



Biodiesel oxidative stability from Rancimat data



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ARTICLE INFO

Article history:

Received 14 January 2016

Received in revised form 10 March 2016

Accepted 16 March 2016

Available online 18 March 2016

Keywords:

Oxidative stability

Induction period

Rancimat method

Antioxidants

Biodiesel

ABSTRACT

It is conventional to quantify the oxidative stability of oils and biodiesel through an induction time determined by a Rancimat instrument. European Standard EN 14112 for the Rancimat method describes two procedures for determining this induction period. The automated method relies on finding the position of the peak in the second derivative of the conductivity vs. time curve. The manual method is based on the intersection of two tangents lines. It is shown that this method can also be automated by a curve fitting approach based on a novel Rancimat response function. This analysis demonstrates that the induction period values determined by the two methods differ with the second derivative method returning slightly higher estimates for the induction period.

Biodiesel was prepared using base-catalysed methanolysis of sunflower oil. It was stabilized using the hindered phenol antioxidant tetrakis[methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]methane. It was found that stability increases linearly with stabiliser concentration and that the effect of the measurement temperature follows Arrhenius kinetics. The effectiveness of the antioxidant stabiliser diminished with increasing temperature.

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1. Introduction

Biodiesel is a renewable fuel produced by reacting vegetable oil or animal fat with methanol in the presence of an alkali catalyst to produce fatty acid methyl esters (FAME). It is more susceptible to oxidative degradation than petroleum diesel as it contains unsaturated long-chain fatty acids [1,2]. The oxidative stability can be improved by adding suitable antioxidants [2–4].

Currently the reference method for the measurement of the oxidative stability of biodiesel is EN14112 [5]. It prescribes the Rancimat method [6,7] for gauging the induction time of the biodiesel. In this procedure autoxidation is accelerated by passing a constant flow of air through the biodiesel sample while controlling the temperature at an elevated level, i.e. 110 °C. The oxidation process is driven by radical reactions that involve the unsaturated fatty acid structures. During an initial induction phase virtually no secondary products are formed. This is abruptly followed by an oxidation phase characterized by a rapid increase in peroxide value and the formation of volatile products. The Rancimat method relies on the fact that the greater part of the volatile matter consists of formic acid. This is trapped by passing the exiting air through

distilled water where its accumulation is recorded conductometrically. The length of the induction period (*IP*) is taken as a measure of oxidative stability. EN14112 [5] describes two methods for the evaluation of the *IP* from a conductivity vs. time curve. An example is shown as an insert in Fig. 1(a). Furthermore, there is a tacit assumption that the two methods yield comparable if not identical results. The “manual method” relies on the determination of the point of intersection of two optimal tangents to the conductivity vs. time curve. The first tangent is drawn along the first, moderately increasing part of the curve. The second is drawn along the upper part of the rapidly increasing portion of the curve. The problems associated with this manual approach is that it is operator dependent. It relies on subjective judgment of the “optimal” tangents. The “automatic method” identifies the *IP* with the location of the position of the maximum in the second derivative of the conductivity vs. time curve. Determining the second derivative from noisy data is not a simple problem, in fact it is considered to be an ill-posed problem [8]. Occasionally problems are experienced with this method too [9]. For example, the second derivative generated by the instrument from the conductivity-time curve may show multiple maxima and it then becomes necessary to revert to the “manual method” [9].

The main objective of this communication was to explore ways to automate the “manual method” for evaluating the *IP* from the Rancimat curves and to critically compare the results returned by the two methods. If this can be done, the corresponding *IP* value can

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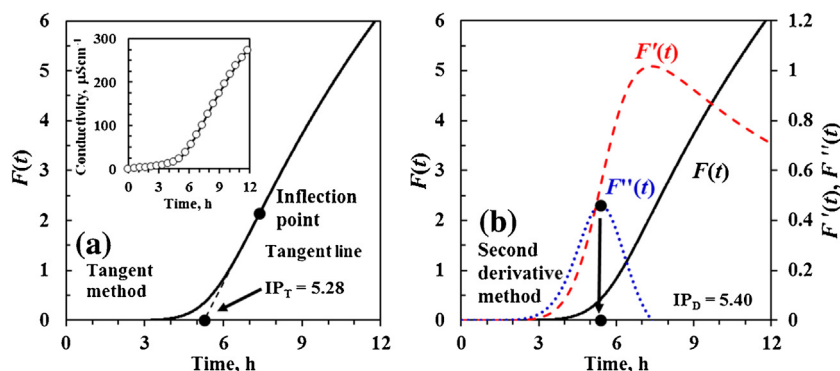


Fig. 1. Schematic illustration of the data reduction methods used. The experimental conductivity vs. time curves (insert in (a)) were fitted to the response function $F(t)$ defined by Eq. (1). The parameter values were determined from the experimental data using least square fits. The IP values were directly determined from the sigmoidal response curves parameters based on two different methods: (a) the first approach is based on the assumption that the IP corresponds to the intersection, with the time axis, of the tangent line drawn to the inflection point of $F(t)$; (b) The second methodology associates the IP with the position of the maximum in the second derivative of $F(t)$, i.e. $F''(t)$.

be generated directly by the instrument software without operator intervention. Another objective of this study was to study the stabilization of sunflower oil-based biodiesel with a hindered phenol antioxidant at different dosage levels. The oxidation stability of the sunflower biodiesel was also tested at different temperatures using the Rancimat method.

