Fuel Processing Technology 125 (2014) 223–235

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Experimental study of the factors affecting the oxidation stability of biodiesel FAME fuels

James Pullen, Khizer Saeed *

Low Carbon Energy Research Group, School of Computing, Engineering and Mathematics, University of Brighton, Lewes Road, Brighton BN2 4GJ, United Kingdom

ARTICLE INFO

Article history:
Received 19 December 2013
Received in revised form 19 March 2014
Accepted 22 March 2014
Available online 4 May 2014

Keywords:
Biodiesel
Fatty acid methyl esters (FAME)
Transesterification
Oxidation stability
Rancimat
Autoxidation

ABSTRACT

Oxidative stability of fatty acid alkyl esters or biodiesel during storage is very important as it yields products that degrade biodiesel quality and consequently affect engine performance. Accurate measurement, prediction and control of the oxidative stability of biodiesel from different feedstocks remain a challenging problem in biodiesel research. The current study relates to the investigation of the impacts of variation in feedstock on the oxidative stability of biodiesel, efficacy of various stability models (APE, BAPE, and OX) at predicting biodiesel oxidative stability, and the impacts of antioxidant loads in controlling oxidative instability of biodiesel. Firstly, oxidation stability for twelve different fatty acid methyl ester (FAME) biodiesels was measured to establish the effects of feedstock type on it. Then, fatty acid compositions were measured to establish the efficacy of the various models known as APE, BAPE, and OX proposed for characterizing the susceptibility of FAME to oxidation. Results showed oxidative stability and stability indices did not correlate well indicating that these models are inaccurate indicator for biodiesel stability. The response of the four biodiesel (Palm, Olive, Soyabean, and Jatropha) to the loading of the antioxidant (tertiary butyl-hydroquinone, TBHQ) was investigated to establish antioxidant threshold loading for delaying needed to delay oxidative degradation. It was found that biodiesel with high polyunsaturated fatty acids showed little improvement in oxidative stability to the same antioxidant dose. Finally, the efficacy of Rancimat methods in predicting the storage life of biodiesel was carried out by developing and extrapolating the oxidative stability Arrhenius temperature curves. The results for Sesame and Rapeseed FAME kept at 40 °C showed under prediction of the storage life by the Rancimat method than obtained in real conditions.

1. Introduction

Biodiesel is a drop-in replacement for petro-diesel that can be derived from renewable sources, including a wide range of plant-seed oils, animal fats and even certain lipid-rich algal species. Biodiesel is made via the transesterification of the range of vegetable feedstock oils or animal fats with alcohol; usually methanol to yield fatty acid methyl esters (FAME). Therefore, the chemical composition of biodiesel can vary significantly resulting in extremely varied physical properties. However, biodiesel is biodegradable, less toxic and can reduce harmful tailpipe combustion emissions (CO_2, CO, UHC and PM) relative to petro-diesel [1]. Biodiesel is miscible with petro-diesel, compatible with fuel delivery infrastructure, has high flashpoint for safer handling, and can be used in standard diesel engines requiring no engine modification. Biodiesel also offers improved lubricity over certain low-sulphur petro-diesels and thus can help reduce wear of engine components [2]. Running diesel-engine equipment on biodiesel can be beneficial in terms of environmental impact and energy security.

Biodiesel is susceptible to a process called autoxidation. Autoxidation process in biodiesel occurs when biodiesel is exposed to and reacts with ambient oxygen, and this is accelerated by elevated temperatures exposed to and reacts with ambient oxygen, and this is accelerated by elevated temperatures. Oxidative degradation can occur when biodiesel is kept in storage, or when circulating in an engine fuel system, or even when biodiesel is present as a contaminant within engine oil (after dilution of lube oil with unburned fuel). Biodiesel tends to be less resistant to oxidation than petroleum diesel [3], due to its chemical composition and results in the degradation of fuel properties which can affect on engine performance. A measure of the resistance of fuel to degradation by oxidation is referred to as it's 'oxidation stability'.

A recent detailed review by Pullen and Saeed [5] on the previous research efforts related to biodiesel oxidation stability identified the areas which need urgent research attention to address oxidative degradation [5].

Degradation of biodiesel due to auto-oxidation can cause fuel properties to significantly alter, including: flash point, ester content, the amount of insoluble contaminants (polymeric species), heating value

* Corresponding author. Tel.: +44 1273 642304; fax: +44 1273 642405.
E-mail address: k.saeed@brighton.ac.uk (K. Saeed).

http://dx.doi.org/10.1016/j.fuproc.2014.03.032
0378-3820/

of the fuel, Cetane number, acid value, kinematic viscosity and density. Changes in these properties and in colour from yellow to brown can thus indicate the progress of oxidation [5,6]. The products of biodiesel oxidation such as acids and polymer sediments cause engine fuel filters and injector blockages. Most polymers forming from degradation of biodiesel are difficult to filter out, rendering useless many industry standard stability tests for insolubles in diesel fuels. Formation of acids and polymer sediments [7] can block engine fuel filters and injectors, while acids form a corrosive environment for fuel injection equipment. Degraded biodiesel has been observed to result in coking of injectors due to an increase in viscosity caused by the formation of polymeric species in the degraded fuel. Undesirable oxidation products can affect the performance of fuel pumps and injectors due to increased wear [5,8]. Fuel lines, filters, pumps and orifices can clog [9] and exhaust emissions are performance affected [10]. Such concerns have also been expressed by leading manufacturers of fuel injection equipment [11] who declared that the resistance to oxidation is an inherent characteristics of any biodiesel, since degraded biodiesel has acids and polymers that significantly reduce fuel injection equipment performance and life. Sediments and gums can form plugging pump orifices, fuel filters and leave deposits on fuel system components [12]. Clearly, in order to deliver confidence in the quality of biodiesel fuels it is imperative to understand oxidative degradation and how to prevent associated problems. Clearly, in order to deliver confidence in the quality of biodiesel fuels it is imperative to understand oxidative degradation and how to prevent associated problems.

Exact modelling of oxidative stability of biodiesel is problematic because many factors can play significant roles in it such as fatty acid (FA) composition (unsaturation configuration, molecular weight), impurities (metals, free fatty acids, additives and antioxidants, water), physical parameters (sample mass, agitation, viscosity, temperature, light and air exposure), as well as the degree of prior sample ageing [6,10,16,19,22]. Decoupling and establishing the effects of individual effects can lead to a better understanding and prediction of oxidative stability of biodiesel. Bannister et al. [6] observed that oxidation is exacerbated (catalysed) by the presence of metals (e.g. Zn, Cu) that can be present in an engine fuel system [6]. The effect of alcohol type was investigated by Stavinoha et al. [23] who found that the OS of Soybean ethyl ester was slightly more than for Soybean methyl ester. However, the opposite was found for Sunflower-oil-based alkyl esters; currently there is no clear indication that methyl and ethyl esters have different oxidative stabilities. The blending of the biodiesel and diesel also causes improvement in the oxidative stability of the blend fuel due to the presence of sulphur in diesel fuel [6]—which acts as inhibitor to oxidative degradation of biodiesel [6], and because it is diluted from its neat form.

Recent review by the present authors [5] providing the underlying oxidation chemistry and the implications of oxidation for biodiesel use. It showed that the underlying chemistry of oxidative degradation is fundamentally a consequence of fatty acid composition and structure of the biodiesel FAME. The degree of chain unsaturation i.e. carbon double bonds (C═C) present undergo free radical attack causing hydroperoxide formation. The process of biodiesel oxidation is a self-sustaining chain reaction, proceeding by the general mechanism: initiation, propagation and termination [5]. Hydroperoxides form and decompose to problematic secondary products (acids, polymers). The allylic sites in a fatty acid chain (a methylene CH_2 adjacent to only one double bond) are vulnerable to oxidation. Similarly, a methylene CH_2 group present between two double bonds called bis-allylic sites is twice vulnerable to oxidation. Linolenic acid has two bis-allylic sites and two allylic sites. Linoleic acid has one bis-allylic site and two allylic sites; oleic acid has two allylic sites. For these unsaturated fatty acid components the order of greatest susceptibility to oxidation is linolenic > linoleic > oleic. Hence the levels of unsaturated fatty acids that are present in biodiesel FAME shall fundamentally determine relative susceptibility to oxidation. Therefore, it is necessary to decouple and establish the exact impact of biodiesel FAME composition and structure on oxidative stability to understand the role of individual feedstock types on its biodiesel oxidative stability. Researchers have developed different oxidative stability indices based upon fatty acid composition, which are discussed in detail in Section 2. Efficacy of these indices in predicting oxidative stability of biodiesel fuel has been fully established yet and needs detailed investigations.

Research has shown that it is extremely difficult to completely prevent oxidation in biodiesel and it can only be delayed. Therefore, a number of strategies to delay have been proposed in the literature which includes such as managing the impurities, storage conditions, fatty acid composition and antioxidant dosing in the biodiesel. Previous experimental studies carried out by several authors [4,21,24] have examined biodiesel oxidative stability at varying conditions of storage. Generally, similar trends of deterioration were recorded in oxidative stability and other important fuel properties (ester content, kinematic viscosity, acid value, insoluble contaminants) over extended storage periods. It was found that degradation could occur relatively rapidly in storage. For example Bondioli et al. [25] found that biodiesel stored at 43 °C deteriorated significantly on several key properties after only a few weeks. More detailed study of influencing factors (fatty acid composition, water content, storage temperature, exposure to air, agitation, and light) would be useful to understand biodiesel behaviour in storage. Researchers have investigated loading of anti-oxidants as a potential strategy for delaying biodiesel oxidative degradation during storage.

Typically, antioxidant addition in biodiesel acts to inhibits the oxidation process which can be used to control the oxidation of biodiesel. In the literature, authors have investigated the effects of different antioxidants loading on biodiesel oxidative stability [9,13–20] ranging from naturally occurring Tocopherols, to synthetic tertiary butylhydroquinone (TBHQ), pyrogallol (PY), propyl gallate (PG), butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) antioxidants. It has been found that the concentration between 200 and 1000 ppm is where most of these antioxidants are most effective. A detailed review on the efficacy of biodiesel anti-oxidants has been presented by Dunn [19]. Commercially, synthetic antioxidants (TBHQ, BHA, BHT and PG) have been preferred over natural antioxidants because of their better effectiveness as 1000 ppm dosing of TBHQ improves the oxidative stability of biodiesel by more than two times [20]. TBHQ is therefore considered most effective antioxidants amongst synthetic antioxidant [21]. Also, addition of anti-oxidants in high quantity did not alter the other properties of the biodiesel [20] except slight increase in acid value. However, in the literature the relationship, if any, between the fatty acid composition of biodiesel and amount of the antioxidants have not been fully investigated and established. Establishing this relationship will be useful to establish the threshold limits for antioxidants for different biodiesel types in order to attain the same high level of oxidative stability (OS).

