Technologies for processing fat waste and technical fish oils

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Abstract. Current economic and environmental conditions require a more rational approach to use of industrial waste. It is necessary not only to clean industrial effluents from pollution, but also to find rational ways of using pollutants extracted from the industrial effluents. This is especially relevant for fatty foam masses, which are formed during flotation treatment of the fat production runoff. The issue of their rational use has not been resolved yet. Traditionally, these products are buried at specialized landfills. Also, the question of using soap water flows, which are formed during refining the semi-finished fish oils with a solution of alkali, remains. Usually soap water flows are not used and are sent to the combined stock of fat production. An equally urgent problem of the fishing industry is the processing of semi-finished technical fish oils with a high acid number (over 20 mg KOH / g). Traditional cleaning of such semi-finished products is unprofitable. It requires a significant expenditure of material resources. In this case, the yield of purified fish oil is not more than 60 %. At the same time, the listed objects contain a significant amount of polyunsaturated fatty acids. Therefore, after additional processing, they should be considered as a secondary material resource for obtaining surface-active, film-forming, and anti-friction substances.

1. Introduction
Currently, the implementation of low-waste and non-waste technologies is a priority in the fishing industry. In the fish production, waste from cutting the raw material ranges from 20 to 70 %. Traditionally, these wastes are used for the production of feed products and fish oil [1], [2].

The problem of waste processing has an environmental pillar. The semi-finished fish oil obtained during the processing of waste products needs to be cleaned of associated impurities. The modern fish oil market requires highly refined products. Purification of semi-finished fish oil is associated with high water consumption. This leads to the formation of significant volumes of industrial effluents [3].

Industrial effluent from fat processing plants is an emulsion with a high concentration of fat components. For example, in the process of alkaline neutralization of semi-finished fish oils, a soap water flow is formed. It is an aqueous-fatty emulsion with a high content of sodium salts of fatty acids (soaps). Fat production enterprises do not use the soap water flow separately. It is discharged into combined industrial effluents. This leads to a significant loss of valuable components [4].

The combined industrial effluent of fat production is also a water-fat emulsion with a high content of fat components. Before being discharged into a body of water, it must undergo physico-chemical treatment to extract pollutants. Fatty foam masses resulting from such treatment are disposed of through burial in the specialized landfills. This leads to environmental pollution by fatty substances, which could be used as secondary material resources for various industries [5].
An equally urgent problem in the fishing industry is the processing of semi-finished technical fish oils with a high acid number (over 20 mgKOH/g). Traditional cleaning of such semi-finished products is unprofitable. It requires a significant expenditure of material resources. A large amount of waste is generated in the form of soap water flow. In this case, the yield of purified fish oil is not more than 60%. It is appropriate to extract valuable fatty components from semi-finished technical fish oils with a high acid number and use them as secondary material resources for various industries [6].

2. Research objects
The research objects were as follows: fatty foam masses - the products formed during purification of the combined industrial effluents of fat production by the flotation method; semi-finished technical fish oil with an acid number of more than 20 mgKOH/g, a soap water flow - a product resulting from neutralizing the semi-finished fish oil products with an alkaline solution.

Fat foam masses contain 20 ... 56% water, 33 ... 70% lipids, 0.06 ... 0.28% nitrogenous substances. The semi-finished technical fish oil contains up to 10% water and 0.10 ... 0.20% nitrogenous substances.

Soap water flow is a water-in-oil emulsion containing 3 ... 10% lipids and 9 ... 16% sodium soaps. The fatty acid composition of the lipids of the studied objects is represented by high molecular weight polyunsaturated (37 ... 46%) and monounsaturated (31 ... 38%) fatty acids.

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The research objects should be considered as a source of polyunsaturated fatty acids. After additional processing, they can be used as a secondary material resource for obtaining surface-active, film-forming and anti-friction substances.

