Lube-Tech
PUBLISHED BY LUBE: THE EUROPEAN LUBRICANTS INDUSTRY MAGAZINE
No.81 page 1

Research of Natural Antioxidants Influence on Oxidation Stability and Tribological Properties of Rapeseed Oil

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Abstract: Vegetable oils have good tribological and viscosity properties together with excellent biodegradability and non-toxicity. Unfortunately, their wider use is restricted by poor oxidation stability. Durability of vegetable oil based lubricants depends mainly on oxidation. This problem has been analysed in many research works. Nevertheless, scientists agree that there still remain many unanswered questions in this field. In this study the sage and thyme extracts and attars are suggested for use as antioxidants in rapeseed oil. The influence of natural antioxidants on oxidation stability, kinematic viscosity and tribological properties of rapeseed oil was measured. The sage and thyme extracts studied showed good oxidation stabilisation properties and had no negative influence on tribological properties of rapeseed oil.

Keywords: lubricants, natural antioxidants, rapeseed oil, extracts, attars.

1. INTRODUCTION

The consumption of mineral based fuels and lubricants as well as environmental pollution will increase over time as a result of the annually increasing number of trucks, buses, high power tractors and personal cars. The greatest part of energy consumed in the world is obtained using non-renewable, fossil fuel. The use of such an energy source has a negative impact on the environment. Furthermore, the fossil fuel resources will soon dramatically decrease. Therefore, there is great interest in alternative renewable resources. Environmentally friendly bio-based lubricants are one of the alternative ways to save fossil resources and decrease pollution [1].

According to usage lubricant can be divided into two groups [2]:

- **Long-term** - for enclosed systems (engine oils, transmission lubricants, hydraulic fluids et al.);
- **Total loss** - for open systems (railway applications, chain saw oils, two stroke engines oils et al.).

The long-term lubricants used in the enclosed systems can only escape into the environment during an accident or leakage, whereas total loss lubricants will enter the environment after their first use. A technical solution of this problem is not possible and therefore the usage of environmentally friendly readily biodegradable lubricants is essential for total loss lubricants.

Lubricants must satisfy many requirements. One of the greatest influences on a lubricant's properties are its base oil and durability, which indicates the period the lubricant can be used. Ageing through oxidation is the predominant process that determines durability of lubricants. During the ageing process base oil and completely formulated oils change their physical, chemical and tribological properties [3, 4].

Oxidation is caused by working conditions and external factors. During use lubricants are affected by temperature, metal surfaces and secondary products (combustion products in engine). Also, external factors such as moisture, air oxygen and sunlight can also have an effect. Most of these factors are not only demonstrated in usage, but also during handling [2, 5].

Measuring the oxidation stability of lubricants involves the induction period, acidity, viscosity, peroxide value, formed polymers and other parameters. The chosen estimation parameters must be closely related to the purpose/use of the tested lubricant. This is especially important when testing biolubricants as a result of its poor oxidation stability. The limited use of antioxidants in vegetable oils and animal fats cannot compete with mineral or synthetic based lubricants.

Oxidation can be slowed down by elimination factors that stimulate oxidation, and/or using antioxidants. Modification with natural or synthetic antioxidants can greatly increase oxidation stability of vegetable oils. Especially effective are synthetic antioxidants, however their compatibility to the environment is usually poor and the use of this improved efficiency is not always rational. Therefore it is important to study new environmentally friendly, renewable antioxidant products, which can be used for the modification of total loss lubricants [6, 7].

The purpose of this study is to estimate the influence of natural antioxidants on oxidation stability and the tribological properties of rapeseed oil.

2. EXPERIMENTAL

Conventionally refined, bleached and deodorised Low Erucic Acid Rapeseed Oil (RO) was obtained from an oil manufacturer and stored in closed jars away from direct sunlight.

The sage and thyme extracts and attars were used as natural antioxidants. Preparation of extracts was performed using Sokslet apparatus. 46.6g of both sage and thyme plant dried leaves were mixed with 700ml of acetone and extracted for 24 hours. The obtained products were concentrated by distillation. Attars were prepared by hydro-distillation method using Clevenger apparatus. 100g of both sage and thyme plant dried leaves were mixed with 600ml of distillate water and distilled for 2 hours. Prepared extracts and attars were kept in the closed jars at -10°C, away from direct sunlight.

The extracts and attars were mixed with rapeseed oil by weight (accuracy 1 mg). All the samples were stirred with a magnetic stirrer for 2 hours. The mixing temperature was 20… 60°C.

Kinematic viscosity of both pure and natural antioxidant modified rapeseed oil (at the temperature of 40°C) was measured according to standard LST EN ISO 3104+AC: 2000.

