Fuel 156 (2015) 158–162

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Thermogravimetric analysis as a rapid and simple method to determine the degradation degree of soy biodiesel

T. Vega-Lizama, L. Díaz-Ballote *, E. Hernández-Mézquita, F. May-Crespo, P. Castro-Borges, A. Castillo-Atoche, G. González-García, L. Maldonado

Centro de investigación y de estudios avanzados – Unidad Mérida, km 6 antigua carr. a Progreso, Apdo. Postal No 73, Mérida, Yucatán 97310, Mexico

HIGHLIGHTS

- Thermogravimetric analysis is used for measuring the biodiesel oxidation degree.
- A very small amount of biodiesel is required for determining its oxidation degree.
- Biodiesel pre-treatment is not needed to apply thermogravimetric analysis.
- Thermogravimetry is a simple alternative for monitoring biodiesel oxidation.

ARTICLE INFO

Article history:
Received 9 February 2015
Received in revised form 17 April 2015
Accepted 20 April 2015
Available online 27 April 2015

Keywords:
Biodiesel oxidation
Thermogravimetric analysis
Biodiesel degradation

ABSTRACT

This work describes the use of the residual mass observed in a thermal decomposition curve for a soy biodiesel sample as a measure of its degradation degree. The difference in thermal stability between esters and oxidation products is the key point to make the determination. Using residual mass, the acceptance or rejection of a biodiesel becomes a non-subjective process and does not require knowledge of the biodiesel oxidation process. The residual mass data were compared with those of kinematic viscosity, UV spectroscopy and nuclear magnetic resonance. The good agreement found between these data justifies the utilization of this method to determine the biodiesel oxidation degree.

1. Introduction

The use of biodiesel is becoming more common worldwide. This energy source has several benefits that promote its acceptance; it is bio-renewable, non toxic and biodegradable. Its liquid state allows its use in diesel engines currently in circulation without the need for significant changes. A disadvantage of biodiesel is its susceptibility to degradation by oxidation [1,2], a phenomenon that affects the quality of biodiesel. Commonly reported mechanisms of degradation are: oxidation, photo-oxidation and enzymatic oxidation among others [3]. The first has received the most attention [4], because typical storage conditions favor this mechanism (exposure to air and room temperature). Biodiesel oxidation during storage is a concern of producers and distributors since it produces deviations in its physical and chemical properties that can cause a significant deterioration in its quality. The maximum and minimum of the biodiesel properties are specified in standards, the most used are the American (ASTM D6751) and the European (EN 14214). Clearly, for studying and improving the oxidation stability of biodiesel, a simple and precise method for its measurement is required. Biodiesel oxidative behavior has been studied by following the changes in some of their properties related to oxidation, such as: iodine value, acidity, peroxide, viscosity, and density. Advanced analytical techniques like thermogravimetric analysis (TGA), nuclear magnetic resonance (NMR), infrared spectroscopy (FTIR), and ultraviolet (UV) spectroscopy are increasingly used in the oxidation study. The method specified in EN 14214 is the rancimat method. This method [3], consists of passing a flow of oxygen (10 L/h) through a biodiesel sample (3 g) at 110 °C. Oxygen drags the volatile compounds and leads them to a water trap with a conductometer in it. A sharp increase in conductivity indicates an accelerated degradation process. The time it takes the test from the beginning to the sudden increase in conductivity is called induction period. The standard (EN 14214) for biodiesel establishes a minimum induction period of 6 h to consider that the biodiesel passed the oxidative test. In general, these methods or analytical techniques allow us to compare between biofuels to estimate which one will have longer storage life.

This paper proposes a method to determine the oxidation degree of biodiesel based on residual mass of the

* Corresponding author. Tel.: +52 999 942 9437; fax: +52 999 981 2917.
E-mail address: luisdiaz@mda.cinvestav.mx (L. Díaz-Ballote).

http://dx.doi.org/10.1016/j.fuel.2015.04.047
0016-2361/

thermogravimetric curve. The key feature to use the residual mass as a measure of oxidative degradation is the difference between the thermal decomposition temperature of the esters and the oxidation products. The main vegetable oils to produce biodiesel (canola, soybean, sunflower, ...) have a composition dominated by the fatty acids: palmitic, stearic, oleic, linoleic and a bit of linolenic [5–8]. Boiling points of the esters derived from these fatty acids, according to their respective security sheets, are: 181.0 °C for methyl stearate (CAS 112-61-8), 185 °C for methyl palmitate (CAS 112-39-0), 192 °C for methyl linoleate (CAS 112-63-0), 182 °C for methyl linolenate (CAS 301-00-8), and 218 °C for methyl oleate (CAS 112-62-9) [9]. Data of the boiling point safety sheets suggest that the thermal decomposition expected of a typical biodiesel derived from vegetable oils should be in the range of 181–218 °C. Several reports agree with this range. Chand et al. [10] investigated the thermal decomposition of biodiesel derived from soybean oil and found that this biodiesel starts its decomposition at 150 °C. Chien et al. [11] studied the biodiesel derived from soybean and reported a range of thermal decomposition for this biodiesel from 119 to 237 °C. Focke et al. [12] investigated the thermal stability of biodiesel derived from oils; sunflower, soybean and canola. The authors found that the rate of decomposition of biodiesel independently of the vegetable oil, is almost the same until it reaches the temperature of 200 °C, point at which it starts to change. The residual mass in this study was associated with the amount of unsaturations. The use of the difference in thermal decomposition temperatures has also proven to be effective in determining the degree of conversion of biodiesel [13].

