

Influence of the storage on the thermo-oxidative stability of methyl and ethyl esters by PDSC

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Abstract Biodiesel oxidation is a complex process widely influenced by the chemical composition of the biofuel and storage conditions. Several oxidation products can be formed from these processes, depending on type and amount of the unsaturated fatty acid esters. In this work, fatty acid methyl and ethyl esters were obtained by base-catalyzed transesterification of soybean oil and physico-chemically characterized according to standards from ASTM, EN, and ABNT. The thermal and oxidative stabilities of biodiesel samples were investigated during the storage process by pressure differential scanning calorimetry (PDSC) and by viscosity measurements. Absolute viscosities of biodiesels after accelerated aging were also determined. The viscosity increased as the aging temperature and time were raised. The results showed that oxidation induction can occur during storage, decreasing the biodiesel stability. PDSC analysis showed that during storage under climate simulation the values of high-pressure oxidative induction times (HPOIT) were reduced for both FAEE and FAME.

Keywords Soybean biodiesel · Storage · Accelerated aging · Oxidative stability · PDSC

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Introduction

Vegetable oils have been considered an appropriated biomass source for the consolidation of renewable energy programs, since they offer alternatives to economic, social, and environmental problems [1–3]. The most common method to produce biodiesel is through the transesterification of vegetable oils and animal fats via alkaline catalysis, where the triglycerides are converted into fatty acid esters by reaction with alcohol, usually methanol or ethanol [4–6].

The biodiesel quality obtained from several oil sources is associated to different parameters, which can be divided in two groups—the physico-chemical parameters (cetane index, flash point, viscosity, distillation, etc.) and the chemical composition (free and total glycerin, iodine index, mono-, di-, and triacylglycerides, etc.) [7].

Several studies have been carried out in order to monitor the biodiesel quality during storage in different conditions [8–12]. Storage stability may be affected by interaction with contaminants, light, and factors causing sediment formation, changes in color and other changes that reduce the clearness of the fuel [13]. Oxidative degradation during storage can hamper the fuel quality, with effects in kinematic viscosity, acid value, cetane number, total ester content, and with the formation of hydroperoxides, soluble polymers, and other secondary products [14].

Monyem et al. [15] reported steady increases in acid value and kinematic viscosity when soybean oil fatty acid methyl esters were subjected to simulated in-use diesel engine conditions. The peroxide value (PV) first increased, and then leveled off at a maximum value near 350–400 meq/kg oil. Dunn [16] showed a decrease in PV with increasing reaction temperature for soybean biodiesel under severe thermal-oxidative reaction conditions. In

another study Dunn [17] reported that, increasing the temperature accelerated the oxidation reaction, causing a decrease in the oil stability index (OSI) of soybean oil fatty acid methyl esters (SME). On the other hand, antioxidant additives are commonly employed to improve the oxidative stability of biodiesel. Tang et al. [18] investigated the effectiveness of various antioxidants to improve the storage stability of soybean biodiesel. The results indicated that the induction period (IP) of untreated biodiesel significantly decreased with the increasing storage time, while the IP values with the addition of *t*-butylhydroquinone (TBHQ) to biodiesel remained constant for up to 30 months. Other works with natural and synthetic antioxidants have reported an improvement in the stability of biodiesel [19–21].

The oxidation of saturated fatty acids by free radical formation is thermodynamically unfavorable. On the other hand, the presence of double bonds in the chain decreases the energy necessary for the homolytic breakage of C–H bond in the allylic position, favoring the biodiesel oxidation [22, 23]. The oxidation mechanism results from successive radical reactions over the fatty acids unsaturations, initiated by singlet oxygen [2]. The overall mechanism presents three stages: initiation, propagation, and termination (Fig. 1). The final products derive from hydroperoxide decomposition that leads to the formation of aldehydes, ketones, acids, and other oxygenated compounds [24]. However, double bonds can also be oriented by means of side polymerization reactions producing insoluble species that can obstruct lines and pumps of the engine system and increase the biodiesel viscosity.

The oxidative stability is defined as the sample resistance to oxidation and it is expressed by the induction time (period between the beginning of the test and the moment in which there is an abrupt increase of the product formation) [26]. The induction period, also called the oxidative stability index, is widely used for quality control of raw materials and processes. Several methods can be employed to determine the oxidative stability of the

biodiesel: Greenhouse Method and Active Oxygen Method, Rancimat, Oil Stability Instrument, Nuclear Magnetic Resonance and Infrared Spectroscopy, Pressure Differential Scanning Calorimetry, and others [20, 27, 28].

The present work aims at evaluating the thermo-oxidative stability of methyl and ethyl soybean biodiesels as a function of oxygen exposition time, aging test temperature, and long-term storage. The oxidative processes were identified by means of absolute viscosities, UV–Vis absorption spectroscopy and PDSC techniques.

