

Short communication

FTIR assessment of the oxidation process of castor oil FAME submitted to PetroOXY and Rancimat methods

Susana V. Araújo, Breno S. Rocha, F. Murilo T. Luna, Estélio M. Rola Jr.,
Diana C.S. Azevedo, Célio L. Cavalcante Jr. *

Universidade Federal do Ceará, Departamento de Engenharia Química, Grupo de Pesquisa em Separações por Adsorção – GPSA, Campus do Pici, 709, Fortaleza, CE, 60.455-900, Brazil

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ABSTRACT

This short communication reports an assessment of the oxidation process of castor oil fatty methyl ester samples submitted to Rancimat (EN 14112) and PetroOXY (ASTM-D7545) oxidation methods. Fourier Transformed Infrared Spectroscopy (FTIR) was used to evaluate the FAME degradation products resulting from the accelerated oxidation, following the area of the carbonyl band ($\sim 1740\text{ cm}^{-1}$) of the samples at different oxidation times. Our results indicate that the level of oxidation of castor oil FAME, using the Rancimat method, follows a similar pattern of the oxidized samples using the PetroOXY method.

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1. Introduction

One of the main uncertainties about biodiesel fuel quality is its susceptibility to oxidation during storage conditions or engine operations [1,2]. The raw materials employed to produce biodiesel are generally composed of long-chain fatty acids connected by ester-glyceride bonds. Biodiesel usually has high contents of unsaturated methyl esters, especially poly-unsaturated methyl esters which may effortlessly be oxidized to methyl linoleate (C18:2) and methyl linolenate (C18:3). These are directly involved in the formation of decomposed compounds such as acids, aldehydes, esters, ketones, peroxides, alcohols and polymeric species, which not only affect the biodiesel properties, but also can cause problems to engine operation [3–7].

The oxidative susceptibility increases exponentially from an allylic methylene to a doubly allylic methylene. Thus the oleic acid (18:1) oxidation stability rate increases two-fold from linoleic acid (18:2) and ten-fold from linolenic acid (18:3). Therefore, the polyunsaturated fatty acyl chains are those most prone to oxidation with their doubly allylic methylenes [3]. With respect to the unsaturations in allylic methylene, it has been reported that the susceptibility to oxidation of a biodiesel increases with the number of double bounds found in its composition [2]. Commonly, the rate of oxidation of fatty compounds depends on the number of double bonds and their

position. Oxidation happens by contact with air, heat, light and pro-oxidants (metals and hydroperoxides) and leads to the enhancement of decomposed components, for which some of them can boost up further oxidation [8–10].

Currently, the analytical method to determine biodiesel oxidation stability (EN 14112 [11]) corresponds to international specifications to commercialize biodiesel. In food chemistry, the Rancimat test is normally used to determine the oxidative stability in view of the Rancimat Induction Period (RIP). The lesser the RIP value, the sample is more vulnerable to oxidation. This European standard method (EN 14112) of determination of oxidation stability of fatty acid methyl esters is an accelerated oxidation test which sets a lower limit of 6 h as the minimum Rancimat induction period [12].

The two main assessments of biodiesel fuel quality use chromatographic and spectroscopic methods [13]. The most employed chromatographic methods reported for biodiesel are gas chromatography (GC) and high-performance liquid chromatography (HPLC) analyses. Currently, the first one has been broadly used to quantify minor components. A large amount of papers on GC analysis deals with the determination of a precise contaminant or group of contaminants in methyl esters. Those contaminants may be anticipated, such as free glycerol or methanol, or also nonglyceridic materials, such as sterols and sterol esters. In other hand, due to its high sensitivity, HPLC is also used to determine the amount of free glycerol in vegetable esters as well as to detect residual alcohol in biodiesel [14,15].

