PHYSICAL AND CHEMICAL PROPERTIES OF THE PROCESS OF SAPONIFICATION OF COTTON SOAPSTOCK UNDER ULTRASONIC INFLUENCE

Shamuratov Sanjarbek Khusinbay ugli
Ph.D. student, Urgench State University
Baltaev Umid Satimbaevich
Associate professor, Tashkent Institute of Chemical Technology
Sagdullaeva Dilafruz Saidakbarovna
Leading scientist, Institute of Bioorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan
Kuramboev Bekhzod Farkhodovich
Assistant, Urgench State University

ABSTRACT

The article shows the possibility of assessing the transportability of soapstock, saponified by various methods - classical and ultrasonic. It was found that after ultrasonic treatment, the density and viscosity of the soapstock significantly decreased compared to the classical method of processing branch waste from edible oil industry. At the same time, the foaming capacity of the soapstock increased with an increase in the saponification temperature after the initial and 5 minute soak. In a 5 minute settling, the foaming ability of the soapstock turned out to be lower than its initial settling.

The foam ratio of the soapstock, saponified by the ultrasonic method, is relatively from 1.5 to 2.5 times less than by the classical method of soapstock saponification. Indicators of rheological properties of saponified soapstock proved the acceptability of pumping soapstock from one apparatus to another. Whereas, the foaming properties and the foam ratio indicate premature foam control in the production of soap, as well as the properties of the resulting detergent based on the basic solution - saponified soapstock.

Key words: *soapstock, ultrasonic method, density, viscosity, foaming properties.*

INTRODUCTION

The problem of rational processing of fat waste from the oil and fat industry in order to obtain competitive products is relevant today. Depending on the type of oilseeds (soybean, canula, palm, sunflower, etc.), soapstock is about 5-9% of the total crude oil and is used for the production of fatty acids, animal feed and soap products

for synthetic detergents. Although soapstock is a secondary resource for the production of the necessary crude fatty acids from it, the issue of disposal does not always have its potential. Difficult to process among the waste products of the oil and fat industry is cotton soapstock due to its complex colloidal system.

Analysis of the results of studies of soapstock from cottonseed, carried out by gas chromatography-mass spectroscopy (GC-MS), showed that the soapstock mainly consists of moisture and solvent (about 49%), fatty acids (about 60% in terms of dry weight), organic phosphates, monoglycerides, diglycerides, triglycerides, sterols, waxes and waxy substances as well as unsaponifiables such as polyhydric alcohols, carbohydrates, sterols, tocofelores,. In addition, it has been proven that gossypol (a polyphenolic compound) is contained in cottonseed soap stock in an amount of 7.5% [1-4].

Existing methods of processing this fatty waste using catalysts, turbulent mode using live steam with a pressure of more than 3 atm, or other technical solutions do not allow to achieve the expected results. This can be attributed by the presence of undesirable saponifiable substances such as gossypolic acid, phospholipids, etc., which are ballast (NaOH, KOH).

The Republic has its own oil and fat industry, which processes 1.4 million tons of cotton seeds to produce 0.25 million refined oil and 25 thousand tons of soap stock. The classical technology of cotton soapstock saponification, including circulating mixing with pumps under the violent turbulent effect of steam, needs serious improvement. Until now, on the basis of such a method, a duration of about 4-6 hours is required, which is not effective from the point of view of overspending both material and energy resources. The output of the final product, soap glue, does not exceed 90%.

Due to the fact that the saponification process proceeds through heterogeneous reactions, foaming is observed. This phenomenon occurs due to the formation of strong films of soaps and surfactants over the soap stock, the results of which are the proper mixing of free fatty acids, phosphatides, color pigments, as well as the desertification of triglyceride with alkalis. In this case, the rheological and foaming properties of saponification products play a key role.

Scientific and technical literature provides the results of studies of the rheological properties of triglyceride and soap stock.