Experimental

Fatty acid methyl and ethyl esters (FAME and FAEE, respectively) were obtained by base-catalyzed transesterification of soybean oil [29, 30]. The physicochemical characterization of the samples was carried out according to the standards from ASTM, EN, and ABNT, in order to assess if the requirements from ANP (Brazilian National Agency for Petroleum, Natural Gas and Biofuels) were met.

For the aging tests, the biodiesel samples were maintained under airflow of 30 mL min^{-1} produced by a commercial pump. The air humidity was controlled using trap systems containing H_2SO_4 and silica. The contact temperatures between air and biodiesel were 150, 170, 190, and 210 °C. For each temperature samples, 50 mL were collected after 1, 6, 12, 24, 36, and 48 h. The absolute sample viscosities were determined at 25 °C, using a Brookfield LV-DVII viscometer, with a small sample adapter coupled to a temperature controller. The storage tests were carried out as follows: biodiesel samples were stored for a total period of 90 days in steel–carbon containers with nylon caps. The containers were exposed to external conditions (sun radiation and rain) in order to simulate the ordinary gas station conditions. At each 15 days, samples were collected being identified as 15, 30, 45, 60, 75, and 90 days. These samples were immediately analyzed by PDSC and UV–VIS absorption spectroscopy.

The PDSC curves were obtained in a differential scanning calorimeter DSC 2920 TA Instruments, coupled to a pressure cell. For the dynamic mode, 10 mg of sample were analyzed in a platinum pan under oxygen atmosphere with a pressure of 1400 kPa at a heating rate of 5 °C min^{-1} in the 25–500 °C temperature range. The isothermal measurements were carried out at the same conditions of atmosphere, pressure, and sample quantity but at a constant temperature of 110 °C (for samples stored from 0 to 45 days) and 100 °C (storage between 60 and 90 days) for 60 min. The high-pressure oxidative induction times (HPOIT) were determined by the difference between the exothermic peak onset and the initial time when isotherm temperature was reached.

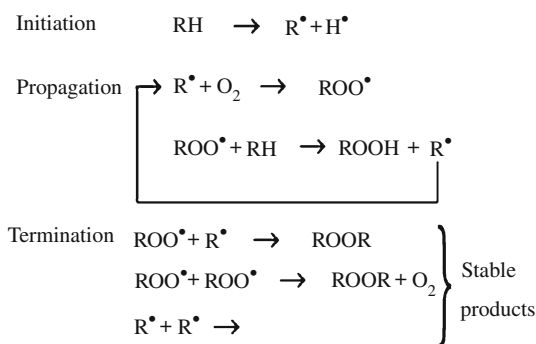


Fig. 1 Scheme of auto-oxidation reaction of fatty acids [25]: R^\bullet = free radical, RH = unsaturated fatty acid, ROO^\bullet = peroxide radical, ROOH = hydroperoxide

Table 1 Physicochemical parameters of FAME and FAEE

Parameter	FAME	FAEE	ANP specifications
Iodine index/g I ₂ /100 g	114	105	NC
Humidity/% water	0.04	0.05	0.05
Free glycerin %/m/m	0.01	0.01	0.02
Total glycerin %/m/m	0.19	0.17	0.25
Kinematic viscosity at 40 °C/mm ² s ⁻¹	5.75	5.83	3.0–6.0
Specific mass at 20 °C/kg m ⁻³	882.8	878.4	850–900
Distillation/°C			
Initial boiling point	327	335	(1)
50% recovered, max	334	341	
85% recovered, max	340	348	
Final boiling point	352	362	
Flash point, min/°C	168	170	100
Total sulfur, max/%	0.00	0.00	50
Cetane index, min	56	60	45
Cold filter plugging point	-5	10	19 (2)
Copper corrosion, 3 h at 50 °C, max	1	1	1

NC = not cited; (1) Temperature equivalent to atmospheric pressure; (2) Valid for South, Southeast, Center-west regions and for Bahia State from Brazil

Table 2 Fatty acid composition of FAME and FAEE

Fatty acid	FAME/%	FAEE/%
C 14:0	0.083	0.09
C 16:0	13.32	16.08
C 18:0	4.81	5.82
C 20:0	0.42	0.52
C 22:0	0.52	0.67
C 16:1 (9)	0.069	0.098
C 18:1 (9)	24.54	25.46
C 18:2 (9,12)	55.39	50.09
C 18:3 (9,12,15)	0.11	0.180
Other	0.74	0.99

Results and discussion

Table 1 shows the physicochemical parameters of FAME and FAEE, indicating that all samples were in agreement with the standards, emphasizing good quality of the obtained biofuel.

