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OBTAINING FATTY ALCOHOLS FROM VEGETABLE RAW MATERIALS AND THEIR USE

Abstract. This work is devoted to the production of fatty alcohols from plant materials, which were used as the initial and used sunflower oil, as well as their esters obtained by esterification / using a catalyst containing compounds Cu-Cr oxide. The highest yield of fatty alcohols was observed when sunflower oil esters were used as raw materials at a temperature of 200 ° C (contact time is 240 minutes) and reaches 79.3%. The main characteristics of fatty alcohols were studied and it was revealed that they can serve as a non-polar part for the production of nonionic surfactants. The synthesis of nonionic surfactants based on glucose and fatty alcohol in a molar ratio of 1:1.5 respectively, in the presence of an acid catalyst- hydrochloric acid. The process proceeds at a temperature of 90-100 °C for 3-4 hours with vigorous stirring, at the end of the reaction, the catalyst is neutralized with alkali to a pH of 9-11. It was revealed that the most favorable reaction temperature is 95 °C, after which increase by 5 °C a rather sharp decrease in the selectivity of the reaction was noted. The best surfactant yield was observed when fatty alcohols obtained by hydrogenation of esters of plant materials were used as raw materials, and amounts to 73%, while the yield of fatty alcohols from esters of used plant materials reaches 62%. The main physicochemical characteristics of the obtained surfactants were investigated, and it was found that the studied alkyl glucosides have a fairly good washing and emulsifying ability.

Keywords: fatty alcohols, hydrogenation, vegetable raw materials, used sunflower oil, plant esters, surfactants, hydrophilic-lipophilic balance, emulsifiers.

Introduction. Fatty alcohols are surfactants widely used as emulsifiers, emollients and thickeners in alimentary and cosmetic industries [1]. Moreover, they can be substrates for the production of other surface-active materials, such as alkylamines and alkylsulfates.

Selective modification of these alcohols could allow to use them as a new resource for producing desired products that are valuable intermediates for the fine chemical, pharmaceutical [2] and agrochemical sectors. For instance, behenic acid ($C_{21}H_{43}COOH$) is used in cosmetics, hair conditioners and creams, due to its high wettability [3], and lignoceric acid ($C_{23}H_{47}COOH$) is used in pharmaceutical [4,5] and health-care preparations [6] and as additives in foods [7].

Fatty alcohols are mainly produced through catalytic hydrogenation of fatty acids, methyl esters or wax esters.

Oils and fats have important applications in the food and pharmaceutical industries[8]. They are composed of triglycerides of even numbered carbon fatty acids [9], which also are starting to be used as low cost renewable resources for the

fatty alcohol production. Another promising source of higher alcohols are fatty acid esters obtained by the esterification of vegetable oils.

Taking into account all the above, it would be of much interest to find a stable and suitable raw materials for the production of fatty alcohols, as well as the best reaction conditions for high product yield.

EXPERIMENTAL PART

Density determination was carried out using a areometer according to GOST 3900. The essence of the method is to immerse the areometer in vegetable oil and take readings on the hydrometer scale.

Viscous studies were carried out according to GOST 33–2000 (ISO3104 - 94). The essence of the method consists in measuring, with a calibrated glass viscometer, the expiration time, in seconds, of a certain volume of the test liquid under the influence of gravity at a constant temperature. Kinematic viscosity is the product of the measured expiration time by a constant viscometer. Dynamic viscosity is equal to the product of kinematic viscosity and oil density.

Tests for determining the acid number of sunflower vegetable oil were carried out according to GOST R 52110-2003 «Vegetable oils. Methods for determining the acid number».

Studies to determine the pour point of organic hydrocarbons were performed according to GOST 20287–91.

The flash point was determined in an open crucible according to GOST 4333-87.

Hydrogenation of vegetable oil and ester of fatty acids was carried out in a column in the presence of hydrogen, obtained in a TRH-300E hydrogen generator. To obtain fatty alcohols, a hydrogenation reaction was carried out using a catalyst containing Cu-Cr oxide compounds.

Synthesis of higher alcohols by the hydrogenation of sunflower oil samples and its esters was studied using catalysts such as compounds of Cu-Cr oxide at 150- 200˚C within 60- 240 minutes.

The mixture of raw material and catalyst was reacted at 150-200 °C for 1-4 h in a high-pressure reactor [10]. The hydrogenated product fatty alcohol was obtained after removing n-heptane and toluene by reduced pressure distillation.

