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Antioxidant studies for animal-based fat methyl ester

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Abstract. The aim of this study was to test an antioxidant, BioSineox, for animal-based fat methyl ester, AFME, in order to determine the optimal concentration of this antioxidant for meeting the six-hour oxidation stability requirement as set in the EN 14214:2010 standard. Oxidation stability was measured using a Biodiesel Rancimat 873, which meets the requirements of the EN 14112 standard. The variety of raw materials used in the production of methyl esters, i.e. biodiesels, renders a variety of fatty acid profiles. Consequently, the reaction of biodiesels with various antioxidants must be individually tested for each combination. Before the antioxidant is added during the manufacturing process, it must be tested in laboratory conditions. As the main result of this study it can be stated that the process requires a relatively high (2,000 ppm) BioSineox concentration in order for the biodiesel to meet the six-hour oxidation stability requirement. In March 2013, the standard EN 14214:2010 was replaced by the EN 14214:2012. One of the changes was an increase in the oxidation stability requirement from 6 hours minimum to 8 hours minimum. To reach this target, the concentration of the antioxidant must be further increased.

Key words: Antioxidant, biodiesel, methyl ester, oxidation stability, Rancimat.

INTRODUCTION

The interest in biofuels as engine fuels is increasing in both developing and industrialized countries. The trend covers many engine applications from transport to agricultural mechanization and electricity production. The growing interest in biofuels correlates to increasing energy consumption, a decline in crude oil resources and hence the obligation to replace fossil fuel products, the obligation to reduce greenhouse gas (GHG) emissions, and the desire to improve energy self-sufficiency by utilizing waste-derived feedstock in distributed energy production – often managed by minor local companies (Sidibé et al., 2010).

Accordingly, in the year 2007 the EU set an ambitious target for increasing the use of renewable energy sources to 20% of the total energy consumption, as well as for increasing the energy efficiency to 20% in comparison with the baseline scenario under development in the EU by 2020. Also, the share of biofuels in transportation shall be increased to 10% (The EU Climate and Energy Package, 2011). In 2014, the EU's framework 2030 presents even more ambitious targets; the green house gas emissions should be decreased 40% below the 1990 level and the renewable energy consumption should increase up to 27% of the total energy consumption by 2030 (The European Commission, 2014).

To achieve this target, even smaller-scale production of biofuels requires further attention and development. Biodiesels produced from oils and fats through the transesterification reaction with alcohol is one of the smaller-scale alternatives needed on a national level to maximize overall energy production and efficiency. The optimal raw material for the production of biodiesel is waste or non-edible oil.

In Finland, biodiesel production is focused on certain raw materials, such as rapeseed oil, animal fat and spent edible frying oil. In particular, increasing attention has been placed on the manufacture of waste-derived fuels in order not to compete with food production when promoting biofuel launching.

In the Ostrobothnia region of Finland, in the surroundings of the city of Vaasa, animal fat containing waste is widely used as feedstock for biofuels. The production of animal-based fat methyl ester, AFME, studied in the current project, does not compete with food production. Much to the contrary, the utilization of waste feedstock for fuels reduces environmental loading, since the uncontrolled decomposition of wastes in landfills is avoided (Lagus, 2010). According to Cooper (Cooper, 2010) the CO_2 production per megajoule is very low for waste animal oil biodiesel.

In many respects, biodiesel is similar to fossil diesel fuel, which poses a great advantage. Its potential as an alternative fuel for compression ignition engines is significant. The production and processing of biodiesel is, however, not always sufficiently controlled, and thus the fuel's chemical and physical properties may vary depending on the adopted feedstock and thermal parameters, as well as on the chemical components applied to develop the final product. The various processes involving oils and fats produce fuels with varying compositions and properties (Knothe, 2010; Varde & Veeramachineni, 2011).

In order to replace fossil fuel consumption by biodiesel, the latter must be of good quality and meet the requirements set in the EN 14214 standard. The oxidation stability limit has proven to be one of the most difficult requirements to fulfill and is thus an obstacle for the widespread commercialization of biodiesels. In March 2013, the standard EN 14214:2010 was replaced by the EN 14214:2012. One of the changes was an increase in the oxidation stability requirement from 6 hours minimum to 8 hours minimum.

