ENVIRONMENTAL PROBLEMS

Vol. 8, No. 1, 2023

THE USE OF OIL AND FAT WASTE IN TECHNOLOGICAL SYSTEMS FOR SUSTAINABLE DEVELOPMENT

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https://doi.org/10.23939/ep2023.01.001

Received: 23.12.2022

Abstract. The paper shows the possibility of efficiently using oilseed production and processing waste. The methods of chemical transformation of by-products of oil and fat production into technological systems for sustainable development have been developed. They have been used to create surfactants and lubricant systems for hydrocarbon production and wwllorkover of wells; polyfunctional additives used as components of lubricants and cutting fluids to improve their antioxidant, extreme pressure, antiwear, lubricating, and cooling properties of metalworking processes. Technological systems have been developed that, along with increased functional properties, have improved biodegradability and caused minimal environmental harm.

Keywords: surfactants, lubricants, polyfunctional additives, lubricants, metalworking fluids.

1. Introduction

Living nature exists through well-coordinated processes of sustainability, interconnection, and cycling of matter and energy. Deepening our knowledge of biological and chemical processes and using the rich opportunities of the biosphere is the basis for the sustainable development of humanity. Ukraine's potential for renewable sources of raw materials and energy is enormous. At the same time, we buy many different substances, products, materials, and their production technologies in other countries, without noticing our developments. Human life and activity in the natural environment invariably lead to the destruction of natural links. Therefore, only technologies inscribed in the Earth's natural laws are humanity's future. Solar energy accumulated by plants in biosynthesis creates a tremendous amount of biomass – raw materials and energy potential for the industry. There is no waste in nature. By-products of one process become raw materials for another. This principle of maximum use of oilseeds through the entire chain – cultivation, processing, and service – is laid down in the ideology of our research as an integral part of the “green economy” and sustainable development.

The relevance and purpose of this work are due to both global environmental and energy problems, as well as limited production capacity and the possibility of using waste from the oil and fat industry for the synthesis of surfactants, lubricants, metalworking fluids, and technological lubricant systems for the processes of stimulation of hydrocarbon production and workover of wells.

To achieve this goal, using already known and own developments and practical experience, a local technological scheme for the energy-efficient use of oilseed production and processing waste has been developed (Fig. 1).

The experimental and applied part includes two interrelated areas. According to the first of them, the study of properties and establishment of the possibility

For citation: Bodachivska, L., Papeikin, O., Safronov, O., Venger, I., Spas`ka, O. (2023). The use of oil and fat waste in technological systems for sustainable development. *Journal Environmental Problems*, *8(1)*, 1–7. DOI: https://doi.org/10.23939/ep2023.01.001

of direct use of by-products from the purification of vegetable oils (phosphatidic sludge, hydrating sludge, phosphatidic concentrate) and their chemical transformations to obtain multifunctional biosynthetic surfactants (biosurfactants) – emulsifiers, stabilizers, hydrophobic agents, structured agents, adhesives, corrosion inhibitors, polyfunctional additives, etc. In the second direction, using synthesized biosurfactants in combination with glycerin and other agricultural wastes, composite systems, lubricants, and metalworking fluids were created and tested in laboratory and pilot conditions.