2. Materials and methods

2.1. Materials

Refined vegetable soybean oil purchased from a local supermarket was used in the preparation of biodiesel. Reagent grade chemicals: KOH, *n*-hexane and methanol purchased from Sigma–Aldrich were used. De-ionized water (18 Mohm) was used in the preparation of solutions and washing of biodiesel.

2.2. Biodiesel preparation

Experimental conditions for the biodiesel preparation were chosen according to those reported in studies of optimization of transesterification reaction. For the soybean oil, an average molecular weight of 874 g mol^{-1} was used for calculations [14–16]. The amounts used were: 100 g of soybean oil, 22 g of methanol and 1 g of KOH. The reaction was maintained at 25 °C with stirring (600 rpm) for 60 min. Subsequently, the reaction mixture was placed in a separatory funnel where it remained undisturbed for 24 h. After this time, the separation of glycerol and fatty acid methyl esters were observed. Glycerin was separated, then biodiesel was washed with deionized water. Biodiesel was placed for 4 h in an oven at 105 ± 2 °C to evaporate the excess of water and alcohol. To determine purity, thermogravimetric analysis (TGA) was used (as described in Section 2.3). Kinematic viscosity was measured according to ASTM-D445 method and for cold soak filtration, the method ASTM D7501 was used. The main fatty acids and the percent amounts of saturated and unsaturated fatty acids, was determined with ^{1}H NMR according to the method described by Knothe [17].

2.3. Biodiesel oxidation

The oxidation was performed by varying the biodiesel area exposed to air (P_{O2} = 0.2 atm) and heating at different temperatures. The procedure was as follows, 30 mL samples of biodiesel were placed in petri dishes with different areas designated as A1, A2, and A3 whose diameters were 50, 90 and 140 mm respectively. A sample without oxidation treatment, designated as B0, was used as reference. The samples subjected to the accelerated oxidation process were designated as B_{A1}, B_{A2} and B_{A3} depending on the exposed area. The petri dishes were introduced in a Fisher Scientific oven at 80, 100 and 120 °C and kept under these conditions for a period of 24 h. Each experiment was performed by triplicate. After oxidation, samples from each biodiesel were taken and were studied using TGA, kinematic viscosity, UV spectroscopy and nuclear magnetic resonance. TGA was performed with a thermobalance Discovery series (TA Instrument). Measurement conditions were: Temperature range of 50–500 °C, heating rate 10 °C/min, average mass of the sample 4.7 ± 0.1 mg, dry air flow 50 mL/min. The UV absorption spectra were obtained with a 4000-U Hach spectrometer in the range of 200–400 nm. All determinations were performed with a ratio of 1:250 dilution in *n*-hexane. Kinematic viscosity was measured according to ASTM D 445 method using a glass viscometer "Ubbelohde" immersed in a thermal bath at 40 °C. The quantitative ^{1}H NMR spectra were recorded at 25 °C on Varian/Agilent Premium Compact 600 NMR spectrometer at frequency of 599.74 MHz with $\pi/2$ pulse of 8.7 μs and 10 s of recycle delay. The lock and shimming were done with internal D_2O in sealed capillary and the chemical shifts (ppm) were referenced to residual signal HOD at 4.80 ppm. In all cases neat samples were used.

3. Results

3.1. Biodiesel characterization

Table 1 shows the results of the characterization of B0 and its percentage amount of the principal fatty acids. The unsaturated fatty acids are the most important indicators that show the biodiesel tendency to oxidation.

3.2. Thermogravimetric analysis

Fig. 1 shows the typical TGA curve (solid line) of B0. A single transition with starting point at 183 °C and final at 218 °C is observed, consistent with the range of boiling points found in the safety sheets of the dominant methyl esters in the composition of biodiesel [18,19]. Nakatani [20] reported the use of the thermogravimetric curve to determine the content of methyl esters. According to the method described by these authors, B0 has a purity of 98.5%. Therefore it meets the minimum requirement of purity (ester content) 96.5% specified in the quality standard EN 14214.

Table 1
Properties of biodiesel (B0) properties and its fatty acids composition.

Properties	
Kinematic viscosity	4 mm^2 s^{-1}
Acid value	0.9 mg KOH g^{-1}
Cold soak filtration	250 s
Purity[a]	98.5%
Density@15 °C	0.87
Fatty acid composition (% weight)[b]	
C18:1	28.3
C18:2	43.6
C18:3	10.0
Total insaturated	81.9
Saturated	18.1

[a] From TGA.
[b] From NMR.