Spectroscopic methods have been used to evaluate biodiesel properties as well as to monitor the transesterification reaction. These methods are ^1H and ^{13}C nuclear magnetic resonance (NMR) and

* Corresponding author. Tel.: +55 85 3366 9611; fax: +55 85 3366 9601.
E-mail address: celio@gpsa.ufc.br (C.L. Cavalcante).

infrared spectroscopy [14]. Fourier Transformed Infrared (FTIR) spectroscopy may be used to verify the biodiesel degradation products resulting from accelerated oxidation, evaluating the size of the carbonyl bands. Biodiesel oxidation may present several degradation mechanisms, like reverse transesterification, secondary products and carbonyl compounds formation [5].

A novel method to perform a faster accelerated oxidation test has been described in details in Neumann et al. [16] and Araújo et al. [17]. In that method (PetroOXY-ASTM D7545), the biodiesel sample is oxidized inside a hermetical chamber, pressurized with oxygen. Meanwhile the progress of the oxidation process is followed through the pressure drop into the chamber, which means oxygen consumption.

In this study, castor oil FAME samples were oxidized using the PetroOXY method and the Rancimat method (EN 14112). The oxidation process was evaluated from the increase of the area of the carbonyl band in a FTIR spectrum.

2. Experimental section

2.1. Materials

The FAME samples used were obtained from castor oil, through alkaline (NaOH) transesterification using methanol (JT Baker, USA) in excess. The reaction was carried out homogeneously in liquid phase at room temperature (25 °C) under intense stirring. The glycerin was removed by decantation after the reaction and the resulting FAME samples were washed twice with deionized water. An extra washing step using chloridric acid 0.1 M followed the first two steps of water washing. The main properties of the castor oil FAME samples were evaluated using standard methods [11,18,19] (see Table 1). It may be observed, as already reported in previous studies [20], that castor oil FAME does not meet all specifications for pure biodiesel, but can still be used in blends with oils from other vegetables.

2.2. Accelerated oxidation tests

2.2.1. Rancimat method (EN 14112)

The oxidative stability of the biodiesel samples was evaluated using a Rancimat equipment (Metrohm, model 743). Essentially, the oxidation process happens inside a reaction vessel heated at 110 °C (with 3 g of biodiesel sample) under air flow of 10 L h⁻¹. The volatiles oxidation products formed during the oxidation experiment are collected in a vessel containing 50 mL of distilled water, and the water conductivity is monitored continuously. A sudden change in electric conductivity of this water is noticed in the induction period point, indicating the propagation launch of an oxidation process. After that, a rapid increase in oxidation rate, peroxide value and oxygen absorption are observed.

2.2.2. PetroOXY method (ASTM D7545)

Another accelerated oxidation method was performed using a PetroOXY (Germany) equipment following ASTM D7545. In this

method, the induction period is the time between the start of the test and the detection of a specific pressure drop, which indicates that the resistance to oxidation has been overcome. The oxidation speed will be dependent on the degree and configuration of olefinic unsaturations, the presence of antioxidants and storage conditions. The test is performed inside a sealed chamber, where a sample of 5 mL is pressurized with oxygen. As the pressure is raised to 700 kPa, the inside temperature is also increased up to 140 °C. Thereby the pressure increases until the moment that the oxidation process starts. Then the oxygen begins to be consumed and the pressure begins to decrease. After a pressure drop of 10%, it is assumed that the sample has oxidized. The induction period is therefore the elapsed time between the start of the test and the breaking point when the 10% pressure drop detected.

2.3. Fourier Transformed Infrared Spectroscopy (FTIR)

A BIO-RAD FX-3000 spectrophotometer was used, equipped with a DTGS cooled detector and KBr beam splitter. Wavelengths were scanned in the range 400–4000 cm⁻¹, with a resolution of 8.0 cm⁻¹. The samples were diluted in cyclohexane (1:10 v/v) and analyzed in a standard cell (CaF₂) with an optical path of 0.5 mm. The infrared range from 1500 to 2000 cm⁻¹ was used, where an outstanding peak was observed, corresponding to the carbonyl group absorption, typical of esters compounds. This band is characteristic of the axial deformations of carbonyl bonds, present in the majority of the oxidation products [21]. The oxidation of the biodiesel samples was quantified by calculating the area of the spectral band around 1740 cm⁻¹, measured from 1620 to 1860 cm⁻¹.

