INFLUENCE OF AN ELECTROLYTE SOLUTION ON THE SEPARATION OF THE AQUEOUS PHASE FROM SOAPSTOCK-DERIVED SAPONIFIED MASS

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Abstract. *The three-stage technology for the production of fatty acids from a 50/50 mixture of cottonseed and sunflower soapstocks has been developed. The primary objective of the study presented in this article is to determine the optimal concentration, quantity, and duration of washing with an electrolyte—specifically, a sodium chloride solution—required for the effective separation of the aqueous and oily phases of the carbonate-saponified mass subsequently treated with a caustic soda solution.The research findings demonstrate that, for efficient separation of the soapstock mass from the aqueous phase, washing with a 20% sodium chloride solution at 50% of the total mass after both processing stages significantly enhances the intensity of accompanying substance removal, compared to the theoretically calculated electrolyte concentration of 5.83%.*
Keywords: *fatty acids, hydrolysis, saponification, soap, electrolyte.*

Introduction

In our previous research, we developed a technology for separating crude fatty acids through a three-stage processing of cottonseed and sunflower soap sludge. In this technology, a 50/50 mixture of cottonseed and sunflower soap sludge was prepared and, in the first stage, saponified with a 35% aqueous solution of soda ash at 90-95°C for 60 minutes.

During carbonate saponification (using soda ash), the triglycerides in the soap sludge are not completely saponified, and the saponification degree reaches 80%. The saponified mass was washed at this temperature with an intermediate product formed in the process—acidic soaps—a 20% concentrated solution of table salt (NaCl) with electrolyte properties, using up to 50% of the saponified mass. The aqueous phase was then allowed to settle for 1-4 hours. During leaching, the salt electrolyte transfers dyes, phospholipids, fatty acid degradation products, and various water-soluble gossypol compounds contained in the soap into the brine. After leaching, the aqueous phase, containing glycerin, associated substances, soda ash, carbonic acid, and table salt, is drained from the bottom of the reactor.

In the second stage, the primary saponified mass is completely saponified with a 42% caustic soda solution at 90-95°C for 180 minutes, then washed with a 20% sodium chloride solution (50% of the soap mass) and poured into the leaching aqueous phase. After leaching and settling for 4 hours, the alkaline soap solution is separated and fed to an acid digestion tank. The resulting alkaline soap solution is sent to separate the glycerin along with the water formed in the first stage, or to neutralize the water formed during acid digestion.

The yield of fatty acids obtained from processing the soap sludge from our own production and from industrial processing was 97.0% and 90.9%, respectively. The resulting oil phase contained 2.9% and 5.7% additives for each sample, respectively.

The subsequent studies examined the effect of the amount and concentration of the sodium chloride solution used in the carbonation and complete saponification processes on the physicochemical properties of the resulting oil and aqueous phases.

Literature Review

It can be seen that during the alkaline refining of vegetable oils, in addition to the neutralization of fatty acids to form soap salts, the presence of numerous oil-soluble by-products and the surface activity of the soap precipitate, due to its adsorption properties, results in the transfer of most of the oil-insoluble and unsaponifiable substances, as well as some of the neutral oil, to the precipitate. Specifically, during cottonseed oil refining, unlike other soap masses, a dark mass with a high content of non-fatty substances containing gossypol and its derivatives is separated [1]. While light-colored soap masses (soybean, safflower, rapeseed, etc.) are used in soap production, the fatty acids are separated from the cottonseed oil [2, 3]. The color of soap masses depends on the content of coloring agents and other accompanying substances in the refined oil and can vary greatly. In any case, the composition of soap masses can be divided into two groups: fatty substances – neutral oils in the form of mono-, di-, and triglycerides, fatty acid salts, free fatty acids, and waxy substances; and non-fatty substances – water-soluble organic acids and their salts, pigments, metal compounds, hydrocarbons, alcohols, ketones, and a number of other compounds.