Several studies have indicated that even the six-hour oxidation stability could not be reached without the addition of an antioxidant (Chen et al., 2011; Karavalakis et al., 2011; Vauhkonen et al., 2011). The increase of the six-hour requirement to a minimum of eight hours aims to ensure the usability of biodiesel as a blending component in fossil diesel grades, a part of paraffinic diesel fuels, as well as pure diesel fuel even after prolonged storage times (AGQM, 2010; AGQM 2011).

Resulting from the wide variety of biofuel origins and manufacturing processes, the properties and suitability of each fuel have to be studied individually. The paucity of data on animal fat based fuels also calls for examining such new fuel options that may be of importance in promoting distributed energy production and self-sufficiency of farms, local communities, and factories.

In this study, the oxidation stability of AFME was determined in dependence on antioxidant concentration. Several measurements were conducted. The main targets were to further the work of a local biodiesel producer and to gather additional general information about biodiesel antioxidants. Antioxidant concentrations are usually relatively high which increases the overall costs of biodiesel production. Testing several antioxidants aims at finding an antioxidant that would improve oxidation stability to the desired level in the smallest possible concentration. The results presented in this paper were measured in the end of the year 2011 and in the beginning of 2012. At the time, the desirable oxidation stability level for biodiesel was still 6 hours and it was therefore used as the target when the optimum antioxidant concentration was determined.

MATERIAL AND METHODS

Samples

The examined animal-based fat methyl ester was produced by Feora Ltd in Nykarleby, Finland. Feora Ltd is a Finnish animal feed company that commenced biodiesel production in 2010. Feora produces ester-type biodiesel using a two-stage process that combines acid-catalyzed esterification and alkali-based transesterification. The product is mainly used as heating fuel and as fuel in non-road engines (Bengts, 2010).

Antioxidants

The tested antioxidant was BioSineox^{TM} Liquid, a product of Antioxidant Aromas and Fine Chemicals Ltd, KZN, South Africa. It is a synergistic blend of hindered phenolic compounds with a chemical name of mixed butylated hydroquinones (Fig. 1). The major components are MTBHQ (mono t-butyl hydroquinone) and DTBHQ (2.5-di-tert-butylhydroquinone) (AAFC, 2009).

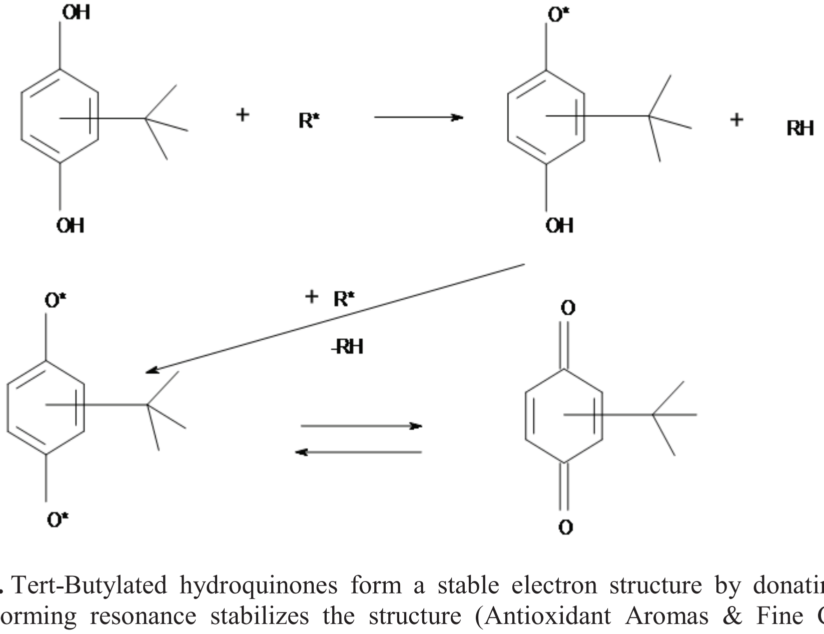

Figure 1. Tert-Butylated hydroquinones form a stable electron structure by donating two H atoms. Forming resonance stabilizes the structure (Antioxidant Aromas & Fine Chemicals /Pty Ltd, date not available).