In [5], the rheological properties of two complex mixtures of short-chain triglycerides were experimentally determined. The dynamic or absolute viscosity of the mixtures was measured at a shear rate of 0.32 to 64.69 s^{-1} at a temperature of 25 to 80°C. The compositions of the mixtures were based on the oil of the plant species Cuphea viscosissima VS-320, a natural source of short-chain triglycerides.

In [6], the rheological properties of confectionery fat (shortening) with similar physicochemical characteristics, but different functionality at small and large vibrational shifts were studied. Particular attention was paid to the mechanical behavior of shortening, characterized by resistance to softening during operation and the formation of continuous thin fat films during rolling and rolling of the dough. All confectionery fats had a weak frequency dependence and comparable G' values from 0.6 to 4.5·106 Pa, resembling viscoelastic solids (G' > G").

Valishevsky et al. neutralized the soapstock mixture with acid and reduced the viscosity by adding ethanol before GC analysis [7, 8].

Studies have been carried out to obtain thickeners, which are a soap and non-soap component that holds together liquid lubricants and additives. Soap thickeners mainly consisted of lithium, calcium, sodium, aluminum or barium fatty acid soaps obtained from cotton soap stock. The chemical structure, viscosity and rheological properties of greases have a direct impact on their performance [9].

It was found that the viscosity of sodium soap based on saponified cotton soapstock decreases with increasing temperature 25, 45 and 85°C 21.5; 16.2 and 10 Pa·s, respectively [9-11].

As for the issue of soapstock transportation, the paper [12] studied the rheological property of a by-product of vegetable oil refining and neutralization (soapstock), a product of potential economic interest, but currently underestimated. According to the authors of the work, it is possible to increase the economic value of soapstock by increasing its fat content, since the selling price of soapstock depends on its fat content. A high fat content results in a higher viscosity, making it difficult to transport. It has been established that the soapstock has a complex rheology: at 20% fat it behaves like a pseudo plastic, and at more than 30% fat it behaves like a Bingham plastic. Thus, it is necessary to dilute the soapstock with water, which reduces its viscosity (and fat content) and facilitates transportation. The information given in the literature indicates the insufficiency of studying the foaming and rheological properties of cotton soapstock as an intermediate in order to obtain soap, crude fatty acids, esters, biofuels, detergents, etc. on its basis.

METHODS

The object for the study was the cotton seed soapstock of JSC "Urganch yog'-moy" (Khorezm, Uzbekistan) composition (wt.%): neutral fat 9.9; total fat 35.1 moisture and volatile substances 55.

Sodium hydroxide of 99% purity was used as an alkaline reagent, which was purchased from JSC :Fortek"-PE (Uzbekistan).

The studied soapstock was diluted with water with a hardness of 7 mmol equiv/l at a ratio of soapstock : H_2O = 1 : 1.

The density of soapstock samples was determined by the pycnometric method and its value was calculated by the formula:

$$\rho = \frac{m}{V} \quad (1)$$

where m – mass of soapstock pulp, g; V– pycnometer capacity, cm^3. The measurement accuracy is ± 0,05%.

Since cotton seed soapstock has a complex colloidal system and does not obey Newton's law [13]. In this study, in contrast to [9-11], where the kinematic viscosity was determined, the dynamic viscosity of the soapstock was studied. To determine the viscosity, a rotational viscometer HAAKE Viscotester 1 plus (Germany) was used. When measuring viscosity, the HAAKE Viscotester 1 plus is switched off when the button is pressed for 3 seconds. The operating hours are then displayed for 3 seconds and the last measuring range is saved. The measurement accuracy is ±3.

Prior to determining the rheology, soapstock samples were subjected to saponification by the classical method using a 42% sodium hydroxide solution at 95°C for 120 min without the use of any additional catalysts or technical approaches.

In the second case, soapstock samples were saponified with 42% sodium hydroxide solution at 95°C for 120 min under sonication using a surface Cavitator Ultrasonic Cleaner (USC-3L, China) at Power: 220 VAC/20 Hz.

