Fuel Processing Technology 130 (2015) 245–251

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Assessment of shelf life of Bulgarian industrial FAME by the use of modified ASTM D2274 as accelerated oxidation method

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ARTICLE INFO

Article history:
Received 17 July 2014
Received in revised form 3 October 2014
Accepted 13 October 2014
Available online 4 November 2014

Keywords:
Biodiesel
Shelf life
Peroxide value
Induction period
Q rule

ABSTRACT

Kinetic data for hydroperoxide formation in a commercial biodiesel, produced from 50% sunflower oil and 50% rapeseed oil were obtained by using rapid, higher than standard temperature procedure with sufficient oxygen solubility in the samples. Three different mathematical methods for processing the data and shelf life determination of the studied biodiesel are compared. The applicable methodologies are hydroperoxide concentration abrupt increase graphical determination and Q rule. The calculation shows that shelf life of the studied stabilized Bulgarian biodiesel amounts between 1.17 and 1.27 years. It was also found that peroxide value for induction period at 15 °C is 71.8 meq O_2/kg biodiesel.

1. Introduction

EU legislation promotes and even obliges the use, within the territories of the member countries, of biodiesel — fatty acid methyl esters (FAMEs) as it is very promising for achieving 2020 European transport sector renewable fuel targets. Along with its ecology favorable properties, biodiesel can reduce the shortage of diesel production in Europe, to some extent. Unfortunately, this diesel substitute has some drawbacks like poor stability [1–8] and cold flow properties [8–11], in which these properties are subjected to vigorous research activity recently. Susceptibility of a biodiesel to oxidation is related to [1,12,13]: its chemical composition (configuration of double bounds in unsaturated FAMEs — presence of bis-allylic or allylic methylene groups and their concentration); the presence of synthetic and naturally occurring antioxidants; contact duration with air, heat, and light; interaction with contaminants; construction materials of storage tanks; etc. The aforementioned prerequisites define low oxidative stability of row biodiesels and the last property is the main issue concerning the storage of biodiesel. A lot of researches have been conducted for determination of shelf life (expiration date) of vegetable oils but there is no information in the literature about expiry determination for FAMEs. Some researchers [14–18] determine expiration date of vegetable oil based on the increase of concentration of secondary oxidation products (aldehydes, aliphatic alcohols, formic acid, formate esters, shorter chain fatty acids and species with higher molecular weights), registered indirectly by acid and anisidine values, viscosity, density and Rancimat Test Method [19]. The same researchers [14–16,18] and others [20–24] count mainly on primary oxidation products (conjugated diene and hydroperoxides) concentration sheer increase measured by the following physical properties — UV adsorption at 232 nm as per standard ISO 3656 and peroxide value (PV) [25]. Most of the studies describe the long term storage behavior of oils, produced only from a single vegetable type [14,20–24] and only a few from a blend of two types of vegetables [15,24]. Another [2,12] investigates the influence of naturally occurring (polyphenols and four isomers of tocopherol — a, b, g and d) and synthetic antioxidant (pyrogallol, gallic acid, propyl gallate, nordihydroguaiaretic acid, butylated hydroxyanisole, butylated hydroxytoluene, tert-butyl hydroquinone, etc.) type and concentration.

The shelf life of a biodiesel can be determined by both accelerated stability testing and real time stability testing. In the real time testing, the continuance of the experiment should be long enough to allow significant biodiesel degradation under recommended storage conditions. Real time storage at ambient temperature is the preferred shelf life methodology, but it can be characterized also as a time consuming and not always successful in onset of rapid oxidation or induction period (IP) recording. Frequently IP exceeds planned experimental aging time. Bondioli et al. [15] for example was unable to register expiration dates (falling of oxidation stability below 6 h) of eleven different

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http://dx.doi.org/10.1016/j.fuproc.2014.10.016
0378-3820/

biodiesel samples after one year storage study. Other researchers [16,18] have found that some types of biodiesels were very stable because they did not demonstrate rapid increase in peroxide value, acid value, viscosity and insoluble impurities according to results from a 30 month study.

The potential for long term storage of biodiesel commodity, which is supplied to fuel hubs, distribution networks and refineries for blending with mineral diesel fuel, is very alternating as there is a variety of feedstocks for its production, different types and quantities of antioxidative additives are used and the fuel itself has been stored for definite time before blending.

The concept of this study is to evaluate the shelf life of a Bulgarian commercial biodiesel fuel through a methodology for determination of induction periods (start of rapid oxidation expressed with sharp peroxide value increase) at several higher than normal storage temperatures. Then, based on the relationship which expresses Arrhenius equation between storage temperatures and degradation rate, the long term storage at ambient temperatures can be extrapolated.

2. Experimental

2.1. Feed

Fatty acid methyl ester (FAME), from rapeseed/sunflower = 1/1 oil originally manufactured by Astra Bioplant Ltd (Slivo Pole, Bulgaria), was supplied to LUKOIL Neftohim Burgas JSC for mandatory blending for EN 590 diesel fuel production. Table 1 summarizes the studied FAME composition determined according to the gas chromatography–mass spectrometry analysis. Fig. 1 represents the biodiesel chromatogram. The GC is equipped with a flame ionization detector and a fused-silica capillary column is used. The column temperature was programmed from 170 °C to 280 °C at a rate of 6 °C/min. More detailed description of GC operating conditions is presented in [26].

