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# Review of aspects of processing and use of waste cooking oils as effective lubricants

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## Abstract

In connection with environmental pollution and the depletion of oil reserves, biologically based lubricants have received great interest as a replacement for mineral oil-based lubricants. Biolubricants have a number of advantages over mineral lubricants, including high biodegradability, low toxicity, lubricating properties and minimal environmental impact. The presented review describes the main characteristics and properties of biological lubricants, various vegetable oils, which are used as raw materials for the production of biolubricant materials. The physicochemical properties of biological lubricants were analyzed from the point of view of improvement. The technological processes used for the chemical modification of vegetable oils, ensuring the lubricity and anti-wear properties of the obtained biolubricants are determined. Various additives used to improve the properties of biolubricants are also recommended. This review material will provide researchers and practitioners with additional information on the practice of using biolubricants.

**Keywords:** vegetable oils, food industry waste, environmental friendliness, chemical modification, physical processing, lubrication, wear resistance

## Introduction

Worldwide concern over the massive use of petroleum-based products is affecting the production of lubricants in a way that also requires the search for new oil-free technologies. Nowadays, environmental protection requirements [1-6] have turned biodegradability into one of the main parameters from the point of view of choosing base oils and improvers of lubricating properties of materials. It is known that various vegetable oils are suitable as base oils for lubricants. However, the large acreage devoted to industrial oil crops competes with the use of land for food production, and this is a major controversial issue. Thus, the production of biolubricants based on edible vegetable oils has recently been considered an unsustainable practice. In addition,

## Main material

Edible vegetable oils are widely used for frying, which is usually carried out at a temperature of 160 to 180 ◦C in the presence of air and moisture. At the same time, chemical changes occur as a result of thermo-oxidative and hydrolytic reactions, isomerization of double bonds, oligomerization and degradation of triglycerides. Thus, the chemical composition of the oil after frying is different from the original fresh oil, it undergoes undesirable physico-chemical changes (among other things, color, smell, viscosity, acidity, general polar compounds). In recent decades, the amount of waste cooking oil (WCO) generated by the food industry, restaurants, fast food establishments and homes has been continuously increasing, at a rate of up to 2% per year, due to the increase in food products and, above all, the consumption of fast food by the population.

There is inadequate disposal of WCO through the sewage system, causing both economic problems and pollution of rivers and soils. On the one hand, the irrational disposal of used cooking oil in the sewer creates problems with the operation and maintenance of municipal sewage treatment plants, which significantly increases the costs of their cleaning.

On the other hand, one liter of waste vegetable oil poured into the environment can pollute 0.5 million liters of water, which will cause serious environmental problems [1-4]. Therefore, proper management of WCO is mandatory to reduce its impact on the global environment and improve their availability for reuse in various industrial processes such as bio-lubricants, biodiesel, asphalt additives and others.

The use of WCO as a feedstock in biodiesel plants is an established practice. However, demand for biodiesel is currently declining to reduce harmful emissions, and many biodiesel plants are closing around the world. Therefore, other methods of reuse should be explored to reduce the negative environmental impact and greenhouse gas emissions of WCO. With this in mind, bio-lubricants can be a way to use waste cooking oil with a dual purpose. First, it can prevent non-food land use; secondly, it can prevent their potential impact if disposed of in the environment. Therefore, other methods of reuse should be explored to reduce the negative environmental impact and greenhouse gas emissions of WCO. With this in mind, bio-lubricants can be a way to use waste cooking oil with a dual purpose. First, it can prevent non-food land use; secondly, it can prevent their potential impact if disposed of in the environment. Therefore, other methods of reuse should be explored to reduce the negative environmental impact and greenhouse gas emissions of WCO. With this in mind, bio-lubricants can be a way to use waste cooking oil with a dual purpose. First, it can prevent non-food land use; secondly, it can prevent their potential impact if disposed of in the environment.

In general, most of the research work related to waste cooking oils focuses on the use of their fatty acid methyl esters for the production of WCO-derived molecules and elucidating their physicochemical characteristics [1-3]. There is insufficient information about the full physicochemical characteristics of the used WCO and the relationship between its physicochemical properties and tribological characteristics.

