Study of the composition of oil and fat waste - soapstock obtained by a combined method of cottonseed oil refination

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Abstract. The article considers the characteristics of the composition of soap stock and wash water obtained during the purification of cottonseed oil in a miscella using a combined method. Soap stock contains soap, oil, phosphorus compounds, dyes, mineral and mechanical additives, etc., and has a solution in water. To separate free fatty acids from soap stock, it is treated with mineral acids or alkalis (to saponify neutral oil), followed by distillation. Comparative indicators of the lipid composition, neutral oil, and color of soap stock obtained by traditional (control) and mixed methods, as well as indicators of multiple washing of refined cottonseed oil in a miscella are presented. It was found that due to hydrogen bonds of polarized substances in a cotton micelle, their molecular structures are formed, that reducing the intensity of cottonseed oil hydration and alkaline neutralization processes in the micelle.

1 Introduction

In our country, the oil and fat industry has entered a new stage of development: the range of products is expanding, their quality is improving, new types of products are being created, more advanced technological processes are being mastered and they are equipped with new equipment. Consumers of vegetable oils are various sectors of the baking, confectionery, canning, food concentrates, as well as the chemical, metallurgical, medical and cosmetic industries [1]. Vegetable oils are produced using various technological schemes, the choice of which is based on the properties of the raw materials and the method of their preparation for pressing: primary pressing; secondary pressing; pressing - extraction; direct extraction. One of the main technological processes for processing vegetable oils, in particular cottonseed, is their hydration and alkaline purification using aqueous solutions of NaOH, KOH and others. There are many technologies for purifying cottonseed oil, which are classified as: periodic and continuous. Moreover, depending on the nature of the organization of the main processes, they are divided into emulsion, cottonseed oil purification in micelles, etc. [2].

The combined use of cottonseed oil pressing, extraction and refining processes allows us to produce up to 500 tons of product per day at our plants. Extrusion technology increases oil yield and reduces solvent consumption. First, the oil refining technology allows us to

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abandon the traditional alkaline refining and water rinsing process, which not only saves water, but also reduces wastewater by 40 cubic meters per day. Second, the technology starts from the production of crude oil and ends with its phenolization, and decolorization and deodorization allow us to improve the effect of dephenolization [3]. Third, the technology replaces the deacidification process with a solvent extraction process, which significantly simplifies the cottonseed oil production process, reduces space and reduces production costs. This oil production technology can also be applied to rapeseed oil and rice bran oil [4].

Currently, the problem of finding effective methods for alkaline refining of difficult-to-clean cottonseed oils, combining the neutralization process with the elimination of modified and derived forms of gossypol and other coloring substances, is being solved [5].

Rzhekhin V.N. together with his colleagues proposed to improve the quality of refined oils and to obtain light-colored soapstock from high-acid oils for two-stage schemes and to obtain oil from defective seeds or to treat the miscella with anthranilic acid before cleaning the oils or miscella with an aqueous solution of alkali [5,6].

In the production of cottonseed oil and fatty acids, a large number of secondary by-products and wastes are formed, depending on the technological scheme and methods of separation of the main products [7]. One of the most common methods is the treatment of fats with alkaline solutions (chemical refining). As a result of chemical refining, neutral fat-insoluble salts, soaps, and aqueous solutions are formed. The resulting soap mass, having a high stabilizing and absorbing ability, is called soapstock, which attracts a significant part of the impurities in the oil [8]. Soapstock is a sediment formed as a result of alkaline refining of vegetable oils and fats in the oil refining industry; it belongs to the category of recyclable waste. It has a complex and variable composition, depending on the nature of the oil and its properties (acid number, amount of components, etc.), as well as the refining method and the accuracy of the technological process [9]. The fatty acid composition of fatty soapstock is close to the fatty acid composition of the raw materials being processed. Soapstock contains a solution of soap, fat, phosphorus compounds, dyes, mineral and mechanical impurities, etc. in water. The weight composition of soapstock obtained by refining sunflower, cottonseed oils and hydrated oils, approximately %: fat 8-50%, including soap 8-30, neutral fat 1-20, water and decomposition of non-fatty components 50-92, including unreacted NaOH, NaCl, dyes, phosphatides, proteins and carbohydrates in small amounts [10].

