The effect of synthetic antioxidants on the oxidative stability of biodiesel

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Abstract

Biodiesels were prepared using base catalyzed methanolysis of sunflower, soybean and canola oils. Rancimat oxidative stability measurements showed that the induction period (IP) for neat canola biodiesel conformed to EN 14214, the European specification for biodiesel (IP > 6 h). Stability was enhanced when 0.5 wt. % of the synthetic anti-oxidants di-*tert*-butylhydroquinone (DTBHQ) or poly(1,2-dihydro-2,2,4-trimethylquinoline) (Orox PK) was added. Soybean-based biodiesel spiked with 0.5 wt. % DTBHQ also reached this specification. Orox PK improved the stability of sunflower biodiesel but the 3 h induction period specified by ASTM D-6751 could not be reached. Curiously, canola biodiesel was destabilized on adding the antioxidant Naugard P (tris(nonylphenyl) phosphate).

KEYWORDS: anti-oxidants, biodiesel, oxidation induction time, oxidative stability, Rancimat method

1. Introduction

Conventional biodiesel comprises Fatty Acid Methyl Esters (FAME) derived from animal fats or vegetable oils [1]. It is a renewable resource because the raw materials used for its production can be replenished through agricultural activities. This is widely presented as its main advantage [2]. In addition, biodiesel fuel is biodegradable [3][6] contains insignificant amounts of sulphur [1] and is considered safer than mineral diesel owing to its higher flash point [7]. Lubricity is an important issue because the moving parts in many fuel pumps are actually lubricated by the diesel fuel itself [1]. Biodiesels feature superior lubricity to conventional mineral diesel so their use does not affect engine endurance [1]. Biodiesel is completely miscible with petroleum diesel fuel. It can therefore used as a blend component to reduce particulate matter emissions, improve fuel lubricity and increase cetane number [1]. On the negative side, NO_x emissions tend to increase when the mineral diesel is replaced with biodiesel [1]. Biodiesel also has a much lower oxidative stability than mineral diesel [1],[2],[5],[8]-[12].

Knothe [11] reviewed the susceptibility of biodiesel to oxidation. Oxidative degradation during transport and storage causes deterioration of the physical properties of the biodiesel making it unstable and unusable [5],[10],[13]. The reaction with atmospheric oxygen is accelerated by elevated temperatures, contact with metal surfaces [19], exposure to sunlight and air [14],[15] and by the presence of metal compound impurities [16].

Oxidation leads to the formation of hydroperoxides that attack elastomers in contact with the fuel or initiate polymerization to form insoluble gums [1],[8],[15]. The oxidation products formed in biodiesel affect fuel storage life, contribute to deposit formation in tanks, and they may cause clogging of fuel filters and injection systems [1],[17]. The volatile

organic acids formed as secondary by products of the oxidative degradation, may stimulate corrosion in the fuel system [2].

FAME is more sensitive to oxidative degradation than fossil fuel because of its chemical composition [14]. The quality and performance of a biodiesel clearly depends on the fatty acid composition of the parent vegetable oils [17]. For example, low cetane numbers and poor oxidation stability are associated with the more highly unsaturated components (C18:2 and C18:3) [18],[19]. Soybean, sunflower and grape seed oils contain high levels of these components [17]. In general the susceptibility to oxidation of a biodiesel increases with the number and degree of conjugation of double bonds present [8],[19]. Unsaturation, and especially the presence of multiple double bonds such as *bis*-allylic moieties [11] in the fatty acid chains, is the main source of instability in biodiesel fuels [1].

Oxidation rates of FAME depend on many external variables including temperature, light exposure and radiation intensity, etc. [21]. The presence of natural anti-oxidants, e.g. tocopherol, is also a crucial factor determining the oxidative stability of a biodiesel [22]. In general, natural anti-oxidant concentrations are high in undistilled fuels prepared from fresh vegetable oil [19],[23]. Distillation of biodiesel often results in a decrease in the oxidative stability owing to the removal of natural antioxidants [24],[25].

The oxidative stability of biodiesels can be enhanced by adding additional natural or synthetic anti-oxidants. However, naturally occurring anti-oxidants were shown to provide relatively poor oxidation stabilization of biodiesels compared to synthetic anti-oxidants [21]. The antioxidants improve the oxidative stability by removing free radicals formed during the oxidation initiation stage. Fatty peroxyradicals are thereby stabilized and the chain reaction is stopped [21]. Anti-oxidants also retard polymerization but do not inhibit it completely [2].

