

## PROPERTIES COMPARISON OF VEGETABLE OILS AS LUBRICANTS

### Summary

The analysis of the properties of vegetable oils used in tribology as lubricants is presented. Oil-based lubricants, which get into the natural environment during exploitation, have a destructive effect on living organisms. Petroleum products, depending on the biodegradation environment, have a low biochemical degradability of 15 to 35%. Vegetable oils show significantly better biodegradability, namely from 80 to even 100%, therefore according to the sustainable development policy they are the most frequently mentioned equivalents for oil bases. Depending on the geographical region, availability and production costs of oilseeds, vegetable oils such as rapeseed, charlock, soy or algae oil are used to produce lubricants. Rapeseed and sunflower oil is mainly used in Europe, while in Asian and American countries, soybean oil is dominant. Vegetable oils are a mixture of triglycerides that determine the properties of fats. As lubricants, vegetable oils are used, as well as oils with modified structure, e.g. by chemical modification or from genetically modified crops. Physico-chemical properties such as viscosity, density or acid number have influence on lubricating properties. The literature analysis shows that both vegetable oils and lubricating compositions can be used as lubricants. Vegetable oils are much more environmentally friendly, nevertheless, due to their chemical structure, this kind of oils oxidizes faster, which badly affects their durability.

**Key words:** vegetable oils, anti-wear properties, lubricants, tribology

## PORÓWNANIE WŁAŚCIWOŚCI OLEJÓW ROŚLINNYCH JAKO ŚRODKÓW SMARNYCH

### Streszczenie

Przedstawiono analizę właściwości olejów roślinnych stosowanych w tribologii jako środki smarne. Środki smarne pochodzenia naftowego, które podczas eksploatacji przedostają się do środowiska przyrodniczego, wpływają destrukcyjnie na organizmy żywe. Produkty naftowe w zależności od środowiska biodegradacji wykazują niską zdolność biochemicznego rozkładu od 15 do 35%. Oleje roślinne wykazują znacznie lepszą biodegradowalność od 80 do nawet 100%, dlatego zgodnie z polityką zrównoważonego rozwoju stanowią najczęściej wymieniane odpowiedniki dla baz naftowych. Do produkcji środków smarnych w zależności od regionu geograficznego, dostępności oraz kosztów produkcji roślin oleistych używane są oleje roślinne m.in.: rzepakowy, gorczycowy, sojowy czy olej z alg. W Europie stosuje się głównie olej rzepakowy i słonecznikowy, natomiast w krajach azjatyckich i amerykańskich dominuje olej sojowy. Oleje roślinne to mieszanina trójglicerydów, które decydują o właściwościach tłuszczów. Jako środki smarne używane są oleje roślinne, a także oleje o zmodyfikowanej strukturze, np. przez modyfikację chemiczną lub pochodzące z upraw na drodze modyfikacji genetycznej. Na właściwości smarne mają wpływ takie cechy fizykochemiczne jak lepkość, gęstość czy liczba kwasowa. Z analizy literatury wynika, że zarówno oleje roślinne, jak i ich kompozycje smarne mogą być wykorzystywane jako środki smarne. Oleje roślinne są znacznie bardziej proekologiczne, jednak ze względu na strukturę chemiczną szybciej ulegają utlenianiu, co niekorzystnie wpływa na ich trwałość.

**Słowa kluczowe:** oleje roślinne, właściwości przeciwzużyciowe, środki smarne, trybologia

### 1. Introduction

Friction is a basic physical phenomena that allow machines and units parts cooperation. Tribology is a science of interaction processes occurring in solids in relative motion. During processes the changes in functional values, such as: motion, work and material occur. Tribology allows to determine friction, wear and lubrication processes for better recognition of these processes and optimization of friction conditions [1].

In late '60s, precisely in 1966, British Government evaluated British economy losses caused by machine wear. Better technique and exploitation of machines were stated to ensure about 515 million pounds of savings per annum. Many sources report that applying tribology in technology brings huge profits confirming previous historical data [1]. Sustainable development policy of EU countries as basic assumption determines the reduction of negative human activity on environment [2, 3]. Current pro-ecological activity concerns finding new, alternative biodegradable raw materials.