Accurate method for determining biodiesel storage life is urgently needed to predict the biodiesel stability under certain storage conditions. Typically, oxidative stability measured by Rancimat method shows a linear relationship between $\log_{10}$(oxidative stability) vs. temperature, which is Arrhenius equation describing increased reaction rate at higher temperature. Xin J et al. [17] extrapolated oxidative stability results obtained at higher temperatures (T) to predict oxidative stability at lower temperatures. Storage life estimates can be obtained by this method, however such estimates may not represent real time conditions as the process of oxidation may be different in real lower temperature conditions than assumed by Xin J et al. [17] be unreliable since it is assumed that the oxidation mechanism does not alter under less severe conditions. Xin J et al. [17] concluded that biodiesel fuel stored at lower temperature is favourable for long time storage of biodiesel without degradation. However, in real-world storage conditions at temperatures nearer ambient may result in different oxidation behaviour. Study of the reliability of storage life estimates derived from Rancimat oxidation stability measurements represents a promising strategy which needs to be investigated further to establish its

effectiveness in predicting storage life for biodiesel before degradation. Also, Rancimat method typically measures the induction period in hours as stability conditions, which is mentioned 6 h for EN 14214 biodiesel standards. However, it is unclear what the Rancimat OS result (h) actually means in terms of the anticipated storage life for biodiesel fuel, or for its performance in a diesel engine.

2. Indices for oxidative stability calculations

A method to predicting oxidative stability of biodiesel and confidently estimate the storage life of biodiesel fuel is necessary but not yet possible [26]. Biodiesel fatty acid profile based models or indices have been proposed in the literature such as *Iodine Value (IV)*, *Allylic Position Equivalent (APE)* and *Bis-allylic Position Equivalent (BAPE)* and *Oxidizability (OX)*. The compositional indices can be necessary to interpret fatty acid profile data and enable calculation of the relative susceptibility of different biodiesel FAMEs to oxidation.

Iodine value (IV) or iodine number measures the degree of unsaturation in organic compound and has been most commonly used to infer oxidative stability [27]. Typically, it is measured by the equations below:

$$IV_{pure} = 100 \times \frac{253.81 \times db}{MW_f} \quad (1)$$

where IV_{pure} is the iodine value of the fatty compound; MW_f is molecular weight of the fatty compound, db is the number of double bonds present in the fatty acid chain, and 253.81 is the atomic weight of the two iodine atoms that are theoretically added to one double bond [28].

The IV of a mixture of FAMEs can be calculated according to the fatty acid profile by Eq. (2).

$$IV_{mixture} = \sum X_{ME}(wt.\%) \cdot IV_{pure} \quad (2)$$

where X_{ME} is the weight percentage of each fatty compound. Eqs. (1) and (2) assume full iodination. The idea behind the use of IV as a biodiesel quality parameter is that it should indicate the propensity of FAME fuel to autoxidize, which can lead to fuel quality degradation. The limit of *IV is 120* in EN 14214 prevents use of highly unsaturated fatty oils for biodiesel production. However there is a debate whether an IV limit is necessary in EN 14214. The argument for having an IV specification has long been related to OS, since higher IV supposedly indicates greater propensity of FAME to oxidize. However, this argument is questionable since it has been reported that IV does not correlate well with OS [29].

Alternatively, Knothe [28] showed that APE and BAPE indices can be used as biodiesel stability indices. Oleic (18:1), Linoleic (18:2) and Linolenic (18:3) acid each contain two allylic sites, hence APE is calculated according to Eq. (3).

$$APE = 2 \times (A_{C18:1} + A_{18:2} + A_{18:3}) \quad (3)$$

where A = wt.% amount of respective C18 compounds.

Linoleic acid contains one bis-allylic site and linolenic acid contains two, hence BAPE is calculated according to Eq. (4).

$$BAPE = (A_{18:2} + 2 \times A_{18:3}). \quad (4)$$

McCormick et al. [16] showed that Oxidizability (OX) index can be used as stability index which can be calculated using Eq. (5):

$$OX = 0.02(A_{C18:1}) + (A_{18:2}) + 2(A_{18:3}) \quad (5)$$

where A = wt.% amount of respective C18 compounds. The coefficients in Eq. (5) represent the relative rates of oxidation of the compounds. The OX formula and APE and BAPE are similar as all of them put importance on the allylic and bis-allylic carbons [27] but OX index is applicable to biodiesel containing 18 carbons chains [16].

These indices (APE, BAPE and OX) quantify the degree of unsaturation of a particular FAME, where a greater index value indicates an increased level of fatty acid unsaturation. It is noted that OX and BAPE are very similar, except that OX also considers monounsaturated oleic (C18:1) content; weighted to be a factor of 50 times less reactive than linoleic (18:2). Eq. (5) for OX thus infers relative rates of oxidation: 1 for Oleates, 50 for Linoleates, and 100 for Linolenates. However, linoleic acid has twelve times faster oxidation rate than oleic acid and linolenic acid has al least 25 times higher rate than oleic acid [30,27].

Waynick [27] and Yamane et al. [30] suggested an inversely proportional relationship between oxidative stability with the presence of different acid compositions in the biodiesel:

$$\frac{1}{OS}\alpha[C18:1] + 12[C18:2] + 25[C18:3]. \quad (6)$$

However, there is disagreement in the literature for the different rates used in Eq. (1) as some authors have assigned rates of 1, 41 and 98 to Oleates, Linoleates and Linolenates respectively [10,31].

A general stability index (SI) can be calculated (Eq. (7)):

$$SI = \frac{\sum(A_{18:i} \times R_{rate})}{D} \quad (7)$$

where i = 1, 2 or 3; and R_{rate} is the relative rate of oxidation for the unsaturated C18 compound. E.g. using rates (1, 41, 98), if D (the denominator) is chosen (=49), then maximum SI is 200 (for 100% linolenate). Eq. (7) becomes Eq. (8), which has coefficients very similar to Eq. (5).

$$SI = 0.02(A_{C18:1}) + 0.84(A_{18:2}) + 2(A_{18:3}). \quad (8)$$

Using rates of oxidation (1, 12 and 25) reported by Yamane et al. [30], setting D = 12.5, (max SI is 200), Eq. (7) becomes Eq. (9):

$$SI = 0.08(A_{C18:1}) + 0.96(A_{18:2}) + 2(A_{18:3}). \quad (9)$$

Compared to Eqs. (5) and (8), Eq. (9) infers greater reactivity for 18:1 (by a factor of 4). Eqs. (8) and (9) infer slightly lower reactivity for 18:2 compared to Eq. (5). Investigation of whether or not these differences are significant appears warranted. Correlation of OS has been reported with BAPE and APE which characterize the distribution of fatty acid unsaturation [9]. However limited data exists on the correlation between OS and recognised stability indices so that further study is warranted.

3. Aim and objectives

It is evident from the literature review in Sections 1 and 2 that modelling oxidative stability of biodiesel is problematic because of many factors that play significant roles in biodiesel stability. However, fatty acid composition of biodiesel plays important role in oxidative stability of biodiesel from different feedstocks. The general aim of the present experimental study was to better understand the meaning of oxidative stability of biodiesel as measured by the Rancimat method in terms of fatty acid composition and the efficacy of various composition based models at predicting oxidative stability of biodiesel. The specific objectives of the current study are:

1. To study the relationship between oxidative stability and fatty acid based stability indices.
2. To study the oxidative stability response of variation in biodiesel fatty acid composition to under antioxidant loading, to assess the correlation between oxidative stability response and stability indices.

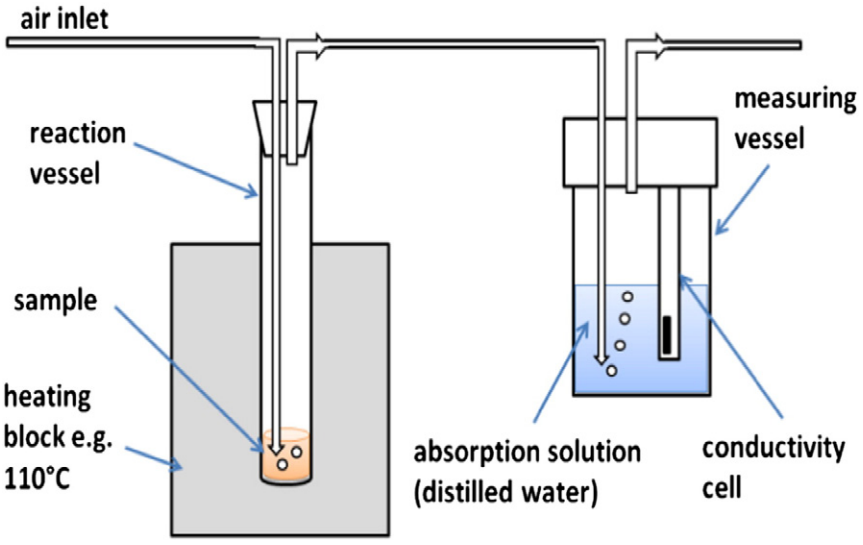


Fig. 1. Principle of the Rancimat method.

3. To obtain storage life estimates derived from Rancimat oxidative stability measurement and evaluate these estimates, as well as biodiesel oxidation behaviour under controlled storage conditions.

4. Experimental procedure

A range of biodiesel FAME samples (500 ml aliquots) was prepared from different oil/fat feedstocks by a consistent base-catalysed transesterification method: (6:1 methanol:oil molar ratio, 1%m/m NaOH catalyst, 60 °C reaction temperature, 60 min reaction time, >600 rpm stir speed). After decanting glycerol, samples were purified by washing with water and dried by open-to air stirring in a beaker. Preparation of each biodiesel sample consisted of two principle stages: (i) transesterification of vegetable oil to methyl ester (reaction with methanol and catalyst), and (ii) purification of crude esters: decanting glycerol, water-washing esters until pH neutral, final drying and filtration.

