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## Full Length Article

# Stabilizing sunflower biodiesel with synthetic antioxidant blends

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## G R A P H I C A L A B S T R A C T



### A R T I C L E I N F O

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### $A \ B \ S \ T \ R \ A \ C \ T$

Biodiesel was prepared using base catalyzed methanolysis of sunflower oil. The oxidative stability of the neat biodiesel, as well as samples spiked with 0.15 wt% antioxidant was quantified by induction periods (*IP*) obtained with the Rancimat method according to the tangent method. The neat stabilizers, binary blends and a ternary mixture of poly(1,2-dihydro-2,2,4-trimethylquinoline) (Orox PK), tetrakis[methylene(3,5-di-t-butyl-4-hydro-xyhydrocinnamate)]methane (Anox 20), and tris(nonylphenyl)phoshite (Naugard P) were tested. Of these, Anox 20 was the most effective stabilizer while Naugard P proved ineffective for the sunflower biodiesel. Synergistic improvement of oxidative stability was observed on partial substitution of this phenolic-based compound with the Orox PK. Combinations of the latter amine-based stabilizer with other phenolic antioxidants did not show any synergy, with perhaps the exception of DTBHQ. At a dosage of 0.15 wt%, only TBHQ, propyl gallate and pyrogallol, as well as their 2:1 blends with Orox PK, provided *IP* values that exceeded 8 h as required by the European Standard EN 14,214 for biodiesel.

#### 1. Introduction

Biodiesel is a renewable fuel produced by the methanolysis of vegetable oil or animal fat in the presence of a catalyst (usually an alkali) to produce fatty acid methyl esters (FAME). The presence of unsaturation on the long-chain fatty acid makes it much more susceptible to oxidative degradation than synthetic petroleum diesel [1,2]. Oxidation commences as soon as the biodiesel has been produced and continues during long term storage. The oxidative stability can be improved by adding suitable antioxidants [2–4]. The effectiveness of a synthetic antioxidant depends on its chemical structure as well as the compounds present in the biodiesel. Antioxidants act by interrupting the degradation process and they are usually consumed in the course of stabilization. Primary antioxidants terminate the propagation reaction by a chain breaking mechanism. Primary antioxidants typically are hydrogen donors (e.g. phenolic hydroxyl groups) that trap the free

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radicals formed by the degradation reaction. They inhibit oxidation by donating the hydrogen from the hydroxyl group to the free radical present [5]. Amine-based primary oxidants are also known but most studies on vegetable oils and other ester derivatives are limited to the phenolic types. Secondary antioxidants are hydroperoxide decomposers and include organic sulfur or phosphorus compounds [2,3,6–8]. They function by converting the hydroperoxides to inactive non-radical compounds such as alcohols.

Some antioxidants combinations show synergistic activity [5,9,10]. According to Ingold [11] synergism can arise when the two component antioxidants perform different roles during inhibition. A few studies explored this avenue for improving the oxidative stability of FAME. Examples include *tert*-butyl hydroquinone (TBHQ) combinations with butylated hydroxyanisole (BHA), propyl gallate (PG) and pyrogallol (PY) and  $\alpha$ -tocopherol with myricetin. In these instances the mechanism appears to involve the regeneration of the more efficient oxidant by the other one [12].

EN14112 [13] is currently the preferred procedure for determining the oxidative stability of biodiesel. This is quantified by the induction time measured with a Rancimat instrument. In this method, a constant flow of air is passed through a small biodiesel sample held at 110 °C. During an initial induction phase virtually no secondary products are formed. This is abruptly followed by an oxidation phase characterized by a rapid increase in peroxide value and the formation of volatile products, mainly formic acid and acetic acid. These volatile acids are transported via the stream of air into a measuring cell filled with deionized water. The volatile acids formed during the oxidation process dissolve in the deionized water and increase its conductivity. This increase in conductivity is measured as a function of time in the Rancimat method. The induction time (IP) is then evaluated from the experimental conductivity vs. time curve.

Compared to other biodiesels, the one derived from sunflower oil is particularly prone to oxidative degradation [14]. Hence, the main objective of this study was to study the stabilization of sunflower oil-based biodiesel. Secondly, it was of interest to determine whether synergistic activity occurs in mixtures of phenolic-, phosphite- and amine-based antioxidants. Therefore, such combinations were explored using the Rancimat method while keeping the overall antioxidant concentration fixed at 0.15 wt%. The aims were (a) to determine whether antioxidants commonly used in polyolefin polymers such as polyethylene (which features no double bonds) and in natural rubber where there are numerous double bonds present have any merit as biodiesel stabilisers, and (b) to establish whether synergistic effects are present when they are used in suitable combinations.