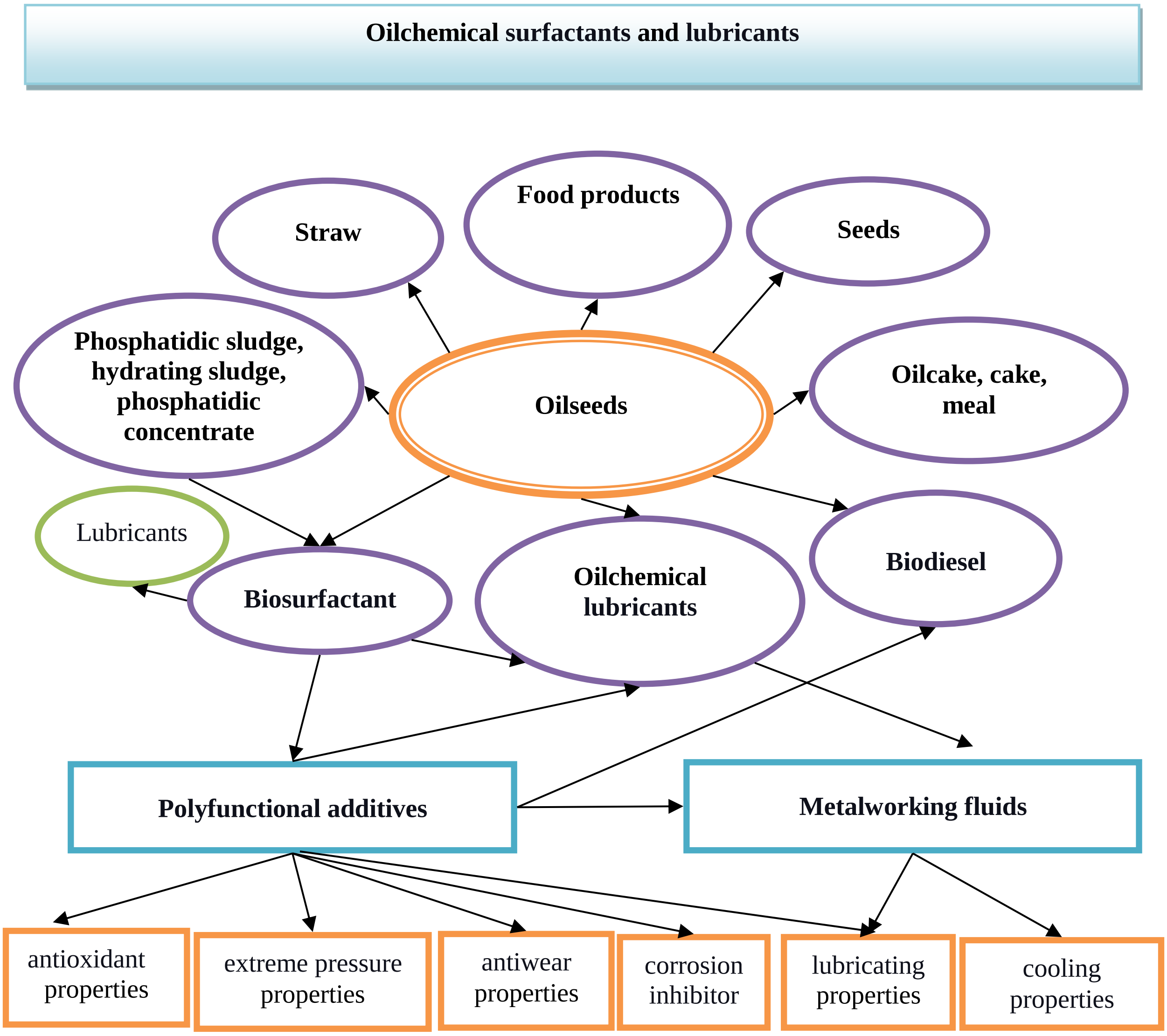

Fig. 1. Scheme of energy-efficient use of oilseeds production and processing waste

2. Materials and Methods

Materials. The research used phosphatidic sludge (PS), hydrating sludge (HS), phosphatidic concentrate (PC), waste food oils (WFO) from the production of sunflower and rapeseed oils, unrefined rapeseed oil (URO). These materials comprise triacylglycerides with saturated (palmitic, stearic) and unsaturated (oleic, linoleic, linoleic, gadoleic, erucic) fatty acid chains, along with phospholipids, such as phosphatidylcholine, phosphatidylethanolamine, phosphatidylserine, phosphatidylinositol, and phosphatidic acids. Due to their structure, phospholipids are amphiphilic since they consist of a hydrophilic polar head formed by a charged phosphate group and two hydrophobic non-polar tails formed by the remains of fatty acids. All other materials, including alkanol amines, calcium hydroxide, and others, were used as received from commercial sources.

General methods. The synthesis of bioFAA was carried out by amidation of PS, HG and PC with amines of different basicity taken in the ratio of

0.1 mol and 0.3 mol under the action of calcium oxide catalyst (40 mol %, in terms of PS, HG and PC) or without catalyst under constant stirring at 80–100 °C for 0.5 hours and at 110–125 °C for 2.5 hours (Fig. 2). By physical properties, the synthesized product is a brownish oily mass with a density of 920 kg/m^3, with solubility in organic non-polar solvents. The composition and structure of biosurfactants were proved by physical and chemical methods (Pop et al., 2012; Bodachivska, 2021).

