THE INFLUENCE OF OXIDATION ON TRIBOLOGICAL PROPERTIES OF RAPESEED OIL

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Abstract. Approximately a half of all consumed lubricants, in one or another way, end up in the environment. Some countries put forward recommendations or even requirements for the use of environmentally friendly bio-lubricants the purpose of which is to reduce a negative influence of lubricants. The priority areas of using environmentally friendly lubricants cover water transport, hydraulic systems in forestry machinery, railway applications, road building machines etc. Particularly it is the case when an increased possibility of putting a lubricant in the environment occurs. Regarding good lubricity and excellent biodegradability, vegetable oils are widely used as environmentally friendly lubricants. The biggest disadvantage of vegetable oils as base stock for lubricants is pure oxidation stability. This article deals with the influence of thermal oxidation on tribological properties of rapeseed oil. The obtained results show that oxidation decreases lubrication ability due to structural changes in oil. The greatest negative influence of oxidation is obtained at the end of the induction period.

Keywords: vegetable oil, rapeseed oil, lubricants, thermal oxidation, ageing, tribology, four ball test rig, lubricity.

1. Introduction

In the pursuit of alternative mineral oils and reduction in environment pollution, the use of environmentally friendly biological origin lubricating materials are foremost promoted. Considering the properties and cost of using environmentally friendly lubricating materials to be of paramount importance, it is expedient to apply them where they have the greatest potential to fall directly into the environment, namely, water transport, hydraulic systems of forestry machinery, railway applications, road building machines etc. Particularly it is the case when an increased possibility of putting a lubricant in the environment occurs. Regarding good lubricity and excellent biodegradability, vegetable oils are widely used as environmentally friendly lubricants. The biggest disadvantage of vegetable oils as base stock for lubricants is pure oxidation stability. This article deals with the influence of thermal oxidation on tribological properties of rapeseed oil. The obtained results show that oxidation decreases lubrication ability due to structural changes in oil. The greatest negative influence of oxidation is obtained at the end of the induction period.

Keywords: vegetable oil, rapeseed oil, lubricants, thermal oxidation, ageing, tribology, four ball test rig, lubricity.
cating properties because their molecules are short and of rather insignificant polarity (Cao et al. 2000; Fox, Stachowiak 2007).

During the process of oil oxidation, an immense variety of non-volatile products the life cycle of which is frequently very short are formed. Therefore, it is inexpedient to determine all their influence on lubrication. Long living oxidation products having an unmistakable impact on lubrication are epoxides (Wu et al. 2000; Adhvaryu, Erhan 2002). Epoxidized vegetable oil is of higher viscosity, resistant to oxidation and less inclined to form sediments, lacquers and burnings; nevertheless, it retains similar boundary lubrication properties as appropriate fresh vegetable oil. Due to above mentioned reasons, oil epoxidation is used for improving its properties (Wagner et al. 2001).

At the final stage of oxidation during the polymerization process, high-molecular weight compounds are formed. When oil polymerized resin and lacquers are formed, viscosity increases. Consequently, the oil aging process is unwelcome.

Experiments on the thermal oxidation of sunflower oil have proved that when oxidation takes longer oil polymerizes and acids emerge inside it. However, when lubricating with this oil is under limited conditions, friction and wear decreases on the interacting surfaces (Fox, Stachowiak 2003). Polymerization may take place under EP conditions lubricated with vegetable oil. Oil containing a great amount of polyunsaturated fatty acids is found to possess good lubricating properties at high temperatures because it forms friction polymers on the interacting surfaces (Murakami, Sakamoto 2003).

The aim of this research is to analyze the impact of thermal oxidation on tribological properties of rapeseed oil.

2. Materials and Methods

Conventionally refined, bleached and deodorised rapeseed oil (RO) was obtained from an oil manufacturer. Its oxidation was carried out using the Rancimat 743 apparatus.