Monteiroa *et al.* [26] reviewed analytical techniques for the characterization of biodiesels while Hoshino *et al.* [7] reviewed the methods available for characterizing oxidative stability. Oxidation in the condensed phase is characterized by a seemingly quiescent induction period (IP) followed by a sudden increase in the rate. It is commonly assumed that the length of this induction period provides a relative measure of the oxidative stability of the material [24]. As oxidation is an exothermic process, the abrupt onset can be detected by thermo-analytical techniques such as DSC or DTA. The oxidation induction time (OIT) corresponds to an IP measured under isothermal conditions. It is also possible to detect such an onset using a dynamic temperature scan. With a linear increase of temperature this yields the so-called oxidation onset temperature (OOT). These two procedures have been standardised for evaluation of the oxidation stability of lubricating oils. ASTM D 6186 [26] and ASTM E 2009-99 [28] correspond to the isothermal and non-isothermal techniques, respectively [9]. The OIT is conducted at a predetermined isothermal temperature [29] and the OOT at a fixed scan rate, most commonly 10°C/minute. In both methods high pressure is used to enhance the rate of oxidation; suppress evaporation of the oil at elevated temperatures, and to shorten the experimental time to minutes instead of hours [30]. Blaine *et al.* [31] noted that the OIT is shortened by conducting the experiments at elevated oxygen partial pressures. The O_2 pressure dependence of OIT follows a power law [32]. However, the exponent depends on the system. So oil that is actually less stable at ambient conditions might, when tested at very high oxygen pressures, appear comparatively more oxidation resistant than a more stable oil [32].

In the secondary oxidation phase of FAME, volatile acids, mainly formic acid and acetic acid, are generated. This provides the basis for the Rancimat method [33] for evaluating the oxidative stability of biodiesel. In this procedure a sample is aged at an

elevated temperature (usually 110°C) by passing air through it at a constant rate [7]. The effluent gases are collected in a measuring cell filled with distilled water, where the conductivity is constantly recorded [19]. The formation of the carboxylic acids is indicated by the increase in conductivity in the measuring vessel. The time elapsed until the secondary oxidation is detected is termed the induction time and provides a measure of the oxidation stability of the sample [29]. According to Ball *et al.* [21], this induction time of a few hours correlates well with the shelf life of a product measured in years. The European biodiesel standard EN 14214 [33] requires the determination of oxidation stability at 110°C with a minimum induction time of 6 hours by the Rancimat method [11]. The method detailed in the similar ASTM standard D-6751 **Error! Reference source not found.** specifies a minimum induction period of 3 h [16]. The Oil Stability Index (OSI) determination described in Method Cd 12b-92 established by the American Oil Chemists' Society is also essentially similar to the Rancimat procedure [8].

Neumann *et al.* [34] proposed the PetroOXY oxygen-contact degradation test. The methodology is based on the induction time observed when a sample is contacted with pure oxygen at an elevated pressure (e.g. 1 MPa) and temperature (e.g. 120 to 140°C). The induction period is taken as the time between the start of the test and the detection of a specific pressure drop, which indicates that the resistance to oxidation has been overcome. Neumann *et al.* [34] and Araújo *et al* [2] found a linear relationship between the induction times obtained with this test and those obtained with the standard Rancimat method [33].

The stabilization behaviour observed with the Rancimat test can be quantified by a stabilization factor (SF) [37]. SF is defined as the ratio of induction times corresponding to the biodiesel containing anti-oxidant and the neat biodiesel respectively. Therefore, a higher oxidation induction time conforms to a higher stabilization factor which in turn conforms to

higher biodiesel stability. Polavka *et al.* [24] defined a similar quantity, the protective factor (PF), as the corresponding ratio of induction times measured by isothermal DSC (OIT).

The suitability of several synthetic antioxidants for biodiesel stabilization have been investigated [10],[16],[24],[37]-[41]. Oxidative inhibitors considered include tert-butyl hydroxyquinone (TBHQ), butylated hydroxytoluene (BHT), butylated hydroxyanisol (BHA), pyrogallol, i.e. propyl 3,4,5-trihydroxybenzoate (PY), propyl gallate (PG), N,N'-diphenyl-p-phenylenediamine (DPPD) and a natural inhibitor called α-Tocopherol. The outcomes of these studies generally support the contention of Mittelbach and Schober [37] that the efficiency of a synthetic anti-oxidant depends on its chemical structure but also on the raw material and the technology employed in producing the biodiesel [8].

Xin *et al.* [40] used Rancimat to study oxidation of unsaturated biodiesel (safflower and rapeseed) and low unsaturated biodiesel (palm biodiesel). Stability increased when the biodiesel was subjected to a supercritical methanol treatment. This was attributed to decomposition of the hydroperoxides present at the elevated temperatures used in the treatment. Safflower biodiesel, which had highest content of poly-unsaturated fatty acids, had the shortest induction period, whereas palm biodiesel, which is high in saturated fatty acid content, had the longest one. They also found that PG was a more efficient oxidation inhibitor than DPPD.

Mittelbatch and Schober [37] used Rancimat to study samples of methyl esters from sunflower and canola oil, oils from deep-frying and animal tallow; distilled and not distilled; and containing antioxidant concentrations ranging from 100 to 1000 ppm. They found that the antioxidants PY, PG, TBHQ, and BHA significantly increased the oxidative stability while BHT was not very efficient. The latter observation was not supported by later studies [10],[39]. Dunn [10] used dynamic PDSC (scan rate 5°C/min heating) with air (2 MPa) as

oxidizing gas to study the oxidation stability of methyl esters from soy oil. His results showed that the antioxidants PG, BHT and BHA were most effective and α-Tocopherol least effective in increasing OOT.