The diverse and complex nature of the substances contained in the soap residue causes it to undergo rapid changes during storage and processing. Its fats and phospholipids are partially hydrolyzed during storage. Phospholipids also decompose under the influence of acids [4, 5]. The presence of polar and non-polar hydrocarbon radicals in phospholipids gives them strong emulsifying properties [6, 7]. During the decomposition of the soap residue, they remain in the emulsion layer between the oil and water phases, which slows the process. A method for the stepwise acidic decomposition of the fully saponified mass with the formation of acidic soaps has been proposed. In this case, the acidic soaps were salted using sodium sulfate formed during the acidic decomposition. The first stage was carried out at a pH of 4-5. As a result of salting, water-soluble acids (WSA) and their salts were formed, which precipitated. Complete decomposition was carried out at a pH of 1.5-3.0. Timely removal of the VRC accelerates the process and reduces sulfuric acid consumption by up to 4%.

Research Methods

Determination of the Color Index of Fatty Acids. The color index was determined using a Lovibond apparatus in accordance with ISO 15305:1998 [8]. This method is based on determining the color of oil or fatty acid mixtures in a single-layer mode, i.e., in cuvettes with a volume of 133.35 mm³ for light oils and 25.4 mm³ for dark oils. This method is used to determine the color of refined and unrefined cottonseed oil. This instrument makes color determination very simple: the sample cuvette size (25.4 or 133.35 mm³) is entered into the instrument's program, the "read" button is pressed, and within 15-20 seconds, three oil color values (red, yellow, and blue) are displayed on the instrument screen.

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Both halves of the field of view must be illuminated equally. This is achieved by correctly positioning the instrument in front of the illuminator.

The oil color is expressed in red units on the Kline scale, indicating the thickness of the cuvette and the number or sum of the numbers of yellow filters. For determining the color, the arithmetic mean of 3-5 measurements is taken. The difference between two parallel measurements should not exceed 1 unit in the range of 2-18 units. Determination of acid number by the salt method. The acid number of the soap solutions and fatty acids used was determined in accordance with ISO 660:2020 [9]. Equipment, reagents, and materials: Class 4 laboratory balance; 100 or 200 cm³ cylindrical special glass container; 25 cm³ burette with 0.1 cm³ divisions; 0.25 N or 0.1 N aqueous or alcoholic potassium hydroxide solution; 35-36% sodium chloride solution; Phenolphthalein.

It is acknowledged that place 20 g of soap solution in a 250 ml conical flask with a stopper. Add 50-60 ml of 15% neutral sodium chloride solution and 0.5 ml of phenolphthalein to the flask. Stopper the flask and shake it, then titrate with a 0.1 N mineral solution (for high acid numbers, a 0.25 N mineral solution can be used). During the titration, shake the liquid after each addition of 4-5 drops of alkali until the lower layer disappears in color. If the color gradually disappears after the next shaking, shake the flask after each addition of 1-2 drops of alkali. Continue titration until a transparent pink color appears in the lower layer of the liquid. The acid number is determined using the following formula (1):

$$Ks = \frac{5{,}611 \cdot a \cdot K}{m} \qquad (1)$$

Here: K_S 5.611 is the titration indicator for a 0.1 N neutral alkali solution, expressed in mg KOH; a is the volume of the 0.1 N solution used for titration, ml; m is the mass of the test sample, g; K is the titration correction.

When determining the amount of organic acid salts in the soap residue and fatty acids, compounds that react with sulfuric acid in the soap residue were taken into account: low-molecular and oxidized acid additives, amino compounds, derivatives of glycerophosphoric acid and gossypol, as well as other saponified substances. The analyses were carried out by potentiometric titration in an alcohol medium. A 0.5-1.0 g sample of soap residue was taken for the study and dissolved in alcohol. A 0.1 mol/dm³ alcohol solution of hydrochloric acid was used for titration. Based on the titration results, potentiometric titration curves were plotted to determine the equivalent volume of titrating agent. The amount of organic acid salts was determined using the following formula:

$$M_{ork.k.t} = \frac{C_{HCl} \cdot V_{HCl}}{m} \qquad (2)$$

Here: $M_{Org.k.t}$ – is the total content of organic acid salts, mol eq/kg; C_{HCl} is the concentration of the alcoholic HCl solution, mol/dm³; V_{HCl} is the volume corresponding to the equivalence point of the HCl solution, cm³; M is the mass of the extract, g.