In general, hindered phenols work best in biodiesels produced from any kind of raw material, and butylated hydroquinones are said to work best in biodiesels produced from vegetable feedstock. Biodiesel is prone to oxidation depending on the raw material it has been produced from. Various raw materials have a variety of fatty acid profiles. The higher the unsaturation level is, the more reactive and unstable the resulting biodiesel becomes, thus requiring a higher antioxidant concentration in order to be stabilized. (Antioxidant Aromas & Fine Chemicals /Pty Ltd, date not available).

Feora previously used the Ionol BF 1000 antioxidant, a product of Degussa Sant Celoni, S.A., Spain, in the production of biodiesel. Ionol BF 1000 contains a blend of butylated phenolic compounds (Oxiris Chemicals S.A., 2009). The concentration of this antioxidant in production was rather high, 2,000 ppm. The new BioSineox^{TM} Liquid antioxidant was tested to determine whether a smaller dosage would prove sufficient for biodiesel to reach the six-hour limit in a Rancimat test.

Experimental

Two types of samples were sent to the University of Vaasa (UV) by Feora Ltd, i.e. biodiesel samples containing the antioxidant and samples without the antioxidant, both obtained directly from the production process. In the following text, the term ‘blank sample’ is used to refer to samples that were obtained before the addition of the antioxidant. The term ‘process sample’ refers to samples obtained directly after the addition of the antioxidant during the production process (Fig. 2). Moreover, in the laboratory at UV, ‘laboratory samples’ were prepared by adding various amounts of the antioxidant into the blank or process samples provided by Feora Ltd. The preparation of the laboratory samples began with the blending of the antioxidant into blank-sample biodiesel to achieve a final antioxidant concentration of 10 m/m%, i.e. the stock solution. The laboratory samples were then prepared using the stock solution and left to react in room temperature (20°C) for at least one day prior to taking measurements. During this time, the samples were shaken by hand several times. The mixing was performed at random time. The reaction times for the measurement sets varied because it was assumed that a few days difference would not have an effect on the obtained results.

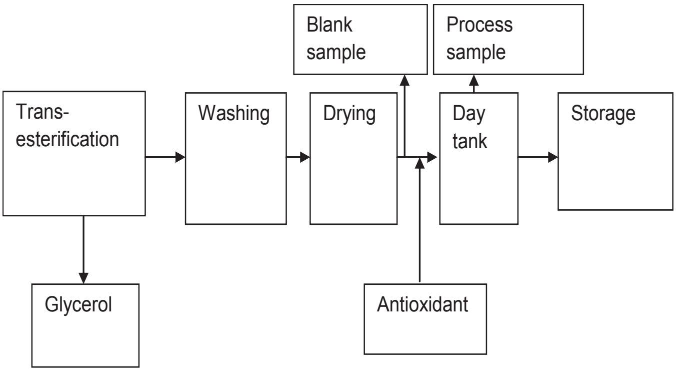

Figure 2. Process diagram of antioxidant addition in the production process (Oxiris Chemicals, 2009).

The oxidation stability of biodiesels was studied using a Biodiesel Rancimat 873 instrument (Metrohm, Herisau, Switzerland), which meets the required EN 14112 standard (European Committee for Standardization, 2003). The air flow rate was set at 10 l h^{-1}, using 3.00 grams of a sample (± 0.01 g) placed in the equipment's heating block at a temperature of 110°C. The vapors coming from the sample were directed into a measuring flask containing 50 ml of distilled water. The conductivity of the water was recorded by a computer. The induction times of the biodiesel samples were determined. Several sets of measurements were made for AFME with various concentrations of the antioxidant (Fig. 3). The measurements were repeated for all of the samples and the presented results show the mean values of these two parallel measurements.