Soapstock saponified by classical and ultrasonic methods were conventionally designated as SP-C and SP-U, and the original raw (crude) soapstock - SP.

Due to the fact that soap stock usually contains sodium soap and other surfactants, the foaming property of raw and saponified soapstock was studied by the method of D. Ross and G. Miles [14].

This method is based on whipping the foam with a freely falling jet of solution. In this case, it is necessary to determine the initial foam height H_o and the foam height after 5 minutes H_5. After that, the stability of the foam can be judged by the ratio H_0 /H_5.

The expansion ratio (S_f) of saponified soapstock foam was determined by classical and ultrasonic methods. The foam ratio is a dimensionless value representing the ratio of the foam volume to the total volume of the solution, liquid, etc.

The foam expansion rate was calculated using the formula [15]:

$$S_f = \frac{V_f}{V_1} \quad (2)$$

where V_f is the volume of foam, cm^3, V_1 is the total volume of the foam concentrate solution.

This value, which characterizes the foaming process, is described using the dependence of the equation between the initial volume of foamy liquid V_0 and the volume of liquid by time τ, or express the volume of liquid flowing from it per unit

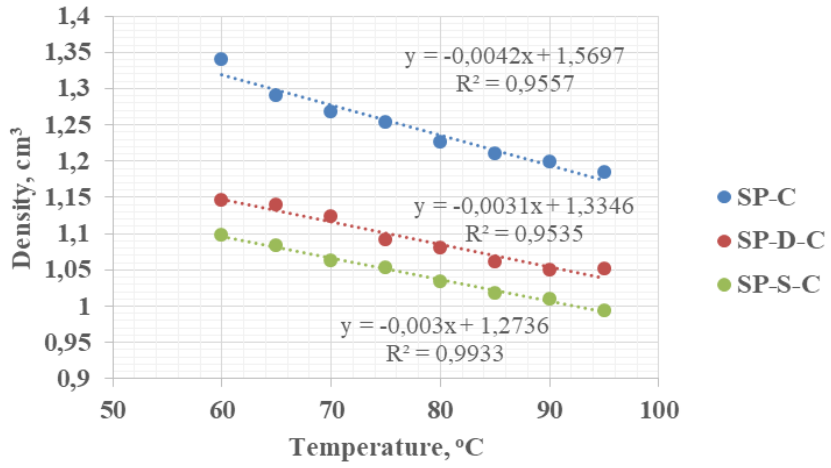
time *(dV/dτ)* [16-18]. In our case, taking into account the foaming ability of soapstock saponification under various conditions, we take the time of 0 and 5 minutes.