The determination of the amount of soap and associated salts is based on the extraction of fatty acids from fully saponified soap residue with an organic solvent [30]. For this purpose, 5-10 g of fully saponified soap residue was taken at a temperature of 80-90°C and decomposed with sulfuric acid in a methyl orange medium with stirring. The separated fatty acids were extracted with petroleum ether, and the precipitate was separated by settling the mass. After removing the ether from the extract, it was dried and its mass was determined. The soap content was determined using three formulas:

$$M_{Soap} = \frac{1000 \cdot m_2}{m_1 \cdot M_e} \quad (3)$$

Here: M_{Soap} – soap content in the soap solution, mol eq/kg; m1 – mass of the solution, g; m2 – mass of the dry extract, g; Me – mass of fatty acids in the soap solution, averaging 280 g/mol eq.

The amount of salt impurities was determined using four formulas:

$$M_{if.miq} = M_{org.k.t} - M_{sovun} \quad (4)$$

Here: $M_{if.miq.}$ - amount of salt compounds, mol·eq/kg soapstock; MOrg.k.t – total content of salts of organic acids, mol·eq/kg; M_{Sovun} – soap content in soapstock, mol·eq/kg.

Results and Discussion

When washing saponified soap solution with an electrolyte solution of table salt, its concentration and quantity significantly affect the color of the resulting product and the additive content, as well as the consumption of the reagent used. The concentration of the electrolyte solution directly depends on the free separation of the saponified mass and alkaline water from the saponified mass, and the concentration that determines the complete separation of the oil phase from the aqueous phase is called the limiting concentration (Ch_k) [10]. This concentration was determined for individual fatty acids, and in our experiments, we determined it by calculating the concentration required to wash the saponified mass of cotton and sunflower soap solution in a 50/50 ratio in salt water. We used the following formula [10]:

$$Ch_k = \sum C_i \cdot K_i/100$$

Where: C_i – is the percentage of fatty acid relative to the total amount, and Ki is the limiting concentration for an individual fatty acid.

Since the limiting concentration is calculated relative to sodium hydroxide, when selecting different electrolytes, their amounts are determined based on their transfer coefficient relative to sodium hydroxide. The transfer coefficient for table salt is 1.15. Based on the fatty acid content of individual soap solutions and their mixtures, as well as the limiting concentrations, the calculated limiting concentration of table salt required to separate alkaline water under soap after saponification of the mixture used in the experiments is given in Table 1.

Table 1. Limiting concentration of table salt solution required to separate alkaline water under soap from a mixture of soap solutions

Type of fatty acids	Fatty acid content in soapstock, %			limit concentration, %	
	cotton	sunflower	mixed acids	counting to NaOH	counting to NaCl
Total fatty acids	50	50	100	5,07	5,83
Saturated fatty acids:	30	11	20,5	4,53	5,21
Stearin	2	4,5	3,25	2,9	3,34
Palmitin	25,7	6,2	15,95	4,6	5,29
Myristin	1,1	0	0,55	7,7	8,86
Araxin	1,2	0,3	0,75	7,9	9,09
Unsaturated fatty acids:	70	89	79,5	5,21	5,99
Olein	22,2	51,2	36,7	4,2	4,83

Palmitolein	2,5	0,2	1,35	3,9	4,49
Linoleum	41,9	33,3	37,6	6,6	7,59
Linolenic acid	0,14	0,3	0,22	8,3	9,55
Others	3,26	4	3,63	4,6	5,29

As can be seen from Table 1, in a 50/50 cottonseed/sunflower blend, unsaturated fatty acids account for 79.5% and saturated fatty acids account for 20.5%. In this case, the maximum concentration for unsaturated fatty acids is 5.99%, for saturated fatty acids 5.99%, and for total fatty acids 5.83%. It is important to note that the maximum concentration required for salting the saponified mass of short-chain fatty acids differs significantly from the maximum concentration of long-chain fatty acids.