3. Results and discussion

The FTIR spectra obtained for the biodiesel samples before the oxidation tests are presented in Fig. 1. The area of the carbonyl band at 1740 cm⁻¹ was used to evaluate the level of oxidation of the samples. Several studies about biodiesel oxidative degradation analyzed by means of FTIR spectra have already been performed, in which the area of the carbonyl band was used for comparison [22–24].

A comparison of the results for castor oil FAME using the Rancimat method (EN 14112) and the PetroOXY method (ASTM D7545) has been reported by Araújo et al. [17]. It was observed that there is essentially a linear relationship between the two methods correlating the PetroOXY values to the Rancimat values, similarly to what had been noticed for soybean oil biodiesel [16].

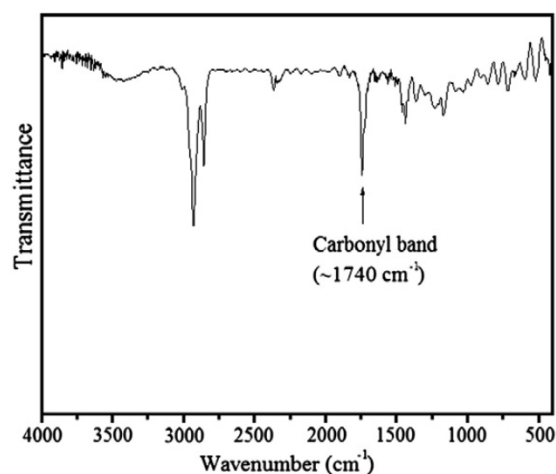


Fig. 1. Infrared spectra of a castor oil FAME sample before oxidation.

Table 1
Properties of castor oil FAME.

| Property | Unit | Result | Method |
|------------------------------|-------------------|--------|------------|
| Specific gravity at 20 °C | kg/m ³ | 846 | ASTM D1298 |
| Kinematic viscosity at 40 °C | cSt | 16.82 | ASTM D445 |
| Water and sediments | % | <0.05 | ASTM D2709 |
| Flash point | °C | 213.0 | ASTM D93 |
| Acid number | mg KOH/g | 0.92 | ASTM D664 |
| Ester content | % m/m | 95.8 | EN 14103 |
| Rancimat induction period | min | 183 | EN 14112 |
| PetroOXY induction period | min | 19 | ASTM D7545 |

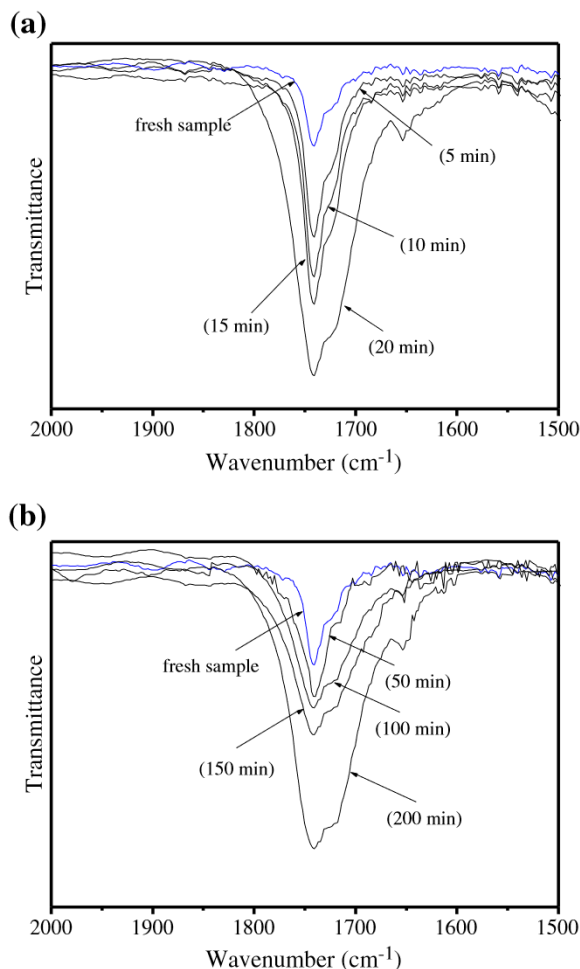


Fig. 2. Magnified region of carbonyl in FTIR spectra of oxidized castor oil FAME in different times. (a) From PetroOXY method; (b) from Rancimat method.

