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A MANUFACTURING METHOD FOR ORGANIC LUBRICANTS FROM REFINING BY-PRODUCTS OF VEGETABLE OIL

Key words

Lubricant, refining of oils, refinement by-products, vegetable oils, tribo-active substances.

Abstract

The requirement for the use of "environmentally safe" lubricants in many areas of technology makes it necessary to search for new raw materials for their manufacture, and its potential source may be the by-products obtained during the refining of natural oils. The article describes a methodology for the isolation of tribo-active substances from refinement by-products of rapeseed oil, which resulted in producing ecologically safe additives. The lubricating compositions obtained in this process were then tested in regards to their physicochemical and lubricant properties. The results obtained have shown that they have a higher effectiveness of anti-wear properties and more advantageous rheological properties in comparison with commercial oils recommended to be used in conditions of moderate loads and node friction velocity. A high degree of the biodegradability of lubricant allows its application in settings where there is a risk of direct contact with natural environment.

Introduction

Lubricating products based on petroleum raw materials have a number of beneficial properties related to their purpose; however, they simultaneously constitute a very high ecological risk, due to their low biodegradability. Biodegradability is defined as the ability of the particles to decompose as a result of the complex interactions of living organisms and their enzymes [1–5]. These processes lead to the transformation of organic compounds into low molecular non-organic forms, such as water or carbon dioxide.

The basic ingredients of the lubricants are lubricant base oils (70–99%), which largely determines the ecological character of the lubricant and additives. The most common additives include oxidation inhibitors, detergents and dispersants, corrosion and rust inhibitors, thickeners, and additives to improve the lubricating properties of the oil (anti-wear, anti-friction, extreme pressure, friction modifiers). Some of them – particularly lubricating additives – contain sulphur, chlorine, phosphorus, and heavy metals in its molecules, which are all elements harmful to human health. Most of them exhibit low biodegradability, which is equivalent to their concentration in the natural environment [3, 6, 7].

A main alternative to the mineral base oils, which are not able not meet the ecological requirement (biodegradability 10–40%), are vegetable oils and a few synthetic oils (ester, polyalkylene, poly-α-olefines) [8–11]. Often, however, their desirable characteristics are negated by their toxic, non-biodegradable lubricating additives. Therefore, the content of these additives in lubricants should be minimised or replaced by a new generation of non-toxic, biodegradable, and ashless additives. These types of additives are required to improve the basic properties of base oil without increasing the emission of pollutants into the environment. The compounds that meet these criteria contain, in their composition, active functional groups, for example, ester, hydroxyl, and carboxyl. Often these are esters of higher carboxylic acids, aliphatic alcohols, or hydroxy-carboxyllic acids.

A potential raw material for organic additives may be the by-products formed during the refining of natural oils. The following components are removed during the refining process that can be used in the manufacture of organic additives: free fatty acids, phospholipids, monoglycerides and diglycerides, provitamins, alcohols, waxes, tocopherols, and sterols.

The aim of the study was to develop a method for the manufacture of additives using refining by-products of rapeseed oil and to create a biodegradable lubricant using these additives.

1. Research objects and methods

The natural waste materials for the manufacture of biodegradable additives for lubricants were technical fatty acids, which is a by-product of the deacidification process (neutralising). These waste products underwent esterification using enzymatic processes.

The manufacturing technology of ecological additives out of natural waste materials consisted of several unit processes, which are the following:

- The production of enzyme preparation;
- The production of esters out of the fatty acids in the presence of the enzyme preparation;
- The separation of biomass; and,
- Final biological product.

A technological diagram of microbiological synthesis is shown in Fig. 1.