The first change we made to the process of extracting fatty acids from soap sludge was to split the complete saponification step into two: in the first step, 50% of the lye in the solution was replaced with a 35% solution of sodium ash. After saponification at 90°C for 60 minutes, the solution was treated with a 20% sodium chloride solution as an electrolyte to separate the oil and water phases and leach water-soluble substances from the oil phase. In laboratory experiments, the amount of solution was added visually, depending on the free separation of the water and oil phases. However, for industrial applications, the concentration and amount of sodium chloride were studied, as it was necessary to determine in practice how much sodium chloride solution should be added during the process relative to the mass of fatty acids in the soap sludge. For this purpose, the optimal concentration of sodium chloride in the solution was analyzed in the studies. During the carbonate saponification of the soap residue, solutions of table salt with concentrations ranging from 5% to 25% were prepared. Upon completion of the process, the temperature was stopped and the mixture was treated with a table salt solution until the oil and water phases were clearly separated. The results are shown in Figure 1.

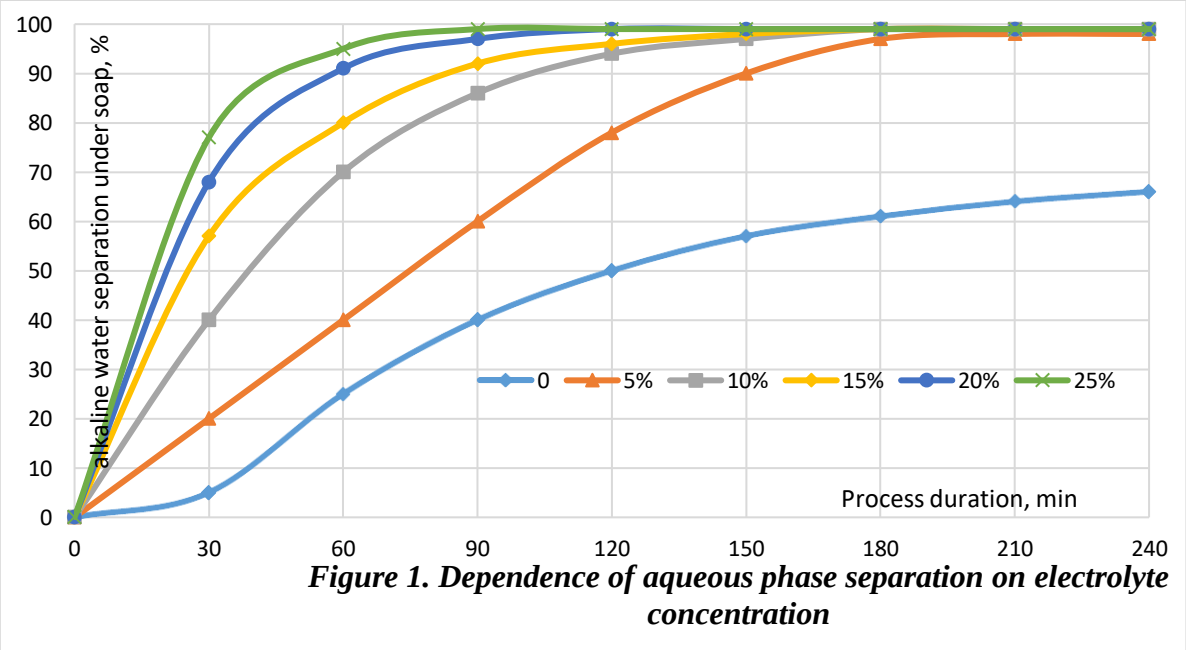


Figure 1. Dependence of aqueous phase separation on electrolyte concentration

As Figure 1 shows, in addition to the weak effect of electrolyte-free water, used as a control during washing of the carbonate soap solution, phase separation occurs very slowly due to emulsion formation. In practice, even after 240 minutes, the oil and aqueous phases do not separate completely.