To separate free fatty acids from soapstock, it is treated with mineral acids or alkalis (for saponification of neutral oil), followed by distillation. Soapstocks obtained from miscella should be used to enrich the sunflower oil in toasters (without pre-treatment with gasoline), or sent to film apparatuses to remove gasoline from them.

The main volume of cotton soapstock is subjected to subsequent saponification, decomposition with sulfuric acid, washing and distillation in the same and other oil factories. If it is necessary to ship cotton soapstock, it is advisable to decompose it, since in this case 50% of the total weight is subject to transportation, and the fatty acids are easily heated and discharged from automobile or railway tanks. The fatty acids purified from cotton soapstock are used for soap making or for the production of technical olein.

The main challenges of soapstock acidization are primarily related to the corrosion hazards of the process and difficulties in separating the acid-oil phase from the acid-water phase, which leads to significant fat losses and wastewater contamination with fats. Federal, state, and municipal legislation aimed at reducing pollution favors more efficient acid effluent treatment methods. Continuous acidization of soapstock and washwater at the refinery outlet has resulted in the formation of acid oil as a byproduct with specified quality standards and an acid effluent containing a smaller amount of more easily removed contaminants. Soapstock should be processed as soon as possible after formation to minimize the potential for fermentation and emulsification. Several different continuous acidization schemes exist.

The primary reason for soapstock deacidification is to remove moisture to reduce its volume for further processing or storage. Soured butter is essentially the fatty portion of soapstock with a moisture content reduced to 1.0 or 2.0%. It is shipped at a total fatty acid content of 95%, and is considered unacceptable for transportation if the content falls below 85%. Impurities present in the crude butter, such as dosphatides, carbohydrates, proteins, pigments, sterols, and heavy metals, are partially or completely transferred to the soapstock during daphnia processing and then converted to soured butter during acidification.

Of the innovations being applied to address these challenges, the most effective are developments in the field of recycling and processing waste from oil and fat production. This is due to their triple effect: a significant reduction in waste disposal costs, additional revenue from the sale of new products obtained through waste recycling, and an improved environmental situation. Given this, the development of new technologies for processing oil and fat production waste is relevant and offers significant innovative potential.

The main objective of the study is to study and optimize the process of extracting free crude fatty acids (FFA) and gossypol from soapstock for use in important industries in order to ensure the reduction of harmful substances to the environment.

2 Materials and methods

Experimental studies were conducted at the regional testing laboratory of the engineering profile "Structural and biochemical materials" of the M. Auezov South Kazakhstan University. In order to solve the problems set in the work, appropriate methods and standards were used to conduct physicochemical studies of raw cotton micelles and products processed from them.

The organoleptic and physicochemical properties of soapstock were studied in accordance with the requirements of GOST 30266-2017. Physicochemical characteristics of soapstock: non-fatty impurities in oil according to GOST 30623-2018, soap and fatty acid content of soapstock according to GOST 5480-59, acid value according to GOST 31933-2012, unsaponifiable matter content according to GOST 5479-64, saponification value according to GOST 5478-2014, peroxide value according to GOST R51487-99, the weight fraction of soap in cottonseed oil according to standard TS 10-04-02-80-91, quantitative determination of gossypol was carried out by HPLC, the concentration of hydrogen ions was measured with an I-160MI ionometer, the mass fraction of fatty acids was determined by liquid chromatography.

In this work, crude, hydrated and purified cottonseed oils obtained by extraction, phospholipid precipitate obtained after hydration and alkali purification of cottonseed oils, and soapstock were used as objects. The composition of the soapstock was as follows: mass fraction of total oil 8-50%, including soap 8-30%, neutral oil 1-20%, water and various non-fatty components, including small amounts of unreacted NaOH, NaCl, dyes, phosphatides, proteins and carbohydrates.