Therefore, a comparative assessment of waste cooking oil from different food enterprises and an analysis of the influence of their physical and chemical properties on tribological behavior is needed.

This review presents the results of the latest research in the field of using waste cooking oils for the production of technical lubricants.

The work [1] reveals the achievements of modern scientists in the creation of environmentally friendly biodegradable lubricants. It is noted that the main problem is the development of a universal biodegradable base oil that could replace base mineral oils taking into account the preservation of the environment. The need for environmentally friendly products has been discussed for a long time in many forums. ASTM reviews the products available today and the tests required to determine performance criteria for biodegradable fluids. Synthetic fluids as a base oil have become widely used in a variety of industrial applications. Some of the applications include engine oils, transmission oils, hydraulic oils, compressor oils, pump and turbine oils. The choice of different base lubricants depends on the type of application, cost and biodegradability requirements. Vegetable oils are widely used for two-stroke systems, open gears, chain saws. For automotive lubricants with extended drain intervals, hydrotreated mineral oils are increasingly preferred. The development of chemically modified esters based on biological resources is a very profitable option for environmentally friendly applications. Development of synthetic esters from cost-effective sources for critical applications (automotive and industrial) is one of the best choices. Additionally, there is a need to develop hydrocarbon-based mineral oils with improved biodegradability and performance. Lubricants should be evaluated on the basis of increased thermal and mechanical stability, environmental safety and rapid biodegradability.

In the review [2], lubricants on a biological basis, various vegetable oils used as raw materials for the production of lubricants on a biological basis are considered in detail. The physical and chemical properties of biologically based lubricants are described. Features of the processes used for chemical modification of vegetable oils, lubricating properties of bio-based lubricants, as well as various additives to improve the properties of bio-based lubricants are highlighted. Vegetable oils have several advantages over conventional mineral oils, as they have a high level of biodegradability and are safe for the environment. The following methods of chemical modification of vegetable oils can be used to increase thermo-oxidative stability: transesterification, epoxidation or selective hydrogenation. The properties of biobased lubricants can also be improved by introducing additives: antioxidants, detergents and dispersants, nanoparticles, corrosion inhibitors, anti-seize additives and anti-wear additives. Bio-based lubricants appear to be promising alternatives for replacing petroleum-derived lubricants. Regarding the use of vegetable oils as lubricants on a biological basis, additional studies are being conducted to understand the lubrication mechanisms of these lubricants and their mixtures.

In [3], two main types of WCO treatment are discussed in detail: chemical transformations to utilize the chemical functional groups present in the waste, and physical treatments such as extraction, filtration and distillation procedures. The first part, which concerns chemical synthesis, is mostly related to the production of fuel. The second part, related to physical processing, focuses on the production of biolubricants. In addition, during the description of the filtration procedures, special attention is paid to the development and application of new materials and technologies for the treatment of WCO materials.

A technology based on a combination of water treatment and filtration on porous materials was made in [4], designing a mini-recycling plant aimed at the production of biolubricants from WCO (Fig. 1) [4].

The proposed technology can be described as follows: WCO is to be purified from water. The refined waste oil is then pushed to the filter module, where it is cleaned by a porous material. The combination of refining and filtration makes it possible to obtain purified processed vegetable oil.

Despite the results achieved in the field of filtration, further efforts are needed to improve performance and cost-effectiveness. In particular, careful research is needed to reduce the amount of oil absorbed by cellulose filters, to reduce the cost of synthesis and regeneration of synthetic materials.

In work [5], several types of cooking oil waste from various food establishments were investigated: a regular restaurant, a fast food restaurant, a fried food establishment, a mixture of used cooking oils of various unknown origins, without segregation

Oil has undergone molecular distillation. Distillation of WCO does not require too much energy, so it can be considered economically feasible. Molecular distillation yields two fractions: a lighter fraction enriched in free fatty acids, and a heavier fraction containing the most polar compounds and a low fraction of undistilled free fatty acids. Both fractions are liquid at room temperature.