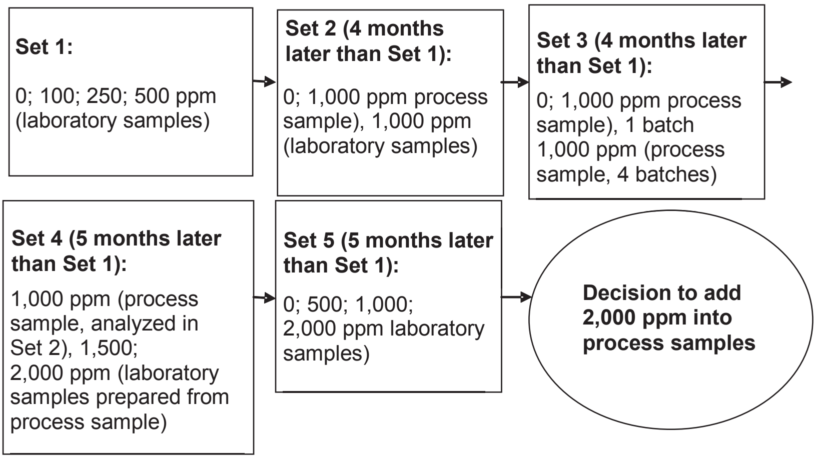

Figure 3. Diagram of the measurement sets, the schedule and the samples.

In addition to oxidation stability, certain other properties of the biodiesel-antioxidant mixtures were measured for some of the samples. These properties are presented in Table 1. The purpose was to detect whether the addition of the antioxidant would alter certain properties of the AFME biodiesel. Measurements were carried out for a blank sample and a sample containing 500 ppm of the BioSineox antioxidant. The biodiesel for both the blank and the 500 ppm sample was obtained from the same production batch.

The water content was determined with a Karl Fischer Coulometer Mettler Toledo C30 according to the EN ISO 12937 standard. The iodine value and the acid value were measured according to the EN 14111 and EN 14104 standards, respectively. Both measurements represent titration methods that were performed employing a Mettler Toledo DL 70 ES titrator. The surface tension was measured with a Tensiometer TD 2 Lauda according to the manufacturer's instructions. The trace elements were measured using an ICP-OES Perkin Elmer Optima 7000 DV according to the EN 14538 standard and the manufacturer's instructions.

RESULTS AND DISCUSSION

Table 1. Properties of animal-based fat methyl ester, blank sample (without antioxidants), and laboratory sample containing 500 ppm of BioSineox

Property (unit)	Limit, EN 14214	AFME, blank	AFME, 500 ppm, BioSineox
Water content (ppm)	≤500	510	430
OSI (h)	≥6	2.5	6.5
Iodine value (g I_2 100 g^{-1})	≤120	77	76
Acid value (mg KOH g^{-1})	≤0.50	0.15	0.17
Surface tension (mN m^{-1})	-	30.0	30.9
Mg+Ca (mg kg^{-1})	≤5.0	<1.0	<1.0
Na+K (mg kg^{-1})	≤5.0	<1.0	<1.0
P (mg kg^{-1})	≤10.0	0	0

As Table 1 shows, oxidation stability reflects the most significant difference in performance between the blank and the 500 ppm sample. The BioSineox antioxidant improved the oxidation stability of the tested biodiesel by 160%, while other properties showed only minor changes. The water content of the 500 ppm antioxidant sample appeared to reduce by 15% in comparison with the blank sample. This may have resulted from a change in the chemical structure, as a number of chemical compounds interfere with water determination.

The first Rancimat measurements were carried out for an AFME series of four laboratory samples containing 0 (blank), 100, 250 and 500 ppm of the BioSineox antioxidant. The results are presented in Fig. 4. The error bars in Fig. 4, (as well as in Figs 5 and 6) are drawn based on the relative standard deviation, 4.5%, measured for this method earlier. The six-hour limit was reached when 500 ppm of the antioxidant was added. It should be noted that the blank sample with 2.5 h yielded relatively high oxidation stability. Normally, the oxidation stability of AFME samples containing no antioxidants measures approximately 0.6 h.

In the second set of measurements, a blank sample was compared to a process sample and a laboratory sample, both containing 1,000 ppm of BioSineox. The Rancimat result for the blank sample was 0.6 h. The Rancimat result for the 1,000 ppm process sample was 3.2 h, while the 1,000 ppm laboratory sample yielded 27 h oxidation stability.

In the third set of oxidation stability measurements, a blank sample was compared to two process samples containing 1,000 ppm of the antioxidant. The process samples consisted of biodiesel from a single production batch and a mixture of four batches, respectively. The blank sample yielded an oxidation stability index of 0.6 h, whereas the one-batch sample reached 2.4 h and the four-batch sample 2.2 h oxidation stability.