The procedure was performed according to the ISO 6886:2006 method using the Rancimat 743 apparatus (Fig. 1).

A 20 ml oil sample was placed into a glass reaction vessel (no metals or catalysts) and heated up to 100 °C. A glass tube was inserted from the top to bubble dry air at the flow rate of 10 L/hr. The exiting air, including volatile oxidation products, was directed to bubble through the measuring vessel with deionised water, the electrical conductivity of which was monitored by a measuring cell. With the beginning of oxidation, the rapid production of volatile degradation products starts during the so-called induction period (IP). Volatile products dissolve in water under this test, which results in a rapid increase in electrical conductivity monitored by the Rancimat apparatus. The period between the samples was determined during primary experiments according to IP time.

The four ball test rig was used for measuring tribological properties of samples (Fig. 2). The load of 150 N was used. The test ran for 1 hour. Prior to each experiment, all appropriate parts of the machine, i.e. bottom and upper ball holders, oil vessel and test balls were washed in an ultrasonic bath and then dried. The testing procedure was adapted from the standard DIN 51350 Part 3 (DIN 51350-3:2010).
The diameters of wear scars on friction surfaces were measured and analyzed employing an optical microscope. For each run, scar measurements were reported as an average of the Wear Scar Diameter (WSD) of three balls in millimetres.

The profile of wear scars was measured using profilometer Mahr GD 25 with a scanning resolution of 0.5 µm.

3. Theoretical Approach

Oils modified by both basic and functional additives are aging, i.e. their physical and chemical properties, friction and wear reducing characteristics are changing. Oxidation is affected by oil operating conditions and environment factors. Oil in operation is subjected to changing temperature, the materials of lubricated machine parts and by products of the process (Mang, Dresel 2007).

Temperature has the greatest impact on oil oxidation. The increasing temperature accelerates the formation and decomposition of peroxides and hyper-peroxides and increases the catalytic effect of metal. The oxidation of hydrocarbons and other organic components is explained by a mechanism of free radicals through alkyl-and peroxy-radicals. This process is described considering three stages: initiation, propagation and termination. These stages consist of complex consecutive and consecutive reactions (Gunstone 2004; Frankel 2005).

At the initial oxidation stage, oxygen adsorbs hydrogen from unsaturated hydrocarbon (RH), thus free alkyl-radical is formed (R) (Mang, Dresel 2007):

\[
\text{RH} + \text{O}_2 \rightarrow \text{R} + \text{O}_2. \tag{1}
\]

Splitting alkyl-hydroperoxides present in oil is stimulated by the temperature (Eq. 2) and metal ions of various valences (Eq. 3 and 4). Acids present in oil and water on the metal surface form free ions stimulating oxidation (Frankel 2005):

\[
\text{ROOH} + t^\circ + \text{C} \rightarrow \text{RO} + \text{OH}; \tag{2}
\]
\[
\text{ROOH} + \text{M}^{2+} \rightarrow \text{RO} + \text{OH}^- + \text{M}^{2+}; \tag{3}
\]
\[
\text{ROOH} + \text{M}^{3+} \rightarrow \text{ROO} + \text{H}^- + \text{M}^{2+}. \tag{4}
\]

The initial oxidation stage is slow; its rate depends on the intensity of the above mentioned factors. At this stage, primary antioxidants neutralize newly formed oxidation products. The further oxidation stage comes when either primary antioxidants are used or due to very intensive oxidation when antioxidants cannot neutralize all forming radicals (Frankel 2005).

During the oxidation propagation stage, alkyl-radical (R-) reacting with oxygen forms alkyl peroxy radicals (ROO- ) (Mang, Dresel 2007):

\[
\text{R} - + \text{O}_2 \rightarrow \text{ROO}. \tag{5}
\]

The latter reaction proceeds very fast and at a sufficient amount of oxygen a great quantity of alkyl peroxy radicals are formed. The following reaction at a propagation stage proceeds much slower – alkyl peroxy radicals take hydrogen from hydrocarbons and form alkyl hydroperoxides (ROOH) and new alkyl radicals (R):

\[
\text{ROO} - + \text{RH} \rightarrow \text{ROOH} + \text{R}. \tag{6}
\]

During this process, more and more radicals are formed and oxidation development accelerates, i.e. a chain of reactions begins (Gunstone 2004). The alkyl hydro peroxides formed during oxidation are unstable; they split and form volatile and unstable materials.