Actual ecological actions tend to limit waste production and storage. Products whose negative influence is inevitable have the highest influence on environment. Widely understood lubricants and technological or processing liquids are produced from crude oil and could infiltrate to the natural environment during exploitation. Wrong lubricating system application, unit depressurization and vaporization of lubricant are the most common reason of lubricants leakage to the environment [2, 4]. Hazard substances generally infiltrate to the environment from machines and units that work on the fresh air, but also from straightway lubricating systems, in which lubricant passes through grinding parts and then it is removed to the environment or spent oil vessel. Such situations occur in agricultural machinery, strip mines, hydraulic structures, diversion dams, etc. [2].

Petroleum products, in various exploitation conditions, have a negative impact on the natural environment [2, 5, 6]. They influence destructively living organisms, while getting into surface waters, soil or underground water. Longer exposure to these substances can also have a toxic impact

on living organisms. Petroleum products show low biochemical degradation ability in environment, which differs in range from 15% to 35%. Biodegradation level is evaluated in laboratory by measuring sample weight loss, chemical structure and morphology changes analysis or mechanical and physicochemical changes in material specification. There are few ways of biodegradation processes operations that are described with appropriate standards, in which emitted CO<sub>2</sub> value is measured [7]. Petroleum lubricants and working liquids with improvers are depicted in group WGK 2, which means they are hazardous for water according to the mischievousness classification of surface and ground waters [2, 8, 9]. According to pro-ecological policy it is very important to reduce the emission of hazardous substances to the environment. Improvement of environmentally friendly products could have positive impact on pro-ecological policy development. Products, that are environmentally harmful (including petroleum products) are being substituted with alternate bioresorbable raw materials. Vegetable oils or synthetic products are the most common equivalents for petroleum oils [2, 10, 11, 12, 13]. Their biodegradation is 80-100%, which is caused by faster biochemical degradation in the environment of vegetable oils in comparison to mineral oils. For this reason fossil fuels are being replaced with biofuels. For fuels production, in Europe rapeseed and sunflower oils are used, while in American and Asian countries mostly soybean oil [2, 9].

Regardless of the source or cultivation, vegetable oils show the highest biodegradability because of quick biodegradation in natural environment, in comparison to all the others which found their application in lubricants production. It is so because they are natural products of nature, but also they are used by heterotroph organisms, as a high energy source of carbon and energy, next to proteins and hydrocarbons [14].

Lubricants provide a different wear intensity, which is caused by friction processes occurring in machines. Both vegetable oils and animal fats could be an alternative for most common mineral oils [15].

## 2. Objective

The objective of this work was to analyze vegetable oils properties, implemented in tribology as lubricants.

## 3. Vegetable oils as lubricants

Vegetable oils are more biodegradable and less toxic for the environment than mineral oils [2]. Different types of oils found application as lubricants: mineral, semisynthetic, synthetic or vegetable oils, which are nowadays analyzed with interest by researchers. Lubricants may be produced from different raw materials. The most common vegetable oils are produced from: rapeseed, charlock, soybean or algae. Raw material selection for lubricant mainly depends on geographical region, availability and oily plants production costs [16].

Vegetable oils are composition of natural esters. It is a mixture of triglycerides, which are the products of glycerol with three fatty acids reaction. Fatty acids decide of fats properties. Unlike the mineral oils, each of carbon atoms that form the acid, could be conjugated with single bond (saturated fatty acid) or with double bond (unsaturated fatty acid). Double bond could also form different spatial configurations cis or trans. The length of chain and number, posi-

tion and shape of double bonds decide of properties and nutritional importance of particular fatty acids and triglycerides that form them. Waxes and ring-structure compounds are also present in vegetable and animal fats, in the amount from 0,5 to 5% [16]. Unlike natural fats, estimation of chemical structure of mineral oils is more complex. Mineral oils properties depend on crude oil composition and treatment of particular crude oil. Base oil composition constitutes hydrocarbons of various structure, saturation ratio and molar mass of greater differentiation degree than vegetable oils. Moreover mineral oils could be contaminated with sulfur, nitrogen or oxygen compounds. Mineral oils produced from crude oil have better and more diverse exploitation and physiochemical properties than vegetable oils, excluding environmental protection aspect [14]. Nowadays, more and more importance is attached to nonedible fats utilization, which may be adapted to technical objectives. Nonedible vegetable and animal fats are produced in many food and industrial production processes [17]. An alternative for base oils could be the implementation of synthetic chemical compounds and natural oils [18].