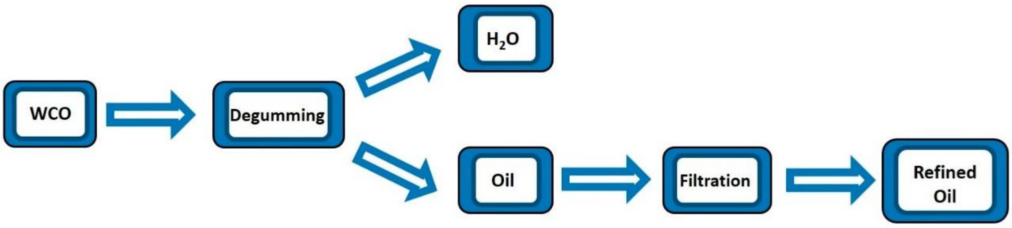

**Fig. 1. WCO recycling process [4].**

Studies of WCOs have shown marked variations in their chemical composition associated with several variables involved in the various roasting processes investigated. Deep-fried oils showed a high content of free fatty acids and diglycerides due to the hydrolysis of triglycerides [5]. In contrast, lightly roasted WCO showed rather low acidity, indicating a lower degree of hydrolysis. Variations in the chemical composition had different effects on the studied properties. WCO with the highest content of molecules (oligomers, dimers and polymers) showed the highest kinematic viscosity. WCOs with the highest values of total polar compounds and acidity showed the lowest viscosity index values, while WCOs with the lowest acidity values showed the highest viscosity index values and were less sensitive to temperature. revealed that acidity also affects the fluidity of oils at low temperature, so oils with the lowest acidity values have the best fluidity at low temperature. It was found that the high acidity and high ratio of unsaturated and saturated fatty acids of the oils gave these WCOs the greatest lubricating ability [5].

Molecular distillation was shown to yield two fractions, light and heavy, with significantly improved tribological properties compared to their parent waste cooking oil. Thus, the low viscosity and high polarity of the light fractions enriched with free fatty acids provide improved lubricating characteristics both in extreme and mixed modes of friction.

In the study [6] methylolpropane triester of fatty acid (TFATE) was obtained as a base oil of biolubricant material. This product was synthesized by transesterification of fatty acid methyl esters from waste cooking oil. The constituent reactions and oxidative stability of TFATE were analyzed. Under the selected conditions, TFATE was obtained with a yield of 85.7%. After purification by molecular distillation at 120 0C, the TFATE content in the product reached 99.6%. It has been proven that the chemical and physical properties of TFATE meet the requirements of ISO VG32.

A study [7] showed that WCO can be successfully hydrolyzed by Candida rugosa lipase to obtain FFA at an enzyme concentration of 1 g L-1 within 30 hours. The resulting FFA can be esterified with a higher alcohol (octanol) using Amberlyst 15H to produce an environmentally friendly bio-lubricant. It was found that temperature, amount of catalyst, molar ratio of reagents (alcohol : FFA) have a significant effect on the reaction rate. Complete recycling can be achieved in minimal time by using a suitable desiccant to remove the water produced during the esterification reaction. It can be concluded from the experiment that the most favorable conditions for the maximum conversion in the minimum time are the molar ratio octanol : FFA 3 : 1, temperature 80 ◦C, catalyst 2 g and desiccant (preferably silica gel powder) 50% by weight of FFA.

Studies have shown that esters based on olive oil have the highest thermal oxidation resistance due to the low content of polyunsaturated acids. While NPG esters have higher stability in thermo-oxidative conditions.

The polyols used during the transesterification process are NPG, TMP and PE. Each of them contains a different number of hydroxyl functional groups. In general, the viscosity of ester-based lubricants increases with polyol functionality. The number of hydroxyl groups affects the viscosity of esters in the following order: PE > TMP > NPG. Similarly, the viscosity of vegetable oil-based TMP esters is higher than that of equivalent esters, which may be due to the presence of three acidic groups in the ester structure.