Domingos *et al.* [39] used the Rancimat method, EN14112 [33] to investigate the effect of the synthetic antioxidants BHA, TBHQ and BHT on the induction time of soybean oil ethyl esters with low oxidation stability. BHT was the found the most effective antioxidant up to concentrations of 0.7 wt. %. However, TBHQ showed a better stabilizing effect at 0.8 wt. %. No evidence was found [39] of any positive synergistic effect when binary or ternary mixtures of these antioxidants were utilized.

Araújo *et al.* [2] used the PetroOXY oxygen-contact degradation test [34] and evaluated the performance of several phenolic antioxidants in castor oil fatty methyl ester (FAME). Their results indicated that BHA outperformed PG, TBHQ, and 2,6-ditert-butyl-4-methylphenol (DBPC).

Polavka *et al.* [24] used temperature scanning PDSC and Rancimat analysis to study the oxidation stability of methyl esters derived from fresh rapeseed oil and waste frying oil, both distilled and undistilled, unstabilized and stabilized by pyrogallol or BHT. Both techniques show that oxidation stability increases considerably with the addition of antioxidants and that pyrogallol is the most efficient inhibitor.

Liang *et al.* [38] used Rancimat to study the oxidative stability of neat and distilled palm oil methyl ester. The outstanding stability of the crude palm oil methyl ester (IP = 25.7 h) was attributed to the presence of natural components such as carotenes and vitamin E that act as antioxidants. The distilled biodiesel was significantly less stable (IP = 3.5 h). Addition of the natural antioxidant or synthetic antioxidants improved stability but it remained less

than that of the crude biodiesel. The efficiency ranking of antioxidants in the distilled biodiesel was as follows: TBHQ > BHT > α-tocopherol.

Rodrigues *et al*. [41] used PDSC and found that addition of cardanol, i.e. cashew nut shell liquid (800 ppm) improved the oxidative stability of cotton biodiesel by approximately four times. Sarin *et al*. [16] used the OSI method to study the destabilizing effect of catalytic amounts of transition metals on palm methyl ester (PME). Addition of the antioxidants BHT, TBHQ, tert-butylated phenol derivative (TBP), and octylated butylated diphenyl amine (OBPA), improved the OS of metal-contaminated PME with TBHQ the most effective.

Studies done to date appear to have been limited to exploring the utility of synthetic phenolic and aromatic amine antioxidants. The objective of this investigation was to determine whether a phosphate and another amine-based antioxidant have anything to offer with respect to stabilizing non-distilled biodiesels synthesized by transesterification with methanol. The activity of the following three synthetic anti-oxidants in soybean, sunflower and canola oils biodiesels was studied: di-*tert*-butylhydroquinone (DTBHQ), poly(1,2-dihydro-2,2,4-trimethylquinoline) (Orox PK) and tris(nonylphenyl) phosphate (Naugard P). The oxidation stability of the biodiesels was tested using the Rancimat induction time method. The fuels were also characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and FAME analysis.

2. Experimental

2.1. Materials

Pure sunflower, soybean and canola oils were purchased from a retail outlet. Table 1 lists the three different types of antioxidant that were used in this study.

<Insert Table 1>

2.2. Synthesis

Biodiesel samples were produced using conventional alcoholysis [4],[42],[43]. The procedure was as follows: An amount of 5 g of potassium hydroxide was completely dissolved in 100 ml of dry methanol. The solution was then poured over 500 mL of the dried vegetable oil in a large jar. The jar was securely closed and the solution vigorously agitated for 15 minutes. The solution was then allowed to settle in a gravity separation setup. In the first hour 75% of the separation appeared complete and after 8 h glycerine was settled at the bottom and biodiesel at the top. A separation funnel was used to remove the glycerol and to wash the product free of catalyst, free fatty acids and methanol. The product was washed three times with 280 mL distilled water. The biodiesels were then placed in an open container in a convection oven at 70 °C to remove the remaining methanol and water. The biodiesel samples were stored in the dark in airtight containers at ambient temperatures. Separate samples were aged in contact with air at ambient conditions.

2.3. Characterization

A thin film of biodiesel was formed between two KBr discs and the Fourier transform infrared (FTIR) spectra recorded on a Perkin Elmer RX I FT-IR spectrometer. The reported spectra represent averages of 32 scans at a resolution of 2 cm^{-1}. The averaged data was background-corrected using a pure KBr pellet.

The Fatty Acid Methyl Ester (FAME) analysis was performed on an Agilent 6890 gas chromatograph equipped with a flame ionisation detector. A polyethylene glycol stationary phase capillary column (Omegawax 320^{TM}, 30m x 0.25 mm ID, 0.25um film thickness) was

used for the separation of the FAMEs. The column temperature was initially set at 140°C for 5 minutes, and then increased to 240°C at the rate of 4°C/min where it was held constant for 10 minutes. Elution of the FAMES was primarily by carbon chain length and secondly by the number of double bonds. Helium was used as the carrier gas with hydrogen and air as fuel gases. Injector and detector temperature were 250°C and 300°C respectively. Injection volumes for samples and standards were 1µL and a split ratio of 50:1 was employed. Biodiesel samples were dissolved in heptane and quantification was performed by internal standard calibration using methyl heptadecanoate. The FAME content was computed according to EN 14103 [44] where the sum of all the peaks from the methyl myristate (C_{14}) peak up to that of the methyl ester in $C_{24:1}$ was accounted for. Identification of the FAMEs in the biodiesel samples was accomplished by comparing their retention times to a reference 37 component FAME mixture (Supelco).