During the oxidation of vegetable oil, polysaturated fat acids are the first to split. They comprise the major part of volatile materials. Linolenic acid (18:3) splits into 2.4-heptadienal and propanal; then splitting linoleic acid (18:2) forms C5…C7 chains. Monounsaturated fatty acids split much slower and form significantly less volatile materials compared to the polysaturated ones. Then, splitting oleic acid (18:1) forms C7…C9 carbon atom chains.

At high temperatures, volatile materials intensively evaporate emitting specific odour. At low temperatures (≤20 °C), they are liquids and possess acid characteristics causing the corrosion of lubricated surfaces (Mang, Dresel 2007).

Since the conversion of peroxides into hydroperoxides is comparatively a slow process, peroxides proliferate when oil is oxidizing. When their accumulation reaches a sufficient amount, peroxides start combining into non-radical products. This is the beginning of the final termination stage (Frankel 2005). When oil intensively oxidizes, non-radical compounds may be formed by two joined alkyl radicals (Mang, Dresel 2007).

At the final stage of oxidation during poly-condensation, large molecular weight products are formed. Therefore, viscosity in oil increases. Further poly-condensation and polymerization of these blends induce the formation of insoluble polymers, residues and resins (Gunstone 2004; Pospišil, Klemchuk 1990).

4. Results and Discussion

Research into the impact of thermal oxidation on tribological properties of RO indicates that time (oxidizing degree) highly affects wear and friction reduction properties of this lubricating material (Figs 3 and 4). In our case, both the disintegrating structure of triglycerides and the newly formed compounds are assumed to influence tribological properties of RO (Fox, Stachowiak 2007). Some of the compounds are formed to improve these properties; some of them act on the contrary and impair them, while in most cases thermal oxidation discussed in this research has a negative effect on lubricating characteristics of rapeseed oil.

Lubricating properties of RO oxidized to the end of IP deteriorate within a stretch of oxidation time. In 10 hours, wear reduction properties of oxidized RO slightly decrease; moreover, when oxidized for 18 hours, RO much less protects the lubricated surfaces against wear. When lubricating with rapeseed oil oxidized at this stage, friction and wear are directly proportional to oxidation time, i.e. longer oxidized rapeseed oil possesses
rather poor friction and wear reduction characteristics. Linear dependence between oxidation time and lubricating properties has been also noticed by other researchers (Fox, Stachowiak 2003; Suzuki et al. 2009).

The compounds formed during the decomposition of the triglyceride structure of oxidized rapeseed oil influence not only wear reducing ability and average torque but also friction variation during the test. When lubricating with non-oxidized RO, friction gradually increases at the outset of the conducted tests (Fig. 5). At a later stage, following approximately 1300 s, its value settles down and remains constant with a slight variation in the end of the experiment. Up to the end of IP, an increasing amount of peroxides cuts the initial assimilation of lubricated surfaces: when lubricating with 10 hours oxidized RO, friction settles down after 800 s while lubricating for 18 hours it takes 400 s (Fig. 5).

Furthermore, with an increase in the amount of peroxides, torque increases more abruptly at the beginning of the experiment. The rate of an increase in the torque of non-oxidized and 10, 18 hours oxidized rape oil is 2.5, 4.4 and 9 mNm/min respectively. When lubricated with non-oxidized and oxidized RO, torque distinguishes for its quite strong variation which increases along with longer oxidation. Such variation of torque reveals unstable lubricating conditions indicated by growing wear and friction.