As soon as the concentration of the sodium chloride solution exceeds 5%, rapid separation of the aqueous phase begins. Specifically, when treated with a 5% sodium chloride solution, 40% of the aqueous phase separates from the soap solution mass in 60 minutes, 78% in 120 minutes, and 96% in 180 minutes. Increasing the solution concentration by the next 10 and 15% accelerates the process and leads to separation of 96-97% of the aqueous phase within 150 minutes. Treatment of the soap mass with a 20-25% sodium chloride solution allows for complete separation of the aqueous phase within 90-120 minutes.

It can be supported from our experiments, separation of the aqueous phase from soap masses treated with 20% and 25% (saturated) sodium chloride solution yielded similar results, it is advisable to use a 20% sodium chloride solution for washing the mixture of cotton and sunflower soap residues after carbonate saponification in the first stage. During the course of our research, we learned that other authors had also reached a similar conclusion [11].

Therefore, there is a difference between the threshold concentration sufficient for separating alkaline water from the soap residue and the actual optimal amounts. It can be concluded that the main reason for this is related to the emulsifying properties of the accompanying substances in the soap mass. It is known that soap residue primarily contains three types of compounds:

1. Compounds that react with alkali to form soap. This type includes phosphatides (lecithin, cephalin, phosphatidic acid), oxidized fatty acids, and some gossypol derivatives. During cottonseed oil refining, almost all phosphorus-containing compounds are transferred to the soap residue. Since sunflower oil is first hydrated, their content in the soap residue is low. Phosphorus-containing substances have strong emulsifying properties, as they capture both polar and non-polar hydrocarbon radicals. As a result, they hinder aqueous phase separation. Depending on storage time and pre-processing conditions, the soap residue contains up to 1-10% oxidized fatty acids (hydroxy acids) [12]. Hydroxy acids are formed by the oxidation of unsaturated fatty acids and have a negative impact on the color of the separated fatty acids and phase separation.

2. Compounds that do not react with alkali, i.e., do not saponify. These compounds include ketones, aldehydes, tocopherols, some water-insoluble derivatives of gossypol, and aliphatic alcohols.

3. Pigments. Cottonseed oil contains significant amounts of gossypol, while sunflower oil contains chlorophylls and carotenoids. During the gossypol refining process, sodium combines with sodium, forming sodium gossypolate. However, this compound is unstable, and gossypol can easily be replaced by oxygen and combine with phosphatides, proteins, and their hydrolyzed derivatives, forming gossyproteins and gossyphosphatides.

The results obtained by adding a 20% solution of table salt to the soap mixture at a rate of 10-70% are presented in Table 2.

Table 2. Effect of electrolyte amount on phase separation of the saponified carbonate mass

Amount of solution, %	Cooling period, min				
	0	60	120	180	240
0	a	a	a	b	B
10	a	a	a	b	B
20	a	a	b	b	B
30	a	b	b	e	E
40	a	e	e	e	E

50	a	e	e	e	E
60	a	e	e	e	E
70	a	e	e	e	E

As can be seen from table 2, when the soap mass was allowed to settle for 4 hours (240 min) without adding electrolyte, the aqueous phase did not separate clearly. Similar results were obtained when treating the soap mass with a 10-20% solution of table salt. When adding more than 30% of the required process, a clear separation of alkaline water from the soap occurred within 60-240 min. Clear separation of the aqueous phase, a minimum amount of water remaining in the soap phase, and the best results in terms of color were obtained using a 30% solution in the range of 180-240 min, a 40% solution in the range of 60-180 min, and a 50% solution in the range of 60-120 min. Subsequent treatment of the soap mass with a 60-70% electrolyte solution also led to similar results. Based on this, a conclusion was drawn on the advisability of washing the carbonate soap mass with an electrolyte solution with a concentration of up to 50%.