Twelve different FAME samples were prepared from respective oils: Sunflower [SN], Rapeseed [R], Cold-pressed Rapeseed [CPR], Palm [P#2], Groundnut [G], Sesame [SES], Grapeseed [GR], Corn [CN], Soybean [S#2], Jatropha [J#2], Olive [O], and Used Cooking Oil [UCO]. Two further FAMEs were made from animal fats: Lard [LME] and Tallow [TME]. All oils/fats were purchased from a local supermarket, except Jatropha and UCO samples which were obtained from a local biodiesel manufacturer. Four further commercially produced FAME samples were also obtained and tested for comparison, respectively made from: Coconut [C], Palm [P#1], Soyabean [S#1] and Jatropha [J#1] oils.

Water content of each FAME sample was checked by titration [mg/kg] using a Karl–Fischer Coulometer supplied by Metrohm Ltd., Herisau/Switzerland., according to standard method (EN ISO 12937 [32-33]). Each sample was dried to <500 ppm and filtered under vacuum

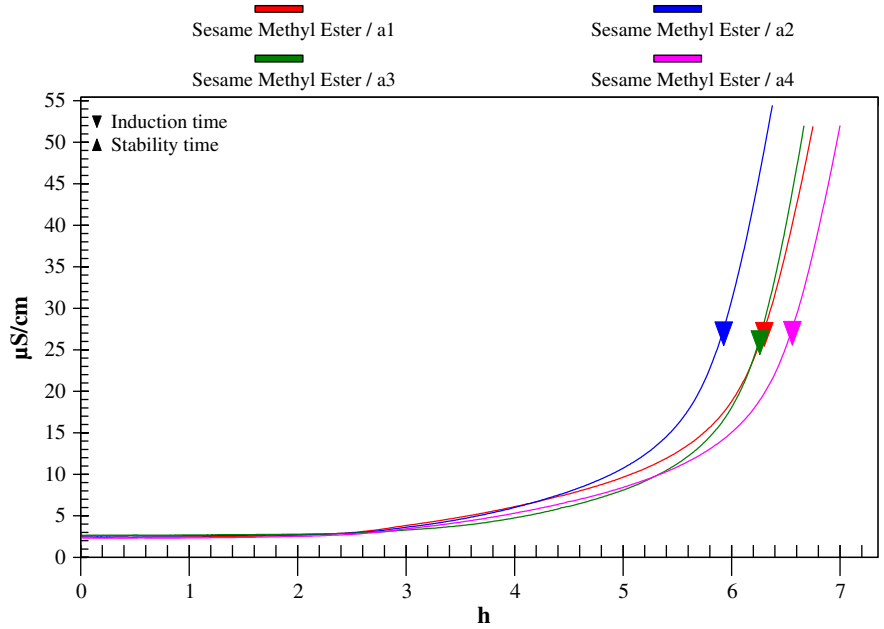


Fig. 2. Four replicate determinations of RIP obtained for Sesame Methyl Ester, showing Rancimat cell conductivity (µs/cm) with test duration (hours). The induction time (RIP) was automatically evaluated by the Rancimat software.

Table 1
Measured composition (%m/m) for 18 different biodiesel FAME samples.

FAME specie	P#1	P#2	S#2	S#1	C	R	CPR	SN	CN	O	G	GR	SES	J#1	J#2	UCO	LME	TME
Caprylate 8:0					6.6													
Caprate 10:0					5.1													
Laurate 12:0					42.2													
Myristate 14:0	1.0	1.0	0.1	0.1	15.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.3	1.1	2.6
Palmitate 16:0	32.7	42.5	10.5	10.0	9.0	6.6	4.6	6.1	10.9	10.6	7.7	7.4	10.1	13.5	13.5	11.2	21.2	19.8
Stearate 18:0	3.6	4.4	4.0	3.9	2.8	2.2	1.6	4.2	3.8	3.2	2.0	3.8	4.0	5.6	5.6	3.1	13.2	17.0
cis-9 Oleate 18:1	47.4	39.5	23.8	26.4	10.4	49.1	59.2	24.6	26.2	75.3	57.2	24.7	37.8	38.4	38.4	45.0	34.0	34.4
Linoleate 18:2	13.3	10.7	52.4	53.8	6.9	30.1	18.5	62.6	50.1	7.4	24.1	61.8	45.1	40.7	40.7	31.2	8.7	1.6
Linolenate 18:3	0.5	0.3	7.1	3.9	0.6	7.4	10.5	0.3	5.5	0.7	0.3	0.4	0.7	0.3	0.3	4.9	2.0	0.2
Arachidate 20:0	0.4	0.4	0.4	0.3	0.1	0.5	0.6	0.3	0.4	0.4	1.0	0.3	0.5	0.2	0.2	0.4	0.2	0.1
Behenate 22:0			0.4	0.5	0.6	0.4	0.3	0.7	0.5	0.2	2.8	0.5	0.2			0.4		
Erucate 22:1					0.3	1.5	0.0	0.0	0.4	0.3	0.0				0.4			
Lignocerate 24:0			0.2		0.2	0.3	0.3	0.3		1.9	0.3	0.2			0.3			
Other[a]	1.1	1.2	1.1	1.1	0.4	3.1	2.8	0.8	2.2	1.7	2.6	0.7	1.3	1.2	1.2	2.8	19.6	24.4

[a] Other components were: LME: Palmitoleic 16:1 (3.5%), Elaidic 18:1 (10.4%), TME: Myristoleic 14:1 (1.3%), Pentadanoic 15:0 (0.3%), Pentadecenoic 15:1 (0.5%), Palmitoleic 16:1 (8.2%), Elaidic 18:1 (9.3%).

through filter paper (Whatman GF/F, 0.7 μm) to remove any particle contaminants before being stored in airtight jars in darkness. Further analysis was carried out according to the following standard test methods, which were all published by the British Standards Institute.

For each sample, Gas Chromatography (GC) standard method (BS EN 14103 [34]) was used to determine FAME content and composition, including linolenic acid content and content of FAME with ≥4 double bonds [%m/m]. The method used a DB-WAX capillary column coated with a polyethylene glycol stationary phase of length 30 m, internal diameter 0.32 mm, film thickness 0.25 μm. The GC system was an Agilent 7890A equipped with a split/splitless injector, flame ionization detector (FID), data log PC with ChemStation software, supplied by Agilent Technologies UK Limited.

Iodine value was determined by titration with sodium thiosulfate solution [g I2/100 g], according to test method (EN 14111 [35]) using an 809 Titrando, auto-titrator, Metrohm Ltd., Herisau/Switzerland. OS was measured by the Rancimat method using an 873 Biodiesel Rancimat instrument, supplied by Metrohm Ltd., Herisau/Switzerland. Rancimat Induction Period (RIP) was determined [h] according to standard method (BS EN 14112 [36]). Results were determined as quadruplicate averages, unless otherwise stated. The test involved a steady flow rate (10 l/h) of air passed in the 3 gramme biodiesel sample, heated to 110 °C. The passed out air contains volatile, water-soluble short chain carboxylic acids (secondary oxidation products) into a distilled water (50 ml) containing flask. An electrode in the water flask continuously measures the conductivity of the water — see Fig. 1. Conductivity was recorded to the Rancimat data logging PC software, and a rise in conductivity indicated oxidation of the sample. Rancimat Induction Period (RIP) measured in hours, was automatically evaluated by the software in Rancimat system by time based second derivative of conductivity and gives automatic values of RIP in hours as the duration of time to reach this maximum point. For example, Fig. 2 shows replicate RIP determinations obtained for Sesame Methyl Ester. The Rancimat instrument allowed simultaneous testing of up to 8 samples.

Four of the FAME samples (Palm, Olive, Soyabean, and Jatropha) were dosed with antioxidant additive (tertiary butyl-hydroquinone, TBHQ) in order to assess OS response. TBHQ was weighed into the pre-weighed FAME sample using an analytical balance (+/−0.0001 g) and dissolved by stirring.

Two FAMEs (Sesame and cold-pressed Rapeseed) were stored at 40 °C in a temperature-controlled water bath, for over 100 days. Kinematic viscosity (KV40) and acid value (AV) of the samples were

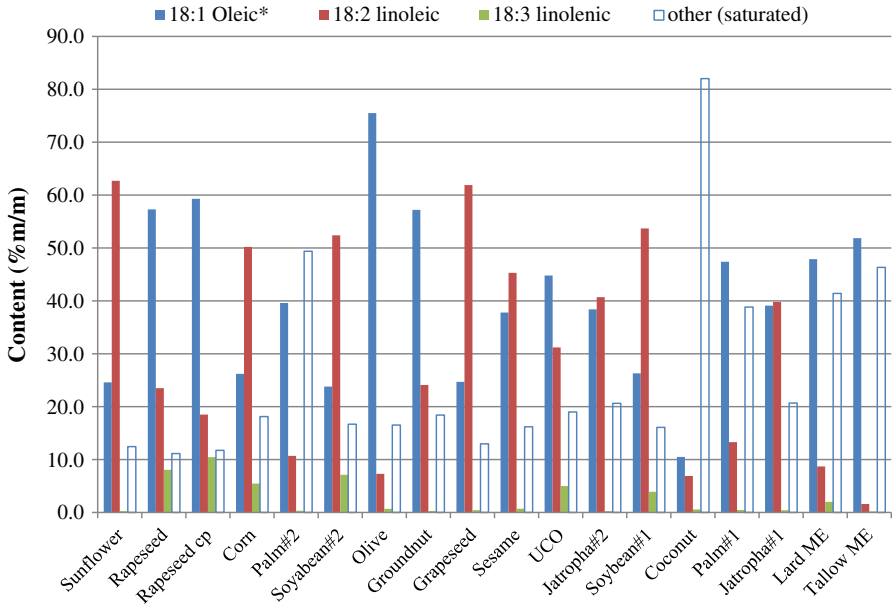
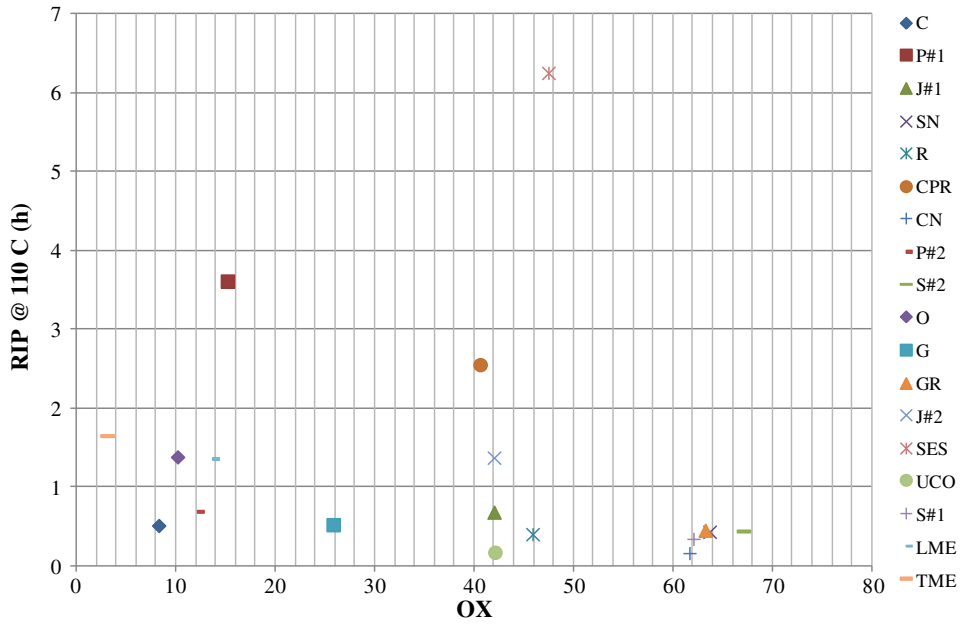