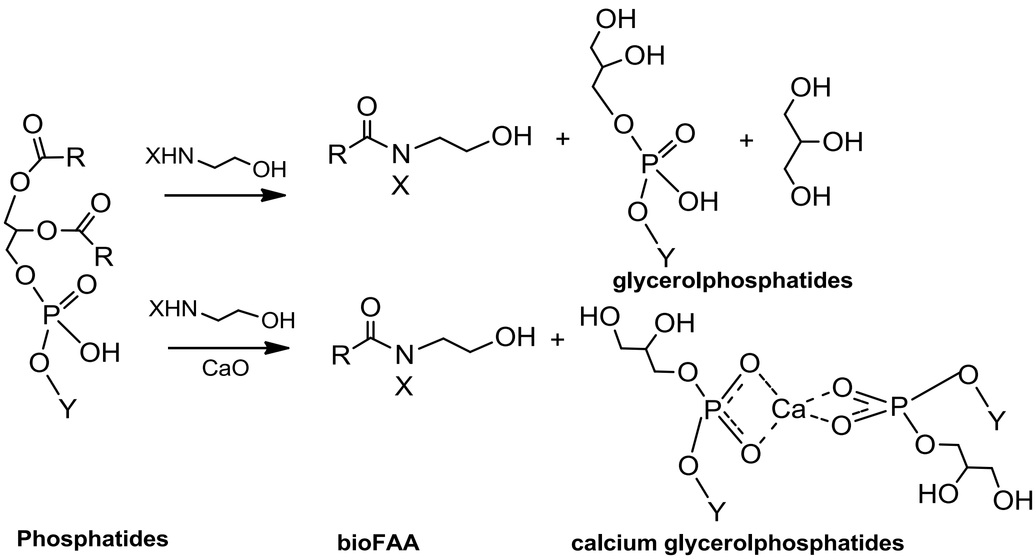

Fig. 2. Proposed conversion of phospholipids into bioFAA. R = alkyl or alkenyl fatty acid residues. X – H, CH_2CH_2OH, $CH_2CH_2N(H)CH_2CH_2OH$ et all, Y – H, $CH_2CH_2N(OH)(CH_3)_3$, $CH_2CH_2NH_2$, $CH_2CH(NH_2)COOH$

3. Results and Discussion

3.1. Use of fat waste for the synthesis of bioFAA

There is no doubt that if oilseeds are used exclusively for biofuel production, their cost will be 1.5–2.0 times higher than the price of diesel fuel. We argue that to improve the technical and economic performance of biodiesel production from rapeseed or sunflower oils, it is necessary to use not only cake, straw, and husk but also by-products from the purification of pressed oil in the context of the integrated complex of fuels and lubricants production, including phosphatidic sludge, hydrating sludge and phosphatidic concentrate for the production of various types of lubricants according to the scheme shown in Fig. 1.

In general, oil-chemical production consists of three parts. One of them is based on oils (refined and unrefined, recycled, etc.), as well as various fatty by-products and wastes from the processing and use of oils. The second part is aimed at the synthesis of multifunctional biosynthetic surfactants. This part also focuses on the catalytic processes of transesterifying triglycerides with methanol, ethanol, or butanol. Finally, the third part is devoted to creating lubricant compositions using bioFAA, lubricants, and cutting fluids, where biosurfactants as multifunctional additives are used as constituent components.

Phosphatidic sludge (PS) is a by-product formed from freshly pressed oil (sunflower, rapeseed, and others) in natural settling or separation in a centrifugal field. It is a thick brown mass with an oil odour and density of 958 kg/m^3, freezing point minus 8–10 °C. It and contains water (2.5–40 %), and residual oil (45–85 %) stabilized by phosphatides (10–45 %).

Hydrating sludge (GS) is a product of refining waste generated during the processing of vegetable oils heated to 45–55 °C by water vapour. They are a stable lubricant of oil (15–20 %) in water (50–75 %) stabilized by phosphatides (10–30 %). The consistency of hydro fusions is the ointment-like product of light brown colour with an oil smell, and a freezing point minus 1–2 °C.

