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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді геология және техникалық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия геологии и технических наук» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК. Серия геологии и технических наук в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по геологии и техническим наукам для нашего сообщества.

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SEPARATION OF FREE FATTY ACIDS FROM COTTON TAR

Abstract. This article presents the results of study of influence of technological factors on the process of cotton tars' fatty acids saponification, necessary to develop technology for synthesis of new surface-active substances used in oil dehydration processes.

To substantiate the choice of alkali concentration (sodium hydroxide) and determine the effective modes of the neutralization process, the method of determining the minimum necessary alkali concentration depending on the boiling time of the "tar – saponified reagent" system was used. Based on the obtained data, it was concluded that the effective alkali solution concentration corresponds to 8-15%, while the alkali excess amount does not affect the "boiling" time. The dependence of the change in the hydroxyl number on the sodium hydroxide concentration in the solution was obtained under real conditions, where it was shown that the saponification degree increases with increasing the alkali solution concentration, but only to a certain concentration value. The effect of temperature on the neutralization process duration was established. It is shown that fatty acids are valuable and fairly affordable raw materials that find their application in various fields of the oil and gas industry, so their extraction from wastes, namely, from cotton distillation tars, with a content of up to 65%, is reasonable and economically sound.

Key words: fatty acids, saponification, oil, gossypol, demulsifier, boiling, viscosity, alkali, hydroxyl number, dehydration, reagent, emulsion.

Introduction. Today, the problem of efficient processing of secondary resources to obtain competitive products is relevant for the oil and gas industry in our country. However, despite the importance and economic feasibility of the most complete processing of secondary resources, the level of their use is still insufficient. Considering the potential of oil and fat enterprises in the south of Kazakhstan, the task of efficient processing of secondary resources of the oil and fat industry and obtaining valuable chemical reagents on their basis is of particular importance. The main component of the secondary resources obtained in the processing of plant oils, in particular, cotton oil, are tars of fatty acid distillation. Free fatty acids are a valuable feed stock for obtaining a number of complex-effect reagents, which are used for dehydration and desalting in complex oil treatment plants [1].

There is a special economic zone in the territory of Turkestan region, focused, among other things, on the cotton cluster development. Thus, it can be considered that tars, being by-products of cotton oil processing, are a renewable source of free fatty acids [2]. In addition, the tars of the fatty acid distillation, as well as soap stocks, must be processed from the point of view of ecology and environmental protection [3-6].

The purpose of the study is to select the optimal method and conditions for the implementation of the fatty acid (FA) extraction process, which will later serve as the feed stock for the synthesis of a non-ionic (non-dissociating) demulsifier from a mixture of cotton tar components (hereinafter referred to as tar) and purification from impurities.

Previously, it was shown that from the tar of the enterprise Shymkentmay JSC with an alkali solution it is possible to obtain a saponified fraction of salts of fatty acids and gossypol, which are then separated in a free from when treated with sulfuric acid [7-9]. Methods used to separate free fatty acids should satisfy the following conditions: determine the maximum selectivity of fatty acids interaction with reagents used for neutralization; provide the highest reaction rate; facilitate rapid and complete separation of the resulting phases; ensure the maximum extraction of fatty acids from the resulting neutralization products.

In the initial exploratory tests, the resulting mixture of fatty acids and gossypol derivatives was oxyethylated and etherified, and the obtained composition showed, in the tests, the properties of a sufficiently effective demulsifier. However, in modern conditions, more stringent requirements are specified to the reagents used for oil dehydration: they must have the highest possible demulsifying activity, must be biologically easily decomposed, non-toxic, cheap, affordable, and must not have bactericidal activity. In addition, these reagents in oil should not lead to equipment corrosion. Therefore, there was a need to study how the feed stock purity affects the process of oxyethylation and etherification. It is necessary to develop the optimal method for extracting the fatty acids from the mixture of tar components, to select optimal conditions for the process of extracting the fatty acids and to choose a method for preparing free fatty acids to obtain the reagent. As an optimization criterion, the quality of the final product – the oxyethylated or etherified product based on the feed stock extracted and purified by various methods was determined [10-14].