3. The main part
It is proposed to use fatty foam masses as a fatty phase for obtaining a direct emulsion (oil-in-water emulsion). A soap water flow was used to stabilize the disperse system, since it contains up to 16% sodium soaps. It is proposed to test the obtained direct emulsion as a release agent for molding the reinforced concrete building structures. A prerequisite for using the direct emulsion in this direction is reducing the lipid content in the product to 5 ... 7%. Exceeding the specified level of lipid content contributes to the formation of grease stains on the surface of the molded products. This is unacceptable [7].

The reduction of lipid content in the direct emulsion was carried out by separation. The introduction of 2% crystalline urea into the composition significantly increased the degree of separating the fat phase from the aqueous phase. Urea is known to have a hydrotrropic property in relation to water-fat systems [8]. After separating, the lipid content in the direct emulsion was 3 ... 6%.

The obtained direct emulsion was comparable in its anti-adhesive properties to a lubricant traditionally used in the construction industry based on spindle oil and synthetic fatty acids.

Fatty masses and semi-finished technical fish oil were used to obtain a fatty acid concentrate. For this purpose, the objects were subjected to enzymatic hydrolysis, then, the fat phase was separated from the aqueous phase.

For enzymatic hydrolysis of lipids, pancreatic lipase in a free and immobilized state was used as a catalyst. The enzyme was immobilized using polyvinyl alcohol. The enzymatic hydrolysis of the objects was carried out at a ratio of the fat phase to the aqueous phase 1: 0.5, continuous stirring, temperature 37 °C, pH 7.0. To increase the activity of free and immobilized lipase, bile salts and calcium chloride were introduced into the reaction mixture [9].

The rate of enzymatic hydrolysis of lipids of fatty foam masses was insignificant. The increase in the depth of lipid hydrolysis for 12 hours of the process was no more than 3 ... 5%. This is most likely to be due to the inactivating effect on the lipase of trace elements, such as copper, zinc, aluminum, which were present in the hydrolyzable object [10].
The lipid hydrolysis of the semi-finished technical fish oil proceeded more actively. The addition of calcium chloride to the reaction mixture had a stimulating effect on the activity of immobilized lipase. Bile salts had a stimulating effect only on lipase in a free state. The use of immobilized lipase for enzymatic hydrolysis allows achieving a greater depth of substrate lipid hydrolysis compared to the use of an enzyme in a free form. It is also noted that immobilized lipase can be repeatedly used in the technological cycle.

An increase in the content of free fatty acids from 20 to 70% in the lipids of the semi-finished technical fish oil after enzymatic hydrolysis was noted. The fatty acid composition of the lipids of the research objects during the hydrolysis did not change significantly.

The hydrolyzed objects were heated to a temperature of 95 °C, then, the fat phase was separated from the aqueous phase. To increase the efficiency of phase separation, hydrotropic additives — sodium chloride or urea — were introduced into the reaction mixture. According to the results of the experiment, it was noted that urea, in comparison with sodium chloride, has a higher degree of influence on the phase separation of water-fat systems.

The fat phase of the objects of study after phase separation was a fatty acid concentrate with a water content of 10...20% and an acid number of 105...125 mg KOH/g. The fractional and fatty acid compositions of the lipids of the research objects during the heat treatment changed slightly.

The fatty acid concentrates have been tested as raw materials for the manufacture of technical soap, salt drying oil, flotation reagent for the enrichment of apatite-nepheline ore and a lubricating component of the drilling fluid.

The technical soap was made by neutralizing a fatty acid concentrate with a 20% aqueous solution of potassium hydroxide at a temperature of the reaction mixture of 90...95 °C. The resulting product was a liquid substance with a saponified fatty acid (soap) content of 40...45%. The product meets the requirements for technical soap.

The technical soap has been tested as a direct emulsion stabilizer based on spindle oil and synthetic fatty acids, which is used in the construction industry as a release agent. The resulting direct emulsion was uniform, stable; the composition delamination was not observed.

The salt drying oil was prepared by neutralizing a fatty acid concentrate with crystalline calcium hydroxide. For this purpose, the fatty acid concentrate was heated to a temperature of 100...105 °C and maintained at the specified temperature until the complete dehydration. Calcium hydroxide was added to the dehydrated concentrate with continuous stirring in small portions. The mixture was kept at the reaction medium temperature of 100...120 °C and continuous stirring until the product was ready.