Fig. 3. Unsaturated vs. saturated FAME content (%m/m) for 18 different biodiesel samples (*For comparison, all mono-unsaturated components of animal fats are shown as 18:1 oleic).



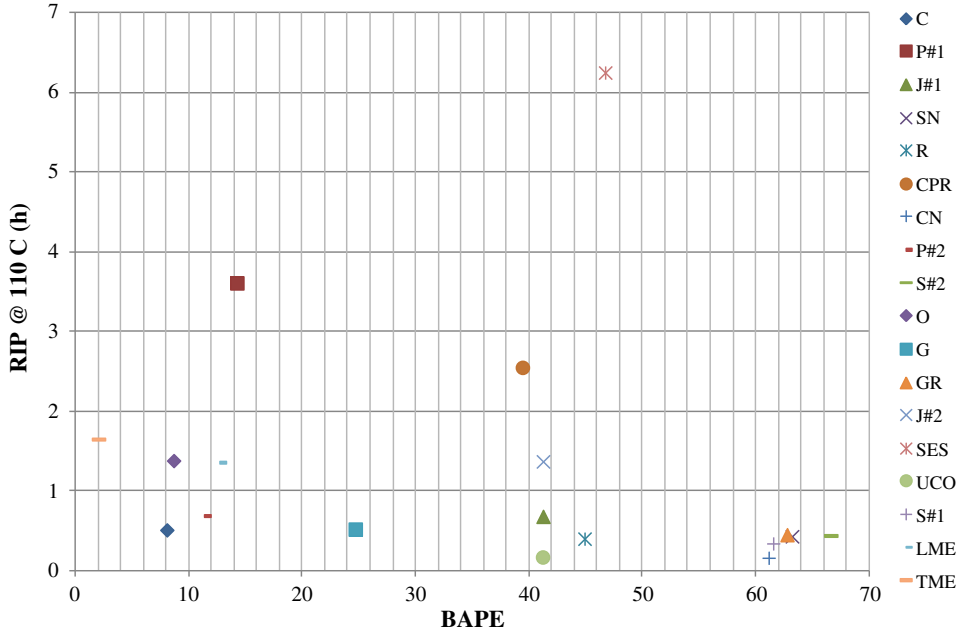
Sunflower [SN], Rapeseed [R], Cold-pressed Rapeseed [CPR], Palm [P#2], Groundnut [G], Sesame [SES], Grapeseed [GR], Corn [CN], Soybean [S#2], Jatropha [J#2], Olive [O], and Used Cooking Oil [UCO]. Lard [LME] and Tallow [TME], Coconut [C], Palm [P#1], Soyabean [S#1] and Jatropha [J#1] oils.

Fig. 4. Correlation of OX with RIP for 18 different biodiesel FAME samples.

periodically monitored. KV at 40 °C was measured by glass capillary viscometer [mm^2/s], according to standard method (EN ISO 3104 [37]) using a temperature controlled water-bath: TCB-7 Mk II, Poulten Selfe & Lee Ltd. AV was measured by auto-titration of samples with potassium hydroxide solution [mg KOH/g], according to standard method (EN 14104 [38]) using a Metrohm 809 Titrando, auto-titrator.

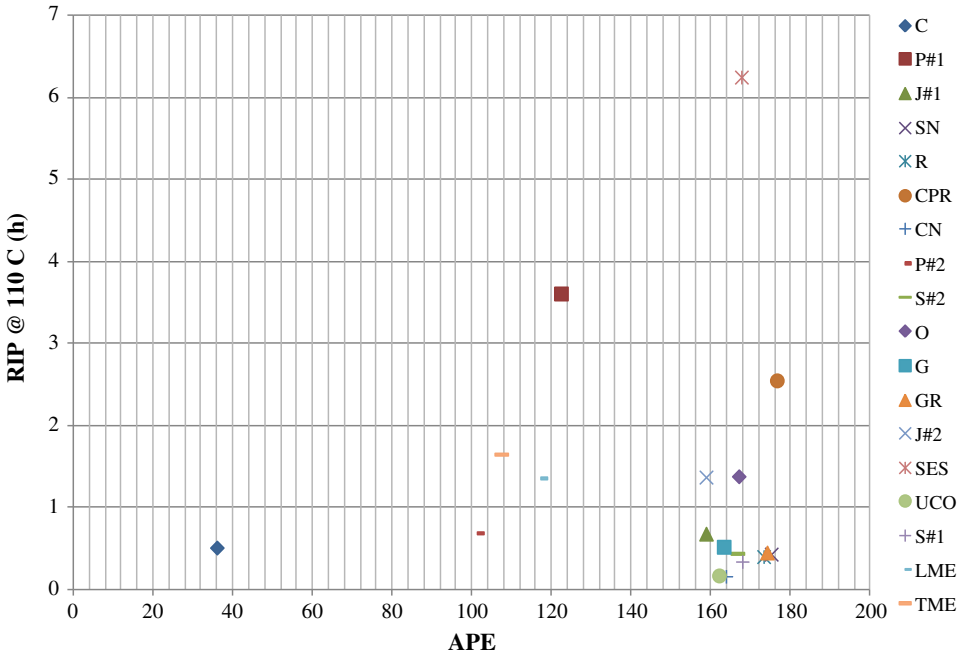
5. Results and discussion

Fatty acid composition results measured for each FAME sample are shown in Table 1. The identity of each FAME specie is abbreviated (X:Y) where X denotes the carbon chain length, and Y is the number of double bonds present in the fatty acid moiety. Saturated fatty acid



Sunflower [SN], Rapeseed [R], Cold-pressed Rapeseed [CPR], Palm [P#2], Groundnut [G], Sesame [SES], Grapeseed [GR], Corn [CN], Soybean [S#2], Jatropha [J#2], Olive [O], and Used Cooking Oil [UCO]. Lard [LME] and Tallow [TME], Coconut [C], Palm [P#1], Soyabean [S#1] and Jatropha [J#1] oils.

Fig. 5. Correlation of BAPE with RIP for 18 different biodiesel FAME samples.

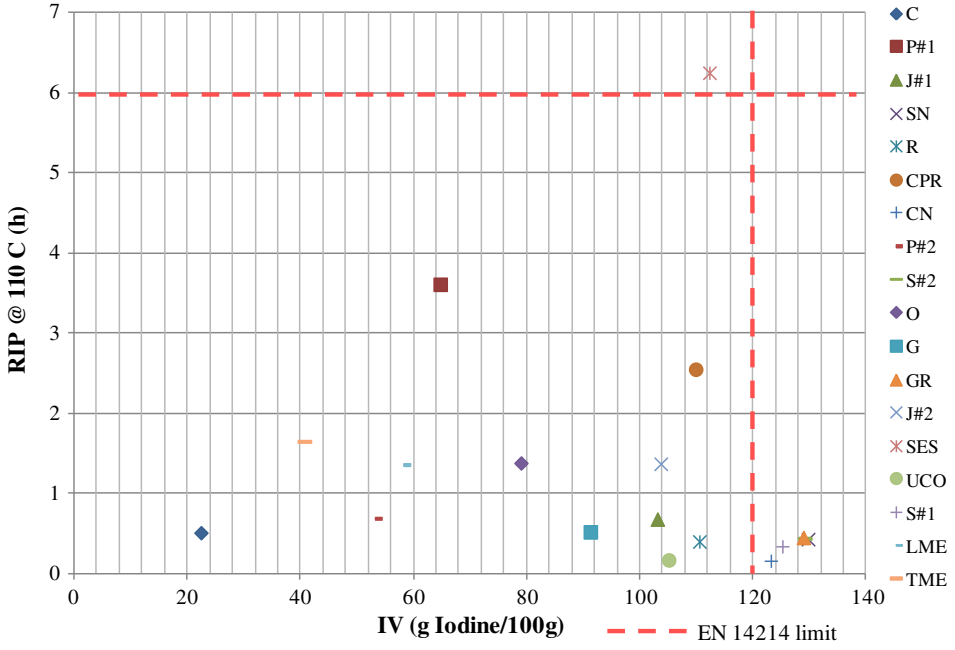


Sunflower [SN], Rapeseed [R], Cold-pressed Rapeseed [CPR], Palm [P#2], Groundnut [G], Sesame [SES], Grapeseed [GR], Corn [CN], Soybean [S#2], Jatropha [J#2], Olive [O], and Used Cooking Oil [UCO]. Lard [LME] and Tallow [TME], Coconut [C], Palm [P#1], Soyabean [S#1] and Jatropha [J#1] oils.

Fig. 6. Correlation of APE with RIP for 18 different biodiesel FAME samples.