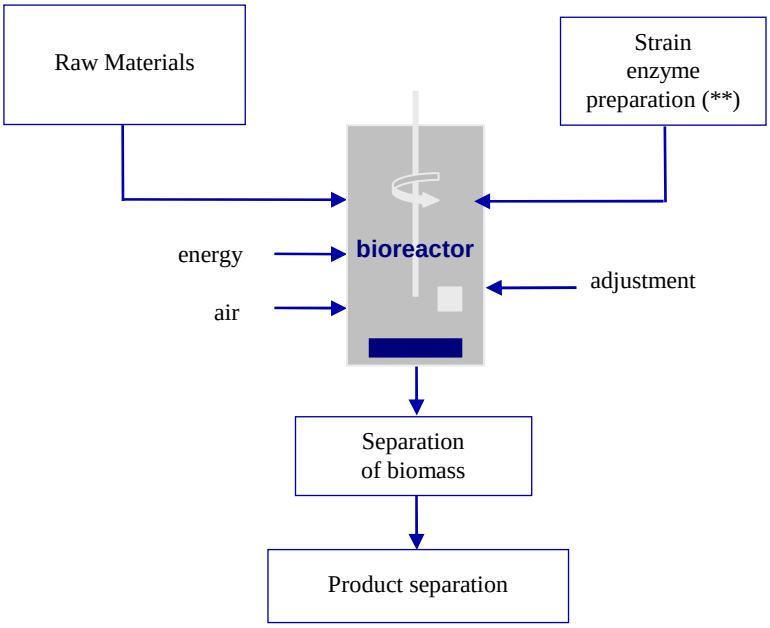

Fig. 1. A diagram for the microbiological synthesis of biological products

Biological material

The cultures used the strains of non-pathogenic *Mucor circinelloides* TB mold, extracted from the shells of shrimp, from the resources of the Institute of Technical Biochemistry of the Technical University of Łodz. The strains were

stored at 4°C, on slanting agar containing brewer wort at a concentration of 8.5° Blg and pH 5.8.

The method for obtaining the enzyme (*Mucor circinelloides* lipase TB80301A) included the following:

1. *Creating mould culture*;
2. *Growing mycelium of mould Mucor circinelloides TB80300A selectant containing a preparation of the lipase*;
3. *Producing a biomass of Mucor circinelloides TB80300A; and,*
4. *The separation, purification, stabilisation of the enzyme preparation.*

The production of TKT_EMC1 in the presence of Mucor circinelloides lipase as an enzyme catalyst

Enzymatic reactions were carried out in a Radleys chemical reactor.

Separation of the biomass, producing the bio-product

The reaction mixture, after being drained in order to separate the biocatalyst, was separated using flash chromatography.

After the separation and ester fraction are collected, they were combined and concentrated in a vacuum evaporator.

The tested additives were synthesised at the Institute of Industrial Biochemistry, Technical University of Lódź by a team headed by Prof. T Antczak. The method of production of these additives is the subject of patent application.

Creating TKT_EMC6b

Ozonizing was conducted in a measuring set made up Ozone Generator 803N and an Ozone analyser BMT 964 meter.

Manufacture of lubricants

Lubricants were prepared in the laboratory conditions by introducing a suitable aliquot of the additive into the oil base (PAO4). The concentration of additives obtained from the post-refinement raw materials of rapeseed oil was 1% of weight for TKT_EMC1 and 2% of weight for TKT_EMC6b. These are the optimal concentrations from the point of view of the anti-wear effectiveness [12]. After thorough mixing of additives with the base oil by using an electromagnetic mixer at a temperature of approximately 50□C, in order to check the stability of the composition. Then, it was stored for 48 hours at room temperature.

To analyse and verify the results of the performance research of bio-additives, they were compared with the lubricating compositions based on selected oils and Acorox 880, a commercial product (by Jaschem, Rafineria Jasło), containing ca. 80% (m/m) ZDTP (Zinc Dialkyl Dithiophosphate) in mineral oil. It is a widely used commercial additive with good AW (anti-wear)

properties and poorer EP (extreme pressure) properties and showing antioxidant and anti-corrosive actions.

Lubricating compositions with the participation of bio-additives were compared with commercial oil EKO-PIL (by EKOMAX, Gliwice). According to the manufacturer recommendation, it is a biodegradable mineral oil, and it probably contains a viscosity modifier, a depressor, and zinc dithiophosphate. It is designed for the lubrication of chains and mechanical saw guides.

Testing lubricating and physicochemical properties of lubricants

Lubricating properties (anti-wear) of the produced composition were evaluated in the conditions of mixed friction, according to PN-76/C-04147 and WTWT-04/MPS-025, in relation to the base oil, and it is based on the wear value of load index G_{oz}. Tribological tests were carried out using the four-ball apparatus (T-02) in the following conditions: running time = 3,600 sec., rotational velocity = 500 rpm, and load = 392 N.