The method of obtaining nonionic surfactants based on glucose and fatty alcohol in a molar ratio of 1: 1.5, respectively, in the presence of an acid catalyst, which was used hydrochloric acid and sulfuric acid.The reaction proceeds at a temperature of 90-100 ° C for 3-4 hours with vigorous stirring of the reaction mass. After completion of the reaction, the catalyst was neutralized with alkali to a pH of 9-11.

The determination of the critical micelle concentration was carried out according to GOST 29232-91.Determination of the surface tension (σ) of surfactant solutions was carried out according to the method of droplet volume corresponding to GOST R 50097-92 on a stalogmometer.

RESULTS AND DISCUSSION

As raw materials for the production of fatty alcohols, sunflower oil, spent sunflower oil, and their esters obtained by the two-stage method of hydrogenation of oils in the presence of alkaline and acid catalysts (table 1).

Table 1 – Characteristics of raw material

Characteristic	Raw materials for fatty alcohols			
	sunflower oil (SO)	used sunflower oil (USO)	ester based on SO	ester based on USO
Density, kg / m^3	921	925	927	929
Viscosity, cSt at 40 ° C	6,17	6,43	7,51	7,59
Acid number, mg KOH / g	0,4	1,1	0,02	0,04
Pour point, ° C	-16	-9	-3	-3

The results for determining the optimal conditions for the release of fatty alcohols using various raw materials are presented in table 2.

Table 2 –The output of fatty alcohols depending on the time and temperature of the reaction with compounds Cu-Croxide as a catalyst

Experience Conditions		Yield, %			
time, min	T,˚C	sunflower oil (SO)	used sunflower oil (USO)	ester based on SO	ester based on USO
60	150	24,4	22,6	25,8	23,9
120	150	33,9	27,4	36,4	34,8
180	150	57,6	47,6	58,1	56,6
240	150	66,2	55,1	70,1	64,7
60	180	29,4	24,5	32,3	31,1
120	180	43,4	28,1	45,6	44,4
180	180	60,2	49,6	67,8	65,1
240	180	69,8	61,5	76,4	74,6
60	200	43,4	34,2	47,7	45,6
120	200	55,6	48,6	59,1	56,7
180	200	67,3	59,4	69,4	68,1
240	200	72,1	63,2	79,3	76,3

According to the results of table 2, it was revealed that the yield of fatty alcohols increases with increasing contact time and temperature.

The highest yield of fatty alcohols is observed when sunflower oil esters are used as raw materials at a temperature of 200 ° C (contact time is 240 minutes) and reaches 79.3%.

It was noted that the yield for samples of raw materials obtained on the basis of spent sunflower oil was slightly lower than for the original oils. So, at 200 °C and a contact time of 240 minutes, the yield of alcohols based on sunflower oil and its spent sample was 72.1% and 63.2%, respectively.

A comparative analysis of the main characteristics of fatty alcohols based on various raw materials is presented in the form of figures 1–3.

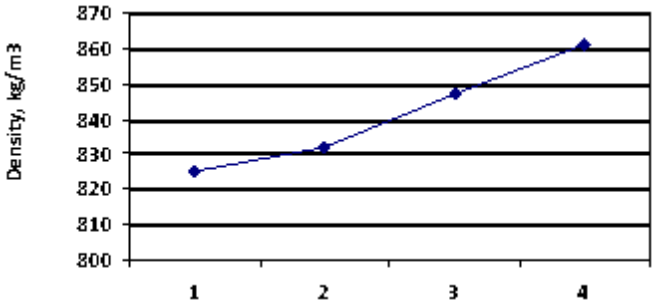

Figure1 – Density of different fatty alcohols, which were obtained on the basis of various raw materials:
1 – ester of vegetable oil; 2 – ester of used vegetable oil; 3 – vegetable oil; 4 – used vegetable oil

Figure 1shows that fatty alcohols obtained from vegetable oils have higher density than those obtained from esters. The highest density of 880 kg/m^3 was recorded for fatty alcohols derived from used vegetable oil, while the lowest density of 815 kg/m^3 was attributed to alcohols obtained from ester of vegetable oil. This proves that molecules of fatty alcohols derived from vegetable oil are spatially arranged more densely than their esters.