RESULTS

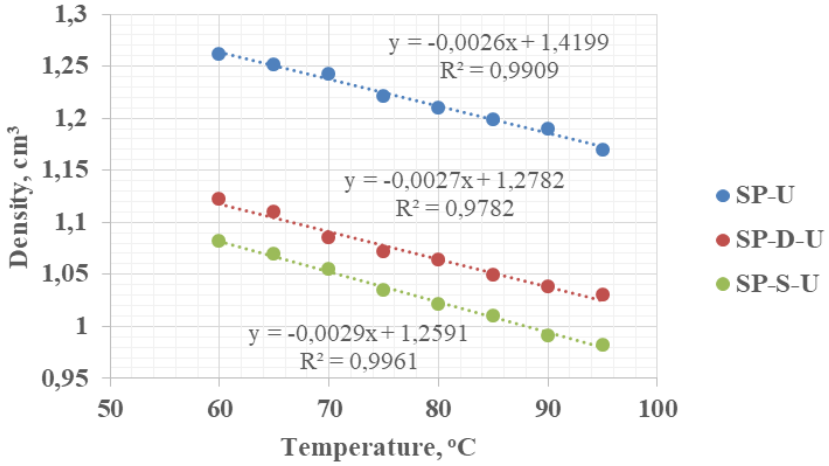
Figures 1 and 2 show graphical representations of the dependence of the change in density and viscosity of raw soapstock and its saponified form, obtained by classical and ultrasonic methods. They have a mathematical straight-line and power dependence, as well as a correlation coefficient, R^2, which varies in the range of 0.95-0.99. Processed by Excel 2019. As can be seen from the figures, raw soapstock under normal conditions has relatively high density and viscosity values compared to raw soapstock under the influence of ultrasound. So if under normal conditions in a raw soapstock the density with an increase in temperature from 60 to 95 °C has a density of 1.3402 to 1.1840 g/cm^3, then the density of the soapstock after ultrasonic treatment at the studied temperatures is in the order of 1.2611 to 1.1692 g/cm^3. In this case, it can be noted that the density of the soap stock under ultrasound is 1.06 and 1.01 times less than the density of the soapstock under normal conditions. A similar pattern is observed in the case of studying the density of the soapstock diluted with water, both under normal and under ultrasonic conditions. It shows that the density of raw and diluted soapstock under normal and ultrasonic conditions is, respectively, from 1.1452 to 1.0514 and from 1.1224 to 1.0303 g/cm^3 under the studied conditions. This means that the density of the soapstock under ultrasonic action is, on average, 1.02 times less than the density of the soap stock studied under normal conditions. In addition, the density of the dilute soapstock compared to the crude undiluted one decreases on average from 1.17 to 1.13 and from 1.12 to 1.13 times, respectively, under normal and ultrasonic conditions.

As for the study of the density of these soapstocks after their saponification by classical and ultrasonic methods, one can see a significant difference between them. For example, the density of the soapstock after saponification by classical and ultrasonic methods decreases from 1.0971 to 0.9931 and from 1.0822 to 0.9821 g/cm^3 with an increase in temperature from 60 to 95 °C, respectively. At the same time, it can be seen that the density of the soapstock saponified by the ultrasonic method is, on average, 1.01 times less than by the classical method.

An important value of viscosity also plays an important role in assessing the rheological properties of the soapstock in various types of its processing. An increase in temperature from 60 to 95 °C helps to reduce the viscosity of the soapstock from 1.94 to 1.25; from 1.29 to 1.12 and from 1.25 to 1.14 m Pa·s and from 1.82 to 1.17; from 1.28 to 1.10 and from 1.24 to 1.01 mPa·s, respectively, in the case of normal and ultrasonic saponification conditions (Fig. 2).