Volatility analyses were conducted using the dynamic method on a Mettler Toledo A851 TGA/SDTA thermogravimetric analyzer (TG). About 20 mg liquid was placed in an open 70 µL alumina pan. Experiments are performed in nitrogen by first purging air from the TGA with ultra high-purity nitrogen for 120 min at 30°C prior to beginning the temperature program. Then the sample was heated from 30 °C to 400 °C at a scan rate of 10 °C/min with nitrogen flowing at a rate of 50 mL/min.

Pressure DSC (PDSC) was performed on a Mettler Toledo DSC 827HP fitted with a FRS5 ceramic sensor. About 5.5 mg liquid was placed in an open aluminium pan. Temperature was scanned from 25 to 300 °C at a rate of 10 °C/min with oxygen flowing at a rate of 50 mL/min. The cell pressure was controlled at 8 MPa.

Oxidation stability was determined with a Metrohm 743 Rancimat instrument. The sample mass of biodiesel placed into the reaction tube was 3 g. The temperature was ramped

to 110 °C and held constant before air, at atmospheric pressure, was allowed to flow at 10 L/h. 50 mL of deionised water was used in the measuring vessel to absorb the volatile acids formed during the oxidation process [2]. The automatic evaluation method (second derivative) was utilised to determine the oxidation induction time. Duplicate measurements of the induction times were carried out for each sample.

3. Results and discussion

The FT-IR spectra for the different biodiesel raw materials are presented in Fig. 1. The band assignments are as follows[45]: The peak at about of 2990 cm^{-1} is due to the H–C= functional group; the two peaks located at ca. 2916 and 2848 cm^{-1} are from the $–CH_2–$ group; the 1740 cm^{-1} absorption is ascribed to the ester C=O stretch deformation; the two medium bands at 1160 and 1180 cm^{-1} are related to the C–O bond in the ester functional group; the band at 710 cm^{-1} is characteristic for the long $–(CH_2)_n–$ sequences in the aliphatic chains of the fatty acids. The three strong bands at wavenumbers of 1100 cm^{-1} (ester C-O), 1740 cm^{-1} (ester C=O) and 3050 cm^{-1} (aliphatic chains) are characteristic of FAME biodiesel. The nonexistence of the O-H bond stretching in the range of 3640 – 3200 cm^{-1} confirms the absence of residual water in the biodiesel samples. The alcohol functional group (O-H bond) is either a strong, broad frequency band in the range of 3500 – 3200 cm^{-1} (H-bonded alcohols) or a strong, sharp frequency band in the range of 3640 – 3610 cm^{-1} (free hydroxyl alcohols) [45]. It is evident from Fig. 1 that no alcohol functionality is present in the three biodiesels. The single sharp ester peak at 1740 cm^{-1}, i.e. the absence of another band adjacent to this ester band, rules outs the presence of carboxylic acids as they feature a strong peak at 1770 cm^{-1}.

< Insert Fig 1 >

The total fatty acid methyl ester contents exceeded the minimum requirement for FAME content of 90 wt. %. They were determined as 90.8 %, 92.2 %, and 96.2 % respectively. As discussed above, the absorption bands in the FTIR spectra of Fig. 1 are consistent with the absence of free fatty acids, methanol and water. This suggests that the present biodiesel samples contained some non-reacted vegetable oil.

Chien *et al.* [46] previously studied soybean biodiesel using thermogravimetric analysis (TG). They observed biodiesel volatilizing and pyrolytic decomposing in the 119-237°C temperature range and were able to model this as a single-stage pyrolysis reaction. Table 2 compares the composition, degree of unsaturation (DU) and long chain saturated factor (LCSF) of vegetable oils used to prepare the present biodiesel samples. Fig. 2 reports the TG results obtained for the sunflower, soybean and canola derived biodiesels. All three samples evaporated at approximately the same rate up to a temperature of about 200 °C. Thereafter the observed mass loss rates were different. The residual mass observed for the biodiesels at higher temperatures decreased in the order sunflower > soybean > canola. This ranking is consistent with the expectation that the amount of pyrolysis residue increases with the degree of unsaturation (DU) of the fatty acids present. See Table 2.

< Insert Fig 2 >

< Insert Table 2 >

< Insert Fig 3 >

Fig. 3 compares the stability measures obtained with PDSC and Rancimat for the three biodiesels samples. The oxidative stability increases in the order sunflower < soybean < canola. The stability ranking accords with the degree of unsaturation indicated in Table 2. However, it is believed that the oxidation stability of an oil is not directly related to the degree of saturation percentage *per se*, but rather to the number of bis-allylic sites in the molecular structure of the fatty acids [17].