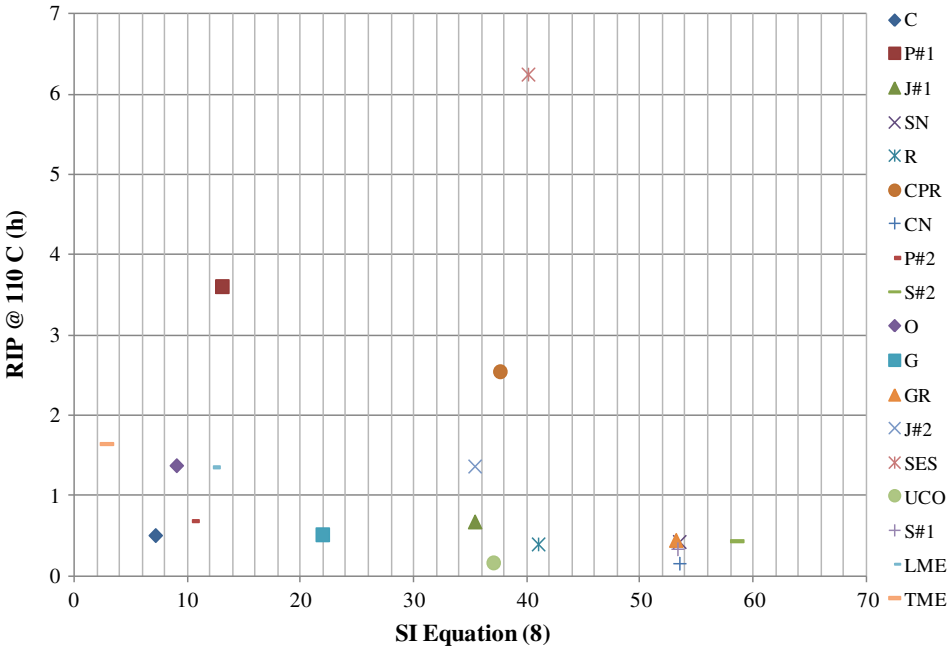
chains contain zero double bonds (Y = 0); mono-unsaturated chains oleate and erucate contain one double bond (Y = 1); di-unsaturated Linoleate (Y = 2); tri-unsaturated Linolenate (Y = 3).

Table 1 shows that fatty acid composition varied significantly according to the feedstock type. In all of the FAME samples (except Coconut), the main methyl ester components were: palmitate 16:0 (5–43%), stearate 18:0 (2–17%), cis-9 Oleate 18:1 (10–76%), Linoleate 18:2 (1.6–63%), and Linolenate 18:3 (0.2–10.5%). Other FAME components were present generally in smaller amounts, not more than a few percent by mass. The composition of Coconut oil methyl ester [C] was notably different to the 17 other samples due to the presence of significant amounts of shorter chain fatty acids (Myristate 14:0, Laurate 12:0,



Sunflower [SN], Rapeseed [R], Cold-pressed Rapeseed [CPR], Palm [P#2], Groundnut [G], Sesame [SES], Grapeseed [GR], Corn [CN], Soybean [S#2], Jatropha [J#2], Olive [O], and Used Cooking Oil [UCO]. Lard [LME] and Tallow [TME], Coconut [C], Palm [P#1], Soyabean [S#1] and Jatropha [J#1] oils.

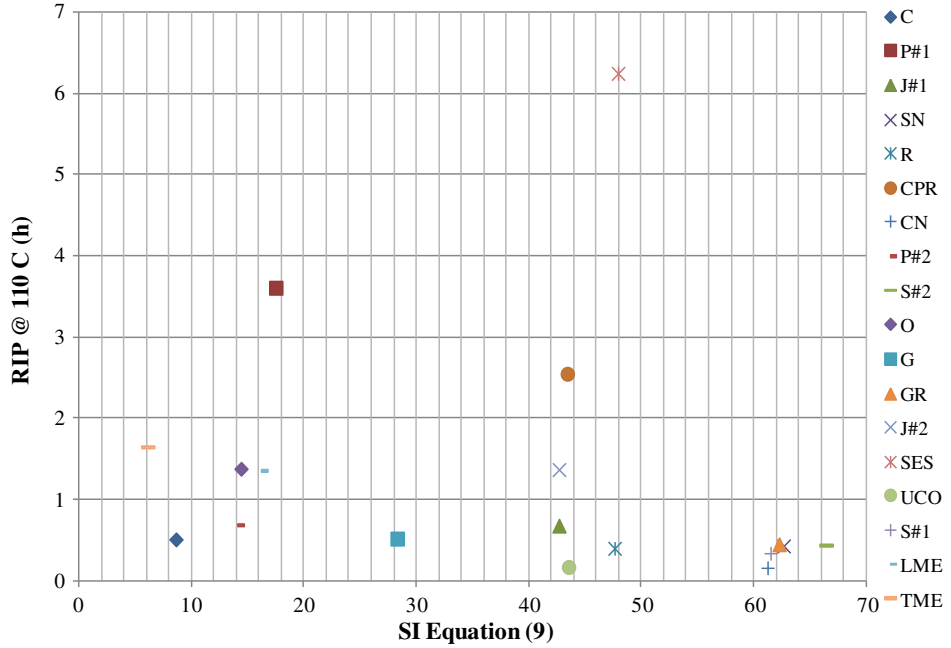
Fig. 7. Correlation of iodine value with RIP for 18 different biodiesel FAME samples.



Sunflower [SN], Rapeseed [R], Cold-pressed Rapeseed [CPR], Palm [P#2], Groundnut [G], Sesame [SES], Grapeseed [GR], Corn [CN], Soybean [S#2], Jatropha [J#2], Olive [O], and Used Cooking Oil [UCO]. Lard [LME] and Tallow [TME], Coconut [C], Palm [P#1], Soyabean [S#1] and Jatropha [J#1] oils.

Fig. 8. Correlation of SI Eq. (8) with RIP for 18 different biodiesel FAME samples.

Caprate 10:0, and Caprylate 8:0). Animal fats: Tallow [TME] and Lard [LME] contained relatively more stearic acid 18:0, as well as 16:1 Palmitoleic acid and 18:1 Elaidic acid (the trans-isomer of oleic). Palm [P#1], Rapeseed [R], Olive [O], Groundnut [G], UCO, [LME] and [TME] contained mostly 18:1, while Soy [S], Sunflower [SN], Corn [CN], and Grapeseed [GR] contained mostly 18:2. Jatropha [J] and Sesame [SES] contained more equal amounts of 18:1 and 18:2. All samples contained <12.0%m/m methyl linolenate; meeting EN 14214 specification. Cold-pressed Rapeseed [CPR] had the highest level of Linolenate 18:3 (10.5%m/m), followed by, [R] (8.1), [S#2] (7.1), [S#1] (3.9), [CN] (5.5), and [UCO] (5.0%m/m). All other samples contained <1%m/m. None of the samples contained any methyl ester with ≥4 double bonds. It is



Sunflower [SN], Rapeseed [R], Cold-pressed Rapeseed [CPR], Palm [P#2], Groundnut [G], Sesame [SES], Grapeseed [GR], Corn [CN], Soybean [S#2], Jatropha [J#2], Olive [O], and Used Cooking Oil [UCO]. Lard [LME] and Tallow [TME], Coconut [C], Palm [P#1], Soyabean [S#1] and Jatropha [J#1] oils.

Fig. 9. Correlation of SI Eq. (9) with RIP for 18 different biodiesel FAME samples.

Table 2
Fuel properties and stability indices for 18 different biodiesel FAME samples measured according to EN 14214 standard test methods.

Test	Method	Units	Specification		Commercial FAME samples				Prepared FAME samples											
			Min	Max	S#1	C	P#1	J#1	SN	R	CPR	CN	P#2	S#2	O	G	GR	J#2	SES	UCO	L	T
Oxidation stability @110 °C			6		0.34	0.51	3.61	0.68	0.43	0.40	2.55	0.16	0.69	0.44	1.38	0.52	0.45	1.37	6.25	0.17	1.36	1.65
Standard deviation	EN 14112	Hours	–	–	0.02	0.02	0.14	0.01	0.02	0.02	0.08	0.02	0.02	0.01	0.16	0.04	0.02	0.21	0.22	0.02	0.12	0.17
Ester content	EN 14103	#m/m	96.5		96.8	87.2	97.4	98.4	98.2	97.3	97.6	97.3	98.1	97.4	98.5	98.1	97.9	99.0	96.8	94.1	95.5	90.2
Linolenic acid methyl ester	EN 14103	#m/m		12	3.9	0.6	0.5	0.4	0.3	8.1	10.5	5.5	0.3	7.1	0.7	0.3	0.4	0.3	0.7	5.0	0.9	0.3
Polyunsaturated methyl ester (≥4 double bonds)	EN 14103	#m/m		1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

understood that this EN 14214 specification serves to exclude highly oxidatively-unstable oils, such as fish oils, as biodiesel feedstocks.

Fig. 3 is a plot of data showing the amounts of unsaturated fatty acids (Oleic, Linoleic, Linolenic) and all other saturated components combined together as 'other' FAME components. Clearly, Coconut, Palm, Lard and Tallow contained the most saturated components. Sunflower, Rapeseed, and Grapeseed contained relatively more unsaturated FAMEs. Stability indices were evaluated from fatty acid profiles (Table 1). IV, OX, APE and BAPE were calculated using Eqs. (2)–(5), and SI values using Eqs. (8) and (9). Calculation results are detailed in Figs. 4–9. Table 2 shows the results for RIP in relation with the ester content, biodiesel with ≥4 double bonds and the amount of linolenic acid.

Figs. 4–9 show stability indices plotted against average RIP measurements. BAPE and OX reported very similar values (Figs. 4 and 5), since the oleic parameter differentiating Eqs. (4) and (5) made very little difference to the index value. Even in the case of Olive [O], which contained 75% methyl oleate, the BAPE and OX values were nearly identical. Comparing Figs. 4 and 5 with Fig. 7, it can be seen that OX and BAPE discriminated between samples differently to iodine value. In Fig. 7, the relative positions of several of the data points are shifted. Two are shifted up the index scale: cold pressed Rapeseed slightly and especially Olive, while Coconut was shifted down the scale. IV predicted a different relative order of susceptibility to oxidation, because IV does not depend on the exact nature of the double bonds in the structure; it establishes average number of carbon double bonds (C═C) per molecule. Serving as a stability index, IV treats all double bonds as being equally reactive. However this is not the case, since bis-allylic sites present in linoleic acid and linolenic acid are far more susceptible to oxidation than allylic sites due to the relatively greater rates of oxidation [10].