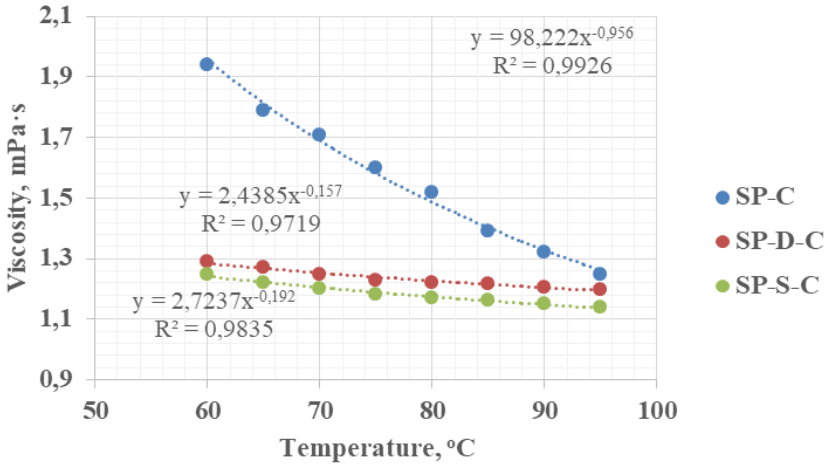


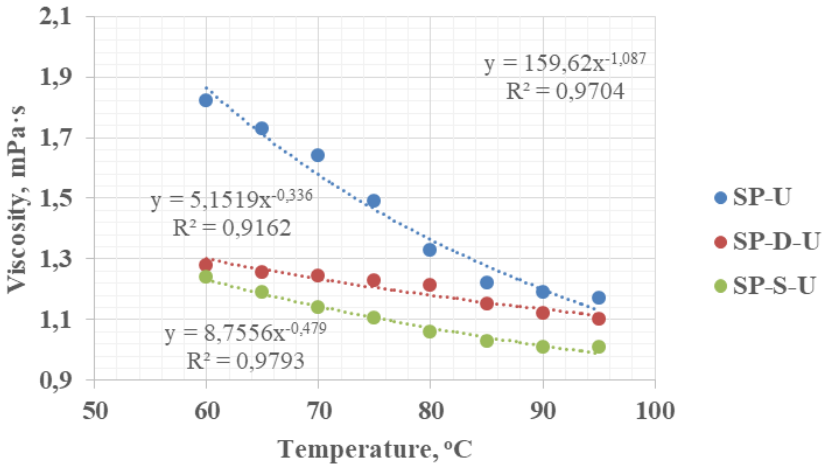
a)



b)

Figure 1. The dependence of the change in the density of raw, (SP-C, SP-U) diluted (SP-D-C, SP-D-U) and saponified (SP-S-C, SP-S-U) soapstock by classical (a) and ultrasonic (b) methods





b)

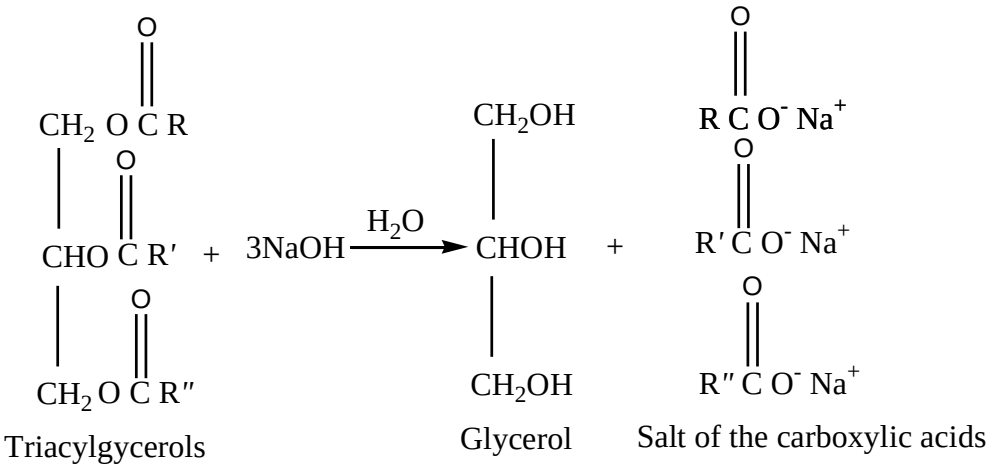
Figure 2. The dependence of the change in the viscosity of raw, (SP-C, SP-U) diluted (SP-D-C, SP-D-U) and saponified (SP-S-C, SP-S-U) soap stock by classical (a) and ultrasonic (b) methods

If we compare the viscosity indicators, we can make sure that the viscosity of the raw, diluted and saponified soapstock by the ultrasonic method is on average 1.06; 1.02 and 1.06 times less compared to soap stock processed by the classical method.