It may be assumed that, during the induction period, the oxidation inhibitors are consumed according to a so-called single step reaction approximation [47],[48]. Thus the reaction follows first order kinetics with a rate constant proportional to the initial antioxidant concentration [49]:

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \tag{1}$$

Here α is a dimensionless degree of conversion, k is the reaction rate constant, and $f(\alpha)$ is a depletion function applicable to the consumption of oxidation inhibitors. Arrhenius-type temperature dependence is assumed for the rate constant k [50]:

$$k = k_o e^{-E/RT} \tag{2}$$

It can be assumed that the isothermal induction time (OIT) and dynamic onset temperature (OOT) values correspond to the situation where the inhibitor is completely consumed [51],[52]. Solving equation (1) in combination with equation (2) leads to the expression:

$$\frac{t_{\mathrm{iso}}}{p(E/RT_{\mathrm{onset}})} = \frac{E}{\beta R} e^{E/RT_{\mathrm{iso}}} \tag{3}$$

Since the Rancimat reaction temperature T_{iso} is constant and the dynamic scan rate β used in the PDSC is fixed, it follows that the right hand side of equation (3) will be invariant provided the notion of a "universal" value for the activation energy (E) is actually valid.

Thus, for the situation at hand, it can be replaced by a constant C_1. The link between isothermal and dynamic data is then given by

$$t_{IP} = C_1 p(E/RT_{onset}) \tag{4}$$

Where t_{IP} is the isothermal induction period, R is the gas constant, C_1 is a constant corresponding to the right hand side of equation (3), and the function $p(x)$ is given by the following approximation valid for $x > 10$ [53]:

$$\ell n\, p(x) = \ell n\left(\frac{x+3}{x^2+5x+4}\right) - \ell n\, x - x \tag{5}$$

Fig. 3 presents a semi-logarithmic plot of the isothermal induction period t_{IP}, determined according to the Rancimat method, against the inverse of the PDSC determined OOT values in absolute temperature units. Relative least squares regression was used to determine the parameter C_1 and the activation energy E in equation (4) for the data obtained with the neat biodiesel samples. The predicted curve is indicated by the solid line in Fig. 3. The good fit suggests that the oxidation reactions occurring during the induction period in the neat biodiesel samples are such that they can be modelled by the same activation energy. The value of the activation energy for the inhibitor depletion reaction is estimated as 413.4 J/mol. It should be emphasized that this energy has no physical meaning other than that it provides an empirical connection between the results obtained for the two measures of oxidative stability.

< Insert Fig 4> < Insert Fig 5 > < Insert Fig 6 >

Fig. 4 shows that the neat sunflower and canola biodiesel samples undergo significant ageing even inside a two-week period when exposed to ambient air. The oxidation induction periods of the sunflower and canola derived biodiesels, spiked with the antioxidants DTBHQ, Orox PK and Naugard P are illustrated in Fig. 5 and Fig. 6 respectively. The stabilization factors were calculated based on the average induction time of the neat (and fresh) sunflower and canola biodiesels (0.55 h and 6.85 h respectively). It is evident from Fig. 5 that the addition of synthetic anti-oxidants increased the stability of sunflower-derived biodiesel. The amine based anti-oxidant, Orox PK, stabilized the sunflower derived biodiesel much better than the antioxidants DTBHQ and Naugard P which showed similar stabilization behaviour.

The best stabilizer for sunflower derived biodiesel was Orox PK. At the highest antioxidant concentration tested (0.5 wt. %) it yielded a stabilization factor of almost 5 (2.7 h). The stabilization factors for Naugard P and DTBHQ anti-oxidants at a concentration of 0.5 wt. % are 2.2 and 1.6 respectively. None of the synthetic anti-oxidants provided sufficient stabilization to the sunflower biodiesel to pass even the lower US specifications of 3 h.

The Rancimat induction time for the neat canola biodiesel already exceeded the European EN 14214biodiesel specification (IP > 6 h). Fig. 6 illustrates that the addition of DTBHQ and Orox PK further increased the oxidative stability of the canola derived biodiesel. The amine-based antioxidant Orox PK performed marginally better than the phenol based anti-oxidant, DTBHQ.

At low addition levels Naugard P caused a decrease in the Rancimat induction time, i.e. the canola derived biodiesel was actually destabilized. This behaviour is counter-intuitive since the oxidation stability is expected to improve with the addition of synthetic anti-oxidants irrespective of the concentration [16]. The destabilization might be caused by complex antagonistic interactions amongst the natural anti-oxidants already present, and the

added synthetic anti-oxidant. Eventually, as more antioxidant was added, the Rancimat induction period increased again but the induction period barely approached the value achieved by the neat biodiesel at the highest concentration tested (0.5 wt. %).

< Insert Fig 7>

Fig. 7 illustrates the effect of varying the concentration of DTBHQ on the Rancimat induction period for all three biodiesel samples. Low level addition of DTBHQ caused a decrease in the stability of the soybean biodiesel. However, at higher concentrations the stability recovered so remarkably that, in fact, the synthetic anti-oxidant DTBHQ was the more effective oxidation inhibitor in soybean at the higher concentrations tested. At a concentration of 0.5 wt. % the stabilization factor reached a value of two and at this level and beyond the fuel conformed to the European specification requiring a Rancimat induction time exceeding 6 h.