Considering Fig. 7, data points for Olive [O] and cold pressed Rapeseed [CPR] showed relatively increased average number of double bonds per molecule amongst the other samples. Whereas O and CPR data points in Figs. 4 and 5, showed relatively reduced average number of bis-allylic positions per molecule. Hence OX (and BAPE) indices predicted relatively lower reactivity for these samples than indicated by IV. In contrast for Coconut [C], the average number of double bonds per molecule was relatively low amongst the other samples, but the average number of bis-allylic positions per molecule was relatively higher; hence OX (and BAPE) indices predicted relatively greater reactivity for Coconut than indicated by IV.

APE values (Fig. 6) are proportional to the average number of allylic positions per molecule; the samples fell into roughly 2 groups, with one low outlier (Coconut). The high APE group identified samples containing more unsaturated C18 fatty acids. Low APE values identified samples that contained the highest levels of saturated components: Coconut, Palm and the animal fats.

Figs. 8 and 9 show SI values calculated according to Eqs. (8) and (9) respectively; comparison of these plots with Fig. 4 shows that the different relative rates of oxidation assumed in each case, only slightly affected the predicted order of susceptibility to oxidation.

Results for RIP (Table 2) varied significantly amongst the samples; all (except Sesame, 6.25 h) failed to meet the EN 14214 requirement (≥6 h). Standard deviations indicated that the differences in average RIP results were statistically significant, with reasonably good result

Table 3
RIP of FAME samples after dosing with TBHQ antioxidant. Bracketed values show the increase in RIP relative to 0 ppm.

TBHQ dose (ppm)	RIP (h) @110 °C (EN 14112)			
	P#2	O	S#1	J#1
0	0.69	1.38	0.34	0.68
2000	3.01 (2.32)	29 (27.6)	2.66 (2.32)	1.65 (0.97)
4000	14.66 (13.97)	43.2 (41.8)	7.83 (7.49)	11.7 (11.02)

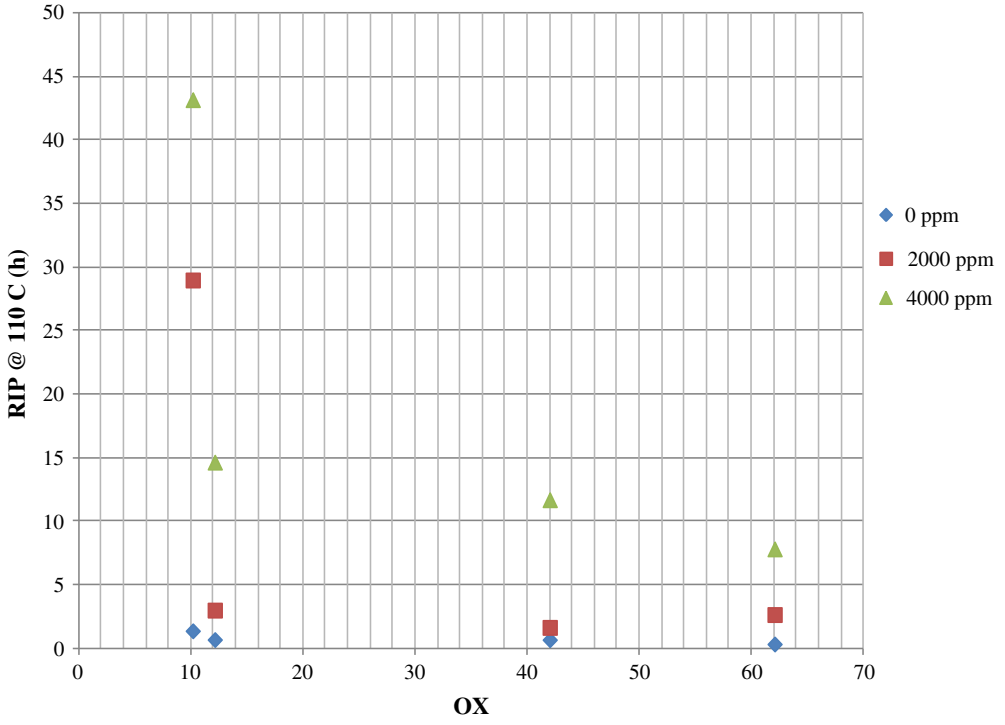


Fig. 10. RIP response to 2000 ppm and 4000 ppm TBHQ dose shown as function of OX stability index value.

precision. The majority (11) of the FAME samples showed very low RIP (<1 h). Palm [P#1] was 3.61 h, though [P#2] was 0.69 h. Likewise, Cold-pressed Rapeseed [CPR] was 2.55 h, though refined Rapeseed [R] only 0.4 h. Jatropha#1 was 0.68 h compared to [J#2], 1.37 h.

Figs. 4 to 9 show that samples with similar stability indices recorded very different RIP results. It is thought that this was probably due to varying amounts of residual antioxidant (e.g. Tocopherol) present in samples. For example, cold-pressed Rapeseed oil would be expected

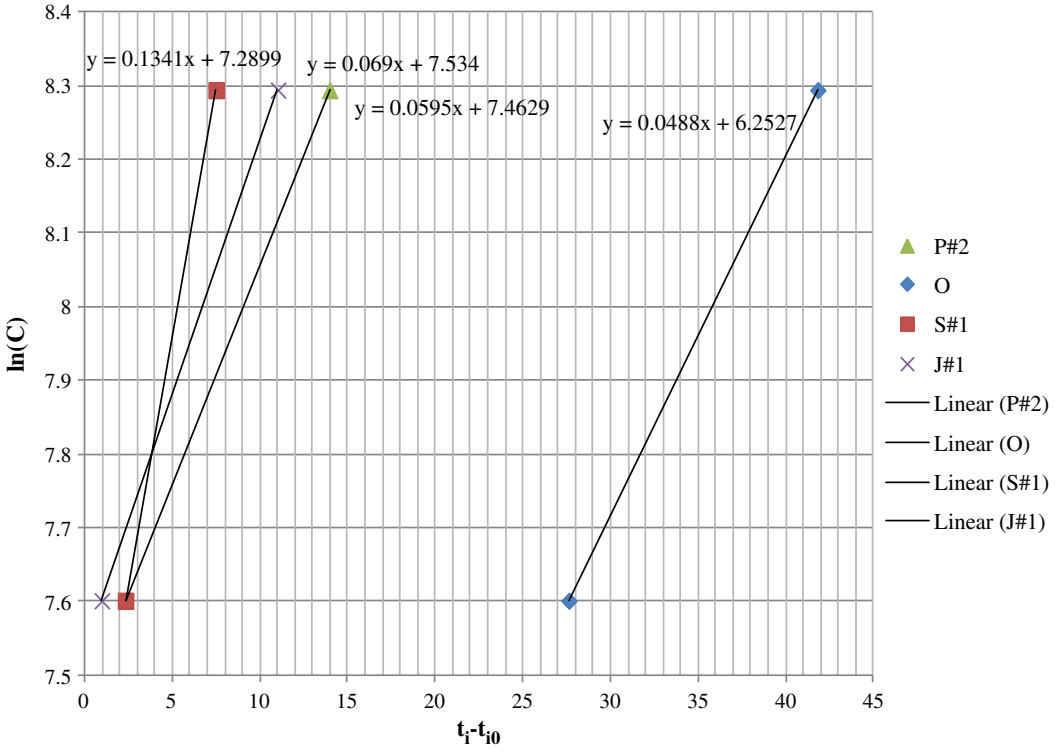


Fig. 11. RIP increase (t_i–t_{i0}) vs. the natural logarithm of antioxidant concentration (C).

Table 4
RIP (h) measured at discrete Rancimat test temperatures for methyl esters of cold pressed Rapeseed (CPR) and Sesame (SES) oil.

CPR		SES	
Test temperature (°C)	RIP (h)	Test temperature (°C)	RIP (h)
110	2.65	110	6.29
110	2.44	110	5.92
110	2.59	110	6.25
110	2.51	110	6.55
100	3.90	100	13.11
100	5.00	100	13.17
100	4.86	100	13.25
100	4.54	100	12.55
90	8.90	90	27.03
90	10.00	90	26.58
90	9.72	90	27.20
90	9.08	90	26.70
80	21.24	–	–
80	21.08	–	–
80	20.48	–	–
80	20.50	–	–

to contain more residual antioxidant compared to refined Rapeseed oil, since natural antioxidant is better preserved by the cold-pressing process. Also, Sesame oil is considered to be more stable than most vegetable oils due to antioxidants naturally present in the oil [39]; it is rich in Tocopherol (Vitamin E), as well as naturally-occurring preservatives, Sesamol and Sesamin. In summary, poor correlation between stability models and RIP suggested that none of the indices can correctly indicate oxidative stability correctly measured by Rancimat method, and indicated RIP strongly depended on other factors, such as the content of antioxidants (not measured by stability indices).

Biodiesel made from Jatropha, Palm, Olive and Soyabean was added with TBHQ antioxidant to evaluate RIP response. These four FAMEs were selected because of their different stability indices (high, medium, and low). Table 3 shows RIP results after dosing each sample with

Table 5
KV40 and AV recorded at intervals of storage at 40 °C for CPR and SES.

Storage time		SES		CPR	
Days	Hours	KV40 (mm^2/s)	AV (mg KOH/g)	KV40 (mm^2/s)	AV (mg KOH/g)
0	0	4.34	0.47	4.42	0.41
4	96	4.43	0.46	4.48	0.47
14	336	4.45	0.41	4.52	0.48
23	552	4.46	0.49	4.65	0.72
32	768	4.46	0.51	4.67	0.82
43	1032	4.46	0.52	4.69	0.88
57	1368	4.46	0.53	4.79	1.07
72	1728	4.46	0.54	4.97	1.36
88	2112	4.52	0.57	5.335	1.52
102	2448	4.60	1.11	5.52	1.81

2000 and 4000 ppm (mg/kg) TBHQ. Values for RIP increase (calculated as RIP_{dosed} minus $RIP_{un\text{-}dosed}$) are shown in brackets. Results indicate that samples did not respond equally to the same TBHQ dose. RIP of Palm, Soy and Jatropha increased slightly though showed relatively little response to 2000 ppm, and the EN 14214 requirement >6 h was not met. In contrast, Olive responded dramatically to the 2000 ppm dose. Fig. 10 shows the effects of the anti-oxidant loading for the OX index. It can be clearly seen from Fig. 10 that the maximum effect of loading the anti-oxidant is observed at low OX value and the effects is seen to be reducing with increasing OX value. RIP of all samples responded well to 4000 ppm (Fig. 10) and the more saturated FAME samples (lower OX) responded relatively better. This trend wasn't so clear at 2000 ppm. Data points are few, but Fig. 10 suggests that FAME of higher OX, needed a relatively greater antioxidant dose in order to achieve the same improvement in RIP.