At the same time, a significant difference between the rheological properties of raw and saponified soap stock is attributed by the formation of free water during the saponification process according to the equation:

$$C_3H_5(RCOO)_3 + 3NaOH \rightarrow 3RCOONa + C_3H_5(OH)_3 \quad (3)$$

or



$$RCOOH + NaOH \rightarrow RCOONa + H_2O \quad (4)$$

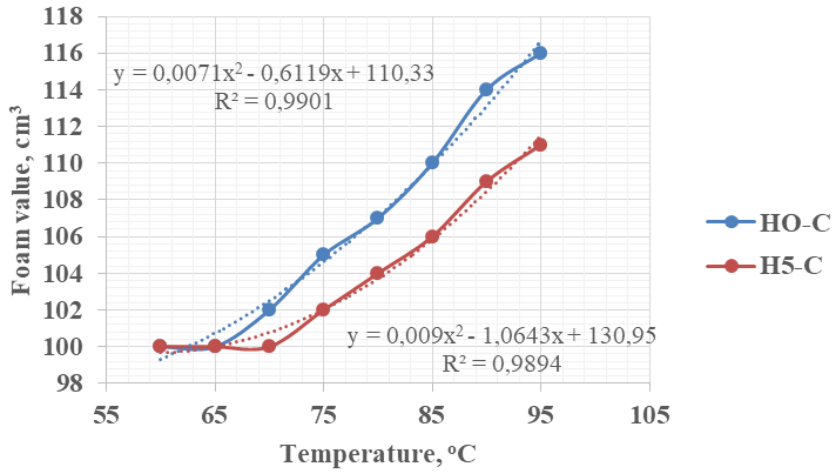
In this case, water dilutes the soapstock, which leads to a decrease in density and viscosity. These indicators are quite suitable for transporting soapstock from one apparatus to another.

Thus, the regularity of the series for the decrease in the indicators of the rheological properties of the soap stock from the data of Fig. 1 was established. 1 and 2 as follows :

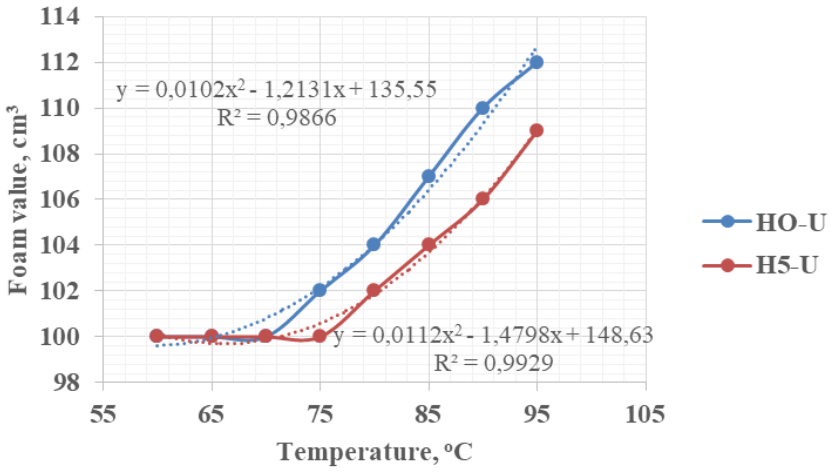
SP-C > SP-D-C > SP-S-C > SP-U > SP-D-U > SP-S-U

Taking into account the fact that ultrasonic impact could destroy the structural and mechanical strength of the cotton soapstock, causing destabilization in general.

The foaming property of cotton seed soapstock in the initial and 5 minutes settling after its saponification by the classical and ultrasonic methods is shown in Figure 3. All the results of the study have a mathematical dependence of the polyminal graphic image and are correlated in the range R^2 = 0.98-0.99.



a)



b)

Figure 3. The dependence of the change in the foaming properties of the soap stock, saponified by classical and ultrasonic methods, after the initial (HO-C) and 5-minute (H5-U) exposure

th

from 70 °C, which is due to the low intermolecular interaction of the constituent substances of various nature in the soapstock.

The foaming ability of the saponified soapstock, as a basis for obtaining detergents, also has sufficient stability due to the presence of viscous high-molecular surfactants in it, which play the role of a stabilizer [19]. In all cases, the results of the study show that the values of the foam volume after 5 minutes of exposure, compared to the initial value, decrease from 105 to 102 at 75 °C and from 116 to 111 cm^3 at 95 °C when the soap stock is saponified by the classical method. Whereas in the case of ultrasonic treatment, the foam volume is relatively low and varies from 102 to 100 and from 112 to 109 cm^3, respectively, at 75 and 95 °C.