4. Conclusions

Biodiesel samples were prepared using base-catalyzed methanolysis of sunflower, soybean and canola oils. FAME analysis results, in conjunction with FTIR spectra, confirmed the absence of water and methanol but indicated that the fuels contained unreacted vegetable oils. The stability of the neat oils correlated with the degree of unsaturation of the fatty acid methyl esters (FAME). The Rancimat induction periods were 0.61 h, 3.3 h and 7.1 h for the neat (and fresh) sunflower, soybean and canola fuels respectively. The measured Rancimat induction periods decreased by about 25 % when the neat oils were exposed to air for twelve

days. The neat canola biodiesel already conformed to the European Rancimat specification EN14214 [33] for biodiesel stability of > 6 h. Its stability was further improved by the addition of the synthetic anti-oxidants di-*tert*-butylhydroquinone (DTBHQ) or poly(1,2-dihydro-2,2,4-trimethylquinoline) (Orox PK). Surprisingly it was found that low additions of the synthetic antioxidant tris(nonylphenyl) phosphate (Naugard P) to canola oil actually resulted in an apparent decrease in the oxidative stability as quantified by Rancimat. Such an effect was also observed, albeit to a lesser extent, with DTBHQ as inhibitor in sunflower and canola biodiesels.

Soybean-based biodiesel samples spiked with DTBHQ at concentrations of 0.5 wt. % and above also satisfied the EN14214 specification. Orox PK significantly improved the stability of sunflower biodiesel. The stabilization factor reached ca. five at a concentration of 0.5 wt. % but even at this level the fuel fell just short of the 3 h induction period specified for biodiesel by ASTM D6751 **Error! Reference source not found.**.

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Table 1 Antioxidants used

Antioxidant	Type	Chemical name (Supplier)
Sineox DTBHQ	phenolic	2,5-di-*tert*-butyl-1,4-dihydroxybenzene (Antioxidants Aromas and Fine Chemicals)
Naugard P	phosphite	tris(monononylphenyl)phosphite (Chemtura)
Orox PK	amine	polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (Orchem)

Table 2 Composition (wt. %), degree of unsaturation (DU) and long chain saturated factor (LCSF) of vegetable oils [18]

Oil	Saturated	Monounsaturated	Polyunsaturated (2,3)	DU	LCSF**
Sunflower	11.1	25.6	63.3	152.2	4.2
Soya	15.3	25.6	59.1	143.8	3.4
Canola	6.5	65.3	28.3	121.9	1.3

*Degree of unsaturation. **Long chain saturated factor calculated using the methyl ester composition.

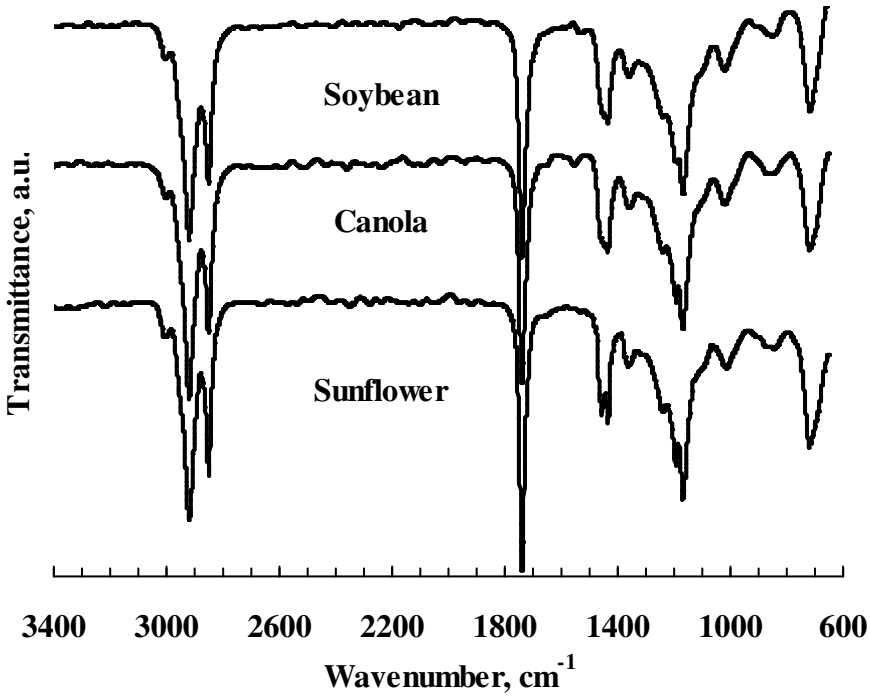

Fig. 1 FT-IR analysis of sunflower, soybean and canola derived biodiesels.