Fig. 11 shows data from Table 3 (RIP increase and antioxidant concentration) plotted according to Eq. (10) given by Xin et al. [17]:

$$\ln C = k(t_i - t_{i0}) + \ln C_{cr} \quad (10)$$

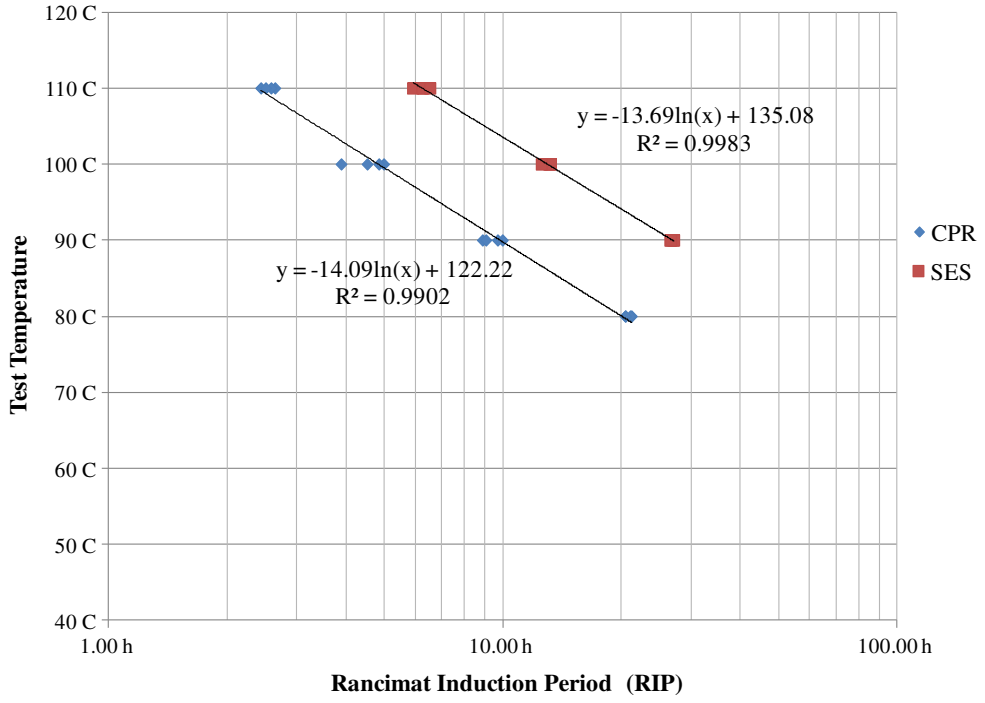


Fig. 12. RIP (h) measured at discrete Rancimat test temperatures for methyl esters of cold pressed Rapeseed (CPR) and Sesame (SES) oil.

where C is the concentration (ppm) of antioxidant added to the FAME; t_i is Rancimat OS (hours) of the dosed FAME (dose = C); t_{i0} is Rancimat OS (h) measured for C = 0 ppm; k is a reaction constant; and C_{cr} is the critical antioxidant concentration (ppm) threshold below which the antioxidant had no effect on retarding oxidation.

Intercept values of trend lines fitted to the data allowed calculation of respective critical antioxidant concentrations (C_{cr}) according to Eq. (10), which were: [O] (519), [S#1] (1465), [P#2] (1742), and [J#1] (1871 ppm). The critical threshold of antioxidant dose for achieving effective control on retarding oxidation (C_{cr}) was much lower for Olive [O], hence why it responded better to the TBHQ. Whereas C_{cr} values for Soy, Palm and Jatropha were higher (closer to 2000 ppm).

Chain-breaking antioxidants work by intercepting peroxide or any radical species, donating their proton to convert the radical back to hydrocarbon (A–H + R* − >A* + R–H). The resulting radical (A*) is generally less reactive, and the main propagation step is then terminated preventing creation of another FAME radical by the autoxidation mechanism. The free radical is then either stable or further reacts to form a stable molecule that does not contribute to the oxidation process. The oxidation chain reaction is thus interrupted, while the antioxidant is consumed [5,12].

Chain-breaking antioxidants therefore effectively neutralize peroxide radicals responsible for autoxidation. Biodiesel FAME containing a higher concentration of radicals shall require a larger antioxidant dose to neutralize them. Critical antioxidant concentration (C_{cr}) probably correlates with radical concentration.

The behaviour of the cold pressed Rapeseed (CPR) and Sesame (SES) samples was examined in storage. Before storing the samples, RIP of each was measured at intervals of test temperature (110, 100, 90, 80 °C). Quadruplicate results obtained are shown in Table 4. Tests for SES at 80 °C were not carried out as excessively long determinations were expected (>50 h) with potentially unreliable results, due to evaporation of distilled water from Rancimat conductivity cells.

As anticipated, test results (see Fig. 12) exhibited Arrhenius temperature dependence, where a lower test temperature exponentially reduced the reaction rate; a 10 °C reduction approximately doubled the RIP result (h). Trend lines fitted to Fig. 12 data enabled extrapolation of RIP results in order to predict RIP at lower test temperatures. Each Arrhenius curve was extrapolated to predict RIP at 40 °C. This method for extrapolation of test data is incorporated into the 873 Biodiesel Rancimat instrument's data logging software. Although the samples had similar stability indices, the predicted RIP result at 40 °C for Sesame was 1038 h, and for Rapeseed it was 342 h.

Predicted RIP values were interpreted as storage life estimates for the samples kept at a storage temperature of 40 °C, i.e. the sample should endure that amount of time before losing its resistance to oxidative degradation, and significant levels of oxidation products form. To test this idea, the FAMEs were stored at 40 °C for over 100 days. Both FAME samples (~300 g of each) were stored in respective air-tight glass jars, which were immersed in a constant-temperature water bath (40 °C). Sample jars were half-full so that a sizeable air pocket was maintained above the liquid. During storage, kinematic viscosity (KV40) and acid value (AV) were periodically measured for signs of oxidation. Table 5, and also Figs. 13 & 14 show KV40 and AV result data recorded at intervals of storage (every 10 days or so).

For Rapeseed, noticeable increases in KV40 and AV occurred after around 500 h. Sesame endured more than 2000 h before increases occurred. Therefore, the predictions did not conform to the real conditions accurately. A conservative prediction might well be anticipated since the samples were not constantly agitated with air bubbles as in the actual Rancimat test, but kept in sealed containers hence oxygen availability may have been a factor limiting oxidation progress. Such predictions may therefore be consistently conservative by some factor. This work demonstrates the significance and potential utility of RIP measurements obtained at different test temperatures, as the basis for estimating FAME storage life at ambient temperature. A more detailed study is needed

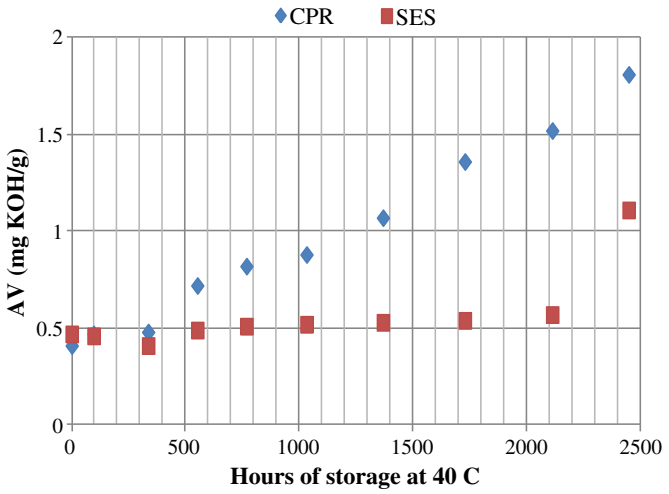


Fig. 13. AV recorded at intervals of storage (every ~10 days) for methyl esters of cold pressed rapeseed (CPR) and sesame (SES) oil.

that would assess the validity of storage life estimates obtained by this method e.g. by repeating the experiment for a larger number of samples, and particularly in application to larger quantities of biodiesel FAME fuel kept in storage.

For RIP equivalent to 6 h at 110 °C (the EN 14214 limit value), using the approximate rule of thumb that RIP doubles with each 10 °C drop in test temperature, then 6 h at 110 °C would correspond to a (likely conservative) prediction of 256 days (~8 months) storage life at a temperature of 20 °C. If RIP was 3 h at 110 °C (ASTM D6751 limit value), predicted life would be half that (128 days). These life spans, although probably conservative, would be useful to keep in mind for quantities of biodiesel kept in storage that are certified to conform to respective standards.

6. Conclusions

In all biodiesel samples tested, FAME components were generally: Palmitate 16:0, Stearate 18:0, cis-9 Oleate 18:1, Linoleate 18:2, and Linolenate 18:3. Though Coconut methyl ester was notably different containing short chain fatty acids, especially Laurate 12:0. Coconut, Palm, Lard and Tallow contained the most saturated components. Sunflower, Rapeseed, and Grapeseed were the most unsaturated FAMEs.

