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Monitoring free radicals formation in the biodiesel oxidation reaction via electronic paramagnetic resonance

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ABSTRACT

Biodiesel is an environmentally friendly alternative for petro-diesel. However, its degradation caused by radical oxidative reactions generates free radicals that damage the mechanics of vehicles. Spin trapping is a powerful resource for quantifying the short-lived and unstable free radicals liberated in these reactions. In this work, the formation of free radicals in samples of corn, soybean, and commercial biodiesel was investigated via electron paramagnetic resonance (EPR) using the spin trapping technique. The samples were incubated using the spin trap α-Phenyl-*N*-*tert*-butylnitrone (PBN) and analyzed via X-band EPR at room temperature and under heating at 70 °C. The experimental and simulated absorption spectra of the entrapped radicals allowed both identifying the presence of a derivative of the hydroxyl radical and characterizing the degradation stages of biodiesel. This result was discussed and compared with the accelerated heating method. The analysis allowed to establish EPR as a suitable, quick, and inexpensive way of probing the degradation of biodiesel in comparison with standard methods.

1. Introduction

Much of the energy used worldwide comes from crude oil products including gasoline, natural gas, and diesel. The use of these fossil substances contributed to several environmental problems such as acid rain and intensification of the greenhouse effect [1]. There is an increasing search for alternative sources of energy in order to avoid these negative impacts. Biodiesel is obtained from renewable sources and is considered a suitable fuel to substitute diesel oil [2].

The most known processes for obtaining this biofuel are cracking, micro emulsification, pyrolysis, and transesterification [3]. The most economically viable form of production is the transesterification reaction of vegetable oils and animal fats [4] which present unsaturated bonds, making the obtained biodiesel more susceptible to undesired oxidative processes [5]. These degradation processes can be initiated due to thermal factors [6], light incidence [6], contamination with metallic ions [7], presence of water [8], and contact with oxygen [9].

The oxidative processes originate a non-reversible and radical reaction, forming various products such as organic acids of low molecular weight, aldehydes, ketones and alcohols. These products are responsible for the increase in acidity as the degradation process increases. Unstable hydroperoxide species are also undesired products because they polymerize and form compounds of high molecular weight, such as dimers, leading to mechanical problems in vehicles using biodiesel [10].

The oxidation stability of the biodiesel may be evaluated via accelerated heating using the Rancimat equipment (EN 14214 [11]/EN 14112 [12]) [7]. However, electron paramagnetic resonance (EPR) is a faster and simpler technique that can be applied to the study of free radicals generated by the oxidation reaction. Some free radicals such as ·OH, $\cdot CH_3$ have a short lifetime and cannot be directly detected via EPR but the spin trapping technique allows their indirect detection. [13].

The spin trapping technique consists of adding to the sample a diamagnetic species that conveniently reacts with the radical released during the oxidative reaction, forming a radical with greater stability, called spin adduct or adduct radical [14]. The adduct radicals are detectable on the EPR.

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The EPR experiment requires a smaller amount of sample and less time of analysis when compared to the accelerated heating method that can take more than 6 h of analysis [15]. From the measured absorption spectra, it is possible to extract information about the type and amount of radicals observed [16]. The spin trap PBN (α-Phenyl-*N*-*tert*-butylnitrone) has been used in several similar studies [17–19] because it is soluble both in lipids and water [20].

In this work, we present a methodology for the quantification of free radicals in the oxidative degradation of biodiesel using spin trapping. We monitored the free radicals formation in biodiesel samples synthesized from different raw materials and compared the obtained results with the current techniques and norms in this field. From the analysis at room temperature, it was possible to observe the relation between the biodiesel degradation process and the spin adducts formation. Through the heated samples we determine the EPR characteristic induction periods (EIP) using methods previously established by Thomsen et al. [19] and Velasco et al. [18], showing a relation with the accelerated heating method. Also, the presence of the hydroxyl radicals concurs with the mechanism of lipid oxidation already known [21].

