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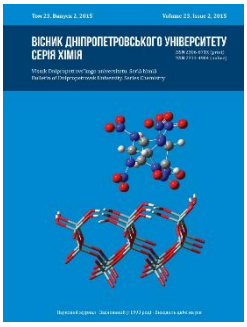

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INDUSTRIAL LUBRICANTS BASED ON RENEWABLE RAW MATERIALS REPORT 1. PROPERTIES OF THE NATURAL ACYLGLYCEROLS

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Abstract
The paper analyzes and generalizes the information available on animal fats that can be used as secondary raw materials in production of lubricants compatible with the new recycling technologies. The paper reviews the current market of lubricants, analyses the environmental problems in manufacturing of petroleum-based lubricants and suggests a new class of alternative raw materials for the lubricant production. The experimental studies showed that sunflower oil contains the highest number of unsaturated bonds as compared to other fats. The iodine number measurements of the beef and chicken fats indicated that the latter contains more unsaturated carboxylic acids. Dynamic viscosity of the beef fat is much higher than that of other studied fats. The synthetic acylglycerols have higher temperature-dependent and shear viscosity as compared to the original fats. The paper presents the results of experimental physicochemical and rheometric studies of animal fats. It is shown that animal fat-based materials may serve as an alternative source of environmentally-friendly lubricants.

Keywords: lubricants, animal fat, recycling, rheometric characterization.

ЗМАЩУВАЛЬНІ МАТЕРІАЛИ ТЕХНІЧНОГО ПРИЗНАЧЕННЯ НА ОСНОВІ ВІДНОВЛЮВАЛЬНОЇ СИРОВИНИ ПОВІДОМЛЕННЯ 1. ДОСЛІДЖЕННЯ ВЛАСТИВОСТЕЙ АЦИЛГЛІЦЕРИДІВ ПРИРОДНИХ ЖИРІВ

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Анотація
Мета статті пов'язана з узагальненням та аналізом доступної інформації щодо вихідних характеристик тваринних жирів, які розглядаються як вторинна сировина при виготовленні змащувальних матеріалів за новими технологіями рециклінгу. Наведено характеристику стану ринку змащувальних матеріалів, здійснено аналіз екологічних проблем виготовлення мастил на нафтовій основі та обґрунтовано пошук альтернативної сировини для виготовлення змащувальних матеріалів. Результати експериментальних досліджень показали, що найбільша сумарна кількість ненасичених зв'язків спостерігається у соняшникової олії в порівнянні з ін. жирами. При порівнянні йодного числа курячого і яловичого жиру видно, що значно більшу кількість ненасичених карбонових кислот має курячий жир. Динамічна в'язкість яловичого жиру значно перевищує відповідні значення ін. жирів. Для синтезованих ацилгліцеридів значення в'язкості в залежності від температури і швидкості зсуву зростають у порівнянні з вихідними жирами. В роботі представлені результати експериментальних фізико-хімічних та реометричних досліджень тваринних жирів. Показано, що альтернативним варіантом розробки екологічно-безпечних змащувальних матеріалів можуть стати матеріали на основі тваринних жирів.

Ключові слова: змащувальні матеріали; тваринний жир; рециклінг; реометричні дослідження.

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СМАЗОЧНЫЕ МАТЕРИАЛЫ ТЕХНИЧЕСКОГО НАЗНАЧЕНИЯ НА ОСНОВЕ ВОЗОБНОВЛЯЕМОГО СЫРЬЯ СООБЩЕНИЕ 1. ИССЛЕДОВАНИЕ СВОЙСТВ АЦИЛГЛИЦЕРИДОВ ПРИРОДНЫХ ЖИРОВ

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Аннотация
Цель статьи состоит в обобщении и анализе доступной информации об исходных характеристиках животных жиров, которые рассматриваются в качестве вторичного сырья при изготовлении смазочных материалов с использованием разработанных новых технологий рециклинга. Представлена характеристика состояния рынка смазочных материалов, осуществлен анализ экологических проблем производства масел из нефти. Дано обоснование необходимости поиска альтернативного сырья для изготовления смазочных материалов. Результаты экспериментальных исследований показали, что наибольшее количество ненасыщенных связей наблюдается в подсолнечном масле в сравнении с остальными жирами. При сравнении йодного числа куриного и говяжьего жиров, видно, что значительно большее количество ненасыщенных карбоновых кислот имеет куриный жир. Динамическая вязкость говяжьего жира значительно превышает соответственные значения др. жиров. Для синтезированных ацилглицеридов значения вязкости в зависимости от температуры и скорости сдвига возрастают в сравнении с исходными жирами. В работе представлены результаты экспериментальных физико-химических и реометричних исследований животных жиров. Показано, что альтернативным вариантом разработки экологически безопасных смазочных материалов могут стать материалы на основе животных жиров.