Phosphatidic concentrate (PC) is a product of dewatering a mixture of phosphatidic sludge and hydrating sludge in a vacuum (266 kPa) at 70–90 °C. This product consists of phospholipids (40–60 %), ester non-soluble substances (1–5 %) and oil (triacylglycerides) (39–59 %) with residual moister content (0.5–3 %).

Phosphatidic sludge, hydrating sludge, phosphatidic concentrate, and the basic phosphatides isolated from them, such as lecithin and kefalin, are soluble in most organic solvents. They dissolve slightly worse in tetradecane and hexadecane. They practically do not dissolve even when heated in methyl acetate, acetone, and other ketones. Dispersion of phosphatides with the formation of milky white dispersions is observed in acids and alkalis.

Due to their natural surface activity, phosphatidic sludge, hydrating sludge, and phosphatidic concentrate were used in technological systems for the oil and gas industry as ecologically safe surfactants. However, lubricants and suspensions formed from the PS, GS, and PC are unstable, so they are used together with other biosynthetic co-surfactants (Pop et al., 2012).

An increase in the activity and complex improvement of emulsifying and stabilizing ability and thermal stability with simultaneous reduction of energy and material costs was achieved by chemical transformation of phosphatidic sludge, hydrating sludge, phosphatidic concentrate, waste food oils, unrefined rapeseed oil with amines (Fig. 2). The resulting biosynthetic surfactants (bioFAA) are a complex mixture of alkylolamides and glycerol phosphatides or calcium glycerol phosphatides. The first has increased surface activity and, accordingly, dispersing ability. The second provides stability of oil-dispersed systems, both due to bulk structure formation and the shape of a mixed adsorption-solvent layer.

Table 1

Composition and technical properties of lubricants prepared with bioFAA

No.	Composition of lubricants					Technical properties of lubricants			
	Surfactant-product, wt%	Co-FAA, wt%	Aqueous phase, wt%		Hydro-carbon phase, wt%	Viscosity, Pa·s	Thermal stability at 80 °C, days	Stability to phase separation, days	Electrical stability, V
			H_2O	$CaCl_2$					
1	FAA (PS) –2.5	0.5	40	7	50.0	0.215	8	>90	220
2	FAA (GS) – 2.5	0.5	40	7	50.0	0.189	7	>90	170
3	FAA (PC) – 2.5	–	40	7	50.5	0.205	>9	>90	180
4	FAA (WFO) – 2.5	–	40	7	50.5	0.192	>9	>90	200
5	FAA (URO) – 2.5	–	40	7	50.5	0.172	>9	>90	230

FAA (PS), FAA (GS), FAA (PC) and FAA(WFO), FAA (URO) = surfactants based on phosphatidic sludge and hydrating sludge derived from sunflower oils, phosphatidic concentrate derived from sunflower oil, waste food oil, unrefined rapeseed oil

Concerning the practical use of synthesized bioFAA, the most important is the developed dispersion systems with controlled structural-mechanical and colloidal-chemical properties while maintaining their high aggregation and sedimentation stability in a wide range of densities from 520 to 1750 kg/m^3 (Pop et al., 2012; Bodachivska, 2021). Synthesized bioFAAs are effective emulsifiers-stabilizers of invert dispersions. Therefore, they can be used to increase the recovery of hydrocarbon raw materials and drilling processes, and workover operations (Table 1). By studying the properties of bioFAA, it was found that forming a micellar structure in a solution and a gel-like structure in the adsorption layer, they solubilize water and other hydrophilic components and thus prevent the course of corrosion processes. The indicator of bio-splitting ability is environmental characteristics according to DSTU 4247 (CECL 33-A-93), and the bio-splitting ability of bioFAA is 80–86 %.

Due to their structure, bioFAA molecules are amphiphilic since a hydrophilic polar functional group (alkylolamide and oxyethyl) contributes to their dispersion in water. At the same time, hydrophobic non-polar aliphatic chains of higher carboxylic acids give them an affinity for organic solvents. Therefore, concentrating bioFAA molecules on the interfacial surface provides for the stabilization of composite systems and reliable protection of metal surfaces against corrosion. Studies have shown that phosphate-containing direct lubricants are corrosive to metals. In contrast, inverted lubricants are protective against steel equipment and ferrous metals in aggressive environments. In this regard, inverted lubricants using bioFAA are recommended to protect equipment and pipelines in the oil and gas, petrochemical, and chemical industries (Table 1) (Pop et al., 2012; Saikia, Mahto, 2018; Bera et al., 2014).

