The thermal stability of rapeseed oil as a base stock for environmentally friendly lubricants

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1. Introduction

The annual lubricant consumption of the world is rising annually. Recently, there has been a growing concern about pollution reduction. This concern has increased the pressure on research and industry to find environmentally friendly, biologically based lubricants to replace materials of petrochemical origin, and this is now considered a research priority in the fuel and energy sectors [1].

High-level automotive lubricants are required to have high quality and high performance, and to be multipurpose. In addition, primary lubricant additive compounds such as sulphur, phosphorus and zinc are restricted. In some cases, their use is completely forbidden [2]. In particular machinery applications such as forestry, agriculture, and water treatment, the use of environmentally friendly bio-based lubricants is determined by Eco Labels. In these cases, the use of readily biodegradable base stocks of vegetable origin is required. This includes pure and modified vegetable oils and animal fats, as well as various esters sintered from vegetable oils. The sintered esters have excellent properties but are also expensive, which leads to limited usage for such esters [2]. Vegetable oils have good natural lubricity together with environmental compatibility and a low price [1]. Unfortunately, they are susceptible to oxidation and have problems at low temperatures. Despite these issues, vegetable oils remain the most attractive base materials for environmentally friendly lubricants.

The lifetime of vegetable based lubricants is predominantly limited by thermal oxidation. This problem has been discussed in many works of research [3-5]. Oxidation causes a decrease in the oil’s tribological properties. As was shown by Fox and Stachowiak [6], the oxidation of sunflower oil has a strong influence on its boundary lubrication properties. They conclude that the decrease in lubrication properties when oxidation begins is related to the destruction of triglycerides and an increase in the level of peroxides. Additionally, severely oxidised sunflower oil demonstrates an improved friction coefficient. Mano et al. [7] observed that the oxidation of rapeseed oil could improve both the wear and friction reduction properties, depending on the lubricated surface material. The influence of oxidation time on the tribological properties of rapeseed oil was studied by Kreivaitis et al. [8]. It was found that the worst tribological properties are seen when rapeseed oil is in the oxidation propagation stage, while oxidation products formed in the final stage soften the negative effects. The tribological properties in the above study were evaluated by using only the oxidation time to represent the oxidation rate. The literature survey shows that more comprehensive relationship, between tribological and physicochemical properties, should be found. The present study was performed to further investigate the physicochemical changes of the oil and elucidate the relationship between the main physicochemical parameters and the tribological properties. Visible light spectroscopy is suggested as an easy and fast method for determining the oxidation rate.

2. Testing procedures

Conventionally refined, bleached, and deodorised rapeseed oil (RO) was obtained from an oil manufacturer (SV Obeliai, Lithuania). Rapeseed oil was used without any additional preparation. The reagents used to determine the peroxide and acid numbers were procured from (Penta, Czech Republic). All of the solvents used were analytical grade.

Oxidation was carried out with reference to the standard method ISO 6886:2006 “Animal and vegetable fats and oils - Determination of oxidative stability”. Oxidation was performed using a Rancimat 743 (Metrohm AG) apparatus. A 20 ml oil sample was placed into a glass tube and heated to 100°C. A stream of dried and purified air (10 litres/h) was passed through the sample, intensifying the oxidation. To reach the different stages of oxidation the samples were oxidised for 5, 10, 15, 18, 20, 30, 35 and 40 hours. After the oxidation, they were cooled to -10°C and held until the appropriate test.

The kinematic viscosity of all samples, at temperatures of 40 and 100°C, was measured according to standard LST EN ISO 3104+A1:2000. Kinematic viscosity measurements were performed in a Stabinger Viscometer, model SVM 3000 (Anton Paar). The viscosity index was calculated using the ISO 2909:2002 method. The acid and peroxide numbers were measured using methods LST EN ISO 660:2000 and LST EN ISO 3960:2001, respectively. The acid number measurements were performed in a potentiometric titrator, model 877 Titirino plus (Metrohm AG). The density was measured according to LST EN ISO 12185:1999.
Tribological properties were investigated using a four-ball type test rig in accordance with standard DIN 51 350, part 3. The 12.7 mm diameter balls were made of 100Cr6 bearing steel. A load of 150 N was used. The test duration was 1 h. At least three repetitions were performed to determine the mean wear and friction.