Ключевые слова: смазочные материалы, животный жир, рециклинг, реометрические исследования.

Introduction

High efficiency, low energy consumption and financial expenses, easy availability of the raw materials, operation and recycling with minimal negative impact on the environment are the governing tendencies in development of modern technologies. This pertains in particular to automotive industry, agricultural machinery and aeronautical engineering.

Modern ground, air and water transportation, agricultural, mining and forestry engineering machinery, industrial equipment, chemical, oil-producing, metallurgical, mechanical-engineering technologies are all energy-intensive. Under these conditions, the rational and efficient use of fuel and lubricating materials is one of the crucial issues.

Lubricants must provide high resource efficiency of the operated equipment, they must not change its technical properties during the exploitation period [1]. Due to reinforcement of the regulations on environmental control and equipment operating conditions, the problem of development and improvement of lubricants based upon renewable secondary raw materials has arisen.

Under the pressure of a global economic crisis, the market of lubricants is not developing steadily. In 2009, it had decreased by one-fourth but since 2010–2013 the growth of 9% took place [2]. In Ukraine, the importance of high quality lubricating materials for the equipment efficiency was being underestimated for a long period of time.

Therefore, development of the lubricant production was not given due regard. As a result, it negatively affected the national market where the demand for lubricants was dependent on the import. Nowadays, the Ukrainian manufacturers produce lubricants according to State Standards of the USSR. A large part of the products does not have globally recognized quality certificates and a number thereof does not meet the modern requirements.

The vast majority of lubricating materials is produced on the basis of mineral or synthetic oils (polyolefins, polyethers, esters of organic and inorganic acids, esters of polyatomic alcohols, polyhalogenated hydrocarbons, siloxanes etc.).

Since the production of lubricants accounts for only about 1% of the overall oil products consumption, the problem of their recycling does not deserve much attention from the environmental point of view. However, it is the environmental safety that is stipulated in the first place since a considerable part of the used products ends up in the environment. Oil products are slowly biodegradable. The manufactured lubricants are particularly resistant to biodegradation. Their high hydrophobic properties are conducive to their retention in soil. In water bodies, a film of used lubricants on the surface hampers the processes of air-water gas transfer. A considerable number of oil-based lubricants accumulates on the bottom forming sediments that have a pernicious effect on flora and fauna.

A lot of consumers do not recycle used lubricants, rather leave them on city dumps or waste into a sewerage system. Used lubricant compositions can have more than 140 condensed polycyclic hydrocarbons the number of which grows as long as lubricants are used. Pollution of water bodies with used lubricants alone constitutes 20% of the general anthropogenic pollution and 60% of the oil-induced pollution.

Therefore, at the present stage of economic globalization and environmental pollution, the central issue is the choice and realization of an environmentally friendly path of energy development, rather than separate improvements of utilization processes. One of the priority directions of solving energy and resource saving problem is the search and use of substitutes for mineral raw materials based upon renewable natural resources. The validity of such choice is supported by high dynamics of the world markets and considerable increase in industrial use of vegetable oils. The most illustrative examples of such tendency are the USA and Western Europe where vegetable oils are widely used in chemical industry for production of "green" surfactants, high-quality compound feed, biodiesel, base of engine, hydraulic and plastic lubricants, and various additives to lubricating materials. Over the past several years, the practical use of vegetable oils has grown substantially in the following areas: agriculture, construction industry, sports and medical equipment. Nowadays, they are widely used for lubrication of petrol-powered saws, outboard motorboats, motorcycles, snow-mobiles, air pumps etc. [3].

Analyzing the agriculture of rapeseed and other industrial crops in Ukraine, current conditions of their export, technical difficulties of the rapeseed oil production and environmental aspects of its processing in Ukraine, one can come to a conclusion that there are certain ambiguities and problems, especially regarding the orientation of production of lubricants based upon vegetable oils [4; 5].

Rapeseed oil has a number of essential drawbacks in regard to independent lubricating properties and if used as a dispersion medium for plastic lubricants: a) rather high chemical activity and, consequently, thermodynamic instability due to, first of all, a large number of unsaturated bonds in the structure; b) high content of erucic acid; c) insufficient viscosity for a dispersion medium; d) relatively low anti-welding and wear-resistant properties, as well as reduced protection of metal surfaces from welding in sites of contact and in the course of friction and wear-out [6].