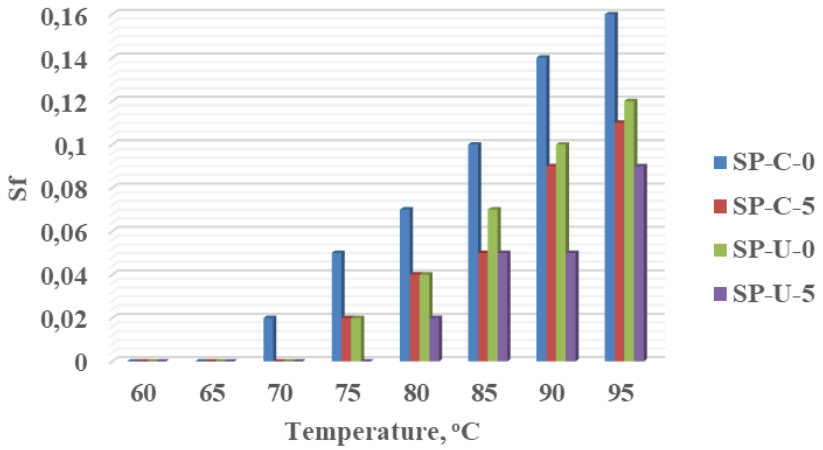


Figure 4. Dependence of the change in the foam ratio (S_f) of the soap stock saponified by classical and ultrasonic methods after the initial (SP-C-0, SP-U-0) and 5-minute (SP-C-5, SP-U-5) exposure on temperature

Comparative results of the study show that under ultrasonic treatment, the volume of foam is reduced by an average of 1.03 times compared to the classical method of soapstock processing.

The indicators of the foaming property served to calculate the foam ratio (equation 2) of the soapstock during its saponification by the studied methods. The results of the calculated data are presented in Figure 4. The data show a trend towards an increase in the foam ratio with an increase in the soapstock saponification temperature. For example, with an increase in temperature from 75 to 95 °C, the foam

expansion ratio increases from 0.05 to 0.16 and from 0.02 to 0.11, respectively, after the initial and 5 minute exposure of the saponified soapstock by the classical method. At the same time, the same picture is observed in the case of an increase in the expansion ratio of the foam of saponified soap stock, saponified by the ultrasonic method, which varies from 0.02 to 0.12 and from 0 to 0.09 with an increase in temperature from 75 to 95 °C. The foam ratio of the saponified soapstock is almost 1.5 to 2.5 times less than that of the saponified soapstock by the classical method, respectively, after the initial and 5 minute exposure.

CONCLUSION

Thus, the dependence of the change in the rheological properties of saponified soapstock by classical and ultrasonic methods on temperature has been studied. It was found that the density and viscosity of the saponified soapstock by the ultrasonic method is from 1.06 to 1.02 times less than in comparison with the classical method. In any case, with an increase in temperature from 60 to 95 °C, the density and viscosity of the soapstock, saponified by two methods, significantly decrease, which is attributed by intermolecular interactions inside the soapstocks.

On the one hand, the indicators of foaming ability and foam ratio increase with increasing temperature, but on the other hand, a 5-minute exposure of the saponified soapstock mass is 1.03 and from 1.5 to 2.5 times less compared to the initial stage.

The rheological properties of the saponified soapstock reveal the availability of their transfer from one apparatus to another. As for the foaming properties and the foam ratio, they give a characteristic of the premature control of the foam in the production ofsoap, as well as the properties of the resulting detergent based on the base solution - saponified soapstock.