2. Materials and methods

2.1. Materials

Pure triple distilled sunflower oil was manufactured by Sunfoil. The antioxidant considered was the hindered phenol tetrakis[methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinamate)]methane (Anox 20 ex Addivant). The antioxidant was added to the biodiesel at different loadings up to a maximum of 0.25 wt.%.

2.2. Biodiesel preparation

The biodiesel was prepared at ambient conditions ($28\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$) from sunflower oil using the following procedure: A catalyst, potassium hydroxide, was dissolved in 100 mL of dry methanol. The solution was then poured over 500 mL of the sunflower oil in a large Mason jar. The jar was securely closed and the solution vigorously agitated for 15 min. The solution was then transferred to a gravity separation funnel and allowed to settle. In the first hour the separation appeared about 75% complete. After 8 h the glycerine reaction product had settled at the bottom with a biodiesel or FAME layer on top. The lower glycerol phase was removed. The FAME was then washed to remove residual catalyst, free fatty acids and methanol. The product was washed five times with 140 mL distilled water portions. The biodiesel was then placed in an open container in a convection oven at $70\text{ }^{\circ}\text{C}$ to remove the remaining methanol and water. After drying the biodiesel sample was stored in airtight container in a fridge.

2.3. Characterization

The fatty acid methyl ester (FAME) analysis was performed by Analytical Services, Food and Beverage Laboratory, CSIR on an Agilent 6890 GC-FID. An Agilent J&W GC column CP-SIL 88 ($100\text{ m} \times 0.25\text{ mm } \varphi$ with a film thickness of $0.20\text{ }\mu\text{m}$) was used for the separation of the FAME's. The column temperature was initially set at $60\text{ }^{\circ}\text{C}$ for 1 min, and then stepwise increased first to $150\text{ }^{\circ}\text{C}$ at a rate of $20\text{ }^{\circ}\text{C min}^{-1}$, then to $215\text{ }^{\circ}\text{C}$ at a rate of $5\text{ }^{\circ}\text{C min}^{-1}$

and finally to $240\text{ }^{\circ}\text{C}$ at a rate of $1.5\text{ }^{\circ}\text{C min}^{-1}$ where it was held constant for 40 min. Hydrogen was used as the carrier gas with hydrogen and air as fuel gases. Injector and detector temperatures were $230\text{ }^{\circ}\text{C}$ and $260\text{ }^{\circ}\text{C}$ respectively. Injection volumes for samples and standards were $1\text{ }\mu\text{L}$ and a split ratio of 150:1 was employed.

The biodiesel sample was dissolved in heptane and quantification was performed by internal standard calibration using methyl heptadecanoate. The FAME content was computed according to EN 14103 [10,11] where the sum of all the peaks from the methyl myristate (C_{14}) peak up to that of the methyl ester in $\text{C}_{24:1}$ was accounted for. Identification of the FAMES in the biodiesel samples was accomplished by comparing their retention times to a Supelco FAME reference mixture containing 37 components.

FTIR spectra of the neat biodiesel was obtained using KBr plates on a PerkinElmer Spectrum RX I FTIR spectrometer. The reported spectrum represents the average of 12 scans recorded at a resolution of 2 cm^{-1} .

Additional physical properties of the biodiesel samples were determined, using standard procedures, by Bio Services CC, Randburg, South Africa. These included free glycerine, methanol content, water content, acid value, iodine value and flash point.

2.4. Antioxidant formulations and determination of the oxidative induction times

The effect of antioxidant concentration on the induction time was determined by spiking the biodiesel with different amounts of Anox 20 as indicated in Table 3. The variation of the induction time with temperature was studied at 80, 90, 100, 110 and $120\text{ }^{\circ}\text{C}$.

The oxidation stability of the neat biodiesel as well as the stabilised biodiesel samples was determined using a Metrohm 895 Professional PVC Thermomat. It was set up with the required accessories to analyse biodiesel according to the EN14112 [5] Rancimat method. A typical procedure was as follows: The cellblock temperature was ramped to $110\text{ }^{\circ}\text{C}$ and held constant. A 3.00 g biodiesel sample was transferred into the reaction vessel and placed in the cellblock. The air flow rate was set at 10 Lh^{-1} . It was passed through the sample and then through a measuring vessel containing 60 mL of deionised water. The increase in conductivity was measured as a function of time. The Rancimat induction time (IP_R) was determined automatically using the instrument software using the second derivative method. Repeat measurements of the induction time were carried out for each sample.

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