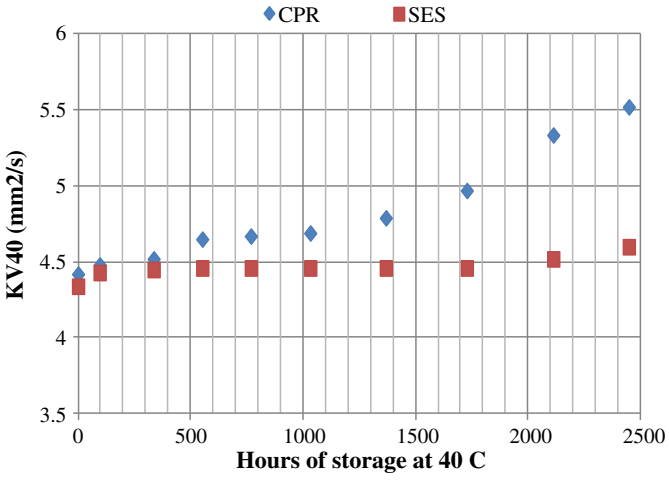


Fig. 14. KV40 recorded at intervals of storage for CPR and SES.

All samples met EN 14214 specification on methyl linolenate content and methyl ester content with ≥4 double bonds.

Stability indices: BAPE and OX were calculated and found to be very similar values, since the oleic parameter made very little difference to OX value. OX and BAPE discriminated between samples differently to IV, which predicted a different relative order of susceptibility to oxidation, as it treats all double bonds as being equally reactive which is not the case. The BAPE value is the more significant for oxidation.

Assuming different relative rates of oxidation for Oleates, Linoleates, and Linolenates: either respectively: 1, 50, 100 (OX), or 1, 41 and 98, or 1, 12.5, 25 in calculation of stability indices, the different values had little effect on the predicted order of susceptibility to oxidation.

Poor relationship between stability indices and RIP showed that none of the indices can reliably indicate oxidative stability as measured by Rancimat method, and that RIP strongly depended on other factors not measured by the stability indices such as content of natural antioxidants.

All samples except Sesame, failed to meet the EN 14214 requirement on OS (>6 h). The majority (11 samples) showed very low RIP (<1 h), hence would require dosing with antioxidant.

Four samples (Palm, Olive, Soyabean, and Jatropha) were dosed with antioxidant (TBHQ) and did not respond equally to the same dose. RIP results suggested that more unsaturated FAME (of higher OX) responded less well to the same antioxidant dose, and that a critical concentration was exceeded before the antioxidant had significant effect.

RIP results showed Arrhenius temperature dependence, where a 10 °C reduction in test temperature approximately doubled RIP. Extrapolation of RIP results for two FAME samples down to 40 °C was used to predict RIP at this lower temperature. Predictions were interpreted as storage life estimates, but in actual storage tests, were found to be conservative. The method is potentially useful, though a more detailed study is needed that would assess its validity.

Acknowledgements

Authors wish to express thanks to Rye Biofuels Ltd (UK) and the Engineering and Physical Sciences Research Council (EPSRC) of the United Kingdom for their support.

References

[1] R.L. McCormick, A. Williams, J. Ireland, M. Brimhall, A.A. Hayes, Effects of biodiesel blends on vehicle emissions, Colorado: Milestone Report NREL/MP-540-40554, National Renewable Energy Laboratory, 2006.
[2] G. Knothe, J. Van Gerpen, J.E. Krahl, The Biodiesel Handbook, AOCS Press, Illinois, 2005.
[3] H. Tang, N. Abunasser, A. Wang, B.R. Clark, K. Wadumesthrige, S. Zeng, M. Kim, S.O. Salley, G. Hirschlieb, J. Wilson, K.Y.S. Ng, Quality survey of biodiesel blends sold at retail stations, Fuel 87 (13–14) (2008) 2951–2955.
[4] A. Bouaid, M. Martinez, J. Aracil, Long storage stability of biodiesel from vegetable and used frying oils, Fuel 86 (16) (2007) 2596–2602.
[5] J. Pullen, K. Saeed, An overview of biodiesel oxidative stability, Renewable and Sustainable Energy Reviews 16 (2012) 5924–5950.
[6] C.D. Bannister, C.J. Chuck, M. Bounds, J.G. Hawley, Oxidative stability of biodiesel fuel, Proceedings of the Institution of Mechanical Engineers. Part D, Journal of Automobile Engineering 225 (1) (2010) 1–16.
[7] J. Van Gerpen, B. Shank, R. Pruszko, D. Clements, G. Knothe, Biodiesel analytical, Colorado: Report NREL/SR-510-36240, National Renewable Energy Laboratory, 2004.
[8] S.R. Westbrook, An evaluation and comparison of test methods to measure the oxidation stability of neat biodiesel, Texas: Report NREL/SR-540-38983, National Renewable Energy Laboratory, 2005.
[9] G. Knothe, Some aspects of biodiesel oxidative stability, Fuel Processing Technology 88 (7) (2007) 669–677.
[10] G. Knothe, R.O. Dunn, Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals, Journal of the American Oil Chemists' Society 80 (10) (2003) 1021–1026.
[11] F. Manufacturers, Fatty acid methyl ester fuels – diesel fuel injection equipment manufacturers common position statement – issued Jan 2007, cited; Available from http://www.motorconsult.co.uk/images/stories/news/fame%20statement%20march%202007.pdf 2007.
[12] A. Monyem, J.H. Van Gerpen, The effect of biodiesel oxidation on engine performance and emissions, Biomass and Bioenergy 20 (4) (2001) 317–325.
[13] S. Loha, S. Chewb, Y. Chooa, Oxidative stability and storage behavior of fatty acid methyl esters derived from used palm oil, Journal of the American Oil Chemists' Society 83 (11) (2006) 947–952.
[14] R.O. Dunn, Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel), Fuel Processing Technology 86 (10) (2005) 1071–1085.
[15] Y.C. Liang, C.Y. May, C.S. Foon, A.M. Ngan, Y. Basiron, The effect of natural and synthetic antioxidants on the oxidative stability of palm diesel, Fuel 85 (5–6) (2006) 867–870.
[16] R.L. McCormick, M. Ratcliff, L. Moens, R. Lawrence, Several factors affecting the stability of biodiesel in standard accelerated tests, Fuel Processing Technology 88 (7) (2007) 651–657.
[17] J. Xin, H. Imahara, S. Saka, Kinetics on the oxidation of biodiesel stabilized with antioxidant, Fuel 88 (2) (2009) 282–286.
[18] R. Dinkov, G. Hristov, D. Stratiev, V.B. Algayri, Effect of commercially available antioxidants over biodiesel/diesel blends stability, Fuel 88 (4) (2009) 732–737.
[19] R.O. Dunn, Antioxidants for improving storage stability of biodiesel, Biofuels, Bioproducts and Biorefining 2 (4) (2008) 304–318.
[20] S. Schober, M. Mittelbach, The impact of antioxidants on biodiesel oxidation stability, European Journal of Lipid Science and Technology 106 (6) (2004) 382–389.
[21] P. Bondioli, A. Gasparoli, L.D. Bella, S. Taghliabue, G. Toso, Biodiesel stability under commercial storage conditions over one year, European Journal of Lipid Science and Technology (105) (2003) 735–741.
[22] J.Y. Park, D.K. Kim, J.P. Lee, S.C. Park, Y.J. Kim, J.S. Lee, Blending effects of biodiesels on oxidation stability and low temperature flow properties, Bioresource Technology 99 (5) (2008) 1196–1203.
[23] L. Stavinoha, S. Howell, Potential analytical methods for stability testing of biodiesel and biodiesel blends, SAE Technical Paper 1999-01-3520, 1999.
[24] D.Y.C. Leung, B.C.P. Koo, Y. Guo, Degradation of biodiesel under different storage conditions, Bioresource Technology 97 (2) (2005) 250–256.
[25] P. Bondioli, A. Gasparoli, L.D. Bella, Tagliabue, Evaluation of biodiesel storage stability using reference methods, European Journal of Lipid Science and Technology 104 (12) (2002) 777–784.
[26] B.L.T. Wieselburg, BIOSTAB — stability of biodiesel used as a fuel for diesel engines and heating systems, Summary Report: Austria, Federal Institute of Agricultural Engineering, 2003.
[27] J.A. Waynick, Characterization of biodiesel oxidation and oxidation products, Colorado: SwRI Project No. 08-10721, National Renewable Energy Laboratory, 2006.
[28] G. Knothe, Structure indices in FA chemistry. How relevant is the iodine value? Journal of the American Oil Chemists' Society 79 (2002) 823–833.
[29] M. Lapuerta, J. Rodriguez-Fernandez, E.F. de Mora, Correlation for the estimation of the cetane number of biodiesel fuels and implications on the iodine number, Energy Policy 37 (11) (2009) 4337–4344.
[30] K. Yamane, K. Kawasaki, K. Sone, T. Hara, T. Prakoso, Oxidation stability of biodiesel and its effects on diesel combustion and emissions characteristics, International Journal of Engine Research 8 (2007) 307–319.
[31] G. Knothe, Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, Fuel Processing Technology 86 (10) (2005) 1059–1070.
[32] NBB, Specification for biodiesel (B100) — ASTM D6751-07b, cited; Available from http://www.biodiesel.org/pdf_files/fuelfactsheets/BDSpec.pdf March 2007.
[33] BSI, BS EN ISO 12937:2001, Determination of water content — Coulometric Karl Fischer titration method, British Standard Test Method, BSi, 2001.
[34] BSI, BS EN 14103:2003, Fat and Oil Derivatives — Fatty Acid Methyl Esters (FAME) — Determination of Ester and Linolenic Acid Methyl Ester Contents, Standards Policy and Strategy Committee, British Standards Institute, 2003.
[35] BSI, BS EN 14111:2003, Fat and Oil Derivatives — Fatty Acid Methyl Esters (FAME) — Determination of Iodine Value, Standards Policy and Strategy Committee, British Standards Institute, 2003.
[36] BSI, BS EN 14112:2003, Fat and Oil Derivatives — Fatty Acid Methyl Esters (FAME) — Determination of Oxidation Stability (Accelerated Oxidation Test), Standards Policy and Strategy Committee, 2003.
[37] BSI, BS EN ISO 3104, Methods of Test for Petroleum and Its Products, Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity, Standards Policy and Strategy Committee, British Standards Institute, 1996.
[38] BSI, BS EN 14104:2003, Fat and Oil Derivatives — Fatty Acid Methyl Esters (FAME) — Determination of Acid Value, Standards Policy and Strategy Committee, British Standards Institute, 2003.
[39] Thomas-Jefferson-Agricultural-Institute, Growing sesame: production tips, economics, and more, [cited 2011 24 October]; Available from http://www.jeffersoninstitute.org/pubs/sesame.shtml