The influence of natural antioxidant concentration in the rapeseed oil on oxidation stability was investigated increasing concentration of antioxidants from 0.1 to 0.6% (by wt.). The results were compared with 3 different certificated environmentally friendly lubricants. The tests were performed in accordance with ISO 6886:2006 standard. The amount of sample was 2.5g. The test temperature was 100°C, dry air with 10 l/hr flow rate was blown through the sample (Fig. 1).

The tribological properties were investigated using a four ball tribometer in accordance with standard DIN 51 350, part 3. The balls of 12.7 mm diameter were made of 100Cr6 bearing steel (E = 21.98•10^4 MPa; ν = 0.3; 63… 66 HRC). The load of 150 N was used. Test duration was 1 hour. The lubricity evaluation parameters were wear scar diameter (WSD) and mean torque. WSD was measured using optical microscopy MBI – 6.

3. RESULTS AND DISCUSSIONS

The performed experiments show that oxidation stability requirements for total loss lubricants (chain saw et al.) are not precisely specified. Tests were performed using 3 different environmentally friendly chain saw lubricants and showed a wide induction period range, which varied in the range 20 to 60 hours. The rapeseed oil modified with extracts and attars was investigated. It was found that antioxidants obtained by extraction (Fig. 2) are more efficient. The efficiency of attars was poor. The effect of using extracts up to 0.2% concentration of antioxidant greatly increases the induction period of rapeseed oil. Further increases in concentration were not so efficient.

In the performed investigation the greatest effect was observed using sage

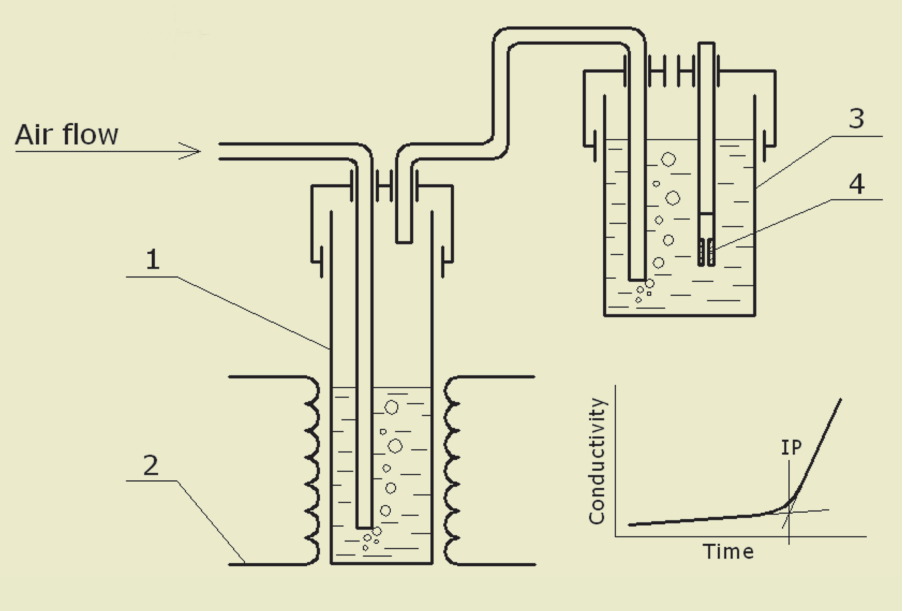


Figure 1
Schematic view of Rancimat 743 oxidation performing cell and induction period (IP) measuring curve. (1 - reaction vessel; 2 - heating block; 3 - measuring vessel; 4 - measuring cell).

extract. The induction period of rapeseed oil modified with 0.3% of such extract increased twofold – from 14 to 28 hours. The highest concentration (0.6%) of sage extract increased the rapeseed oil's induction period by 2.3 times. The use of thyme extract was not found so efficient. To increase the rapeseed oil's induction period twofold, 0.6% of thyme extract was necessary.

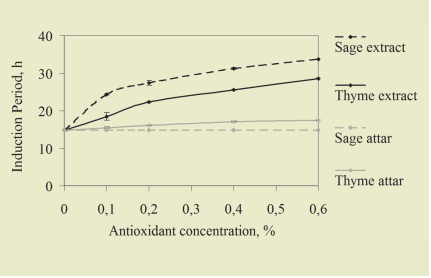


Figure 2
The influence of natural antioxidant concentrations on induction period of rapeseed oil.

The reasons for efficiency variation could be the different compositions. The sage extract may have more tocopherol or its tocophetol's composition could have been different. The poor efficiency of attars could have been explained by small amounts of material, which improve oxidation stability. Moreover, attars are relatively volatile materials, therefore can evaporate with the temperature increase and consequently have not shown any effect. The use of attars was not efficient, therefore further evaluation is made just for extracts. The optimal concentration is 0.3% (by wt.) of both sage and thyme extracts.