2. Material and methods

2.1. Sample preparation

100 g of commercial soybean oil (Suavit®) and corn oil (Suavit®) were used raw material for biodiesel synthesis, producing a sample of soybean biodiesel and a sample of corn biodiesel. The biodiesel samples were produced by methyl ester transesterification reaction with 50 mL of P. A. methanol (Anidrol®, 99.8%). and 0.8 g of sodium hydroxide (NaOH, F.maia®: 97.0%) as a catalyst. The mixtures were submitted to slow stirring, under reflux at 65 °C for 2 h. To separate the triglycerides, the glycerol, and the alcohol from the obtained esters, the biodiesel samples were neutralized with 0.1% (v/v) hydrochloric acid (F.maia®: 36.5%) solution at 80 °C to minimize the formation of emulsions. Subsequently, they were washed with distilled water at 80 °C until the water reached pH 7. After neutralization, the dehumidification of the samples was carried out by adding 8 g of anhydrous sodium sulfate, P. A. (Na_2SO_4, Dinâmica®, 99%), which was previously oven (Odontobras®) dried for 30 min at 120 °C. The blends were shaken and then filtered on quantitative blue strip filter paper (Quanty®, ~8 μm) under vacuum. Dehumidification and neutralization steps were repeated twice. The biodiesel samples produced were stored in a glass bottle under refrigeration and in the absence of light. The commercial biodiesel (BS-BIOS/Marialva-PR) met ANP Technical Regulation No. 3/2014 [22].

2.2. Electronic paramagnetic resonance (EPR)

2.2.1. Spin trap incubation

The samples of corn, soybean and commercial biodiesel were incubated using the α-phenyl-*N*-*tert*-butylnitrone (PBN) (purity ≥ 98%), purchased from Sigma-Aldrich in the proportion of 1 g biodiesel:1 mg PBN. The samples were submitted to manual stirring for approximately 3 min until total spin trap solubilization. After this process, about 0.05 g of each incubated sample was transferred into the 4 mm diameter quartz tubes for EPR analysis. The incubation methodology was adapted from Velasco et al. [23]. No solvent was used in the incubation process.

2.2.2. Spin and magnetic field marker quantification

In order to calibrate the magnetic field and area of the spectra to the number of absorbing species, a preliminary analysis of the EPR spectra of chromium-dopped magnesium oxide (Cr^{3+}:MgO) and of magnesium oxide doped with manganese (MgO:Mn^{2+}) was performed. The Cr^{3+} sample has a known number of paramagnetic species and its spectrum was used to calibrate the number of species in the manganese standard (MgO:Mn^{2+}). The manganese standard was used in all the measurements in order to promote the quantification of the trapped species in the samples.

2.2.3. EPR analysis at 70 °C

The EPR measurements were performed on a JEOL (JES-PE-3X) spectrometer, operating at X-band (~9.5 GHz). All EPR spectra were obtained with a magnetic field modulation of 100 kHz, 1 mW microwave power, 20 G modulation amplitude, and scans of 4 min. The biodiesel samples were analyzed by EPR after the incubation process. The samples were stored in an oven for 21 days at a temperature of 50 °C, indicated as ideal by preliminary tests. EPR data were collected at a constant temperature of 70 °C at 5 min time intervals, for approximately 2 h. Data were collected on days 1, 6, 13 and 21, defined by previous tests. Spectra of the samples and the standard were obtained simultaneously in order to enable quantification of the trapped species.

2.2.4. Analysis at room temperature

The biodiesel samples were incubated once on the first day of analysis and monitored by EPR at approximately every 7 days at room temperature. The samples were kept sealed in the absence of light.

2.2.5. Trapped species quantification

The number of free radicals trapped by the spin trap PBN was determined by using the double integration of the EPR spectra. It is known that the area under the absorption curve is proportional to the number of unpaired spins in a given sample [24]. The number of paramagnetic species (spin adducts) in the samples was determined by comparing the areas of the radical detected and the fourth spectral line of the manganese standard as follows:

$$N_{biodiesel} = \frac{A_{radical} * N_{standard}}{A_{standard}} \quad (1)$$

Where:

$N_{biodiesel}$ is the number of trapped species in the biodiesel sample;
$N_{standard}$ is the number of species in the manganese standard;
$A_{radical}$ is the area of the radical spectrum;
$A_{standard}$ is the area of the fourth spectral line of the manganese standard.

To obtain the trapped species number in the biodiesel samples, $N_{biodiesel}$ values were divided by each samples mass.

2.2.6. Simulation of the EPR spectra

EPR spectra were simulated in the MATLAB software [25] using the *garlic* function of EasySpin, a free toolbox for EPR spectrum simulation [26].

2.3. Oxidative stability

3 g of each sample was submitted to the accelerated heating at 110 °C, according to EN 14112 [12], using an 873 Rancimat (Metrohm®), with air flow of 10 $dm^3\,h^{-1}$, to determine the biodiesel oxidative stability. Induction Periods (IP) are provided by the inflection point of the curve between the electric conductivity in μS and the time in hours.

2.4. Cloud and pour points

The cloud and pour points tests were performed in accordance with ASTM D2500-05 method [27].

2.5. Acidity number

The acidity number tests were performed in accordance with ASTM