Dynamic viscosity (*authors' method*) was determined using a rotational viscosity meter *Physica MCR 101* (by Anton Paar). The apparatus is equipped with a Peltier system with a temperature control range of –40–200°C and external thermostatic system (VISCOTHERM V2), operating in the temperature range of –20–200°C. Rheometer control and the analysis of the measuring data is done using Rheoplus software. The measurements were performed using the cone-plate measurement system in the cutting velocity range of 100 s^{-1} and in the temperature range of 19–200°C.

Flow temperature indicates the lowest temperature at which the fluidity of the oil is still observed during oil cooling in standardized conditions (PN ISO 3016). Flow temperature allows evaluating the behaviour of the oil in changing ambient conditions, and particularly, in temperatures below zero. Flow temperature was determined using the *ISL CPP 5Gs analyser*.

A study of corrosive action on copper, according to PN-EN ISO 2160: 2004 norm, was carried out at a temperature of 100°C for 3 h. After this time, the appearance of the copper plate was compared with corrosion patterns according to ASTM D 130.

Resistance to oxidation (*authors' method*) was measured using the automatic device *Quantum™ Oxidation-Tester* by Tannas in the following conditions:

- Temperature: 140°C,
- Initial pressure: 90 Psi,
- Oxidizing factor: oxygen,
- Sample volume: 50 cm^3.

The measured quantity was the amount of time after which there was a decrease in the maximum pressure of 25 psi. The longer the time of oxidation, the greater is the resistance to the oxidation of the lubricant.

Measurement of *sulphur content* was made with a *SINDIE-7039* device, which uses monochromatic x-rays from a low-powered x-ray lamp, air-cooled with a built-in compressor. The radiation excites the electrons of the K-layer of sulphur atoms, which emit characteristic Kα radiation for the sulphur at a wavelength of 0.5373 nm. The radiation is collected by the monochromator and its quanta are counted by the detector. The measurement was taken at room temperature within 30 to 300 sec.

Testing *biodegradability using CEC L-33-A-94* consisted in measuring the decrease of hydrocarbon concentration in the test samples.

The concentration of hydrocarbons was measured spectrophotometrically in infrared at 2930 ± 10 cm-1, after ultrasound sonification and extraction in 1,1,2-trichloro-1,2,2-trifluoroethane. In parallel, a sample of biocide was set with $HgCl_2$ as a control of the changes in the concentration of hydrocarbons without the participation of microorganisms („poisoned" sample). The absorption in the IR is measured at 0.7 after 21 days of experiment. The concentration of microorganisms was > 10^7/ml. As the biodegradable pattern, di-isotridecyl adipate (DITA) was used.

2. Test results

The results of the study indicated that all the produced compositions in the tested range of concentrations have better anti-wear properties than the base oil [Fig. 2]. The introduction of 1% by weight of the TKT_EMC1 (analogically as in 2% Acorox) additive to PAO-4 resulted in an over 50% increase of the wear load index. The 2% content of TKT_EMC6b results in a slightly smaller increase of the wear load index in comparison to the 2% content of the commercial Acorox additive in the oil base. All lubricating compositions exhibit better anti-wear properties than the commercial oil EKO-PIL.

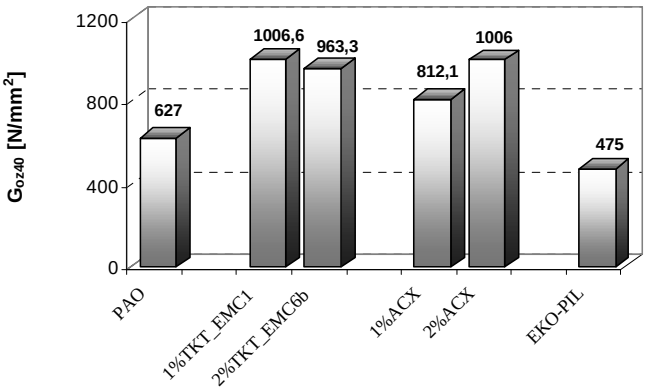

Fig. 2. The effect of additives on the anti-wear properties of oil PAO4

The effects of additives on the viscosity-temperature properties of the synthetic oil PAO4 were examined [Fig. 3].