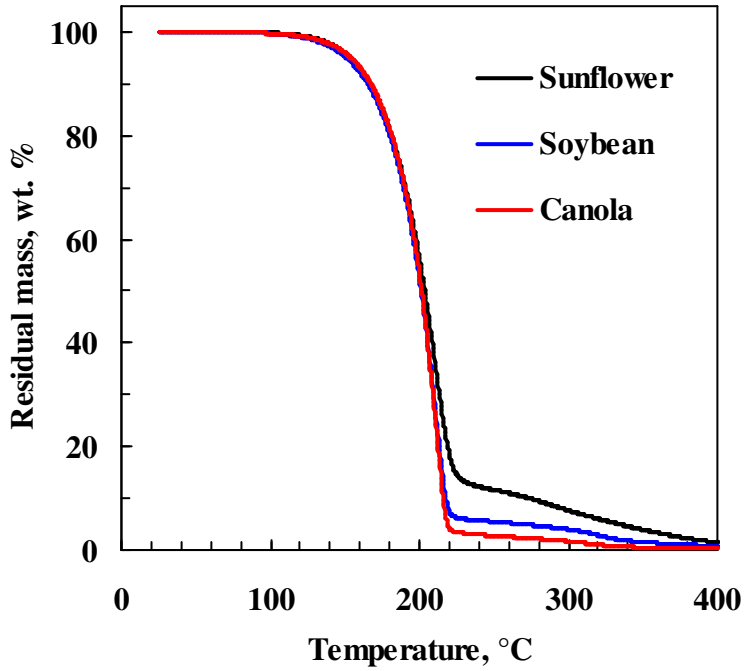

Fig. 2 TG mass loss curves for sunflower, soybean and canola derived biodiesels. Samples were heated from 30°C to 400°C at a rate of 10°C/min with nitrogen flowing at 50 mL/min.

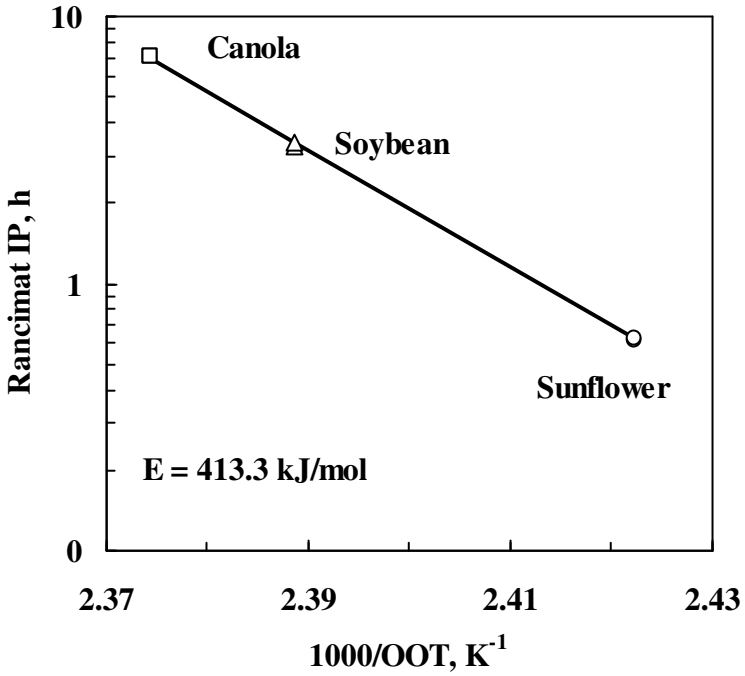

Fig. 3 Plot of Rancimat t_{IP} versus the inverse of the PDSC T_{onset} (=OOT) for neat sunflower and canola biodiesel samples. The solid curve shows the prediction of equation (4) with E = 413.3 kJ/mol and $C_1 = 1.76 \times 10^{56}$.

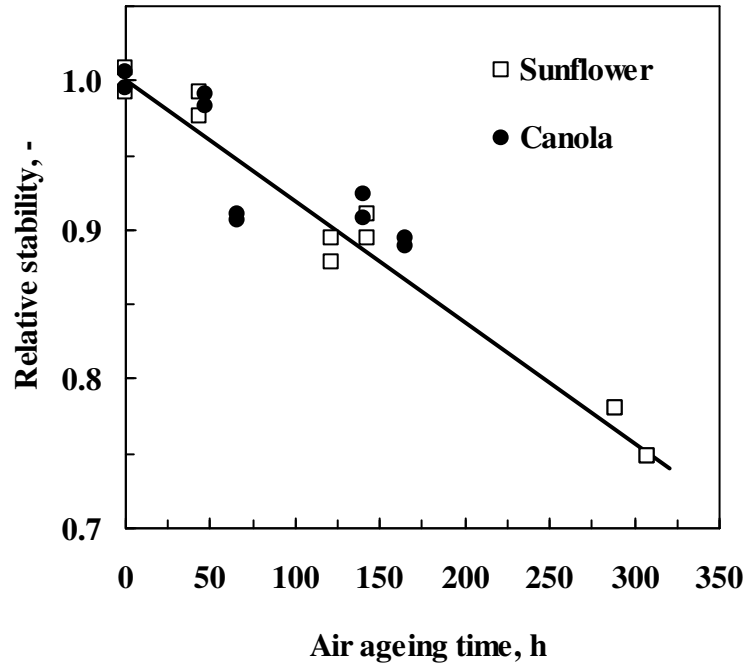

Fig. 4 Rancimat quantified ageing behaviour of sunflower and canola biodiesel samples exposed to air at ambient conditions.