To compare the oxidation process in both methods, the oxidized biodiesel samples were assessed by FTIR. In the PetroOXY method the samples were oxidized up to 20 min, sampling every 5 min, as described in the Experimental section. The magnified region for the carbonyl band of the FTIR spectra for the biodiesel samples submitted to oxidation using the PetroOXY method is illustrated in Fig. 2a. It can be seen that, as the oxidation process proceeds (for times between 0 and 20 min), the area of the band around 1740 cm^{-1} increases, revealing an increasing degradation level of the samples. Using the Rancimat method, the samples were collected up to 200 min, which is essentially equivalent to 20 min in the PetroOXY method [17]. The increase of the carbonyl band was again clearly detected in all samples, as seen in Fig. 2b.

The comparison of carbonyl band areas, for all samples, at different times, is shown in Table 2, for each method.

Table 2
Carbonyl band areas (a.u.) obtained for biodiesel oxidized on PetroOXY and Rancimat methods at different times.

| Time (min) | PetroOXY method (a.u.) | Time (min) | Rancimat method (a.u.) |
|------------|------------------------|------------|------------------------|
| 0 | 338 | 0 | 338 |
| 5 | 633 | 50 | 506 |
| 10 | 696 | 100 | 612 |
| 15 | 950 | 150 | 1012 |
| 20 | 2110 | 200 | 1962 |

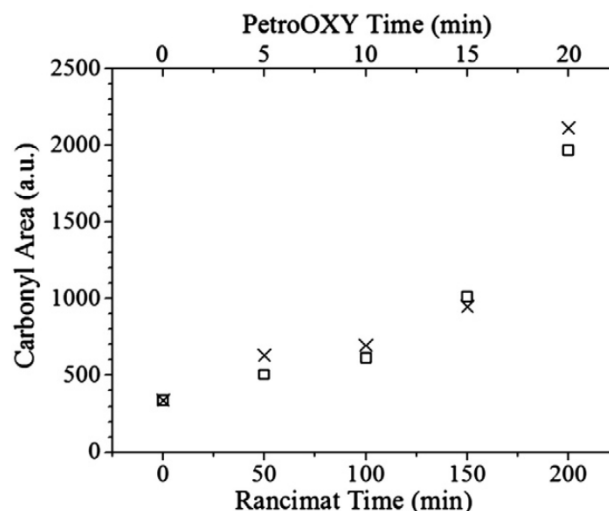


Fig. 3. Areas of carbonyl bands (ca. 1740 cm^{-1}) of oxidized samples with time. (x) PetroOXY method; (□) Rancimat method.

It can be clearly seen that the oxidation products containing the carbonyl group appear in the process to a significant extent for both oxidation methods. It can be also observed that there is a steep increase in oxidation products after 15 min (PetroOXY method) or after 150 min (Rancimat method). This sharp increase lies within the induction period values (given in Table 1) for each method (19 min in PetroOXY; 183 min in Rancimat), point in which the propagation of oxidation reactions determines the value of the oxidation stability of the sample for each method. Finally, a plot of the carbonyl band areas against time (Fig. 3) indicates a similar increasing pattern of the degradation products obtained from the two oxidation methods.

4. Conclusions

A comparison of the oxidation process observed in the PetroOXY method (ASTM D7545) and in the standard Rancimat method (EN 14112) was performed. Fourier Transformed Infrared Spectroscopy (FTIR) was used to quantify the biodiesel degradation resulting from the accelerated oxidation. The carbonyl band ($\sim 1740\text{ cm}^{-1}$) was used to assess the oxidation level of the samples. Our results showed that the pattern of the oxidation process of castor oil FAME, using the Rancimat method, is similar to the oxidation pattern of the same sample oxidized using the PetroOXY method.

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