As an example of oil application we can mention a chainsaw, in which two types of oils are implemented: in cutting system and in the engine. Presence of oils in cutting system prevents from untimely wear of the elements. Oil through causes direct outflow of the oil to the natural environment. In such case biodegradable oils are much better for the natural environment. In Poland, from technical point of view, rapeseed oil is mostly used, because its applications have lots of advantages [15].

## 4. Influence of vegetable oils properties on lubricants application

Presently applied vegetable oils as base lubricants are often oils of chemically modified structure or oils coming from genetically modified cultivations [14, 19, 20, 21]. Triacylglycerols (commonly known as triglycerides, TAG), which form vegetable oils, are subject to chemical processes in organisms, which cause biodegradation of oils [14]. TAG, also called 'neutral fats', are classified as so called 'simple fats'. These are insoluble in water, branched compounds of glycerol with three fatty acids, which may be of one kind or different. Fatty acids have various physical and chemical properties, which decide of triglycerides properties (vegetable and animal). Table 1 shows the profile of fatty acids, which to the highest extent affects vegetable oils and animal fats properties [16]. Chain length and number, position and shape of double bonds decide of the properties and importance of particular fatty acids and triglycerides formed by them. In reality, the number of fatty acids which content in triglycerides of defined fat is high enough, decide of its properties. The shorter the carbon chain of fatty acid, the lower melting temperature it has. Short chain saturated acids are liquids in room temperature, and saturated acids of number of atoms higher than 8 are solids. Presence of double bonds has greater importance for melting temperature, causing collapse of carbon chain, which precludes forming of characteristic crystalline structure for solids. For this reason, isomer trans of single-unsaturated elaidic acid in room temperature is in solid state, while its isomer cis (oleic acid) of the same chain length is in liquid state. Linoleic and linolenic acids have more double bonds, and they maintain in liquid state even in the fridge [16].

Table 1. Fatty acids profile of chosen vegetable oils being potential lubricants [14, 21]

Tab. 1. Profil kwasów tłuszczowych wybranych olejów roślinnych stanowiących potencjalne środki smarne [14, 21]

Type of raw material	Fatty acids						
	Acid	Hexadecanoic	Octadecanoic	Octadecenoic	Octadecadienoic	Octadecatrienoic	Docosenoic
	Common name	palmitic	stearic	oleic	linoleic	linolenic	erucic
	Empirical formula	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	C <sub>18</sub> H <sub>32</sub> C <sub>2</sub>	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	C <sub>22</sub> H <sub>42</sub> O <sub>2</sub>
	Number of unsaturated bonds	0	0	1	2	3	1
		16:0	18:0	18:1	18:2	18:3	22:1
Fatty acids [% , m/m]							
Low erucic rapeseed oil		2-4	1-2	60	20	8	2
High erucic rapeseed oil		2	1	15	15	7	50
Sunflower oil		4-19	3-6	14-35	50-75	0,1	0
High oleic sunflower oil (HOSO)		4,5		89,5	6,0		0
Soybean oil		7-10	3-5	22-31	49-55	6-11	0
Olive oil		7-16	1-3	64-86	4-15	0,5-1	0
Linseed oil		6-7	3-5	20-26	14-20	51-54	0
Palm oil		40	4-6	38-41	8-12	1-2	0
Archid oil		10,4	8,9	47,1	32,9	0,5	0,2
Corn oil		9,9	3,1	29,1	56,8	1,1	0
Castor oil*		4		4-5			0

\* contains hydroxyoleic acid C<sub>18</sub>H<sub>34</sub>O<sub>3</sub> – 89% by mass

It has to be mentioned that inappropriate storage, excessive heating or industrial processing of fats lead to formation of undesired byproducts of fatty acid compounds of changed chemical structure, which may affect organisms negatively. Such changes may result in formation of trans isomers, as well as other oxidation, hydrolysis or polymerization reactions products. Another reason for the presence of changed fatty acids in fats is their industrial processing. Hydrogenation process causes formation of significant amounts of trans isomers and displacement of double bonds through carbon chain [16]. Inappropriate lubricants storage causes long exposure of lubricants on atmospheric factors, which results in formation of viscous or rigid film on the surface, which may cause undesired additional friction during exploitation [22, 23].