The introduction of separation into methyl ether lowers the solidification temperature, disrupting the alignment and construction of hydrocarbon chains. This allows the oil to solidify at lower temperatures.

A specialized batch reactor (1.5 L) made of stainless steel was used to carry out esterification reactions under appropriate operating conditions (Fig. 2). The reactor was equipped with: a stirrer with an electric drive and a digital speed display (rpm); a thermostat that maintained the desired temperature of the liquid in the shirt; inlet channel for pouring the sample; sampling outlet equipped with a valve.

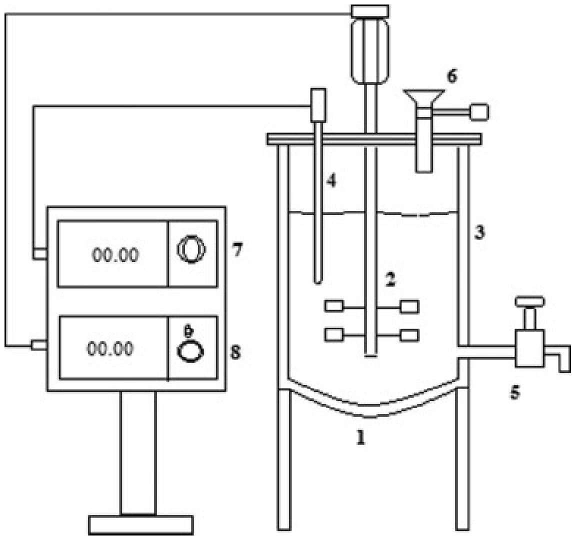

**Fig. 2. Schematic diagram of the reactor for the esterification reaction: 1- reactor, 2- stirrer, 3- reactor casing, 4- thermocouple, 5- material output, 6 - material input, 7 - temperature indicator, 8- stirring speed indicator.**

The review [8] describes in detail biological lubricants, various vegetable oils used as raw materials for the production of biolubricants, physicochemical properties of biological lubricants, processes used for chemical modification of vegetable oils. The properties of biolubricants are considered, as well as various additives used to improve the properties of biolubricants. Low temperature characteristics are the main limitation when it comes to the use of vegetable oils as lubricants. Although vegetable oils have strong intermolecular interactions that provide a strong lubricating film, these interactions also result in poor low-temperature properties.

The life cycle of lubricants obtained from renewable sources is shown in fig. 3 [8]. The main component of vegetable oils are triacylglycerols (98%), as well as various fatty acid molecules attached to the single structure of glycerol.

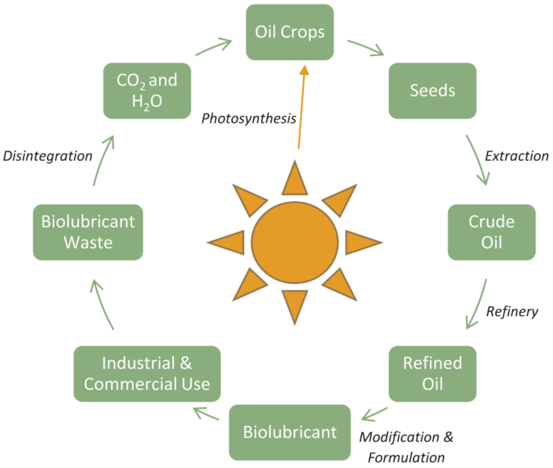

**Fig. 3. Life cycle of biolubricants**

Although the thermo-oxidative stability of vegetable oils can be a problem, this problem can be overcome by chemical modification of vegetable oils through transesterification, epoxidation or selective hydrogenation.

Sunflower oil is extracted from sunflower seeds and is usually used for cooking, as well as for the production of margarine and biodiesel. Sunflower oil is cheaper compared to olive oil. Sunflower varieties differ in the content of fatty acids [9-11]. Sunflower oil with a high oleic acid content has many properties that make it suitable for use in lubricants, with good oxidation resistance and lubricity. [9-11]. One study showed that high oleic sunflower oil (HOSO) can be used to replace mineral oils in textile and leather production without technical problems or equipment modification [11]. The correct composition of sunflower oil can be compared with mineral oil.