REFERENCES

1. Dowd, M. K. (1996). Compositional characterization of cottonseed soapstocks. Journal of the American Oil Chemists' Society, 73, 1287–1295.
2. Dowd, M. K. (1998). Gas chromatographic characterization of soapstocks from vegetable oil refining. Journal of Chromatography A, 816, 185–193.
3. Dowd, M. K., & Pelitire, S. M. (2001). Recovery of gossypol acetic acid from cottonseed soapstock. Industrial Crops and Products, 14, 113–123.
4. Dumont, M.-J., & Narine, S. S. (2007). Soapstock and deodorizer distillates from North American vegetable oils: Review on their characterization, extraction and utilization. Food Research International, 40(8), 957–974. doi:10.1016/j.foodres.2007.06.006
5. D.P. Geller and J.W. Goodrum. Rheology of Vegetable Oil Analogs and Triglycerides. JAOCS, Vol. 77, no. 2 (2000). 111-114.

6. Braulio Macias-Rodriguez & Alejandro G. Marangoni. Rheological characterization of triglyceride shortenings. Rheol Acta (2016) 55:767–779. https://doi 10.1007/s00397-016-0951-6.
7. Waliszewski, K. (1987). Fatty-acid composition of different oils and their soapstocks. Nutrition Reports International, 35, 87–91.
8. K. Barbusinski, S. Fajkis and B. Szelag. Optimization of soapstock splitting process to reduce the concentration of impurities in wastewater. Journal of Cleaner Production 280 (2021) 124459. https://doi.org/10.1016/j.jclepro.2020.124459
9. El-Adly, R. A. (2000). Producing multigrade lubricating greases from animal and vegetable fat by-products. Synthetic Lubrication, 16, 323–332.
10. Adhvaryu, A., Sung, C., & Erhan, S. Z. (2005). Fatty acids and antioxidant effects on grease microstructures. Industrial Crops and Products, 21, 285–291.
11. Delgado, M. A., Valencia, C., Sanchez, M. C., Franco, J. M., & Gallegos,C. (2006). Influence of soap concentration and oil viscosity on the rheology and microstructure of lubricating greases. Industrial & Engineering Chemistry Research, 45, 1902–1910.
12. Ana Filipa Ferreira, Sebastiro Alves, Renato Henriques de Carvalho. Study and transport optimization of a vegetable oil degumming and neutralization byproduct. file:///C:/Users/User/Downloads/Resumo%20Alargado.pdf.
13. Почерников В.И., Ульянов Ю.В., Василинец И.М., Силкина Н.И. и др. Реологические свойства основы хозяйственного мыла. Масложировая промышленность. - 1986. -N7.-С. 18.
14. Руководство по методам исследования, технохимическому контролю и учету производства в масложировой промышленности. Т. 4. /Под ред. В.П.Ржехина и А.Г.Сергеева. - Л.: ВПИИЖ -1963. - 424 с.
15. Г. Г. Лутфуллина, К. С. Гусева, К. Е. Мартынова. Влияние концентрации растворов моющих составов на их пенообразующую способность. Вестник Казанского технологического университета. 2014. С.86-87.
16. Bikerman J.J. Foams.- Appl. Phys. & Eng.-V.lO., N.Y.: Springer -Verl., 1973.- 337 p.
17. Foams. Proc. Symp. 1975 / Akers R.J., eds. L.: Acad. Press, 1976.- 299p.
18. Плетнев М.Ю., Чистяков Б.Е., Власенко И.Г. Современные пенообразующие составы: свойства, области применения и методы испытаний.-М.: ЦНИИТЭНефтехим, 1984.-40с.
19. Нартикоева А.О., Бутина Е.А., Герасименко Е.О., Буханов П.В.Фосфолипидно-гелевосковой соапсток – перспективное сырье для мыловаренного производства / Материалы докл Всерос. научно-практической конф. с межд. участием «Инновационные технологии в создании продуктов питания нового поколения», 1-3 декабря 2005г., г.Краснодар, С. 128-130.