BioFAA can serve as effective polyfunctional additives for metalworking fluids and lubricants under increased technical and environmental conditions (Papeikin et al., 2020; Shah et al., 2018; Abo-Hatab et al., 2018). Polyfunctional additives improve the antioxidant, extreme pressure, antiwear, and lubricating properties of metalworking processes and other friction units of industrial equipment operating under high temperatures, loads, and aggressive environments.

3.2. Lubricants

Wear and tear of moving parts of mechanisms, structural materials, duration, and efficiency of their work depend on the load and intensity of friction processes. Lubricants protect surfaces from premature wear, which significantly increases the durability of various machines and mechanisms. Lubricants are a complex system containing base oil (dispersed phase) and functional biosurfactants (additives), Fig. 1, which regulate numerous operation properties (Papeikin et al., 2021). The special organization of biosurfactants on the interfacial surface has some practically essential properties, such as tribological, anticorrosive, and adhesive, which led to their wide use as part of lubricating compositions. The possibility of using the phosphatidic sludge, hydrating sludge, phosphatide concentrate, and waste food oils from the production of sunflower and rapeseed oils as components of lubricating materials was demonstrated in papers (Papeikin et al., 2020; Bodachivskyi, Pop, 2016; Papeikin et al., 2021; Li et al., 2012; Lazaro et al., 2014; Florea et al., 2003; Korff, Cristano, 2000).

Lubricating compositions were prepared by dissolving the synthesized bioFAA in mineral oil with constant stirring and heating to 60–70 °C for 15–30 minutes. The mass fraction of surfactants in all samples was 5.0 %. Lubricant samples were obtained by the technology described in work (Bodachivskyi, Pop, 2016) and studied by laboratory methods by current standards. The volumetric and mechanical characteristics of the synthesized lubricants were evaluated by penetration, mechanical stability, dropping point, etc.

The main characteristics of the synthesized samples of lubricating compositions and the results of their tests are summarized in Table 2.

Lubricants based on bioFAA are efficient in a wide temperature range, under heavy loads, and in the presence of water, resist oxidation and mechanical destruction, and do not cause corrosion of non-ferrous metals. It is established that biosurfactants with their polar groups bind to the metal surface. Hydrophobic hydrocarbon chains, displacing residual moisture, create a protective barrier for the diffusion of iron ions from the metal surface and the penetration of corrosive agents and water to its surface.

The leading indicators of the thermal stability of lubricants are the dropping point and the maximum operating temperature. As follows from the research results (Table 2), the dropping point of lubricants, at which it changes from a plastic solid to a liquid state, exceeds 250 ºC. But, the upper-temperature limit for the use of the developed lubricants, according to derivatographic studies, is at the level of 180–200 ºC.

Table 2

Physico-chemical properties of developed lubricant with bioFAA

Indicator	Testing method	Values of indicators of lubricant
Appearance of the lubricant	DSTU 38.001	Homogeneous ointment, dark brown in color
Dropping point, °C	ISO 2176	>250
Colloidal stability, %	GOST 7142 method A	6,43
Penetration at 25 °C at stirring, mm·10^{-1}: – 60 double cycles (P_1) – 100,000 doubles cycles (P_2)	ISO 2137	 278 325
Mechanical stability, м·10^{-4} : – change ΔP	ISO 2137	 44
Tribological characteristics on four ball machine at the temperature of (20±5) °C: – welding loading (Pw), N – critical load (Pc), N	GOST 9490	 3283 1098
Resistance to oxidation: increase in acid number (150 °C, 10 hours), mg KOH/g	GOST 5734	2,79
Copper strip corrosion	ASTM D 4048	1a
Biosplitting ability, %	DSTU 4247 (CECL 33-A-93)	38.0

In addition to laboratory methods, samples of lubricants were tested on a special stand, “Dynacorotest”, which evaluates the protective properties of lubricants in dynamic conditions by the value of the corrosion rate of rolling bearings. The data in Table 2 indicate that using biosurfactants as a component allowed us to obtain a lubricant composition characterized by improved protective and tribological characteristics. The presence of phosphorus- and nitrogen-containing compounds, which are part of biosurfactants, strengthened the antiwear properties of lubricants (Pc) and increased the extreme pressure properties (Pw) by more than 1000 N compared to the commercial lubricant Uniol-2, which has antioxidant and antiwear additives.