Inedible animal fats can become an alternative raw material for production of plastic lubricants since they are easily available, non-toxic, fully biodegradable and also possess lubricating properties. Moreover, unlike vegetable oils, animal fat is the waste product of the meat-processing industry. Conclusively, from the environmental point of view (life cycle analysis – LCA) [7], all parameters indicate that animal fats have a significant advantage over vegetable oils.

First compositions of lubricants for industrial needs (which were mentioned as early as the 4th millennium BC) were made of animal fats (lard, beef fat, mutton fat) [8].

Similar lubricants were used until the 20th century. Rendered beef fat and lard were used to grease the wheel spindles of railcars, whale oil was used to produce industrial lubricants for textile machinery, transmissions etc.

The use of animal fat-based lubricants is limited due to their low viscosity and a tendency to oxidize while use. Oxidation may lead to the formation of insoluble compounds with higher molecular weight resulting in the operation instability, problems with removal of friction from the machine elements and damage of their surface [7].

The purpose of the research is to analyze the ways to solve the aforementioned problems *via* production of innovative lubricants based upon modified animal fats. A particularly topical research direction is the use of technologies of high molecular compound waste recycling that will give an opportunity to regulate the viscosity of lubricants as well as enhance their physico-mechanical and tribotechnical properties.

It should be noted that virtually all research projects [9–12] are trying to use vegetable oils as the alternative raw materials for lubricant production. There are relatively few studies, however, devoted to the use of animal fats. Among the scientists tackling this problem are I. G. Fuks from the Russian National University of Oil and Gas [13] and Eiko Furomoto [14], who consider the problems of use of plastic lubricants on the basis of lard, cod liver oil and whale oil.

The research tasks of this paper are to analyze and generalize the information available on animal fats having a potential use as raw materials in production of plastic lubricants that are recyclable in accordance with the new technologies.

Results and Discussion. Fat is a complex mixture of glycerides, i.e. esters of glycerol and high-molecular fatty acids (both saturated and unsaturated) – palmitic $C_{15}H_{31}COOH$, stearic $C_{17}H_{35}COOH$, oleic $C_{17}H_{33}COOH$, linoleic $C_{17}H_{31}COOH$, linolenic $C_{17}H_{29}COOH$ etc.

Content of saturated and unsaturated acids of animal and vegetable origin is given in table 1 [5].

Table 1

Fatty acid content in fats

Name acids	Acid percentage, %						
	Beef fat	Chicken fat	Rape oil	Sunflower oil	Beef fat glyceride	Chicken fat glyceride	Rape oil glyceride
Palmitic	26	–	–	5–7.6	–	–	–
Stearic	23	–	1.6	2.7–6.5	–	–	–
Oleic	41.5	–	22.5	14–39.4	–	–	–
Myristic	31	–	1.5	0.2	–	–	–
Linoleic	1.8	–	14	48.3–74	–	–	–
Linolenic	2	–	2.5	0.3	–	–	–
Hexadecenoic	2.5	–	–	–	–	–	–
Arachic	–	–	1.5	0.1-0.5	–	–	–
Erucic	–	–	60.5	0.3	–	–	–
Lauric	–	–	–	0.1	–	–	–
Gadoleic	–	–	–	0.3	–	–	–
Behenic	–	–	–	0.3–1.5	–	–	–
Lignoceric	–	–	–	0.5	–	–	–
Iodine value*	27	67	89	142	34	42	81

* Iodine value was defined experimentally in accordance with technique [15].

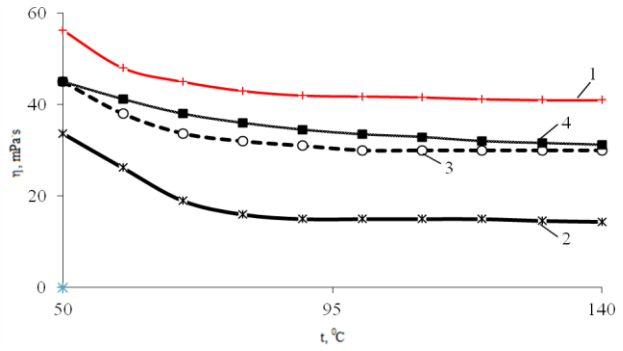

Fig. 1. Dependence of viscosity on temperature for animal fats and vegetable oils. 1 – beef fat; 2 – chicken fat; 3 – rape oil; 4 – sunflower oil (at ẏ =1300 s⁻¹)