The fatty acid composition of the soybean biodiesels (FAME and FAEE) was determined by gas chromatography (Table 2). These samples were mainly constituted by oleic (25%) and linoleic (50–55%) acids. This high proportion of unsaturated fatty acids (75–80%) leads to a low oxidative stability for the biofuel.

To verify the oxidative stability of these biodiesels, accelerated aging, and storage tests were performed. Figure 2 illustrates the values of absolute viscosities as a

function of time and temperature of the aged samples. As expected, the viscosity increased as the aging temperature and time were raised. According to previous degradation studies, different factors are important in the viscosity change, the breakage of the ester chains, release of volatile products, and oxidation of ester chains and polymerization of non-volatile materials [31, 32]. In this study, oxidation and polymerization were more pronounced than the other two factors leading to the viscosity increase especially at higher aging periods. The viscosity of samples aged at 210 °C for 48 h could not be measured due to its high values.

Storage condition of the seeds, extraction procedure and treatment of the extracted oils can also affect the stability of the biofuel and consequently its quality. The oxidative stabilities of the samples were evaluated by PDSC analyses (Fig. 3). The onset and the peak temperatures for FAME oxidation were 146 and 163 °C and 152 and 169 °C for FAEE, respectively (Fig. 3a). At higher temperatures, other oxidation steps were observed, leading to peak temperatures of 216 and 219 °C for FAME and FAEE. These results indicated that these events were related to polymerization reactions, as a meaningful increase in viscosity was observed after aging at 210 °C (Fig. 2) that may related to an increase in chain size. Peaks assigned to combustion reactions were observed at 435 °C for FAEE. For FAME a smaller peak was observed.

The HPOIT values were 24.5 min (FAME) and 50.2 min (FAEE), as determined in the isothermal curves

Fig. 2 Absolute viscosities of aged FAME (a) and FAEE (b)

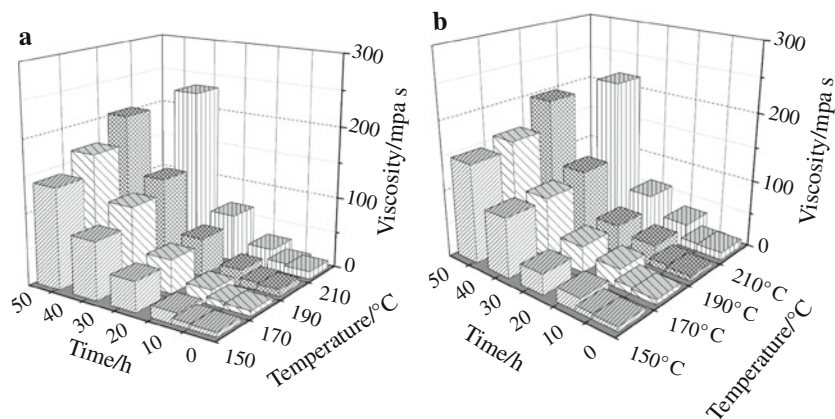


Fig. 3 PDSC dynamic (a) and isothermal (b) curves of FAME and FAEE before storage

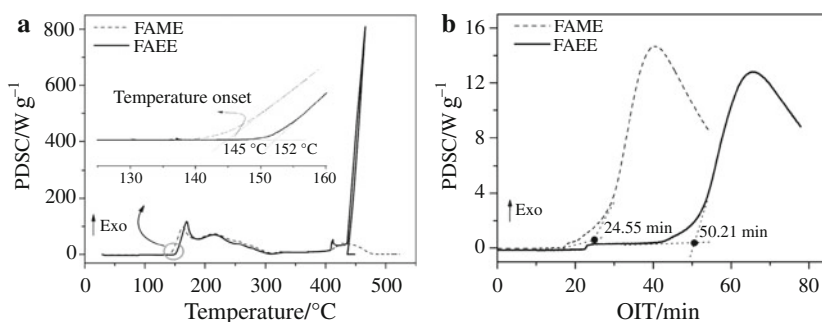
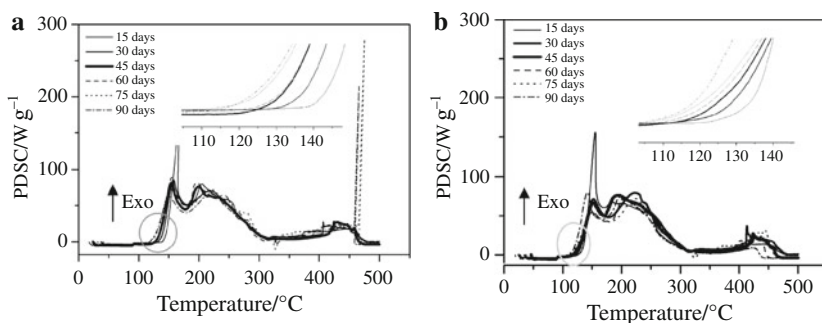