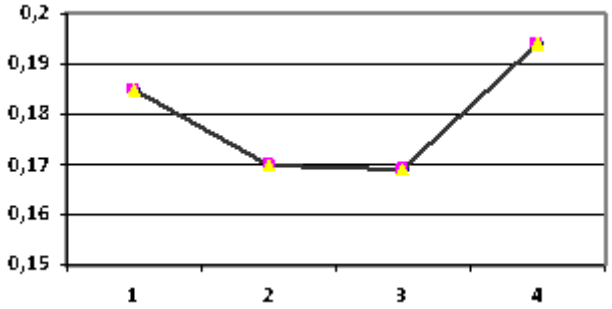

Figure 2 – Dynamic viscosity (Pa*s) of different fatty alcohols, which were obtained on the basis of various raw materials:
1 – ester of vegetable oil; 2 – ester of used vegetable oil; 3 – vegetable oil; 4 – used vegetable oil

As shown in figure 2, the viscosity of fatty alcohols increases when using the initial vegetable alcohols as raw materials, which is confirmed by data on the determination of the flash point of the obtained alcohols shown in figure 3.

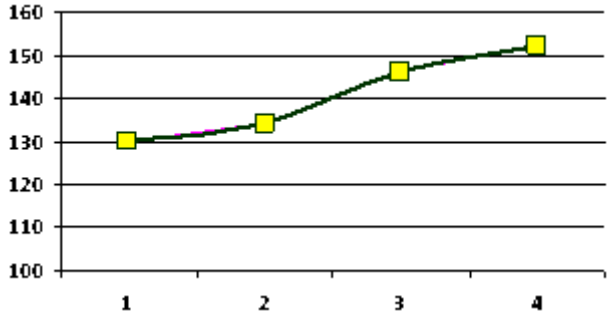

Figure 3 – Flash point (˚C) of different fatty alcohols, obtained on the basis of various raw materials:
1 – ester of vegetable oil; 2 – ester of used vegetable oil; 3 – vegetable oil; 4 – used vegetable oil

These fatty alcohols were used to produce new nonionic surfactants, which are characterized by a high biodegradation rate, low toxicity, lack of carcinogenicity and do not have undesirable effects on the skin and mucous membrane. Alkyl polyglycosides belong to this type, carbohydrate fragments (glucose, maltose, etc.) act as polar groups in their molecules, and the non-polar part is a long-chain hydrocarbon radical.

Based on the above analysis of fatty alcohols, it was revealed that the best yield with optimal characteristics was achieved when vegetable oil esters and its spent sample are used as raw materials.

The reaction for the production of surfactants is the interaction of glucose with excess fatty alcohol, which minimizes the oligomerization of carbohydrates.

The results on the production of surfactants based on fatty alcohols of esters of the source and waste vegetable oil are shown in table 3.

Table 3 – Yield of the surfactant

Temperature, °C	Raw materials for fatty alcohol	Yield, %
90	vegetable oil ester (VOE)	69
95		73
100		68
90	waste vegetable oil ester (WVOE)	59
95		62
100		58

According to the results of table 3, it was revealed that the most favorable reaction temperature is 95 °C, after which increase by 5 °C a rather sharp decrease in the selectivity of the reaction is noted.

Table 4 presents the results of the study of the main physicochemical characteristics of the obtained alkyl glucosides.

Table 4 – Physico-chemical characteristics of surfactants

Reaction temperature, °C	Raw materials for fatty alcohol production	Critical micelle concentration, g/l	Surface tension, mJ/m^2	Hydrophilic-lipophilic balance
90	VOE	0,14	35	8
95		0,04	32	11
90	WVOE	0,12	31	10
95		0,03	28	13

It is known that one of the most important properties of surfactants is the washing action, which is associated with their physicochemical characteristics. Based on the analysis of the data given in Table 4, it follows that with an increase in the reaction temperature, a decrease in the critical micelle concentration of the formed surfactants is observed, which indicates an increase in the washing ability of the studied alkyl glucosides.

The authors of [11] revealed that surfactant compositions for removing oil contaminants should have a low interfacial tension at the interface with the non-polar phase, since surface tension is the main force preventing the removal of liquid contaminants. With increasing temperature, the surface tension decreases, which is justified by an increase in the average distance between molecules and a decrease in the attractive forces between molecules.

When studying the surface tension (σ) of the four obtained surfactant samples, it was found that the surface tension values at the solution – air interface for nonionic surfactant mixtures were low in the range 32–35 mJ/m^2.

According to the results of determining the hydrophilic-lipophilic balance, it can be concluded that the developed alkyl glucosides based on fatty alcohols from esters of plant materials and their spent samples can be effective emulsifiers.