The 1,000 ppm process sample analyzed in the laboratory in the second set of measurements had previously yielded a result of 3.2 h. When the sample was reanalyzed, oxidation stability had declined to 2.7 h. Four weeks had elapsed since the initial measurement. Two more laboratory samples were produced from this 1,000 ppm process sample by adding the BioSineox antioxidant to final concentrations of 1,500 ppm and 2,000 ppm, respectively. The results for both of the new samples exceeded the six-hour limit. The result for the sample containing 1,500 ppm reached 7.1 h and for the sample containing 2,000 ppm 12 h (Fig. 5).

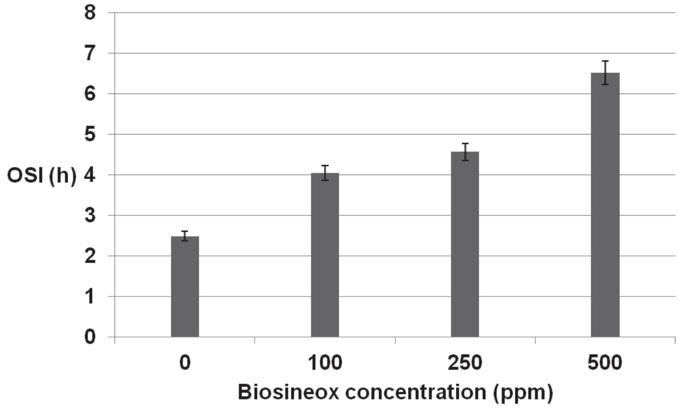

Figure 4. Measured oxidation stability indexes (h) for methyl ester samples containing different concentrations between 0 and 500 ppm of the BioSineox antioxidant.

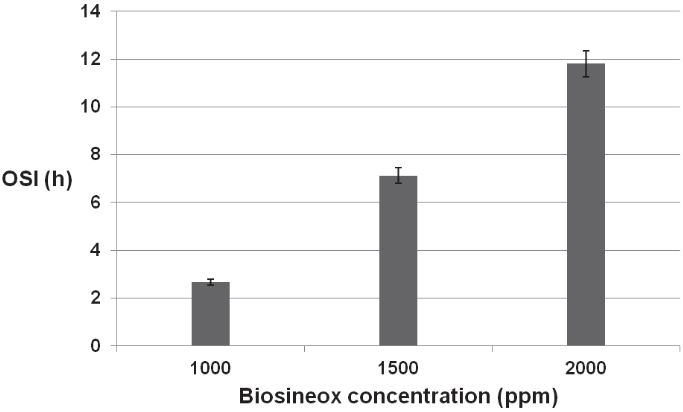

Figure 5. Measured oxidation stability indexes (h) for methyl ester samples containing concentrations of 1,000, 1,500 and 2,000 ppm of the BioSineox antioxidant.

In the final series of analysis, biodiesel samples were prepared in the laboratory containing the antioxidant at concentrations of 0, 500, 1000, 1,500 and 2,000 ppm. The results are presented in Fig. 6.

The blank sample rendered an oxidation stability of 0.6 h, corresponding to the results from the two earlier blank samples. Also, the OSI for the 1,000 ppm process sample was comparable to earlier results. However, the results for the 500 ppm, 1,500 ppm and 2,000 ppm laboratory samples proved lower than the previous results for these concentrations. While the 2,000 ppm sample reached 57% (Fig. 5), the 500 ppm and 1,500 ppm samples equaled the previous OSI results (Figs 4 and 5) only by 12% and 19%, respectively. One possible explanation for this contrastive outcome is that the samples in Fig. 6 were allowed a shorter reaction time than the samples of

Fig. 5. The earlier samples (Fig. 5) were prepared in the laboratory by adding the antioxidant to a process sample that already contained 1,000 ppm of the antioxidant. The first antioxidant addition had already been carried out in the process line four weeks prior to the measurements.

