ENVIRONMENTAL ENGINEERING
The 8th International Conference
May 19–20, 2011, Vilnius, Lithuania
Selected papers

ISSN 2029-7106 print / ISSN 2029-7092 online
ISBN 978-9955-28-826-8 (1 Volume)
ISBN 978-9955-28-827-5 (3 Volumes)
http://enviro.vgtu.lt

INVESTIGATION OF ENVIRONMENTALLY FRIENDLY LUBRICANTS

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Abstract. Many of the lubricants used in the world today cause environmental pollution. To reduce pollution environmentally friendly lubricants should be used. The attractive base oil for environmentally friendly lubricants is vegetable oil. However it is some disadvantages like pure oxidation stability. This paper discuses the influence of thermal oxidation on physico-chemical, and environmental properties of rapeseed oil. Spectral analysis, viscosity and viscosity index represents physico-chemical properties, while biodegradation in aerobic conditions evaluates environmental properties of tested oil.

Keywords: environmentally friendly, lubricant, rapeseed oil, oxidation, biodegradation, tribology.

1. Introduction

It is estimated that approximately 50 % of all lubricants sold worldwide end up in the environment through total loss applications, volatility, spills or accidents. According to statistical data in 1990 in EU and USA together $2.3 \cdot 10^{+9}$ L of lubricants were lost in the environment (Schneider 2006; Salimon *at al.* 2010; Hörner 2002).

Such environmental problems enforce the industry, forestry and agriculture to use more environmentally friendly lubricants. Particularly the use of environmentally friendly lubricants is essential in water treatment, forestry, agriculture and recreation zones. The driving forces for that are various legislations and Eco Labels: The European Eco-label, The German „Blue Angel“, Nordic countries „White Swan“, Austrian ecolabel, Canadian „EkoLogo“ a.o. (Mang and Dresel 2007; Bartz 2006).

In general environmentally friendly lubricants characterizes high biodegradability, low or non toxicity, renewability and exclusion of specific substances (Bartz 2006). Nevertheless the environmental acceptability of lubricants can also encompass a wide range of potential environmental benefits: resource conservation, pollutant source and emission reduction, recycling and so on (Pirro and Wessol 2001).

Majority of the Eco Labels encompass biodegradability as the most important criteria for the environmentally friendly lubricants. Biodegradability means the tendency of a lubricant to be ingested and metabolized by microorganisms. Complete biodegradability indicates the lubricant has essentially returned to nature. Partial biodegradability usually indicates that one or more components of the lubricant are not degradable. To classify the lubricant as readily biodegradable the degradation of ≥ 60 % in 28 days must be reached according to OECD 301 method, or ≥ 80 % in 21 day according to CEC L-33-A-93 method respectively (Salimon *at al.* 2010; Battersby 2000; Bartz 2006).

The toxicity and renewability are of grate important too. The toxic or R phase containing compounds are unallowed or there content can not exceed 0.1 % (wt.). The fully formulated lubricant shall have the particular carbon content derived from renewable raw materials. This content in various Eco Labels and lubricant categories can vary from 45 % (for grease) to more then 95 % (for chainsaw oils, concrete release agents and other total loss lubricants) (Rudnick 2009).

One of the most attractive base stocks for environmentally friendly lubricants are vegetable oils. Inherently they have both excellent biodegradability and non toxicity. Moreover vegetable oils have excellent tribological properties, high flashpoints, lower friction coefficient, lower evaporation, and higher viscosity index in comparison with mineral based lubricants (Schneider 2006; Erhan and Asadauskas 2000; Miles 1998).

However, vegetable oils have some serious disadvantages. They are thermally less stable then mineral oils, more sensitive to hydrolysis and oxidative attack, and there low temperature behavior is frequently insufficient (Salimon *at al.* 2010; Schneider 2006). Low oxidation stability and pure low temperature behavior are the main problems limiting usage of vegetable oils.

A lot of chemical modification methods for instance epoxidation, alkylation, radical addition, acylation, hydroformylation, acyloxylation are used to increase oxidation stability. Unfortunately chemical modification decrease inherent biodegradability of vegetable oils making the choice between good technical properties and environmental benefits (Schneider 2006). Another way to improve above mentioned performance is to use proper additives. However, amount of additives as well as there biodegradability and toxicity is restricted by Eco Labels.