The lubricity evaluation parameters were the relative wear and the mean friction coefficient. Wear was measured using an optical microscope with 160X magnification.

An Ocean Optics USB4000 visible light spectrometer (1 nm resolution) together with a pulsed xenon visible light lamp PX-2 was used to determine transmission of the samples from all oxidation periods. An integration time of 100 ms and a total of 10 scans to average were chosen. Non-oxidised rapeseed oil was used as a 100% transparent reference.

3. Results and discussion

The oxidation stability of rapeseed oil depends on its fatty acid profile as well as the presence of natural antioxidants in the oil. The rapeseed oil used for experiments in this study contained 4.7% saturated, 61.2% monounsaturated and 34.1% polyunsaturated fatty acids. Due to the comparatively high polyunsaturated fatty acid content, rapeseed oil is sensitive to thermal degradation when compared with other types of vegetable oil or animal fat containing a lower unsaturated fatty acid content. The oxidation stability of oil also depends on the content of natural antioxidants in the oil. A large amount of natural antioxidants are found in cold-pressed and unrefined oils. Natural antioxidants are removed during the oil refining procedure, but natural and synthetic antioxidants are added to the oil after refining to increase its storage stability. Our tested rapeseed oil contained 70 mg/kg of carotenoids and 583 mg/kg of tocopherols and tocotrienols.

Stimulated by temperature and oxygen, the primary oxidation products are formed in rapeseed oil at the beginning of the oxidation process. Initially, antioxidants present in the oil slow down formation of the products, but the antioxidants do not have sufficient effectiveness to maintain oil stability for an extended period of time. This fact is of special importance in cases when oxidation is stimulated by a high temperature and/or oxygen in the air. For this reason, after a particular time, which is specific to each type of oil, the oil becomes unstable, i.e., the oxidation development stage begins. The period preceding the beginning of the development stage is called the induction period [6, 9].

Under experimental conditions the IP of oxidised oil is approximately 18 h. In the primary oxidation stage (0 - 18 h) an increasing number of peroxides indicate the growing quantity of alkylradicals (Fig. 1, a). A slight increase in acidity makes it possible to assume that almost no free fatty acids are formed in this stage (Fig. 1, a). They typically form during hydrolysis, which most often occurs simultaneously with oxidation. Because hydrolysis requires water, it is assumed that the examined rapeseed oil contains a small amount of water, and thus formation of the free fatty acids is unnoticed [6].

By analysing the processes at the end of the induction period, it can be assumed that this period ends between 15 and 18 h. During this stage, the natural antioxidants in rapeseed oil are no longer capable of blocking the oxidation process because of their self-consumption. Therefore, when the alkylradicals react with oxygen, the formation of alkylperoxyradicals and hydroperoxides begins. At the end of the induction period, the acidity slightly increases. This may indicate the formation of free fatty acids due to the decomposition of triglyceride fatty acid chains during the formation of short chain volatile (short-chained hydrocarbons and alcohols) and non-volatile (epoxides, high molecular weight compounds, and fatty acids) compounds [10].

The thermal oxidation of rapeseed oil preceding the end of the induction period does not affect the oil’s kinematic viscosity because the compounds responsible for increasing the viscosity have not yet formed (Fig. 1, b).