The presence of 50% sunflower oil FAMEs and 50% rapeseed oil FAMEs in the studied commercial biodiesel can be linearly calculated from the reference FAME compositions [27]. It is worth to note that only methyl linolenate concentration exceeds linearly calculated esters content and thus a compositional prerequisite for low oxidation stability and shorter shelf life is established. From the normalized FAME content and individual ester molecular weight (Mw_i), one can easily calculate the molecular weight (Mw) of biodiesel which is 294 g/mol.

Chromatographic composition and integrated additives define the chemical and physical properties of the biodiesel under study.

Data in Table 2 reveals the high quality of the commercial biodiesel and complete satisfaction of EN 14214 requirements. The negative effect of biodiesel composition over oxidation stability was compensated by 0.2% antioxidative additive — BHT (2,6-bis(1,1-dimethylethyl)-4-methylphenol).

Table 1
Gas chromatographic composition of Astra Bioplant biodiesel and reference composition of neat sunflower and rapeseed biodiesels.

FAME type	Content in studied biodiesel, wt.%	Reference compositional profiles of biodiesel [27], wt.%	
		Rapeseed oil biodiesel	Sunflower oil biodiesel
Methyl palmitate/C16:0	6.52	4.2 ± 1.1	6.4 ± 1.8
Methyl palmitoleate/C16:1	0.04		
Methyl hexadecatrinoate/C16:3	0.13		
Methyl stearate/C18:0	2.87	1.6 ± 0.7	3.6 ± 1.1
cis-9-Oleic methyl ester/C18:1	35.71	59.5 ± 7.8	21.7 ± 5.3
Methyl linoleate/C18:2	38.59	21.5 ± 2.8	66.3 ± 7.6
Methyl linolenate/C18:3	11.06	8.4 ± 1.3	1.5 ± 2.6
Methyl arachidate/C20:0	0.59		
Methyl eicosenoate/C20:1	0.75	2.1 ± 3.0	
Methyl eicosadienoate/C20:2	0.26		
Methyl behenate, methyl docosanoate/C22:0	0.42		
Methyl erucate/C22:1	0.12		
Unidentified	2.94	4.3 ± 4.4	0.1

2.2. Procedure

It should be mentioned, that the rate of FAME oxidation reaction depends from the velocity of mixing and the pressure of oxygen (air) above the sample at low values of these variables. At such low values oxidation chemical reaction proceeds in the so called diffusion area. In order to eliminate the effect of pressure and mixing (to provide enough oxygen permeability) and to register only the chemical interactions, one should increase their values above a definite threshold, i.e. to lead the chemical reaction in the kinetic area [28]. In this relation the applicability of ASTM D 2274 for kinetic study for shelf life determination can be found in the rate of 3 l/h oxygen which bubbles through the sample. This quantity assures vigorous mixing of oxidizing agent within the sample. The test method itself provides high partial oxygen pressure and oxygen solubility remains stable or at least sufficiently high that the rate-determining step is not oxygen addition.

The standard conditions (95 °C and 16 h) of the test were modified and four experiments were conducted at 80 °C, 85 °C, 90 °C and 95 °C, and different experiment durations at every temperature but up to 24 h for the lowest temperature. At every temperature and on regular time intervals, samples were taken and peroxide values (PV) in mg/kg as per ASTM D3703 were determined. The shelf life of the biodiesel under study is calculated on the base of PV expressed in milliequivalents of peroxide per kilogram of sample (meq O_2/kg ester) because of the wider spread of this dimension. The last value is calculated by the following equation:

$$PV = \frac{V_{Na_2S_2O_3} * Titre_{Na_2S_2O_3}}{m_{biodiesel}} . \quad (1)$$

In this equation PV is peroxide value in meq O_2/kg biodiesel; $V_{Na_2S_2O_3}$ — volume of sodium thiosulfate in ml, spent for oil titration; $Titre_{Na_2S_2O_3}$ — the concentration of sodium thiosulfate solution which in our study is 24.8 mg eq/ml and $m_{biodiesel}$ — mass of biodiesel sample in g, taken for the analyses.

3. Results and discussion on rapid techniques for projecting shelf life

3.1. Hydroperoxide concentration abrupt increase

According to the radical initiated chain mechanism [25,29,30] of FAME oxidation, primary oxidation products — hydroperoxides and conjugated dienes are formed initially during propagation step. Once primary oxidation products have occurred, the oxidation reaction can proceed very rapidly. Lacoste [31] illustrated that oxidation degradation of rapeseed and sunflower biodiesels could be chronologically registered by three analytical techniques and found that occurrence time of oxidation products follows the order: peroxide value of 100 meq O_2/kg; acid value of 0.5 mg KOH/g and last Rancimat IP. When predicting the shelf life of a biodiesel, measurements pertaining to the very beginning of intensive oxidation process are more significant than measurements related to the end of the oxidation process. Negative effect of biodiesel molecule oxidation on engine performance starts at the very beginning of this process. It is proved that the very unstable hydroperoxides have a tendency to attack elastomers [32]. Recording the duration (IP) before sharp peroxide value increases will ensure a reliable shelf life determination of a biodiesel. During this period, there still would not be subsequent, fast accumulation of secondary oxidation products like aldehydes, alcohols, shorter chain carboxylic acids, and higher molecular weight oligomers often called polymers. These compounds are precursors of rancidity and toxicity and their presence in a biodiesel is an indication of already degraded fuel, which is not