Kinematic viscosity is an important oils feature, which is one of the three parameters of rheological characteristics, next to dynamic viscosity and exploitation liquids relative viscosity. Viscosity is a parameter which defines flow resistance of fluid (gas or liquid) during its motion. Fluid motion resistance depends on the structure of a molecule, and so on the force that has to be applied to the system to force the flow. Liquid viscosity is a function of temperature, that means that with the increase in temperature the viscosity of liquid drops. Each exploitation system has its optimal range of applied viscosities of lubricants and exploitation or hydraulic liquids. With the decrease in temperature, the viscosity increases, which results in higher energy losses of the system. In extreme conditions increasing the viscosity may cause serious damage of the machine elements or disable its work. On the other hand, too low viscosity caused by high temperature may be a reason of lubricant leakage, so it may result in higher surface wear or even seizing of the machines [22, 23]. Oils viscosity depends on chemical structure of the substance. Viscosity and boiling temperature of vegetable oils increase with higher carbon chain length of fatty acids. Increase in unsaturated bonds causes

the ignition temperature retardation and viscosity abatement (Table 2) [24, 25, 26]. Oils with saturated bonds are much more effective lubricants than oils with unsaturated fatty acids [27]. Viscosity of working fluids, mostly based on rapeseed oil, decreases with the temperature increase. It is so because the mobility of particles and the outer volume are higher. It was observed that fluids increase their viscosity when their structure tends to be ordered, whilst reaching solidification point the temperature has little effect on viscosity. While increasing the temperature reaching boiling point we observe a strong dependence of viscosity on temperature, because the system disorder occurs, increasing its volume [28]. Oil purity influences viscosity as well. Presence of even trace amounts of glycerin phase in rapeseed oil causes the increase of viscosity even several times [29].

Acid number is a significant fuels parameter, which defines acidic substances content in products, and more precisely the number of free fatty acids [30]. With this parameter oil type examination is possible, as well as its quality, because acid number defines fat hydrolysis degree [31]. For example, refined rapeseed oil has lower acid number than cold pressed rapeseed oils. During refining process free fatty acids are efficiently removed from oil [32, 33]. High acid number may indicate long and inappropriate storage of oil [34]. Acid number is a measure of the oil freshness. It allows to define oils and lubricants quality, basing on physiochemical aging processes and formation of byproducts, without application of other analytical techniques. For this reason suitable lubricants properties, such as acid number, may decide of exploitation system proper work. Increasing oil aging time results in the increase in acid number, viscosity, density, ignition temperature, etc. [35].

Another crucial physiochemical parameter is density, which among others defines usefulness of given oil for system lubrication [15]. Density is one of the basic features of matter, defined as weight of the body volume unit or body mass to its volume ratio.

Table 2. Physiochemical properties of chosen potential raw materials as lubricants [2, 39, 40, 41, 42, 43]

Tab. 2. Właściwości fizykochemiczne wybranych potencjalnych surowców jako środków smarnych [2, 39, 40, 41, 42, 43]