Comparison of the results of environmentally friendly products, which are already in the market show that the properties of antioxidants obtained by extraction are good enough for use in the modification of environmentally friendly total loss lubricants.

Modification of base oils with various additives can cause viscosity changes and therefore, kinematic viscosity at the temperature of 40°C was measured. The results obtained showed a slight decrease in viscosity when rapeseed oil was modified with thyme extract (Fig. 3). However the decrease in viscosity is negligible and should not cause any influence on other characteristics.

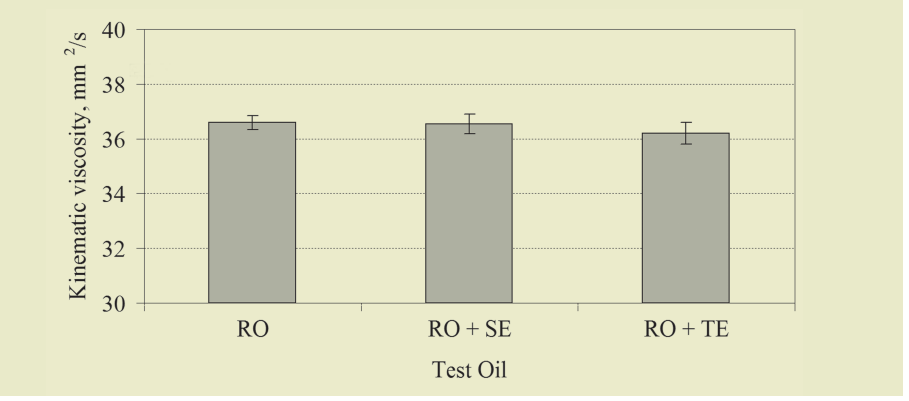


Figure 3
The influence of natural antioxidants on kinematic viscosity of rapeseed oil. (RO – rapeseed oil, RO+SE – rapeseed oil modified with sage extract, RO+TE – rapeseed oil modified with thyme extract).

The tribological tests show that the presence of extracts in the rapeseed oil has no significant influence on its wear reduction properties (Fig. 4 a). and only the results variation is smaller in comparison with pure rapeseed oil. It can be stated that extracts stabilising oxidation results in more stable lubrication conditions.

Figure 4a

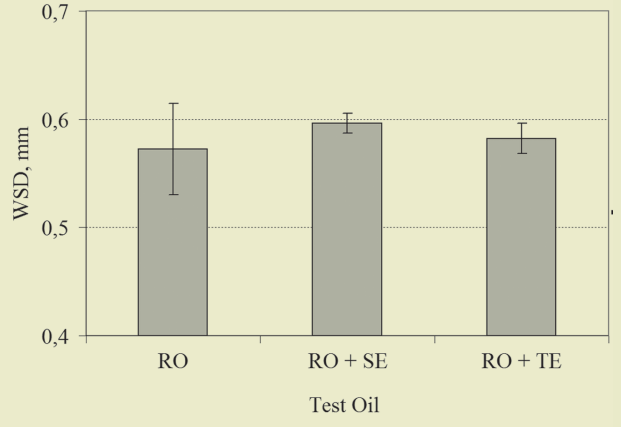


Figure 4b

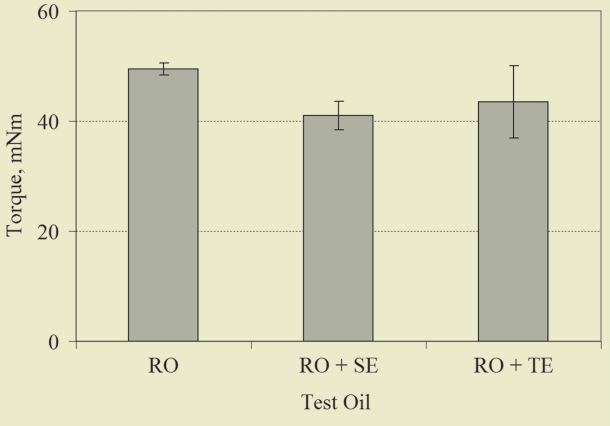


Figure 4a & b
The influence of natural antioxidants on tribological properties of rapeseed oil: a) wear reduction; b) friction expressed by torque (RO – rapeseed oil, RO+SE – rapeseed oil modified with sage extract, RO+TE – rapeseed oil modified with thyme extract).

During the tribological tests of the extract modified rapeseed oil lower friction was noted than for pure rapeseed oil (Fig. 4 b). The lower friction can also be explained by stabilisation effect or by action of natural antioxidants as friction reduction components.

In Fig. 5 the wear scars obtained after conducting tribological tests using pure and natural antioxidant modified rapeseed oil are shown. It is clear that pure and extracts modified rapeseed oil have produced similar wear scars, under similar lubricating conditions. The wear scars obtained after the lubrication with extract modified rapeseed oil differs only in some small wear grooves. These grooves were explained by some hard particles contained within the extracts.