Fig. 4 PDSC dynamic curves of stored samples: a FAME and b FAEE



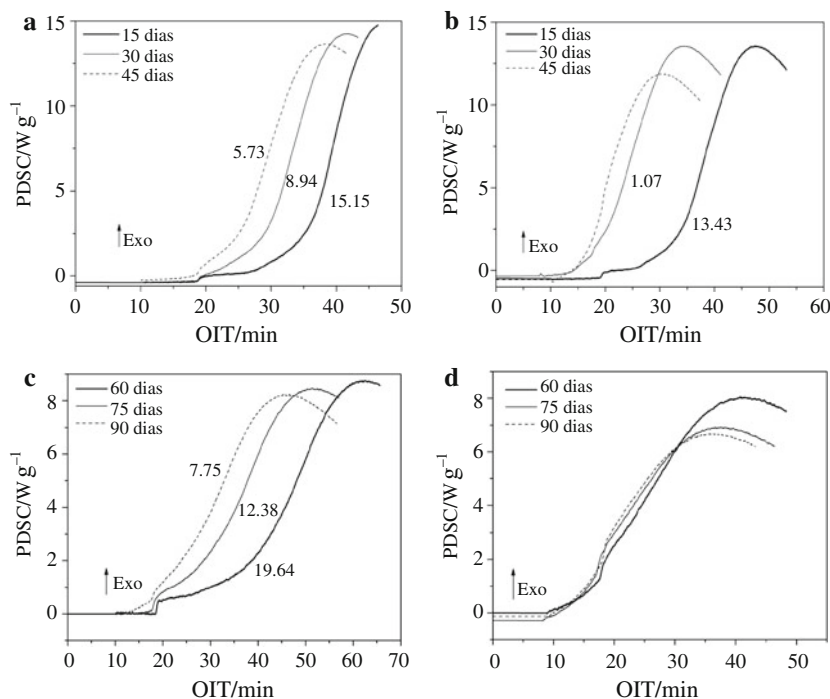
(Fig. 3b), probably due to the higher content of linoleic ester (C 18:2) in FAME, Table 1.

As the soybean biodiesel displays a high proportion of unsaturated fatty acids, it was highly susceptible to oxidation. Therefore, a low oxidative stability was expected for this biodiesel. Figure 4 shows the PDSC dynamic curves of the stored samples. It was noticed that the higher the storage time, the lower the initial oxidation temperatures. This fact should be evaluated considering the oxidation mechanism presented in Fig. 1. The first exothermic reaction occurs at the beginning of the propagation step, being detected in the PDSC analysis. The decrease of this onset temperature indicated that a higher amount of free radicals were formed during the initiation step that probably occurred during storage changing the composition of the biodiesel.

Figure 5 shows the isothermal curves at 110 °C for storages between 15 and 45 days and at 100 °C for samples stored during 60–90 days. This lower temperature was due to the further reduction in the onset oxidation temperatures (OT) for longer storage periods. The HPOIT reduction and the decrease of the energy flow (Fig. 5) were also observed and were proportional to the storage period. These results indicated that for longer storage periods, the oxidative induction probably occurred during the storage, and the propagation and polymerization occurred during the test.

During storage, the biodiesel samples produced by the methanol route demonstrated a higher HPOIT than those obtained by the ethanol route, as observed in Fig. 5. This result indicated that FAEE showed a higher amount of

Fig. 5 Isothermal curves of samples stored for different periods at different temperatures. **a** FAME and **b** FAEE stored during 15–45 days at 110 °C. **c** FAME and **d** FAEE stored during 60–90 days at 100 °C



oxidized molecules and thus fewer free radicals. Therefore, the collision between radicals and molecules is more difficult to occur.

Conclusions

The influence of the storage condition on the thermo-oxidative stability of fatty acid methyl and ethyl esters was suitably evaluated by PDSC analysis and viscosity measurements. At the beginning of the storage sample of FAEE showed higher oxidative stability than FAME but after 15 days of storage similar HPOIT values were obtained. During storage under climate simulation the HPOIT values were reduced for both FAME and FAME indicating that free radicals formation probably occurred during storage. Accelerated aging led to polymerization reactions increasing the biodiesel viscosity.

This study contributes to consolidate the PDSC technique as a powerful tool for oxidative stability evaluation. It is faster than Rancimat method, using lower analysis temperatures and smaller amounts of sample. Moreover, the main advantage of PDSC is that the sample is directly analyzed, differently from Rancimat that analyzes the volatilization compounds produced by the oxidation reactions.

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