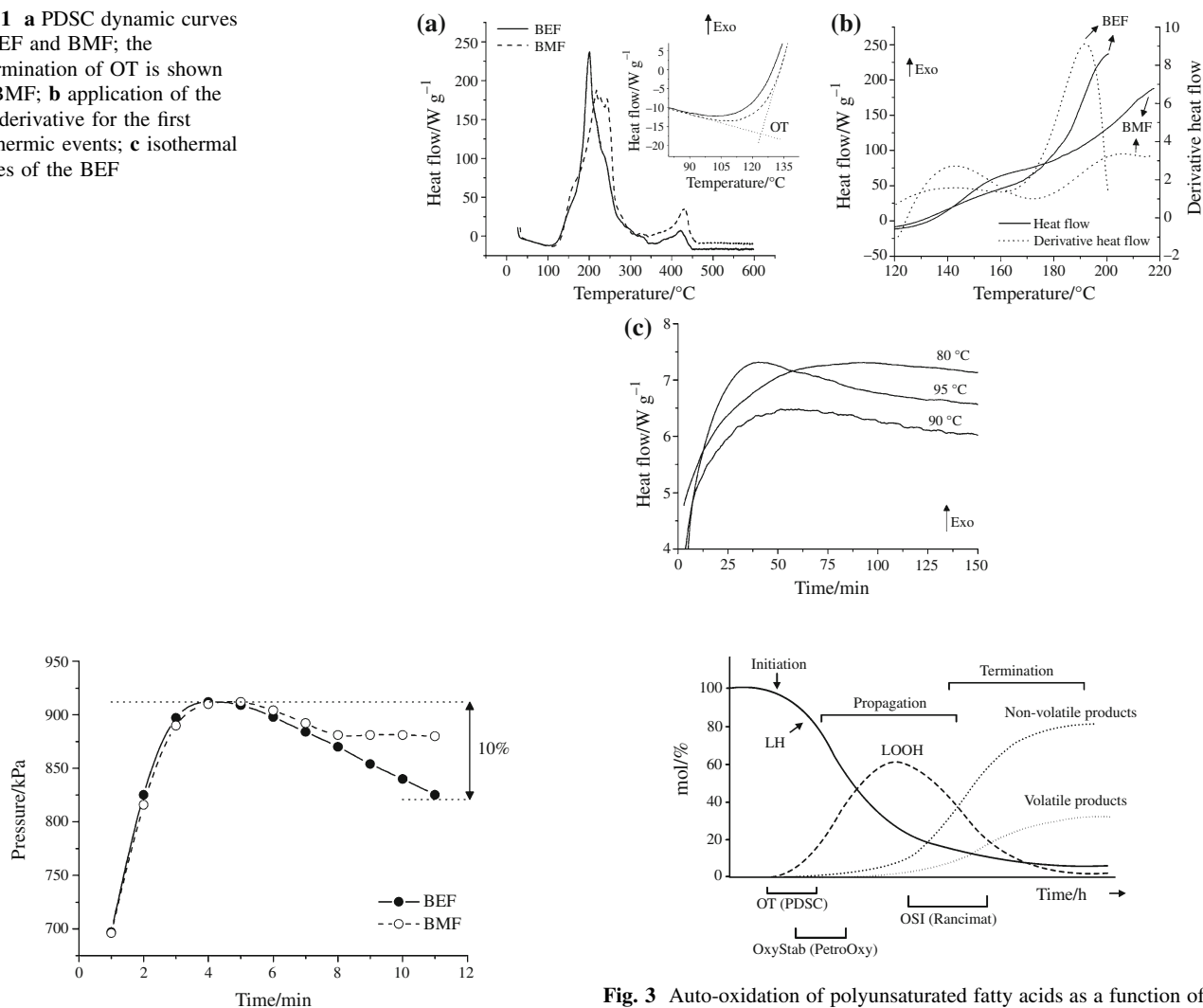


Fig. 2 Pressure as a function of time obtained by the PetroOxy method

measurement, an induction time of about 11 min was verified for the BEF and higher than 11 min for the BMF, which presented pressure stabilization from the 8 min of analysis. The OxyStab result is probably related to the propagation step of the oxidation mechanism as it is related to the oxygen consumption associated to the reaction between free radicals and oxygen for hydroperoxide formation. The OxyStab signal could be accelerated if sample already contains peroxy radicals and retarded for previous formation of volatile products.

As already observed in PDSC curves an atypical behavior was observed in PetroOxy curves of the poultry fat biodiesels. The beginning of the oxidation occurred simultaneously for both biodiesels as showed in the first derivative of the beginning of the exothermic peak in the PDSC curve, while the second oxidation step occurred just after the first one for BEF with the continuous pressure

Fig. 3 Auto-oxidation of polyunsaturated fatty acids as a function of the time, showing the superposing of several reaction steps. (Adapted from Gardner, 1987) [22]

decrease. For BMF biodiesel, the formation of a plateau was observed in the PetroOxy curve, after the first pressure decrease.

The stability order obtained by the three different techniques showed that $OT(BEF) \approx OT(BMF)$, $OSI(BEF) > OSI(BMF)$, and $OxyStab(BEF) < OxyStab(BMF)$. The correlation lack sometimes observed among the different methods can be related to the indicator measured by each technique: exothermic events are observed by PDSC, related to the beginning of the propagation step; conductivity of volatile secondary oxidation products is measured by Rancimat being related to the termination step; 10% of reduction in the oxygen pressure is determined by PetroOxy, assigned to the propagation step (not exactly at the/beginning). This way the authors believe that the different techniques do not reflect the same step of the oxidation mechanism (Fig. 3).

In relation to the accuracy of each technique some important points should be emphasized. In the PDSC analyses the oxidation beginning was accompanied by the exothermic peak, without volatile loss, due to the high O₂ pressure, around 1400 kPa. The volatile polar compounds may influence the oxidation process so that its presence is important to assure the reproducibility and the accuracy of the OT values. Comparing PetroOxy and PDSC curves a similar behavior can be observed at the beginning of curve, related to the peroxidation reactions that lead to the exothermic peak observed in PDSC and to the oxygen consumption observed in PetroOxy. The difference is that OT value in PDSC curve is established as the exothermic peak onset, while the OSI value is related to a 10% of decrease in oxygen pressure. The smaller OSI values in Rancimat analyses can be due to the presence of volatile polar compounds formed due to oxidation reactions during storage. As this signal is assigned to the product formation, the OSI values are more directly related to the sample rancidity than to its resistance to thermal oxidation.

The speed of the initiation, propagation (hydroperoxide formation), and volatile compound formation depend on the stability of each substance in the biodiesel. As a consequence different behaviors can be observed by the different techniques. In that way, correspondence among them depends substantially on the nature of the sample.

Conclusions

No correspondence was observed among PDSC, PetroOxy, and Rancimat techniques in the evaluation of the oxidative stability of biodiesels derived from poultry fat. The stability order presented by the techniques was OT(BEF) \approx OT(BMF), OSI(BEF) > OSI(BMF), and OxyStab(BEF) < OxyStab(BMF). The correlation lack was assigned to the different signals detected by the three techniques, which are assigned to different steps of the oxidation mechanism. PDSC and PetroOxy are related to the propagation mechanism but not exactly the same region, as the onset temperature of the exothermic peak is measured in PDSC curves and 10% of oxygen pressure decrease is measured by PetroOxy. In Rancimat, only the termination step is evaluated by the formation of volatile polar compounds.

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