When estimating the obtained results of wear and friction, it is obvious that the peroxides formed in the initial oxidation period worsen lubricating properties of rapeseed oil. A great amount of peroxides stimulates the decomposition of a fatty acids chain thus affecting the ability of decomposed oil to lubricate surfaces. The analyses conducted by other researchers confirm a negative impact of peroxides on lubricating properties. Peroxides formed during the oxidation of sunflower oils reacting to the lubricated surface are considered to increase wear (Fox, Stachowiak 2003). The input of hydroperoxides into basic mineral and motor oil deteriorated its wear reduction characteristics actually intensified by a further increase in peroxide concentration. Under high loading conditions, a positive effect of hydroperoxides on lubrication is observed (Rounds 1993; Mang, Dresel 2007).

Lubricating properties of 20 hours of oxidized RO were improved comparing with the results of those RO oxidized for 18 hours (Figs 3 and 4). The number of peroxides at this point has substantially grown comparing with the previous ones; nevertheless, the compounds formed after IP have improved lubricating properties of RO. The most likely influence is that free fatty acids were formed during hydrolysis, because they are known as friction reduction additives used under boundary lubricating conditions (Fox et al. 2004; Mang, Dresel 2007).

When lubricating longer with IP oxidized rapeseed oil, friction variation partially changes during the experiment. A tendency towards torque increase at the start remains while an increase in rate continues to grow. When lubricating with 30 and more hours of oxidized RO, a site of constant moderate friction is formed at the beginning of the experiment, whereas the friction torque of all RO oxidized longer than IP reaches the maximal value and decreases during the remaining experimental period (Fig. 6).
The formation of constant friction at the beginning of the experiment may be influenced by saturated free fatty acids which are the last at separation from glycerol during oil oxidation. It is assumed that stearic acid saturated at a rather low temperature in the beginning of the experiment, forms a friction reducing an adsorption layer on the interactive surfaces. When contact temperature increases during the experiment, the adsorption layer disintegrates and friction starts to grow (Fox et al. 2004). As mentioned above, the friction growth rate increases along with the elongation of oxidation time.

Lubricating properties of 30 hours of oxidized RO compared to those oxidized for 20 hours deteriorate again. At this point, the values of wear and friction of lubricated balls are the highest ones obtained in this research. This deterioration of lubricating properties is related to an extremely high number of peroxides and likely reaches the maximal value at this point.

Further RO lubricating properties start improving when prolonging thermal oxidation time. When estimating wear reduction, this improvement is not that strong, but reduction in friction is evident. 40 hours oxidized RO improves the friction of lubricated surfaces 1.3 times compared to that lubricated by non-oxidized RO (Fig. 4). Improvement in RO lubricating properties is related to high molecular weight compounds – polymers, ketons and epoxides formed at this stage. The most likely is the influence of epoxides because they can promote the formation of friction polymers (Fox, Stachowak 2003). The formation of high molecular weight compounds during the late state of RO oxidation increases kinematic viscosity. Growing viscosity might have influence on the improvement of lubricating properties, because the lubricants with higher viscosity more readily separate lubricated surfaces. However, this phenomenon is more typical of hydrodynamic lubrication and is less probable under present experimental conditions. A decrease in the average torque might have been influenced by free fatty acids. This long oxidized RO could contain only saturated fatty acids. In our case, saturated stearic fatty acids have likely had an influence, as mentioned above, on friction variation during research.

In estimating worn surfaces lubricated with oxidized and non-oxidized RO, it is determined that the oxidation period affects not only the extent of wear trace but also has a great influence on the micro-geometry of the surface (Fig. 7) (Kreivaitis et al. 2009).