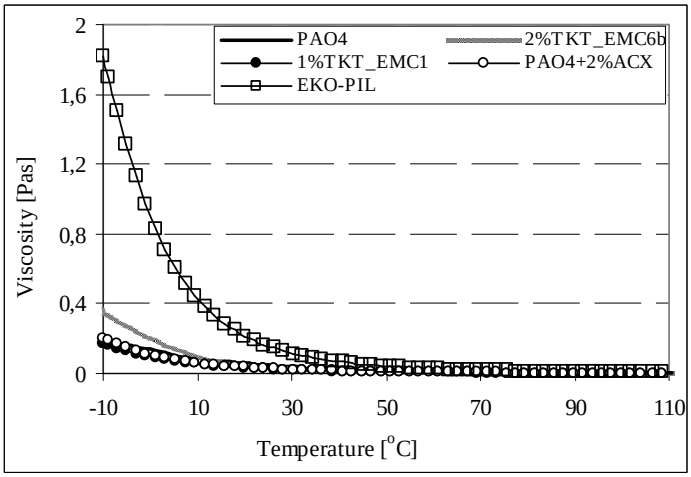

Fig. 3. A comparison of viscosity-temperature properties of compositions based on PAO4 oil and additives and EKO-PIL oil

It was found that the smallest variation in viscosity in the total temperature range was in lubricating compositions containing bio-additive TKT_EMC1 and Acorox. Somewhat more variation in temperature was evidenced by a base oil containing TKT_EMC6b additive. The worst viscosity-thermal properties were evidenced by the commercial oil EKO-PIL. An additional rheological description of lubricating oil is provided by flow temperature [Tab. 1]. It was found that the introduction of bio-additives and the commercial Acorox additive does not affect the low-temperature properties of base oil. For each composition in which bio-additives played the anti-wear role, the degree of corrosion was 1a or 1b (no corrosive effects on copper). The tendency to cause corrosion in copper plates was shown only in compositions containing Acorox, a multi-purpose additive, including anti-corrosive properties.

Table 1. Physicochemical and ecological properties of lubricants

Physicochemical and ecological properties	Lubricant			
	1%TKT-EMC1	2%TKT-EMC6b	PAO_2%ACX	EKO-PIL
Flow temperature [°C]	–72	–73	–75	–25
Corrosion level	1a	1b	3b	1b
Oxidation time [min]	603	607	1.187	2.387
Sulphur content [ppm]	2.7	2.6	2.943	7.108
Biodegradation	96	97	–	–

The table indicates that the compositions with bio-additives practically contain no sulphur (less than 3 ppm). It should be emphasized that the high antiwear efficiency, comparable to Acorox, was obtained for the additives that do not contain sulphur. Lubricants with bioadditives are highly biodegradable, and thus easily decompose in the environment [13].

Conclusions

The obtained results indicate that it possible to replace environmentally harmful additives (e.g. Acorox) in the conventional oil bases with additives that are based on carbon, oxygen, and hydrogen compounds alone, resulting in the improved wear properties of the lubricant composition. The use of ecological lubricants makes their operational and disposal costs lower than mineral lubricants. These lubricants may be used to lubricate friction nodes working under moderate conditions (temperature, load), and working in areas under special protection, such as forests, water intakes, national parks, recreation areas, farm areas, as well as road construction.

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Metoda wytwarzania ekologicznego środka smarnego z produktów porafinacyjnych oleju roślinnego

Słowa kluczowe

Środek smarowy, rafinacja olejów, produkty porafinacyjne, oleje roślinne, substancje triboaktywne.

Streszczenie

Wymóg stosowania „ekologicznie bezpiecznych” środków smarowych w wielu obszarach techniki sprawia, że zasadne stają się poszukiwania nowych surowców do ich wytwarzania. Potencjalnym źródłem mogą produkty uboczne powstające podczas rafinacji olejów naturalnych. W artykule przedstawiono metodykę wyizolowania substancji triboaktywnych z produktów porafinacyjnych oleju rzepakowego, która w efekcie doprowadziła do otrzymania ekologicznie bezpiecznych dodatków uszlachetniających. Otrzymane z ich udziałem kompozycje smarowe poddano badaniom właściwości fizykochemicznych i smarnych. Uzyskane wyniki wykazały, że charakteryzują się one wyższą skutecznością przeciwzużyciową i korzystniejszymi właściwościami reologicznymi w porównaniu z komercyjnym olejem zalecanym do stosowanych w warunkach umiarkowanych obciążeń i prędkości węzła tarcia. Wysoki stopień biodegradacji otrzymanego środka smarnego pozwala na zastosowanie go w skojarzeniach, w których istnieje niebezpieczeństwo bezpośredniego kontaktu ze środowiskiem.