Research methods. The fatty part extracted from the cotton tar (the mixture of tar components) is a thick, viscous mass: the kinematic viscosity is 2340 cSt at 25°C; the color is dark brown; the specific weight is 0.981 t/m^3; the acid number is 112.8 mg KOH/g; the saponification number is 228.3 mg KOH/g; the ether number is 155.43 mg KOH/g; the iodine number is 1.44 g I_2/100 g; the setting point is 37°C. The high mixture viscosity is due to the presence of saturated fatty acids in its composition, which are crystalline substances at temperatures below 50-70°C, but due to the partial solubility in unsaturated acids, the resulting mixture has the consistency of resin. Chromatographic separation of the fatty acid mixture was carried out by two methods: 1) the HPLC method according to the method [15] and 2) the GLC method according to the method GOST 30418-96.

When analyzing samples of the tar, it was found that using the standard method for determining the fatty acids does not allow obtaining adequate results, which is associated with the formation of a stable bulk emulsion layer. In this regard, the standard methods for determining the fatty acids were adjusted as applied to the tar. The content of soap and fatty acids in the tar after alkali treatment was determined by the modified method GOST 5480-59 – Plant oils and natural fatty acids. Methods for soap determination. To control the fatty acid content in model systems and in real resins, the acid number determination method was used according to GOST P 52110 – 2003. The pH of the reaction mixture was measured on the ANION pH meter 4100 (the accuracy class is 0.05). To determine the fatty acid content in the tar, the method of indirect pH-metering – measurement of the pH values of the special reaction mixture was used. The study of the influence of various impurities in the tar composition on the measurement error of the reaction mixture pH value showed that the error reaches 8-10%, therefore, other methods were used in some cases. In particular, the mass fraction of the fatty acids in the tar was determined by the method of high performance liquid chromatography using the technique of “Certificate No. 36-08 dated 04.03.2008 ФР.1.31.2008.04633” [16]. The rheological properties of various technological mixtures from the tar and soap bases were determined on the Polymer Rotation Viscometer RPE-1M instrument. The estimation of the results and their statistical reliability was carried out using the application programs “MathCAD” and “Statistica”.

It was found that the main factors determining the efficiency of the crude fatty acids, gossypol and its derivatives saponification are concentration, amount of neutralizing agent, temperature and duration of the process, as well as amount of the saponified tar additive. In this case, the required neutralizing agent amount depends on the fatty acid content in the tar subjected to saponification [17]. The tar saponification was carried out in the high pressure reactor РВД-2-150, the process efficiency was estimated by the values of the neutralization coefficient [14, 18].

To substantiate the choice of alkali concentration (sodium hydroxide) and determine the effective modes of the neutralization process, the method of determining the minimum necessary alkali concentration depending on the boiling time of the “tar – saponified reagent” system was used [19]. For this, the tar was treated with the sodium hydroxide solution of 1-20% concentration, initially with 10% excess, and then – varying the excess. The resulting "tar – alkali solution" system was subjected to treatment in the electromagnetic field of super-high frequencies until the "boiling" effect. The efficiency of neutralization was estimated in terms of the fatty acid saponification degree. For the reliability of the control of the fatty acid saponification degree, the hydroxyl number index was used [17].

Research results. From the data presented in figure 1, it can be seen that in the concentration range of 1-8%, the boiling time of the system is 5-45 s, starting from the concentration of 5 to 10%, there is increase in the boiling time of the system from 26 to 48 s with formation of characteristic dependencies (figure 1). This dependence can be explained by decrease in the free moisture content in the neutralized tar. The change in the boiling time practically does not occur when the sodium hydroxide concentration is more than 15%.