3 Results and discussion

Although soap stock raw material is considered a by-product of refining, the efficiency of subsequent processing processes depends on its quality.

For example, a high content of neutral oil and unreacted alkali increases its consumption before saponification, decomposition and distillation. Soap stock is difficult to transport through very thick pipes, which negatively affects the operation of pump motors.

It is also known that the composition of soap stock largely depends on the concentration of alkali used in the technological process of oil refining. The fatty acid composition of soap stock changes depending on the concentration of the alkali solution, its properties, in particular its structure and viscosity: the higher the content of bound fatty acids and glycerides in soap stock, the higher its viscosity.

The organoleptic properties of soap stock and the mass fraction of moisture in soap stock were determined using standard methods. The physicochemical characteristics of soap stock were as given in Table 1.

Table 1. Organoleptic and physicochemical characteristics of soap stock.

Index	**Soap stock**	**Research method**
Consistency at 20^0 C	Viscous flowing mass	Visually
Color	Yellow to dark brown with a hint of the color of the original oil	Visually
Smell	Characteristic of cottonseed oil soapstock	GOST 30266-2017
Mass fraction of neutral fats, %	6.9-8.1	TS 10-04-02-80-91
Acid number, mg KOH/g, not less than	90.0-190.0	GOST 30266-2017
Colored number, mg iodine, not more than	69.0-97.0	GOST 30266-2017
Mass fraction of moisture and volatile substances, %	4.1	GOST 30623-2018
Mass fraction of total fat, % not less than	69.0-83.1	GOST 5480-59
Mass fraction of fatty acids, %	67.0	GOST 5480-59
Mass fraction of non-fat impurities, %, not more than	1.0	GOST 5479-64
Mass fraction of unsaponifiable substances in soapsock, %	2.3-2.7	GOST 5479-64
Viscosity of soapstock, g/sm^3	0.998	GOST 30266-2017
Mass fraction of water, %, not more than	1.0	GOST 2196-12

To determine the composition of fatty acids, we used gas-liquid chromatography, which allowed us to study the composition of fatty acids in cotton soap stocks in the form of methyl esters. When analyzing fatty acids, the presence of small amounts of fatty acids in the fatty acid mixture can make it difficult to identify small peaks on the chromatogram. Therefore, fatty acid mixtures are analyzed as methyl esters, which have a lower boiling point than fatty acids. The methyl esters of distilled fatty acids and their fractions were obtained by reacting them with diazomethane.

The experimental data obtained for the separation of cotton soapstock fatty acid methyl esters, unsaturated and saturated fractions, by gas-liquid chromatography are presented in Table 2.

Table 2. Individual composition of cotton soapstock.

Name of acids	**Mass fraction of fatty acids, %**		
	Distilled fatty acids of cottonseed soapstock	**Saturated fraction of distilled fatty acids of cotton soapstock**	**Unsaturated fraction of distilled fatty acids of cotton soapstock**
Lauric acid	2.47	2.37	2.21
Myristic acid	1.61	1.09	1.98
Palmitic acid	47.5	69.2	33.7

Continuation of Table 2.

Name of acids	Mass fraction of fatty acids, %		
	Distilled fatty acids of cottonseed soapstock	**Saturated fraction of distilled fatty acids of cotton soapstock**	**Unsaturated fraction of distilled fatty acids of cotton soapstock**
Stearic acid	5.48	6.97	8.81
Oleic acid	35.37	27.51	50.61
Linoleic acid	37.97	48.63	41.68

The composition of soapstock depends primarily on the concentration of the alkali used for fat refining. It has been established that the structure and viscosity of soapstock vary depending on the fatty acid composition of the soapstock and the concentration of the alkali solution. The higher the content of bound fatty acids and glycerides, the higher the viscosity of the soapstock.

Therefore, changes in technology should not create new problems in the processing of soapstock, taking into account the above-mentioned requirements for soapstock.