As rapeseed oil oxidises further from the end of the induction period to a time of 20 h, the number of peroxides increases almost 3 times (Fig. 1, a). This sudden increase in peroxides is stimulated by both the absence of a natural antioxidant effect and a sufficient amount of oxygen entering with the ambient air, which increases the formation of alkylperoxyradicals and hydroperoxides [9, 10].
To estimate the kinematic viscosity changes that occur in this stage, the assumption can be made that following the end of the induction period a complex oil decomposition process occurs and the formation of new compounds begins. The growing viscosity implies the formation of epoxides and polymer compounds [11]. The formation of these compounds is initiated by a number of reactions beginning with the formation of hydroperoxides and finishing with their decomposition; it is then that short chain volatile and non-volatile compounds develop. Water released during the decomposition of hydroperoxides initiates triglyceride hydrolysis, i.e., the possibility of free fatty acid formation. This process could explain the increase in acidity during this stage, though the possibility of an impact by short chain compounds on the acidity cannot be rejected.

As rapeseed oil oxidation proceeds further, the number of peroxides grows more slowly and reaches a maximum by approximately 30 h. From this point forward, the number of peroxides begins to decline. Other researchers’ analysis of sunflower oil and other oil methyl esters shows similar changes in the peroxide value [6, 11].

The number of acids increases intensively from 20 to 40 h. It is influenced by the decomposition of fatty acid chains that form low molecular weight compounds. In addition, free fatty acids have been forming during this period. In the late oxidation stages, it should be mentioned that the value of acidity is exceptionally sensitive to the end of the induction period. When oxidation was repeated, the position of the induction period slightly changed, and it resulted in substantial variation in the acidity value at times from 30 to 40 h.

In the final stage of oxidation, the kinematic viscosity of rapeseed oil continues to grow. Its growth rate even increases between 30 and 35 h. This phenomenon may be related to the number of peroxides, which starts to decrease from its maximum value after 30 h. In this stage, because of the great quantity of hydroperoxides, the formation of large molecular weight compounds is taking place and the viscosity increases. Thus, the quantity of peroxides is reduced due to their decomposition [6].

The increase in viscosity is also assisted by the evaporation of volatile low molecular weight compounds associated with the operation of a particular unit of oxidation equipment [12]. This is confirmed by an increase in the density of the oxidised oil; after 40 h, oxidised rapeseed oil has approximately a 5% higher density than non-oxidised oil. When oil-dissolving compounds of low molecular weight evaporate, the viscosity must increase.

One of the important parameters that determines the temperature-viscosity relationship of lubricants is the viscosity index. The variation in the viscosity index in oxidised oil is presented in Fig. 1 b. Generally, triglycerides have a very high viscosity index [13]. The rapeseed oil used in our research is no exception. Its initial viscosity index value was 213, and during the first 18 hours of oxidation, this value remained nearly unchanged. Furthermore, in the oxidation process, the rapeseed oil’s viscosity index decreased. The decomposing triglyceride structure and a growing quantity of low molecular weight compounds are assumed to have an impact on this process. At the end of the experiments, the viscosity index value stabilizes and remains steady between 35 to 40 h during the final oxidation stage. It seems likely that the viscosity index of the sample also changes. To find the factors affecting the colour change in the oil after the tribological test, the oil was spectrally analysed and compared with the expected oxidation products.
non-oxidised rapeseed oil and oil after certain times of oxidation (Fig. 4).

Rapeseed oil samples oxidised for 18 and 40 hours and tested in the four-ball tribometer show different changes in their transmission spectra. After the tribological test, rapeseed oil oxidised for 18 h has become more yellowish – the peak at a wavelength of 450-460 nm has increased (Fig. 4, a). Meanwhile, after the tribological test of rapeseed oil oxidised for 40 h, especially distinct changes are observed – the peak at a wavelength of 420 nm disappears, and the former peak at 450-460 nm that was present before the induction period is observed to become broader and more intense (Fig. 4, b).