High oxidation resistance is an important criterion for lubricants, as low oxidation resistance will cause the lubricant to oxidize rapidly if left untreated. As a result, the lubricant thickens and polymerizes into a plastic consistency. Numerous studies were conducted to study the resistance of vegetable oils to oxidation [12-14]. The oxidation resistance of vegetable oils is generally lower than that of synthetic esters due to the higher degree of unsaturation in vegetable oils. Oxidation is undesirable because it leads to polymerization and degradation of the lubricant.

Attempts to improve the low-temperature properties and oxidation resistance of vegetable oils include transesterification of trimethylolpropane and methyl ether from vegetable sources [15–17]. Transesterification is a reaction in which a triglyceride molecule reacts with three moles of methanol in the presence of an acidic or basic catalyst [18-19], resulting in the formation of glycerol and mixtures of methyl esters of fatty acids.

The disadvantages of vegetable oils, such as low thermo-oxidative stability and cold flow, can also be enhanced by the use of additives. Manufacturers of different vegetable oils may choose different additives to meet the requirements of a particular application. For some oils, additives can be up to 5% (by weight). The presence of additives contributes to the improvement of the properties of lubricants and lubricants on a biological basis in terms of corrosion inhibition, as well as friction and wear characteristics. In general, esters with biodegradable additives have superior wear resistance compared to pure oils or blends of vegetable oils.

Antioxidants are used to slow down or prevent the oxidation process by slowing the oxidative degradation of the lubricant, while ensuring that the lubricant meets the technical requirements [20].

Nanoparticles are effective additives for lubricants and bio-based lubricants to reduce friction and wear. Nanoparticles are considered to be more effective compared to conventional additives for protection against high pressure and anti-wear additives due to their environmental properties [21]. The properties of biolubricants depend on the properties of the nanoparticles, such as the size, shape and concentration of the nanoparticles.

Friction in the contact of surfaces from the shear forces required to separate the interacting asperities. Friction and wear can be reduced by adding anti-wear and anti-seize additives to the oil. These additives create strong protective films on the metal surface, entering into a thermochemical reaction with the metal surface. Anti-seize and anti-wear additives usually contain chlorine, phosphorus and sulfur [22]. These elements protect the surface of the metal with layers of sulfides, chlorine, or phosphides that are easily erased, preventing severe galling and wear.

A fairly in-depth analysis of directions for processing used cooking oils is presented in the review [23]. It is noted thatthe use of biomass wastes such as used cooking oil (WCO) does not create competition and is a better source of resource recovery as it allows a second life cycle (Fig. 4).