While thermal oxidation is the great problem for vegetable oils, there were a few studies related to properties of oxidized vegetable oils (Fox and Stachowiak 2003; Castro *at al.* 2006; Mano *at al.* 2009). However, the influence of thermal oxidation on tribological and environmental properties of vegetable oils is not clear yet. Solution of this problem can help evaluate how used vegetable oil based lubricant can impact the environment.

The purpose of current investigation is to evaluate the influence of thermal oxidation on physico-chemical and environmental properties of rapeseed oil.

2. Materials and Methods

Conventionally refined, bleached and deodourised Rapeseed oil (further RO) was obtained from oil manufacturer. Its oxidation was carried out using Rancimat 743 apparatus (Fig 1).

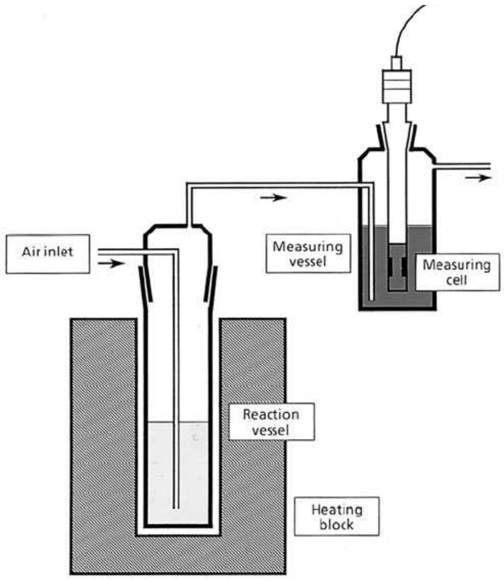

Fig 1. Principled view of Rancimat 743 oxidation performing cell

The procedure was in line with the ISO 6886:2006 method. 20 ml oil sample was placed into a glass reaction vessel (no metals or catalysts) and heated to 100°C. A glass tube was inserted from the top to bubble dry air at flowrate of 10 L/hr. The exiting air, including volatile oxidation products, was directed to bubble through the measuring vessel with deionized water, whose electrical conductivity was monitored by measuring cell. With the onset of oxidation, rapid production of volatile degradation products begins, so called Induction Period (IP). Under this test, volatile products dissolve in the water and result in a rapid increase of electrical conductivity, monitored by the Rancimat apparatus.

The Four Ball test rig was used to measure tribological properties of samples Fig 2. The load of 150 N was used. The test runs 1 hour. Prior to each experiment, all the appropriate parts of the machine, i.e. bottom and upper ball holders, oil vessel and the test balls were washed in an ultrasonic bath and then dried. The testing procedure was adapted from the standard DIN 51 350 Part 3.

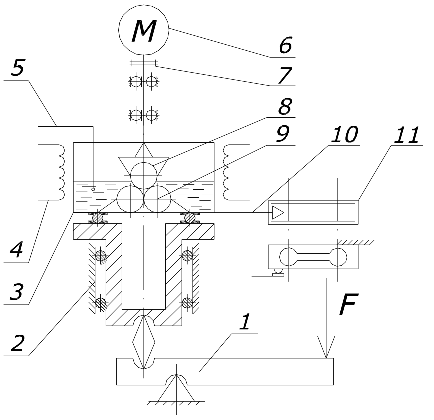

Fig 2. Schematics of Four-Ball tribotester: 1 – load transfer lever; 2 – vertical center bearing; 3 – oil sample compartment; 4 – oil heater; 5 – thermocouple; 6 – electric motor; 7 – clutch; 8 – upper rotary ball; 9 – lower stationary balls; 10 – torque transfer lever; 11- force transducer

The diameters of the wear scars on three stationary balls and the friction surfaces were measured and analyzed with an optical microscope. For each run the scar measurements were reported as an average of the Wear Scar Diameter (WSD) of the three balls in millimeters.

Kinematic viscosities of oxidised samples were determined at 40 and 100°C and viscosity index established according ISO 3104:1994 and ISO 2909:2002 respectively. The Ocean Optics USB4000 visible light spectrometer set with xenon pulsed lamp PX-2 was used to determine absorption of the samples in all oxidation periods. The non oxidized rapeseed oil was used as reference. The 200 ms integration period and 10 scanning samples average was chosen.