We conducted a comparative analysis of the composition of soapstock obtained by the traditional (control) and proposed methods. The conditions for their production corresponded to the above-described mixed method of cottonseed oil purification in micelles.

The results of the analysis are presented in Table 3. As can be seen from Table 3, for example, in comparison with the traditional method of cottonseed oil purification, the proposed mixed method transfers lipids from oil to s0oapstock less, which increases the biological value of the purified oil. Conversely, reducing the amount of neutral fat in soapstock increases the yield of purified oil. The increase in the color of soapstock with the mixed method of cottonseed oil purification in micelles can be explained by the formation of polysilicic acids in the form of a gel when using sodium silicate as an alkaline reagent for neutralizing free fatty acids.

The mechanism of this interaction can be explained as follows: - during the neutralization of free fatty acids with a solution of sodium silicate, free silicic acids are released as a by-product, which, due to the presence of reactive silanol groups (SiOH), undergo polycondensation with each other, forming polystyrene acids of various structures in the form of colloidal solutions (gels). Due to the high adsorption activity, such a gel absorbs the maximum amount of coloring substances from oil, which is confirmed by the data presented in Table 3.

Table 3. Comparative indicators of lipid content, neutral fat and color of soapstock obtained by traditional (control) and mixed methods.

Name of the refining method	The composition of the lipid fraction of soapstock, the mass of lipids %						Neutral oil composition,%	Color
	Glycerides	**Fatty acids (soap)**	**Phosphatidides**	**Total gossypol**	**Sterols**	**Tocopherols**		
Traditional method of refining cottonseed oil in miscella (control)	31.7	31.1	13.8	1.7	1.6	0.13	23.7	Light brown
Mixed method of purifying cottonseed oil in miscella	29.7	30.1	7.9	2.1	1.9	0.13	20.9	Dark brown

In the technological schemes of cottonseed oil purification in miscella, the washing process is carried out after the final distillation of the miscella, since the latter leads to the formation of a water-oil mixture that is difficult to separate.

Therefore, the removal of soap residues from purified cottonseed oil is carried out several times with warm water, which also leads to irreversible loss of valuable oil.

To assess the effect of the mixed method of purifying cottonseed oil in miscella on the frequency and composition of washing water, an analysis was carried out in accordance with the requirements of regulatory documents.

At the same time, the washing conditions of purified cottonseed oil obtained by the traditional (control) and mixed methods correspond to the "Instructions on Production and Processing Technology".

Table 4 presents the comparative results of the analysis of rinsing waters and purified oils obtained by the traditional (control) and mixed methods. The table shows that the weight fraction of soap in cottonseed oil purified by the mixed method (using sodium silicate and electromagnetic effect) is significantly lower, which reduces the consumption of washed water and oil loss.

Table 4. Indicators of multiple washings of refined cottonseed oils in micelles using traditional (control) and mixed methods.

Oil flushing frequency	**Refined cottonseed oil indicators**	
	Mass fraction of soap, %	**Mass fraction of unsaponifiable matter, %**
Purification of cottonseed oil using the traditional method in micelles (control)		
One-time	0.16	0.59
Double	0.9	0.47
Triple	not	0.31
Purification of cottonseed oil in micelles using a mixed method		
One-time	0.02	0.35
Double	not	0.28

A significant decrease in the residual soap content in cottonseed oil purified by the mixed method in the miscella can also be explained by the presence of a gel of polysilicic acids, which, by absorbing a significant part of the soap, passes from the oil into the soapstock.

Thus, the use of a mixed method of purifying cottonseed oil in the miscella allows not only to increase the yield of oil, but also to reduce the frequency of its washing by 1-2 times (depending on the quality of the original oil).

4 Conclusion

Here, it should be noted that when using sodium silicate, the intensity of emulsification of neutral oil into soapstock and the formation of stable emulsions are significantly reduced compared to using NaOH.

Experience has shown that when using sodium silicate, large soapstock flakes are formed, which intensively separate (precipitate) the purified oil, compared to using traditional sodium hydroxide.

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