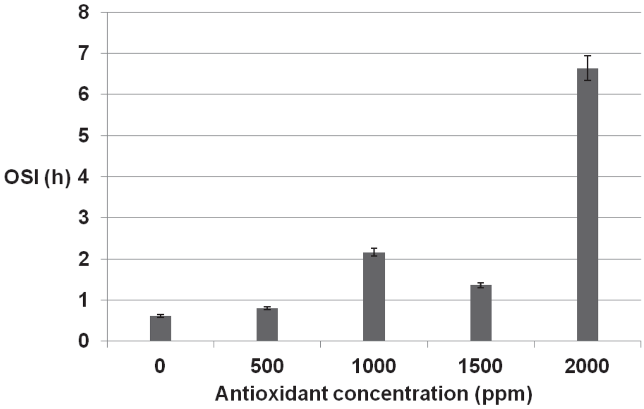

Figure 6. Measured oxidation stability indexes (h) for methyl ester laboratory samples containing different concentrations between 0 and 2,000 ppm of the BioSineox antioxidant.

As for the final series, the samples (Fig. 6) were prepared four days later than the 10 m/m % stock solution, and the samples were analyzed one day after preparation. It is probable that the mixtures of biodiesel and the antioxidant were allowed for an insufficient amount of time to blend and react properly.

The first laboratory samples yielded higher OSI results with lower antioxidant concentrations. A 500 ppm addition of BioSineox sufficed to exceed the six-hour level. The blank sample also yielded a relatively high result, 2.5 h, while the later blank samples yielded only 0.6-hour results. This, along with variation of the raw material, may help explain the smaller amount of the antioxidant reaching the desired level of biodiesel oxidation stability. The promising result that lower concentrations of the antioxidant had achieved high enough oxidation stability for some of the laboratory samples cannot overcome the fact that concentrations of 2,000 ppm were required in process samples.

Some studies on vegetable oil based biodiesels have indicated that lower concentrations of antioxidants suffice to reach the desired six-hour level. According to Chakraborty and Baruah (Chakraborty & Baruah, 2012) a concentration of 500 ppm of the TBHQ (tert-butylhydroxyquinone) antioxidant achieved the limit of six hours for a vegetable oil based biodiesel from *Terminalia belerica*, while a biodiesel sample containing no antioxidant reached oxidation stability of 3.8 h. According to the same study, the PY (pyrogallol) and PG (propyl gallate) antioxidants efficiently rendered the six-hour result with a concentration of only 100 ppm. Ruy (Ruy, 2010) has examined the effect of an antioxidant on soybean oil based biodiesel. With the concentration of 100 ppm, the addition of TBHQ resulted in oxidation stability of more than six hours and the concentration of 2,000 ppm yielded oxidation stability exceeding 40 hours. However, Ruy discovered that the BHA (butylated hydroxyanisole) and BHT (butylated hydroxytoluene) antioxidants helped oxidation stability meet the specification at the 1,000 ppm level (Ruy, 2010). Altogether, these results underline what was previously mentioned, i.e. an antioxidant's efficiency may vary depending on the raw material. Thus, all of the antioxidants and raw materials require individual examining.

The requirement for high antioxidant concentrations has also been observed in studies that have examined certain antioxidants used in the production of AFME. For instance, the Ionol BF 1000 antioxidant has previously been used in the production of biodiesel. The results for BioSineox and AFME mixtures reported here and those for Ionol BF 1000 treated methyl esters presented by Vauhkonen et al. (2011) show that the antioxidant concentrations must be at least 2,000 ppm for these antioxidants to reach the OSI limit of six hours (Vauhkonen et al., 2011). The low reproducibility of the results in this study necessitates further research in order to ensure a sufficient OSI in general and for AFME in particular.

CONCLUSIONS

In the current study, the BioSineox antioxidant was added to animal-based fat methyl ester in order to determine the smallest possible concentration that would improve oxidation stability to the level of six hours.

Based on the results obtained here, the following can be concluded: To ensure biodiesel reaching the six-hour OSI limit in Rancimat tests, a minimum concentration level of 2,000 ppm of the BioSineox antioxidant is required in the process sample.

The increase of the six-hour requirement to a minimum of eight hours in the standard 14214 necessitates further research in order to find the optimum concentration of the antioxidant. Most probably, the concentration needs to be higher than 2,000 ppm.

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