Type of raw material	Kinematic viscosity at 40°C, mm <sup>2</sup> ·s <sup>-1</sup>	The acid number, mg KOH/g oil	Density at 15°C, g·cm <sup>-3</sup>	Lubricating properties, diameter of blemish, mm, PN-C-04147:1976
Rapeseed oil	35,7	0,30	0,92	0,6
Rapeseed oil with E1 (epoxidized soybean oils)	43,94	0,74	-	0,75
Rapeseed oil z E2 (epoxidized soybean oils)	44,26	0,67	-	0,75
Mustard oil	40,17	1,57	0,914-0,923	0,65
Mustard oil with E1 (epoxidized soybean oils)	42,08	2,04	-	0,7
Mustard oil with E2 (epoxidized soybean oils)	50,17	1,86	-	0,8
Soybean oil	31,94	0,35	0,912-0,918	0,6
Soybean oil with E1 (epoxidized soybean oils)	49,02	0,96	-	0,85
Soybean oil with E2 (epoxidized soybean oils)	48,92	0,73	-	0,8
Epoxidized soybean oil E1	171,1	1,95	0,980	0,73
Epoxidized soybean oil E2	163,7	1,36	0,962	0,73
Oil from algae	33,3	0,13	0,919	0,64

For oil products, especially petroleum, density is given at 15°C. It is dependent on temperature, and with the temperature increase density of the material decreases [30, 36]. It is important to maintain suitable density of lubricant, which ensures optimal work conditions. Aging of oil results from increase in density [35]. Density is an important parameter, because it affects the injection system. Increase in density caused by modification of particles size causes lower efficiency of fuel and air mixing, and so the injection efficiency drops [37]. Addition of biocomponents, such as alcohols or refined rapeseed oil are widely used in industry in order to change the density. Such additions also affect other fuels properties, such as viscosity, and especially lubricating properties [38].

In Poland hydraulic oils constitute about 40% of industrial oils consumption. They found wide application in machines, industrial units and vehicles. Lubricating oils properties are checked according to PN-C-04147:1976 regulation on T-02 four-ball extreme pressure tester, under increasing load. Rapeseed, charlock, soybean, algae oils and vegetable oils compositions, obtained by addition of soybean oil E1 and E2 in the amount of 12-16% to epoxidized vegetable oil, were analyzed. Epoxidized vegetable soybean oils E1 and E2 came from different producers and they had the same viscosity class VG 46. Epoxy oils normally are applied as viscosity modifiers. Experiments performed in this article enabled to make precise analysis of the epoxidized oils influence on lubricants for the friction node prevention, basing on physiochemical and anti-wear properties. Data shown in Table 2 show that both vegetable oils and lubricating compositions could be used as hydraulic oils. Anti-wear research showed that epoxidized soybean oils have negative influence on anti-wear properties of analyzed vegetable oils. Tests showed that vegetable oils and synthetic products can be an alternative for petroleum products. Soybean oil is the most common oil in American and Asian countries, while in Europe rapeseed and sunflower oils are the most common [2].

## 5. Conclusions

Different physical and chemical properties of vegetable oils, such as fatty acids profile, acid number, kinematic viscosity, density and lubricating properties have great impact on application of given oils as lubricant. Fatty acids profile to the highest extent influences the properties of vegetable oils and animal fats. Inappropriate storage of fats leads to

formation of undesired fatty acid compounds of changed chemical structure. Oils viscosity is connected to their chemical structure; it increases with the length of fatty acids carbon chains and decreases with the number of unsaturated bonds. Oils with saturated bonds are more effective lubricants than oils with unsaturated fatty acids. Liquid viscosity is a temperature function, so each exploitation system has its own optimal viscosity and temperature working range. Density allows to describe usefulness of given oil for system lubrication. Application of oil of proper density prevents from injection system wear. Lubrication tests showed that both vegetable oils and lubricating composition (Table 2) can be applied as lubricants. Lubricating compositions that contain epoxidized soybean oils could have an adverse impact on anti-wear properties of vegetable oils. Pro-ecological policy urges to find alternative source of raw materials for mineral oils. Vegetable oils and animal fats are surely more ecological, and they could be applied as lubricants, however because of their chemical structure they oxidize faster, which affects negatively their durability and properties. In the next stage of work, the issue of spent vegetable oils and animal fats usefulness as lubricant for various kinematic pairs types will be discussed. As a part of scientific work, the analysis of the knowledge state of rheology and spent food fats market (both vegetable and animal) will be provided, also laboratory research will be conducted. However, there is a lack of information relative to the utilization of spent fats as lubricants. Due to increasing attention for secondary waste management, in this PhD's thesis I will carry out the analysis concerning this subject.

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