The biodegradability was measured according CEC L-33-A-93 Biodegardability of Two-Stroke Cycle Outboard Engine Oils in Water. The biodegradation rate was measured using FT-IR Spectrum RX I method, by disappearance of C – H bonds in 2930 cm^{-1} wavelength.

3. Results and Discussion

During the oxidation of rapeseed oil its color changes from specific yellow to bright yellow at the beginning of induction period. Jest after induction period the oil became transparent and got a quiet yellow at the end of 40 hours oxidation. The changes in rapeseed oil transparency can be easily demonstrated usung visible light spectroscopy

(Fig 3). Taking the pure rapeseed oil as the reference, the 20 hours oxidized oil has the dramatic changes in its absorbance. There is one peak in 380 nm and one slope in 420 nm wavelength. The wide range of these peaks show, that a lot of different compound are formed.

The disappearance of 420 nm slope in the 40 hours oxidized rapeseed oil suggests that it is responsible for yellow pigment. At the same time the 380 nm peak becomes wider and moves a little bit to the longer wave side.

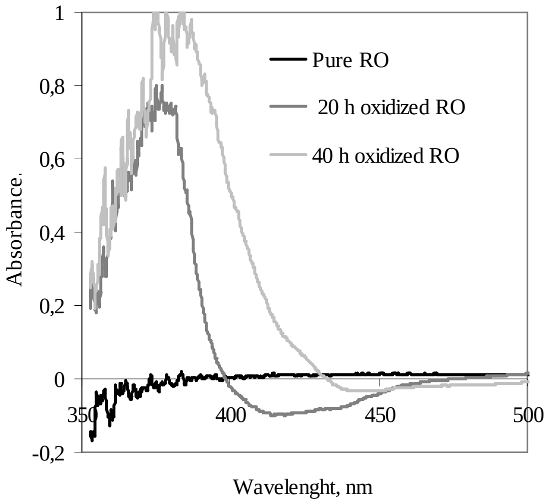

Fig 3. Optical spectroscopy of the pure and different time oxidized rapeseed oil

These changes correlate with the theory of hydrocarbon oxidation by free radical mechanism (Mang and Dresel 2007). According to free radical mechanism a lot of alkyl radicals are formed during the induction period. In this stage oxygen react with hydrocarbons (RH) forming free radicals (R·) Eq. 1.

$$RH \xrightarrow{+O_2} R\cdot \tag{1}$$

When the natural antioxidants can not withstand increasing quantity of free radicals the induction period finishes. At this time alkyl radicals react with the oxygen forming alkyl peroxy radicals (ROO·) Eq. 2.

$$R\cdot + O_2 \rightarrow ROO\cdot \tag{2}$$

When the quantity of oxygen is sufficient (as in the case of Rancimat test) the present reaction has an extremely high rate and a lot of alkyl peroxy radicals are formed. It seams fairly obvious that at the end of induction period 420 nm slope show the alkyl radicals. Following the oxidation mechanism it disappears in further oxidation.

After the induction period the polymerization and epoxidation takes place and the high molecular weight compounds are formed. After induction period extremely increasing kinematic viscosity confirm the polymerization process (Fig. 4). The increasing viscosity is undesirable in lubricating mechanisms because it can cause higher energy consumption and even failure at lower temperature.

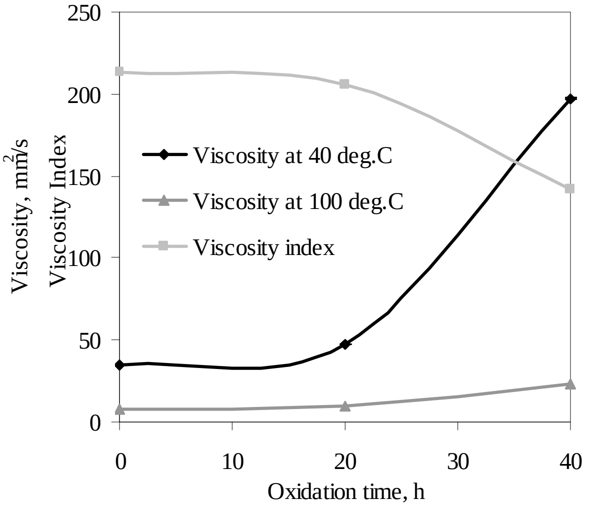

Fig 4. Kinematic viscosity and viscosity index changes during thermal oxidation of rapeseed oil