The resulting calcium salts of fatty acids (salt base) were cooled to a temperature of 90...95 °C and dissolved in white spirit. A desiccant was added to the solution to speed up the drying process of the product. The mixture was thoroughly mixed and filtered through a felt filter. In appearance, the finished product was a transparent solution of dark brown color. The drying time of the product after application to the surface at a given temperature and relative humidity corresponded to the requirements for salt drying.

A flotation reagent was prepared by neutralizing a fatty acid concentrate with a 1% aqueous sodium hydroxide solution at a temperature of 90 °C. The resulting solution of fatty acid sodium salts was introduced in an amount of 25% into the composition of the collective mixture for flotation of apatite from apatite-nepheline ore. Introducing a new component into the composition of the collective mixture increased the extraction of phosphorus oxide from the ore by 0.7...0.9%. The consumption of the proposed mixture for ore flotation was comparable to the consumption of a traditional reagent.

A lubricant additive to the drilling fluid was made by neutralizing a fatty acid concentrate with a 30% aqueous-alcoholic solution of an organosilicon compound (sodium aluminomethyl siloxanolate or ethyl silane triol monosodium salt). The resulting product was added in an amount of 1.5% to the drilling fluid in order to increase its lubricating and anti-wear properties. According to its antifriction properties, the proposed additive is superior to the lubricating components used in oil and gas industry.
based on synthetic fatty acids, vegetable oils and liquid glass, vegetable oils with an additive of boron compounds.

The new lubricant additive is proposed to use in the development of offshore oil and gas fields. This required an assessment of its environmental safety.

To establish the maximum permissible concentration of the test substance in the water of water bodies of fishery importance, the standard test objects were used, such as the lower crustaceans *Daphnia magna Straus* and the unicellular green algae *Selenedesmus quadricauda*; a year old rainbow trout. Bacterial processes were studied by changing the number of saprophyses.

According to the results of the experiments, the maximum permissible concentration of a new lubricant additive for water of water bodies important for fishery was determined as 0.2 mg/dm$^3$.

4. Conclusion

The study of fatty wastes and technical fish oils revealed that they contain a significant amount of polyunsaturated fatty acids. Based on the research results, technology has been developed for obtaining various auxiliary materials from the research objects for the construction, paint, mining and processing, oil and gas and other industries. The developed technology allows reducing the negative impact of fat production on the environment and suggests rational ways to use the fat waste and technical fish fats as secondary material resources.

References

[1] Andrusenko P 1988 *Low-waste and non-waste technology in fish processing* (Moscow, Agropromizdat) 49-59

[2] Windsor M and Barlow J 1981 *Introduction to fishery by-products* (Farnham, Fish. News Books) 187

[3] Petrov B 2009 *Fatty waste from fish processing industries and low-grade fish oils - secondary raw materials* *Rybnuye Khosiatvo (Fisheries)* 5 78-79

[4] Artyukhova S et al. 2010 *Technology of fish and fish products* (Moscow, Kolos) 800-803

[5] Ryabchenko N and Emelyanova E 1981 Recycling of wastewater treatment waste from fish processing enterprises *Rybnuye Khosiatvo (Fisheries)* 12 57-60

[6] Bimbo A and Crowther J 1990 *The Industrial Uses of Marine Oils* *International News on Fats, Oils and Related Materials* 4(1) 295

[7] Petrov B 2011 Release grease based on fatty waste from fish processing enterprises *Khranenie i Pererabotka selkhozsyrya (Storage and processing of agricultural raw material)* 12 54-56

[8] Bengen F 1951 Ang. chem. 63 207

[9] Ruban E 1977 *Microbial lipids and lipases* (Moscow, Nauka) p 143

[10] Wang D et al. 1979 *Fermentation and Enzyme Technology* (A Wiley-Interscience Publication, John Wiley & Sons, Inc.) 283