According to the results of studies of the mechanical stability of the proposed lubricant by the change in the penetration index after prolonged mechanical destruction (Table 2), the use of biosurfactants in the lubricant composition leads to an improvement in the mechanical stability of lubricants (difference ΔP), compared to the commercial lubricant Uniol-2, has significantly decreased. This makes it possible to predict the long-term operation of the lubricant in friction units without destruction and leakage.

Summarizing the results of comparative studies, it can be stated that the antifriction lubricant based on by-products from oil and fat production showed high-performance characteristics. Due to the use of raw materials of plant origin in lubricating compositions, their ability to biodegrade increases up to 38.0 %.

3.3. Microlubricants for metalworking operations

The specifics of the work of modern machines and mechanisms, any metal machining puts high demands on the quality of cutting fluids (MF), which cool the parts of the equipment and prevent wear and corrosion during metalworking. Prevent external influences, such as moisture, dirt, etc., which significantly affects the service life of moving joints of machine parts and mechanisms (Bodachivskyi, Pop, 2016; Korff, Cristano, 2000; Boral, Bohidar, 2012; Negin et al., 2017).

Functional additives (bioFAA) improve the efficiency of MF, especially when machining special steels and alloys, as well as under severe cutting conditions. The lubricating effect of MF is due to the ability to enter into physical and chemical interaction with the activated surfaces of the contact zone and form physical (adsorption), chemisorptions, and chemical boundary polymolecular (up to 500 layers) films on them (Boral, Bohidar, 2012).The higher the resistance of the boundary film to normal loads and the lower the actual loads, the lower the coefficient of friction and the better the lubricating of the medium. The strength of adsorption films, and hence the lubricating effect of bioFAA, depend on the amount of adhesion of the polar group of the bioFAA to the metal surface and the cohesive interaction between its hydrocarbon chains. For these reasons, the acid composition of vegetable oils, particularly the presence of a large amount of oleic acid, is optimal and provides a set of functional, primarily lubricating properties.

Nowadays, organic polysulfanes occupy a prominent place in the field of lubricating materials. These sulfur-rich compounds are effective tribological additives interacting with the metal surface and preventing wear and scoring during processing. Moreover, in contrast to phosphorous or chlorine-containing analogues, polysulfanes have a high degree of biodegradation. As a result, they do not cause harm to the natural environment (Korff, Cristano, 2000).

Works (Bodachivskyi, Pop, 2016) proposed eco-favourable micro lubricant aqueous MF (AMF) with the application of sulfur-rich additives, technical bio-glycerol, and available materials.

Improvement of the lubricating properties of AMF is provided by sulfur-containing ethyl ester and resistance to lubricant stratification – by technical bio-glycerin, which is a by-product of biodiesel fuel production and contains 2–3 % of residual amounts of ethyl esters and 1–3 % of mono- and diglycerides of higher fatty acids of oils.

The positive impact of waste glycerol on micro-lubricant formation and stability should be mentioned. Glycerol is a more relaxed agent and stabilizer of different dispersed systems, especially gels (Bodachivskyi, Pop, 2016; Boral, Bohidar, 2012; Negin et al., 2017). However, waste glycerol from fatty acid esters manufacturing, despite glycerol, also includes contaminants of fatty acid salts and acyl glycerides, which provide emulsifying and stabilizing properties. Hence, waste glycerol is a complex additive that improves the conditions of micro-lubricant AMF preparation and prolongs its storage time.

4. Conclusion

Summarizing the work carried out, it can be stated that surfactants and emulsion systems for the intensification of hydrocarbon production and workover of wells have been developed; polyfunctional additives used as components of lubricants and cutting fluids to improve their antioxidant, extreme pressure, antiwear, lubricating, and cooling properties of metalworking processes.

Furthermore, the developed technological systems which improved performance properties, tested in laboratory and pilot field conditions, have an increased ability to biodegrade and cause minimal environmental harm.

The transition of the petrochemical materials market to alternative oil-chemical products is a time challenge. However, it requires a thorough analysis of raw materials since oils are among the leading food products. Still, using effective methods of chemical transformation of oil and fat production wastes in technological systems for sustainable development is relevant and promising.

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