Another important parameter for lubricants is viscosity index, which sow the temperature – viscosity relationship. As it increase the influence of temperature decrease, and vise versa. Vegetable oils have an inherent high viscosity index which is much higher then that of mineral lubricants. However thermal oxidation decreases the viscosity index of rapeseed oil (Fig. 4). The decrease can be related either to formation of high molecular weight compounds or degradation of triglycerides. Irrefutable both factors influence.

The tribological test results show only a little effect of oxidation time on wear reduction properties of rapeseed oil (Fig. 5). The 20 hours oxidized rapeseed oil having the highest level of free radicals show higher wear, so lesser lubricity. With this result we can predict that aging of rape seed oil till the end of induction period can cause maximum 20 % wear increase.

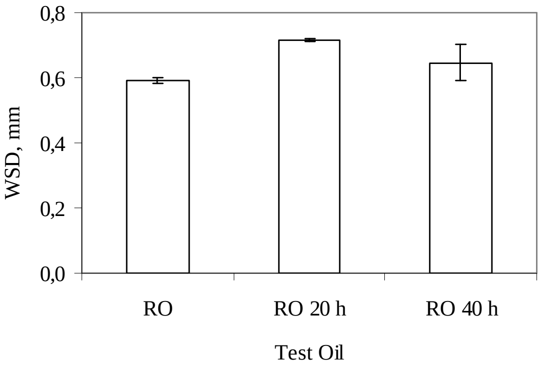

Fig 5. Lubrication properties of pure and oxidized rapeseed oil

The lubrication properties of 40 hours oxidized rapeseed oil can be affected by much more factors. In the first place there is an increasing viscosity which can lead in better lubrication layer formation. The second ones are high molecular weight products formed in the late stage of oxidation. They can lead formation of trobopolymers which also reduce the wear. The lubricity also can be affected by degradation of triglyceride structure, decreasing viscosity index, increasing acidity, and a lot of different non radical products formation. The wear of balls lubricated with 40 hour oxidized rapeseed oil is worse then non oxidized rapeseed oil. Nevertheless even long time oxidized rapeseed oil do not cause dramatic increase in wear as can be expected from changes in chemical composition.

Environmental properties measurement show slightly decreasing biodegradability with increasing oxidation time (Fig. 6). This means that compounds formed during the thermal oxidation are partly biodegradable and show less biodegradability in comparison with pure RO.

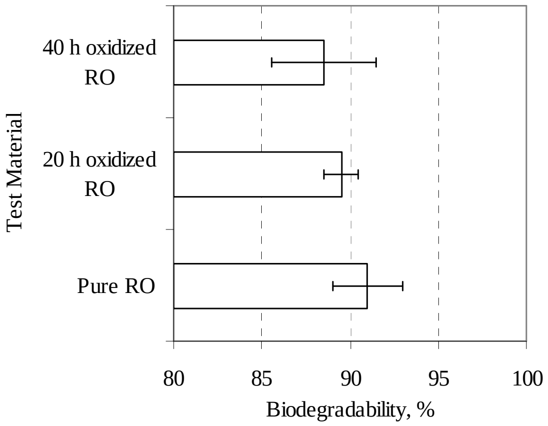

Fig 6. Biodegradability of pure and oxidized rapeseed oil

According to spectral analysis (Fig 3) the 40 hours oxidized rapeseed oil has a lot of high molecular weight compounds while 20 hours oxidized rapeseed oil has less. It is likely that higher molecular weight compounds are less biodegradable. Despite that all investigated samples according to CEC L-33-A-93 standard are readily biodegradable.

4. Conclusion

The study show that obtained results are in the line with classical free radical mechanism. The thermal oxidation has significant negative influence on kinematic viscosity and viscosity index. Although during the oxidation formed products have no or a little effect on biodegradability and lubricity of rapeseed oil.

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