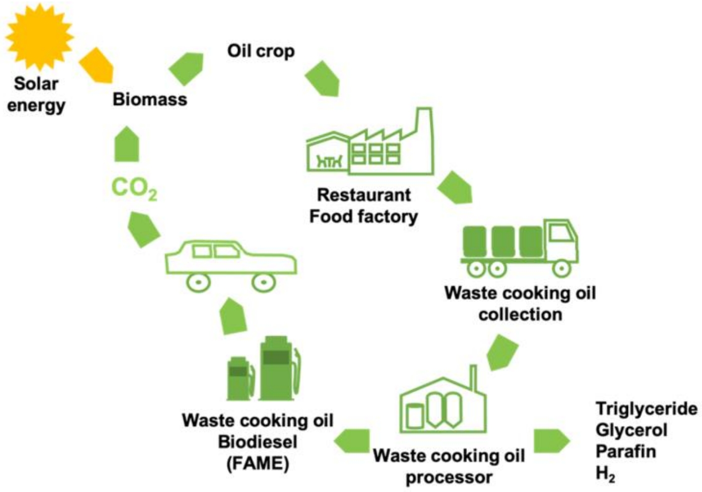

**Fig. 4. Chain of cooking oil waste [23].**

Valorization of WCO was realized by the following processes: transesterification, transesterification, hydrolysis, hydrodeoxygenation, hydrocracking and hydrogenation. Among them, transesterification is the main process that allows the production of biodiesel and bio-lubricant. Biodiesel can be obtained using heterogeneous catalysts having basic centers, acidic centers, a mixture of acidic and basic centers, or enzymes. Among heterogeneous catalysts, magnetic catalysts have been developed for easy separation of catalysts after each cycle. Homogeneous catalysts and enzymes as catalysts also allow the production of biodiesel. Various alternative technologies have been successfully studied, such as electrolysis, ultrasound, microwaves, continuous flow, even continuous flow with microwaves. Compared to transesterification, transesterification makes it possible to obtain biodiesel and triacetin instead of glycerol. Hydrolysis of WCO generates free fatty acids, glycerol, and water, while hydrogenation of WCO yields free fatty acids, free fatty aldehydes, free fatty alcohols, and alkanes via hydrodeoxygenation, hydrocracking using a similar petrochemical process.

In [24], used cooking oil is chemically modified to obtain biolubricants. Three WCO-based fluids were synthesized and considered as base lubricants for environmentally friendly lubricants. Typical properties of these biolubricants, such as viscosity, viscosity index, solidification temperature, cloud point. Corrosion resistance, oxidation resistance and four-ball anti-wear properties were investigated. WCO and its derivatives were tested for friction and wear reduction using a four-ball friction machine. Experimental results indicate that chemically modified WCOs are an economic, sustainable and ecological substitute for mineral oils and will find potential practical applications in the field of lubricants.

In order to reduce environmental pollution as a result of biolubricant synthesis, the study [25] developed an ecological and efficient strategy for the preparation of octylated biolubricant from waste cooking oil (WCO). First, it was hydrolyzed by lipase to obtain unsaturated fatty acids, and the latter were later concentrated by urea complexation. Further, new esters were synthesized by esterification with ethylhexanol using lipase, and new esters were additionally epoxidized. After that, the epoxy group was attacked with a reagent, octanoic acid, to obtain an octylated biolubricant. Articles [26-27] review recent advances in the synthesis of biolubricants from vegetable oils using chemical modification methods, such as esterification/reesterification,

## Conclusions

An overview of the basic properties of biologically based lubricants, the role of chemical functionality and additives, as well as their relationship with the effectiveness of the lubricant is presented. Vegetable oils have several advantages over conventional mineral oils, as they are biodegradable and safe for the environment. Although the thermo-oxidative stability of vegetable oils may be insufficient, this problem can be overcome by chemical modification of vegetable oils by transesterification, epoxidation or selective hydrogenation. The properties of bio-based lubricants can also be improved by adding additives such as antioxidants, detergents and dispersants, viscosity modifiers, nanoparticles, corrosion inhibitors, extreme pressure and anti-wear additives.

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**Диха О., Гетьман М., Старий А., Калачинський Т.** Огляд аспектів переробки і застосування відпрацьованих кулінарних олив як ефективних мастильних матеріалів

У зв'язку із забрудненням навколишнього середовища та виснаженням запасів нафти мастила на біологічній основі викликають великий інтерес як заміна мастилам на основі мінеральних масел. Біомастила мають низку переваг перед мінеральними мастильними матеріалами, включаючи високу здатність до біологічного розкладання, низьку токсичність, змащувальні властивості та мінімальний вплив на навколишнє середовище. У представленому огляді описано основні характеристики та властивості біологічних мастил, різноманітних рослинних олій, які використовуються як сировина для виробництва біомастильних матеріалів. Проаналізовано фізико-хімічні властивості біологічних мастил з точки зору поліпшення. Визначено технологічні процеси хімічної модифікації рослинних олій, що забезпечують змащувальні та протизносні властивості отриманих біомастильних матеріалів. Також рекомендуються різні добавки, що використовуються для поліпшення властивостей біомастильних матеріалів. Цей оглядовий матеріал надасть дослідникам і практикам додаткову інформацію про практику використання біомастильних матеріалів.

**Ключові слова:** рослинні олії, відходи харчової промисловості, екологічність, хімічна модифікація, фізична обробка, змащення, зносостійкість.