When lubricating interacting surfaces with non-oxidized RO, a relatively smooth stain surface is formed, which is typical of triglycerids (Fig. 7 a). If lubricating with RO oxidized for 35 hours, strips are formed on the interacting surfaces and when oxidation time is prolonged, these strips thicken and deepen (Figs 7 b–d). Enlarging irregularities of interacting surfaces are fairly correlating with friction, i.e. at stronger friction, larger strips are expected. 40 hours oxidized rapeseed oil better protects lubricated surfaces, i.e. the worn surface is smoother (Fig. 7 e). When lubricating with 40 hours oxidized rapeseed oil, friction is also lower.
In order to estimate visible micro-irregularities on the worn surfaces, their profiles (across the strips) have been measured, and the obtained profiles are shown in Fig. 8. The measured profiles affirm the strips visible in photographs and make it possible to estimate their size and distribution. In the middle of a trace, the formed strips are found while its periphery is smooth without any strips. It is assumed that in the beginning of the experiment until the balls touch each other on a smaller area, high contact pressure is established, thus oxidizing deteriorating oil cannot withstand and then abrasive wear occurs.

The test shows that when the area of contacting balls increases, pressure decreases; therefore, strips do not form at the wear scar periphery (Figs 8 b, c). Strip formation can be related to the sudden growth of torque at the start of the test (Vekteris, Mokšin 2002). Deeper strips require greater energy and accordingly stronger friction is recorded. 40 hours oxidized rapeseed oil shows less friction; consequently wear scar is smoother without any deeper groves (Fig. 8 c). Some researchers have also noticed a negative influence of prolonged oxidation on the structure of the lubricated surfaces (Minami, Mitsumune 2002).

5. Conclusions
The performed research has arrived at the following conclusions:
1. The great influence of oxidation on tribological properties of rapeseed oil was observed at all stages of oxidation. At the initial stage, lubricity depends on oxidation time – longer oxidation causes worse lubricity. The propagation stage, which begins just after the induction period, has the greatest negative influence on reduction in wear and friction. Oxidation products formed at the final stage soften negative effect but wear reduction properties are still worse than those of non-oxidized oil.
2. Even long time oxidized rapeseed oil does not cause a significant increase in wear.

References
Adhvaryu, A.; Erhan, S. Z. 2002. Epoxidized soybean oil as a potential source of high-temperature lubricants, Industrial Crops and Products 15(3): 247–254. doi:10.1016/S0926-6690(01)00120-0
Bartz, W. J. 2006. Ecotribology: Environmentally acceptable tribological practices, Tribology International 39(8): 728–733. doi:10.1016/j.triboint.2005.07.002

Fig. 8. Profiles of the worn surfaces obtained when lubricating with: a – non-oxidized RO; b – 10 h oxidized RO; c – 35 h oxidized RO; d – 40 h oxidized RO
Cao, Y.; Yu, L.; Liu, W. 2000. Study of the tribological behavior of sulfurized fatty acids as additives in rapeseed oil, Wear 244(1–2): 126–131. doi:10.1016/S0043-1648(00)00445-2

DIN 51350-3:2010. Prüfung von Schmierstoffen – Prüfung im Vierkugel-Apparat – Teil 3: Bestimmung von Verschleißkennwerten flüssiger Schmierstoffe [Testing of Lubricants – Testing in the Four-Ball Tester – Part 3: Determination of Wearing Characteristics of Liquid Lubricants] (in German).

Fox, N. J.; Stachowiak, G. W. 2003. Boundary lubrication properties of oxidized sunflower oil, Lubrication Engineering 59(2): 15–20.

Fox, N. J.; Stachowiak, G. W. 2007. Vegetable oil-based lubricants – A review of oxidation, Tribology International 40(7): 1035–1046. doi:10.1016/j.triboint.2006.10.001

Fox, N. J.; Tyrer, B.; Stachowiak, G. W. 2004. Boundary lubrication performance of free fatty acids in sunflower oil, Tribology Letters 16(4): 275–281. doi:10.1023/B:TRIL.0000152033.08570.82

Frankel, E. N. 2005. Lipid Oxidation. 2nd Edition. American Oil Chemists Society. 470 p.