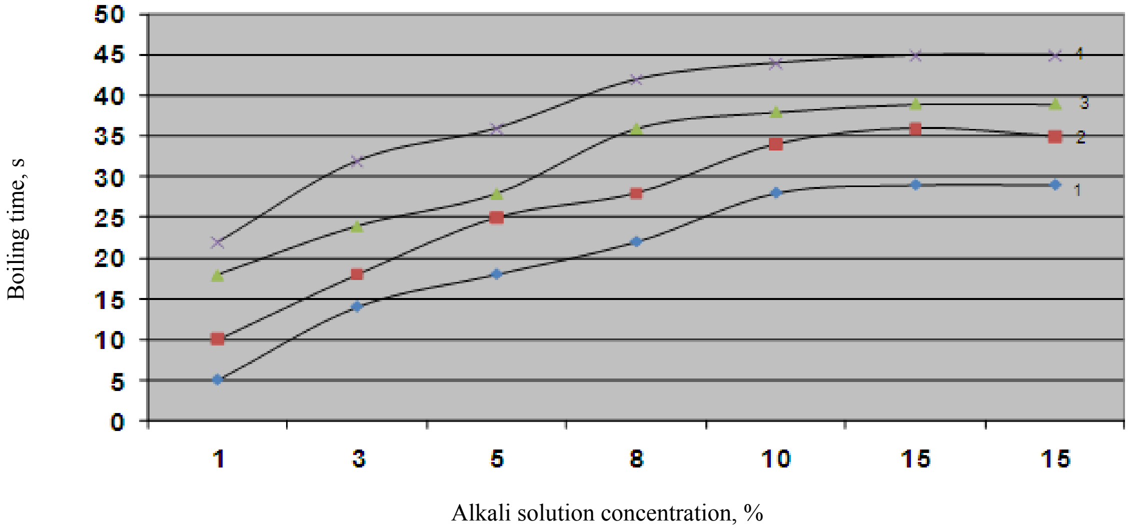
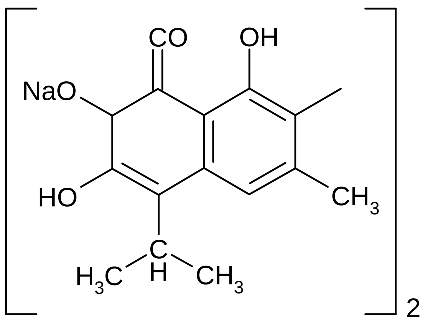


Figure 1 – Dependence of the "boiling" time of the "tar – alkali solution" system on the concentration of the alkali solution and its amount.
Conditions: the alkali excess, %: 1 – 0; 2 – 4; 3 – 7; 4 - 10. The saponified tar additive amount – 5%

The more intense tar interaction with alkali at initial concentrations is explained by the fact that the carboxyl group of the free fatty acids primarily interacts with the formation of R-COONa salts.

The glycerides remaining in the tar, which contain high molecular weight acids, are saponified more difficult compared to glycerides, which contain lower molecular weight fatty acids [12].

Approximately in the same order the gossypol derivatives enter into the reaction, since under conditions of high temperature, the gossypol in inactivated form is more likely to exist during refining and distillation, i.e. without initial aldehyde group at position 8, 8', with the formation of sodium salts of the oxidized gossypol molecule:



The hydroxyl groups of the naphthyl gossypol molecule fragment, according to the distribution of electron density on atoms, are more reactive centers. The most pronounced OH-bond at C_7 and C'_7 atoms, which acts as a strong electron-acceptor group of acid reagent, as the bond is highly polarized (the charges on oxygen and hydrogen atoms are -0.28e and 0.27e, respectively). Thus, the hydroxyl gossypol groups at position 7, 7' of the naphthalene nucleus which are in the ortho-position to the aldehyde group under these conditions form salts of gossypol and its derivatives [20]. Further, when the alkali concentrations are 15 and 20, the boiling time remains almost unchanged, as glycerin, as well as bound fatty acids in the composition of glycerides, remain in the initial mixture.

A similar dependence is also characteristic of change in the hydroxyl number under real conditions, i.e. as the alkali solution concentration increases, the saponification degree increases, but only to the concentration of 15% (figure 2).