#### 2. Experimental

#### 2.1. Materials

Pure, triple-distilled sunflower oil was supplied by Sunfoil. Three different stabilizer chemistries were explored namely phenol-, amine- and phosphite-based antioxidants. A comprehensive study was done on combinations of tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane (Anox 20 ex Addivant) a hindered phenolic antioxidant, poly (1,2-dihydro-2,2,4-trimethylquinoline) (Orox PK ex Orchem) an aminetype antioxidant and tris(nonylphenyl) phosphite (Naugard P ex Chemtura) a phosphite-type antioxidant. The latter is classed as a secondary antioxidant while the first two are considered to be primary antioxidants. The antioxidants were added to the biodiesel at a total loading of 0.15 wt%. Both binary as well as a ternary blends of these antioxidants were evaluated. Additional combinations of the amine with other phenoltype antioxidants were tested at the 1:2 mass ratio. SigmaAldrich supplied samples of BHT, pyrogallol and propyl gallate while TBHQ and DTBHQ were obtained from Aromas and Fine Chemicals, South Africa. All chemicals were used as received, i.e. without further purification.

#### 2.2. Biodiesel preparation

The biodiesel was prepared using alkali catalyzed methanolysis as described previously [15]. Potassium hydroxide was used as the catalyst and several small batches of 500 mL each were prepared and subsequently combined before testing and analysis.

#### 2.3. Characterization

The FAME analysis for sample BD01 was performed by the CSIR Food and Beverage Laboratory (now acquired by Aspirata Certification Auditing and Testing (Pty) Ltd.) using an Agilent 6890 GC-FID. An Agilent J&W GC column CP-SIL 88 was used for the separation of the FAME components. Due to the unavailability of the instrument at CSIR the FAME analysis for sample BD02 was performed at the Tshwane University of Technology using a Varian Crompack CP-3800 gas chromatograph. A Restek Rtx-2330 column was used for the separation of the FAME components.

Quantification was performed by internal standard calibration using methyl heptadecanoate. Identification of the FAMEs in the biodiesel samples was accomplished by comparing their retention times to a Supelco FAME reference mixture containing 37 components. The FAME content was computed according to EN 14,103 [16] and Ruppel and Huybrighs [17]. All the peaks from that for methyl myristate ( $C_{14}$ ) to that for the methyl ester of nervonic acid ( $C_{24:1}$ ) were accounted for. Additional biodiesel physical properties were determined, using standard procedures, by Bio Services CC, Randburg, South Africa. These properties included free glycerine, methanol content, water content, acid value, iodine value, and flash point.

# 2.4. Antioxidant formulations and determination of the oxidative induction times

The effect of antioxidant combinations on the induction time was determined by spiking the biodiesel with different amounts of the antioxidants keeping the total antioxidant dosage constant at 0.15 wt%. In particular, Orox PK, Naugard P and Anox 20 binary mixtures, as well as a ternary blend, were tested. The oxidation stability of the biodiesel samples was determined on a Metrohm 895 Professional PVC Thermomat according to the Rancimat method described in EN14112 [13]. The oxidation tests were done at a constant temperature of 110 °C and an airflow rate of  $10 L h^{-1}$ . Biodiesel samples (3.00 g) were weighed into the reaction vessels, and placed in the heated cellblock. The air was passed through the sample and then through a measuring vessel that containing 60 mL of deionized water. The volatile acids formed during the oxidation process were trapped in this water causing an increase its conductivity. The change in the conductivity was continuously recorded as a function of time. Duplicate runs, and in some cases triplicate runs were conducted on each sample tested.

#### 2.5. Data reduction

The Rancimat instrument produces data corresponding to the initial part of the oxidation reaction. The induction time values were extracted from the experimental conductivity vs. time data using the method described previously [15]. The conductivity vs. time curves ( $\sigma = \sigma(t)$ ) were fitted using the following equation:

$$\sigma(t) = \sigma_{min} + mt + \beta F(t) \tag{1}$$

where  $\sigma(t)$  is the experimental conductivity vs. time curve;  $\sigma_{min}$  is the conductivity offset at time t = 0; m is the slope of the initial portion of the conductivity curve;  $\beta$  is a proportionality constant with conductivity units and F(t) is an appropriate response function that is dimensionless. The parameter m in Eq. (1) compensates for any linear signal drift over the full measurement time. The response function F(t) should be able to adequately represent the experimental data over the full measurement

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