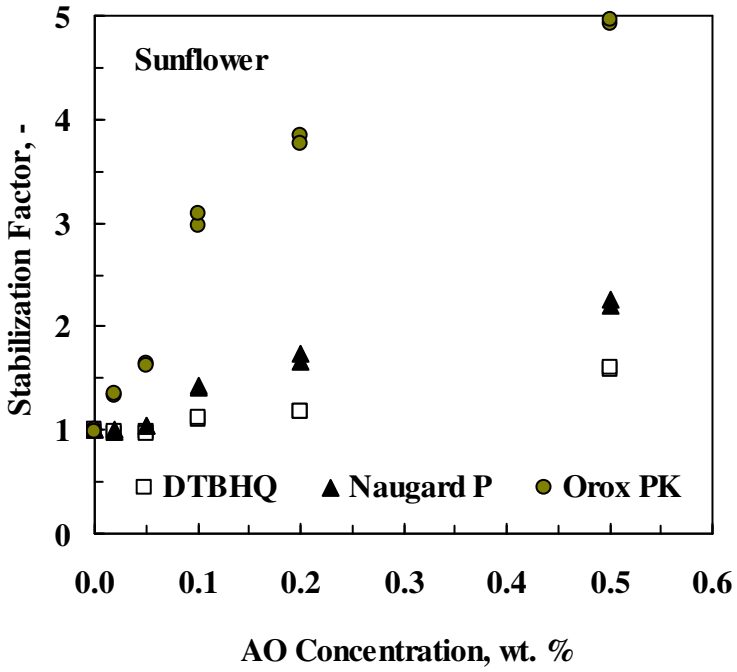

Fig. 5 The effect of varying anti-oxidant concentrations on sunflower derived biodiesel stability.

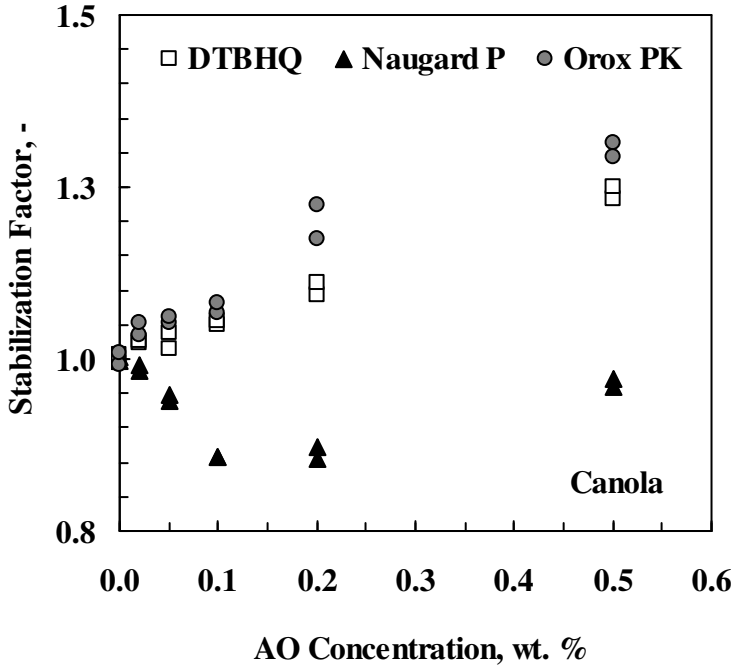

Fig. 6 The effect of varying anti-oxidant concentrations on canola derived biodiesel stability.

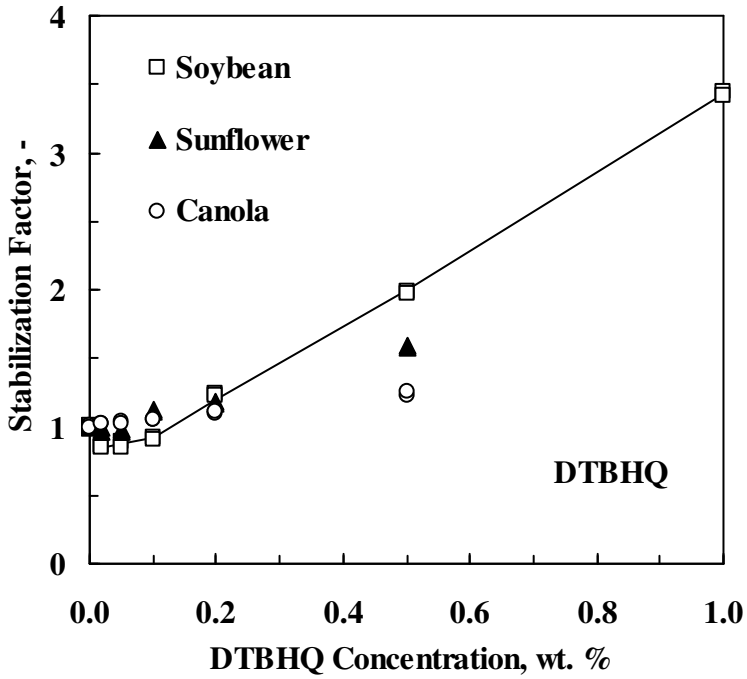

Fig. 7 The effect of varying the concentration of DTBHQ on the Rancimat induction time for sunflower, soybean and canola derived biodiesels.