Conclusions. Thus, the results obtained testify in favor of an economically viable and environmentally friendly method of utilizing vegetable oil waste to obtain fatty alcohols based on it and create new nonionic surfactants.

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Резюме

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ӨСІМДІК ШИКІЗАТЫНАН МАЙЛЫ СПИРТТЕРДІ АЛУ
ЖӘНЕ ОЛАРДЫ ҚОЛДАНУ

Бұл жұмыс өсімдік майларынан (күнбағыс майы ретінде пайдаланылған және пайдаланылған күнбағыс майы ретінде алынған) және олардың эфирларынан Cu-Cr оксиді қосылыстары бар катализаторы қатысында алынған майлы спирттер өндірісіне арналған. Майлы спирттің ең көп шығымы күнбағыс майы эфирлерін 200 °С температурада шикізат ретінде пайдаланылғанда (әрекеттесу уақыты 240 минут) 79,3% құрайды. Майлы спирттердің негізгі сипаттамалары зерттелді және олардың ионды емес беттік белсенді заттаралуда қолданылу мүмкіндігі анықталды. Ионды емес беттік белсенді заттарды синтездеу реакциясын молярлық қатынасы 1: 1,5 сәйкесінше глюкоза мен майлы спиртінен және катализатор ретінде тұз қышқылының қатысында жүргізеді. Процесс 90-100 °С температурада 3-4 сағат ішінде реакция массасын жиі араластырумен жүреді, реакция соңында катализатор сілтімен pH 9-11 дейін бейтараптандырылады. Реакцияның ең қолайлы температурасы 95 °С екендігі анықталды, бұл температура 5 °С жоғарылағанда реакцияның селективтілігі күрт төмендеді. Өсімдік эфирлерінің гидрогенизациясымен алынған майлы спирттер шикізат ретінде пайдаланылған жағдайда 73% құрайды, ал пайдаланылған өсімдік майларының эфирлеріндегі майлы спирттердің шығымы 62% құрайды. Алынған беттік белсенді заттардың негізгі физика-химиялық сипаттамалары зерттелді және зерттелген алкилглюкозидтердің жақсы жуу және эмульсиялық қабілеті бар екендігі анықталды.

Түйін сөздер: майлы спирт, гидрлеу, өсімдік шикізаты, пайдаланылған күнбағыс майы, беттік-белсенді заттар, гидрофильді-липофильді баланс, эмульгаторлар.

Резюме

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ПОЛУЧЕНИЕ ЖИРНЫХ СПИРТОВ ИЗ РАСТИТЕЛЬНОГО СЫРЬЯ
И ИХ ИСПОЛЬЗОВАНИЕ

Данная работа посвящена получению жирных спиртов из растительного сырья, в качестве которого применяли как исходное и отработанное подсолнечное масло, также и их сложные эфиры, полученные путем этерификации/применением катализатора, содержащего соединения Cu-Cr оксида. Наибольший выход жирных спиртов наблюдается при применении в качестве сырья сложных эфиров подсолнечного масла при температуре 200˚С (время контакта - 240 минут) и достигает 79,3%.

Изучены основные характеристики жирных спиртов и выявлено, что они могут служить неполярной частью для производства неионогенных ПАВ. Реакцию синтеза неионогенного ПАВ на основе глюкозы и жирного спирта в мольном соотношении 1:1,5 соответственно в присутствии кислотного катализатора, в качестве которого используют соляную кислоту. Процесс протекает при температуре 90-100°С в течение 3-4 часов при интенсивном перемешивании реакционной массы, по окончанию реакции катализатор нейтрализуется щелочью до pH 9-11. Выявлено, что наиболее благоприятной температурой реакции является 95 °С, после повышения которого на 5 °С отмечается достаточно резкое снижения селективности реакции. Наилучший выход ПАВ отмечается при применении в качестве сырья жирных спиртов, полученных гидрированием сложных эфиров растительного сырья, и составляет 73%, тогда как выход жирных спиртов из сложных эфиров отработанного растительного сырья достигает 62%. Исследованы основная физико- химическая характеристика полученных ПАВ и установлено, что исследуемые алкилглюкозиды обладают достаточно хорошей моющей и эмульгирующей способностью.

Ключевые слова: жирные спирты, гидрирование, растительное сырье, отработанное подсолнечное масло, сложные эфиры растительного сырья, поверхностно-активные вещества, гидрофильно-липофильный баланс, эмульгаторы.