According to our proposed method, the washed (salted) mass, containing 50% carbonate soap mass and 20% concentrated sodium chloride solution relative to the soap mass, is completely saponified in a second step with a 42% caustic soda solution at 90°C for 180 minutes.

In conventional technology, the fully saponified mass is treated with a sodium chloride solution and then held for 4 hours. However, in our process, it is necessary to accelerate the separation of the soap and water phases, as well as the saponification process itself. Furthermore, by washing the saponified carbonate mass with an optimal (50%) amount of salt solution, most of the associated substances are transferred to the alkaline water of the soap base and removed, after which caustic saponification occurs. A sharp reduction in the content of directly emulsifying, water-insoluble, and unsaponifiable substances in the soap mass reduces the consumption of caustic soda and electrolyte for separating soapy water before complete soap formation, or, accordingly, increases its efficiency.

For testing our assumptions in practice, in the second stage, we studied the optimal amount and duration of the process by washing the caustic soap mass with a solution of 10-70% by weight, based on a predetermined 20% concentration of table salt. The results obtained in the experimental studies are presented in Figure 2.

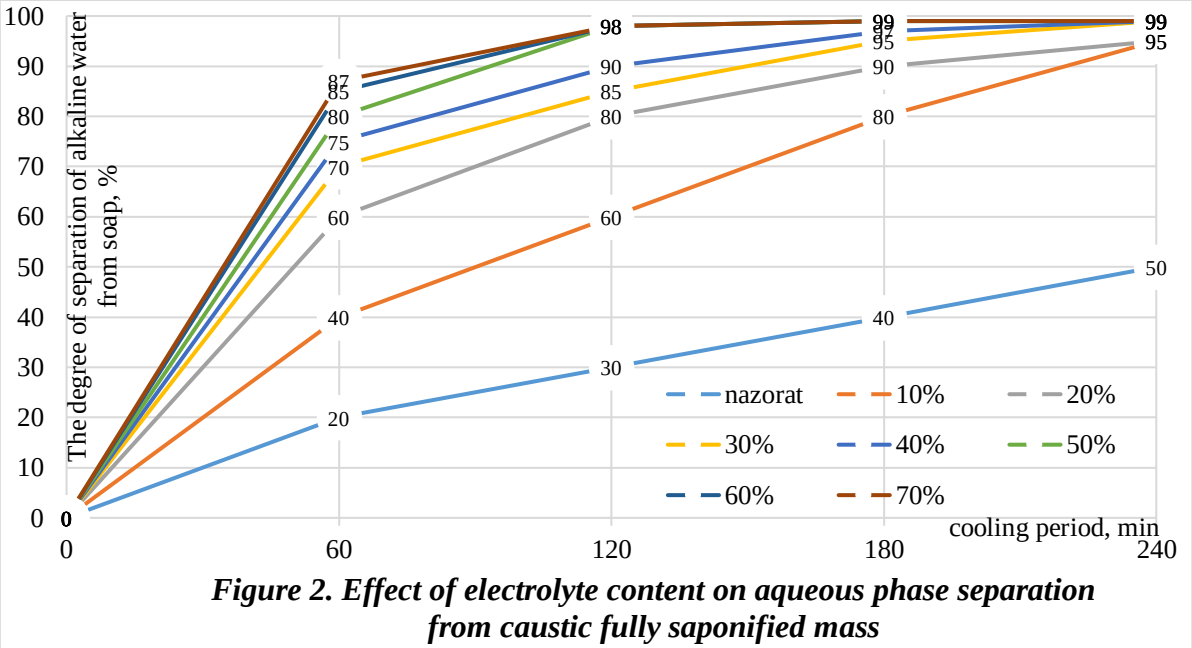


Figure 2. Effect of electrolyte content on aqueous phase separation from caustic fully saponified mass