Figure 5a

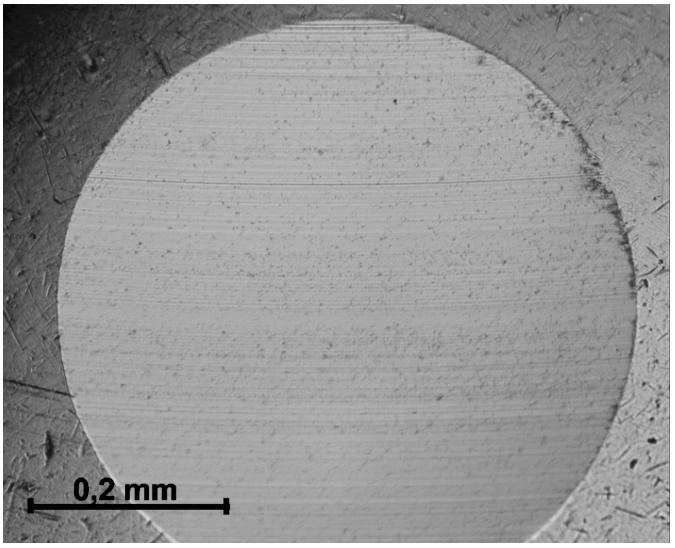


Figure 5b

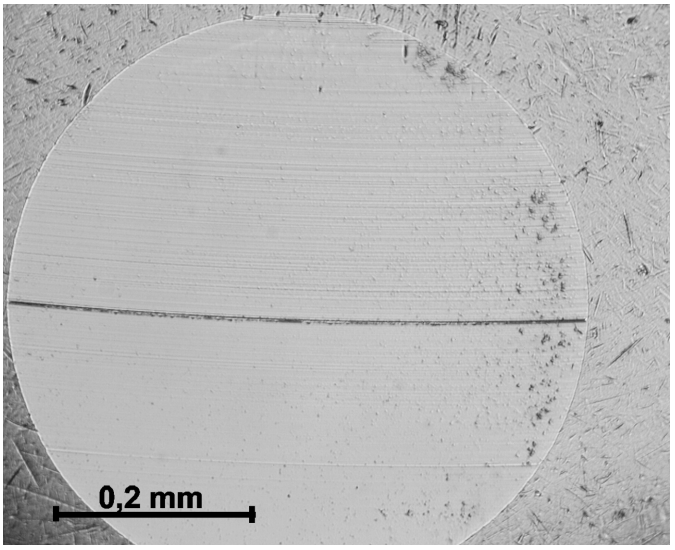
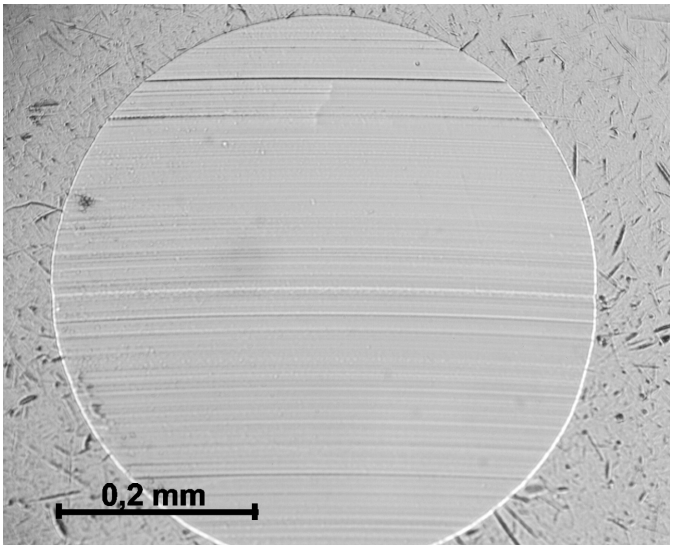


Figure 5a, b & c
The optical microscope pictures of wear surfaces lubricated with: a - pure rapeseed oil; b - rapeseed oil modified with thyme extract; c - rapeseed oil modified with sage extract.

Figure 5c



4. CONCLUSIONS

1) Natural sage and thyme antioxidants obtained by extraction effectively increase the oxidation stability of rapeseed oil. The concentration of sage and thyme extract up until 0.6% increases the rapeseed oil's resistance to oxidation respectively by 2.3 and 1.9 times. The studied attars showed no significant effect on oxidation stability of rapeseed oil.
2) Rapeseed oil modification with natural antioxidants has no influence on kinematic viscosity.
3) There were no reliable differences between the wear reduction properties of pure and extract modified rapeseed oil, whilst the friction of the modified specimens was lower.

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