During the tribological test, the oil is directly in contact with the metal surfaces of machine elements, especially with interacting surfaces where it is subjected to a high temperature. Therefore, it is assumed that, during the tribological test, the decomposition of hydroperoxides into alkyl and peroxyradicals under the action of metals causes changes in the transmission spectrum. The greater changes in the oil oxidised for a longer time can be explained by the greater amount of decomposable hydroperoxides formed after the induction period. It is also possible that
the oil with a greater number of acids intensively acting on the metal surfaces forms metal ions, which intensifies the decomposition of the hydroperoxides.

As was observed in a previous study by Kreivaitis et al. [8], the tribological properties of oxidised rapeseed oil change, but the impact is not significant (Fig. 5). In this case the tribological properties of rapeseed oil are assumed to be influenced by both the decomposing structure of triglycerides and the newly forming compounds. At the end of the induction period (18 h), the lubricating properties of the oxidised rapeseed oil are worse than that of fresh oil. This change could be caused by the increasing quantity of peroxides. Friction at this point is also higher compared with non-oxidised rapeseed oil; however, its increase is not as high as the increases in wear that were observed.

Both the wear and the friction coefficient decrease at the end of oxidation (40 h). The wear reduction properties of rapeseed oil oxidised for 40 h are improved compared with those of oil oxidised for 18 h, but the wear remains higher than that observed by lubricating with fresh rapeseed oil. Meanwhile, the friction of oil oxidised for 40 h is significantly lower than that of fresh oil and rapeseed oil oxidised for 18 h.

As mentioned above, the number of peroxides in and the acidity of rapeseed oil was the highest at the end of the oxidation test. It seems most likely that high molecular weight compounds formed in the final oxidation stage had the greatest impact on wear and friction reduction. High molecular weight polymeric compounds could form friction polymers, which are known to be friction reduction materials [6]. The layers formed by friction polymers are characterised by very low friction. This was the case in both this and previous studies [8]. Nevertheless, friction polymers act by covering and separating the surfaces by a thin layer. If the surfaces are separated, the wear also should be very low. The reason for high wear in this case could be the presence of peroxides, which disturb this layer and increase wear.

The high viscosity can also influence the friction. The viscous oxidised oil can easily separate the surfaces, reducing the friction. The free fatty acids can also have an influence on such lubrication properties [7].

4. Conclusions

The change in physicochemical properties has undisputed influence on lubricity of the oil. The physicochemical and tribological properties of rapeseed oil change substantially during its thermal oxidation. This change particularly intensifies after the induction period. The results show that the measured physicochemical properties of oxidised rapeseed oil do not directly reflect the lubrication properties. In the oxidation initiation stage, the tribological properties of rapeseed oil slightly decrease. After the induction period, during the propagation stage, the tribological properties of rapeseed oil are poorest. In the final stage of rapeseed oil oxidation, high molecular weight compounds are formed, which decreases the wear and friction between the contacting surfaces. All of the oxidation stages can be observed using visible light spectroscopy. The light transmission of rapeseed oil changes substantially with the oxidation stage.

References


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THE THERMAL STABILITY OF RAPESEED OIL AS A BASE STOCK FOR ENVIRONMENTALLY FRIENDLY LUBRICANTS

SUMMARY

It is well known that the good tribological and environmental properties of vegetable oils contrast with their lack of complete thermal and hydrolytic stability. The purpose of the current study is to determine the influence of thermal oxidation on the lubrication and physicochemical properties of rapeseed oil. The oxidation procedure was performed using a Rancimat 743 apparatus. Standard methods were used to determine viscosity parameters, acidity and peroxide values. A visible light spectroscopy method was introduced to estimate the oxidation rate of rapeseed oil. The transmission spectra of rapeseed oil undergoing oxidation show a precise correlation between transmission and degree of oxidation. Using this method, the end of the induction period can be easily observed. The observed results show clear influence of oxidation in the change of physicochemical properties and the lubricating ability of rapeseed oil. Increasing the amount of primary oxidation products decreases the lubrication properties, while the secondary oxidation products that are formed improve the friction reduction properties of rapeseed oil.

Keywords: oxidation, rapeseed oil, tribology, lubrication.

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