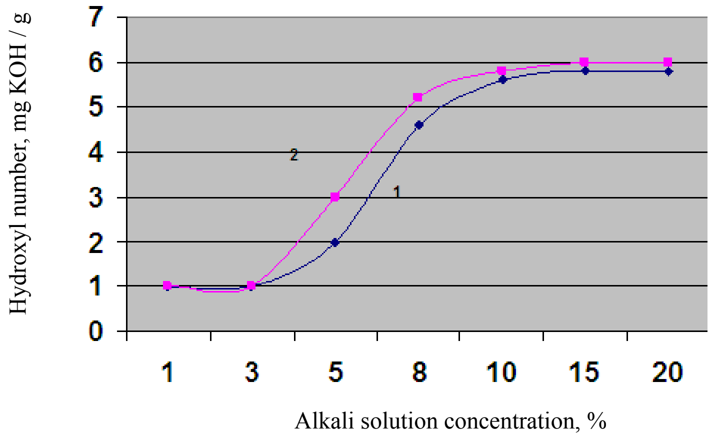


Figure 2 – Dependence of the change in the hydroxyl number on the alkali solution concentration.
Conditions: the alkali excess – 10%, the saponified tar additive amount – 5%,
the temperature, °C – 1 – 105, 2 – 110, the process duration – 120 minutes

Result discussion. Based on the obtained data, it was concluded that the effective alkali solution concentration when saponifying corresponds to 8-15%. It was found that the alkali excess amount does not affect the "boiling" time. However, the analysis of industrial practice on the use of various neutralization schemes confirms the basic point that for effective phase separation in all cases a certain alkali excess has a positive effect. If at the neutralization sufficiently concentrated alkali solutions are used, then the optimal alkali amount creates favorable conditions for the formation of soap flakes and less increase of non-saponified fatty acids. In the case of neutralization in a soap-alkali environment (using low concentration alkali solutions), a decrease in the free alkali content in the soap-alkali solution below the permissible level leads to the formation of acid soaps, reducing the dissolution efficiency of the resulting soap, as a result of which the soap and moisture content can significantly increase in the neutralized phase.

It is known that soap-alkali emulsions are formed by spontaneous emulsification of the mixture of fatty acid – aqueous alkali solution. A distinctive feature of the spontaneous emulsification in comparison with the mechanical emulsification is the emulsifier formation in the dispersed system itself. When neutralizing with the emulsifier in the system itself, the saponified part of the cotton tar acts. The authors studied the change in the saponified tar viscosity with the sodium hydroxide excess introduction, and showed that with increase in the neutralizing agent excess above 20%, the system viscosity increases again due to the change in the colloidal properties of the system, which subsequently leads to decrease in the emulsification degree and saponification rate. With increase in the temperature, the viscosity decreases (figure 3). In order to determine the aggregative emulsion stability, the dispersion of the soap-alkali tar emulsion was tested using electron microscopic images (figure 4). From the above photos it is seen that in the case of using the NaOH excess in the amount of 20%, the size of the dispersed phase droplets in the dispersion medium is the smallest and amounts to 8-10 microns, which has a favorable effect on the saponification process. The reaction that takes place in this system is on the droplet surface, while the internal mass transfer is the limiting stage.

The fatty acids are subsequently separated in the form of associates and individual molecules, the process as a whole follows the model of nonstationary convective diffusion with the introduction of concentration-dependent transfer coefficient. The analysis of the equation describing this model shows