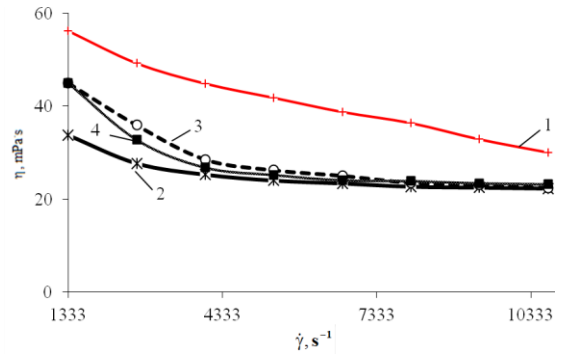

Fig. 2. Dependence of viscosity on shear rate for animal fats and vegetable oils. 1 – beef fat; 2 – chicken fat; 3 – rape oil; 4 – sunflower oil (at t = 50⁰C)

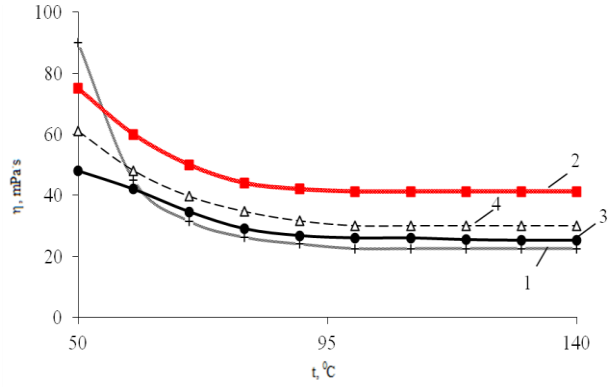

Fig. 3. Dependence of viscosity on temperature for acylglycerols synthesized on the basis of animal fats and vegetable oils. 1 – beef fat acylglycerol; 2 – chicken fat acylglycerol; 3 – rape oil acylglycerol; 4 – sunflower oil acylglycerol (at ẏ =1300 s⁻¹)

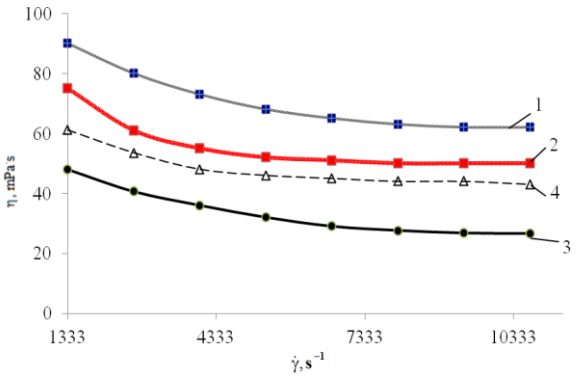

Fig. 4. Dependence of viscosity on shear rate for acylglycerols synthesized on the basis of animal fats and vegetable oils. 1 – beef fat acylglycerol; 2 – chicken fat acylglycerol; 3 – rape oil acylglycerol; 4 – sunflower oil acylglycerol (at t = 50°C)

It should be noted that the acid composition of fats depends on climatic conditions (for plants), feeding conditions (for animals) as well as other factors. At this moment, there are no valid data about chicken fat in the literature.

The results of iodine number measurements show that sunflower oil has the largest total quantity of unsaturated bonds, rapeseed oil has a smaller quantity and beef fat has the smallest one. The comparison between iodine numbers of chicken and beef fat shows that the former has a considerably larger content of unsaturated carboxylic acids.

Rheometric parameters of the systems under study were defined on a rotational viscometer Brookfield CAP2000+, over the temperature range of 50°C to 140°C and at shear rates up to 10670 s^{-1}.

Figures 1, 2 show dependence of viscosity on temperature and shear rate for animal fats and vegetable oils. Figures 3, 4 show dependence of viscosity on temperature and shear rate for glycerides synthesized based on animal fats and vegetable oils.

Rheometric characterization shows that initial basic viscosity of beef fat is considerably higher than that of vegetable oil. Taking into account a substantially smaller number of unsaturated bonds in the fat composition, it is possible to consider beef fat as a prospective renewable, environmentally friendly raw material for the further research towards development of novel lubricant compositions.

Conclusions. As a result of decreasing oil reserves, rises in oil production costs and harmful effect on the environment, minimi-zation of the loss of oil products is becoming a hot topic. Development and use of lubricants based upon renewable secondary raw materials may be one of the keys to this problem. Lubricants on the basis of animal fats modified with compounds synthesized in accordance with the plastic waste recycling technology can be alternative to oil products and synthetic oil-based lubricants. This approach will enable to regulate the viscosity of lubricants and enhance their tribotechnical properties.

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