Gunstone, F. D. 2004. The Chemistry of Oils and Fats: Sources, Composition, Properties, and Uses. 1st edition. Blackwell. 288 p.

ISO 6886:2006. Animal and Vegetables Fats and Oils – Determination of Oxidation Stability (Accelerated Oxidation Test).

Jankauskas, V.; Belyaev, S. 2010. Influence of counterbody surface hardness of a friction pair ‘steel-steel’ on tribological behaviour of zinc nanopowder in oil, Mechanika (3): 45–50.

Kellaci, A.; Mazouzi, R.; Khelidj, B.; Bounif, A. 2010. The effect of lubricant rheology on piston skirt/cylinder contact for an internal combustion engine, Mechanika (1): 30–36.

Kreivaitis, R.; Padgurskas, R.; Jankauskas, J.; Kučinskas, V.; Makarevičienė, A.; Gumbytė, V. 2009. Tribological behavior of rapeseed oil mixtures with mono- and diglycerides, Mechanika (5): 74–78.

Kumar, M. S.; Thyila, P. R.; Anbarasu, E. 2010. Numerical analysis of hydrodynamic journal bearing under transient dynamic conditions, Mechanika (2): 37–42.

Mang, T.; Dresel, W. 2007. Lubricants and Lubrication. 2nd completely revised and extended edition. Wiley-VCH. 890 p.

Minami, I.; Mitsumune, S. 2002. Antiwear properties of phosphorous-containing compounds in vegetable oils, Tribology Letters 13(2): 95–101. doi:10.1023/A:1020152615786

Muralikumari, T.; Sakamoto, H. 2003. Lubricating properties of vegetable oils and paraffinic oils with unsaturated fatty acids under high-contact-pressure conditions in four-ball tests, Journal of Synthetic Lubrication 20(3): 183–201. doi:10.1080/07400190308983162

Newley, R. A.; Spikes, H. A.; Macpherson, P. B. 1980. Oxidative wear in lubricated contact, Journal of Lubrication Technology – Transactions of the ASME 102(4): 539–544. doi:10.1115/1.3251592

Patel, H. C.; Deheri, G. M. 2009. Characteristics of lubrication at nano scale on the performance of transversely rough slider bearing, Mechanika (6): 64–71.

Pospíšil, J.; Klemchuk, P. P. 1989. Oxidation Inhibition in Organic Materials. 1st edition. CRC Press. 384 p.

Russell, F. 1993. Effects of hydroperoxides on wear as measured in four-ball wear tests, Tribology Transactions 36(2): 297–303. doi:10.1080/1040209308983162

Sari, M. R.; Ville, F.; Haimem, A.; Flamand, L. 2010. Effect of lubricant contamination on friction and wear in an EHL sliding contact, Mechanika (2): 43–49.

Suzuki, A.; Ulfiati, R.; Masuko, M. 2009. Evaluation of antioxidants in rapeseeds oils for railway application, Tribology International 42(2): 987–994. doi:10.1016/j.triboint.2009.02.001

Vekteris, V.; Mokšin, V. 2002. Use of liquid crystals to improve tribological properties of lubricants. Part 1: Friction coefficient, Mechanika (6): 67–72.

Wessol, A. A.; Pirro, D. M. 2001. Lubrication Fundamentals. 2nd edition. CRC Press. 544 p.

Wu, X.; Zhang, X.; Yang, S.; Chen, H.; Wang, D. 2000. The study of epoxidized rapeseed oil used as a potential biodegradable lubricant, Journal of the American Oil Chemists’ Society 77(5): 561–563. doi:10.1007/s11746-000-0089-2

Wagner, H.; Luther, R.; Mang, T. 2001. Lubricant base fluid s based on renewable raw materials: Their catalytic manufacture and modification, Applied Catalysis A: General 221(1–2): 429–442. doi:10.1016/S0926-860X(01)00891-2