As can be seen, the separation of the aqueous phase from the carbonate saponified mass using a salt electrolyte accelerates the caustic complete saponification process and the subsequent separation of the aqueous phase, due to the fact that most of the accompanying substances are removed in the previous stage. As can be seen from Figure 2, in the industrial method (control), the process of washing the completely saponified mass with caustic soda in one stage with a salt solution and settling it, due to the large number of accompanying substances in its composition, including emulsifiers that prevent phase separation, the settling decreases by 50% within 4 hours (240 min). The process takes 6-8 hours to complete. Two-stage saponification and washing the soap mass with salt water at each stage facilitates the separation of accompanying substances from the completely saponified mass. In particular, the use of salt water in the amount of 10-50% relative to the saponified mass accelerates the sedimentation process, leading to the separation of 40% to 98% of the aqueous phase within 60-120 min. Subsequent salting with a solution of 60-70% does not significantly affect the process speed. Therefore, it is advisable to wash the caustic finished saponified mass in the second stage using 50% of a 20% solution of table salt. Thus, the composition of the saponified mass obtained as a result of two-stage complete saponification is given in Table 3.

Table 3. Indicators of two-stage complete saponified mass

Samples	Color	Saponified fatty acids, %	Triglycerides, %	Gossypol and its derivatives, %	Phospholipids, %	Others, %
A blend of cotton and sunflower soapstone						
Experience -3*	dark brown	27,8	18,85	4,53	13,4	2,45
Experience -4**	light brown	35,85	19,1	0,92	2,2	2,25
After washing with carbonated soap and salt water						
Experience -3	light brown	40,2	5,75	0,96	2,9	0,83
Experience -4	light brown	47,07	7,1	0,14	1,2	0,67
After washing the caustic soaped mass in salt water						
Experience -3	Yellowish brown	45,33	0,31	0,36	0,98	0,79
Experience -4	Dark yellow color	53,27	0,43	0,11	0,65	0,57

*-50/50 blend of cotton/sunflower soapsacks obtained from emulsion-refined oil;

**-50/50 blend of cotton/sunflower soapsacks obtained from emulsion-refined oil treated with MEA.

As shown in table 3, after the second stage of complete saponification with alkali, the saponification rate of the soap residue relative to the total fat fraction was 45.33 (94.9%) in Experiment 3 samples and 53.27 (95.8%) in Experiment 4 samples, while the unsaponifiable triglyceride content was 0.31% and 0.43%, respectively. It is also evident that the amount of gossypol derivatives, phospholipids, and other substances, including color additives, in the oil

phase significantly decreased after the first and second stages of saponification and washing with an electrolyte solution.

Conclusion

In the 50/50 cottonseed/sunflower soap residue mixture, the unsaturated fatty acid content was 79.5%, and the saturated fatty acid content was 20.5%. In this case, the maximum concentration for unsaturated fatty acids is 5.99%, for saturated fatty acids 5.99%, and for the total concentration 5.83%. However, in practice, this value is significantly higher. It is important to note that the maximum concentration required to salt the saponified mass of short-chain fatty acids differs significantly from the maximum concentration of long-chain fatty acids.

By washing the saponified carbonate mass with a 35% solution of soda ash and an optimal amount of 50% of a 20% concentrated salt solution, the majority of the associated substances are transferred to the alkaline water of the soap base in the first stage and removed. The resulting mass is then completely saponified with a 42% caustic soda solution at 90°C for 180 minutes, and then washed with another 50% of a 20% concentrated salt solution at the end of the second stage. This significantly reduces the amount of gossypol, phospholipids, and other additives, including coloring agents, in the oil phase.

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