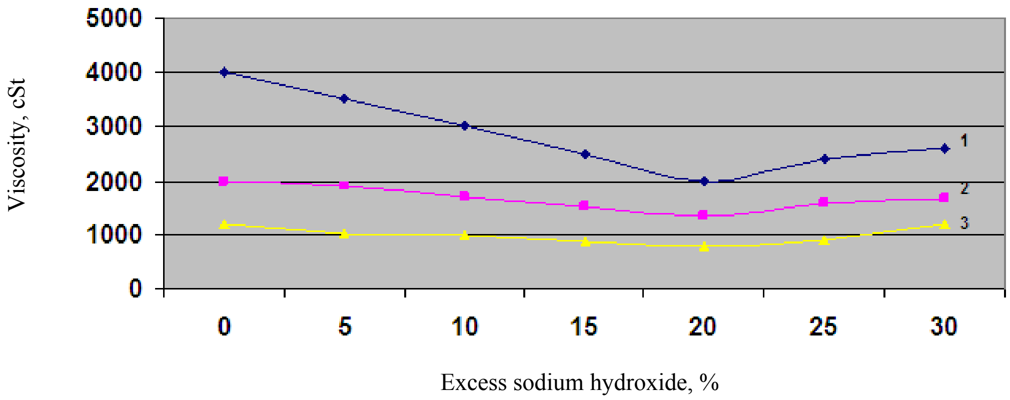


Figure 3 – The effect of the NaOH excess on the viscosity of the “cotton tar – fatty acids – alkali” system. Conditions: the alkali solution concentration – 10%; the saponified tar additive amount – 5%, the temperature, ºC: 1 – 65; 2 – 90; 3 – 115. the process duration – 120 minutes. The viscosity was determined 10 minutes after the start of the process

that the saponified fatty acids concentration on the drop surface is maximum at the beginning of neutralization and is proportional to the initial acid concentration in the tar mass and the saponified part concentration in the solution. Table shows the technological indicators of the cotton tars before and during the saponification process, which indicate that the alkali excess in the amount of 20% contributes to the viscosity decrease and provides the required rheological and filtration properties, as well as good phase separation during subsequent processing.

It is known that with increasing the temperature both direct and reverse reactions are accelerated, but to varying degrees. As a rule, the endothermic process is accelerated to a greater extent than the exothermic. When the temperature in the system of two reactions decreases, the exothermic process flows faster. Therefore, to determine the temperature effect on the chemical equilibrium, it is necessary to know the value of the thermal reaction effect. The greater the thermal reaction effect, the stronger the temperature effect. When studying the temperature effect on the tar neutralization process, it was found that increasing the temperature has a positive effect only up to 110°C, at higher temperatures due to increase in the rate of the reverse reaction, the saponification rate decreases (figure 5).

The soap-alkali emulsion formation process during the saponification of the cotton tar fatty acids takes place in the following order based on the emulsification mechanism [21]:

The fatty acids, gossypol and its derivatives in the tar composition during mechanical action on them in centrifugal pumps are crushed into large and medium drops and dispersed in the alkali solution to form the interfacial surface of the mixture: fatty acids – gossypol and its derivatives – alkali.

On the interfacial surface, the fatty acids, gossypol and its derivatives react with the alkali (the saponification or neutralization reactions) and the soap is formed on the drop surface, the soap begins to act as the emulsifier.

Molecules of the soap emulsifier are adsorbed on the drop surface, while the hydrocarbon chain or the hydrophobic part of the soap molecule is drawn into the inside of the drops, and the hydrophilic polar part of R-COONa is located on the outer surface and forms a protective layer. In addition to the soap molecules, molecules of the dispersion medium, impurities, gossypol polyphenols and its derivatives are also included in the protective layer. As a result, the protective layer becomes adsorption-solvate, and the interfacial surface tension decreases tenfold compared with the tension at a critical micelle concentration, tending to zero.

Drops in which the soap concentration in the adsorption-solvate layer reaches the equilibrium value and the surface tension becomes small compared to the tension at the critical micelle concentration, break up into smaller drops. The dispersion process continues as long as there is decrease in the work of emulsification. The soap emulsifier concentration in the soap-alkali emulsion at the beginning of the dispersion process is insignificant and decrease in the surface tension is small. Therefore, the development of the spontaneous emulsification process flows very slowly and is ≈1 h in time (in the saponification reaction this time is equivalent to the time of the induction period).

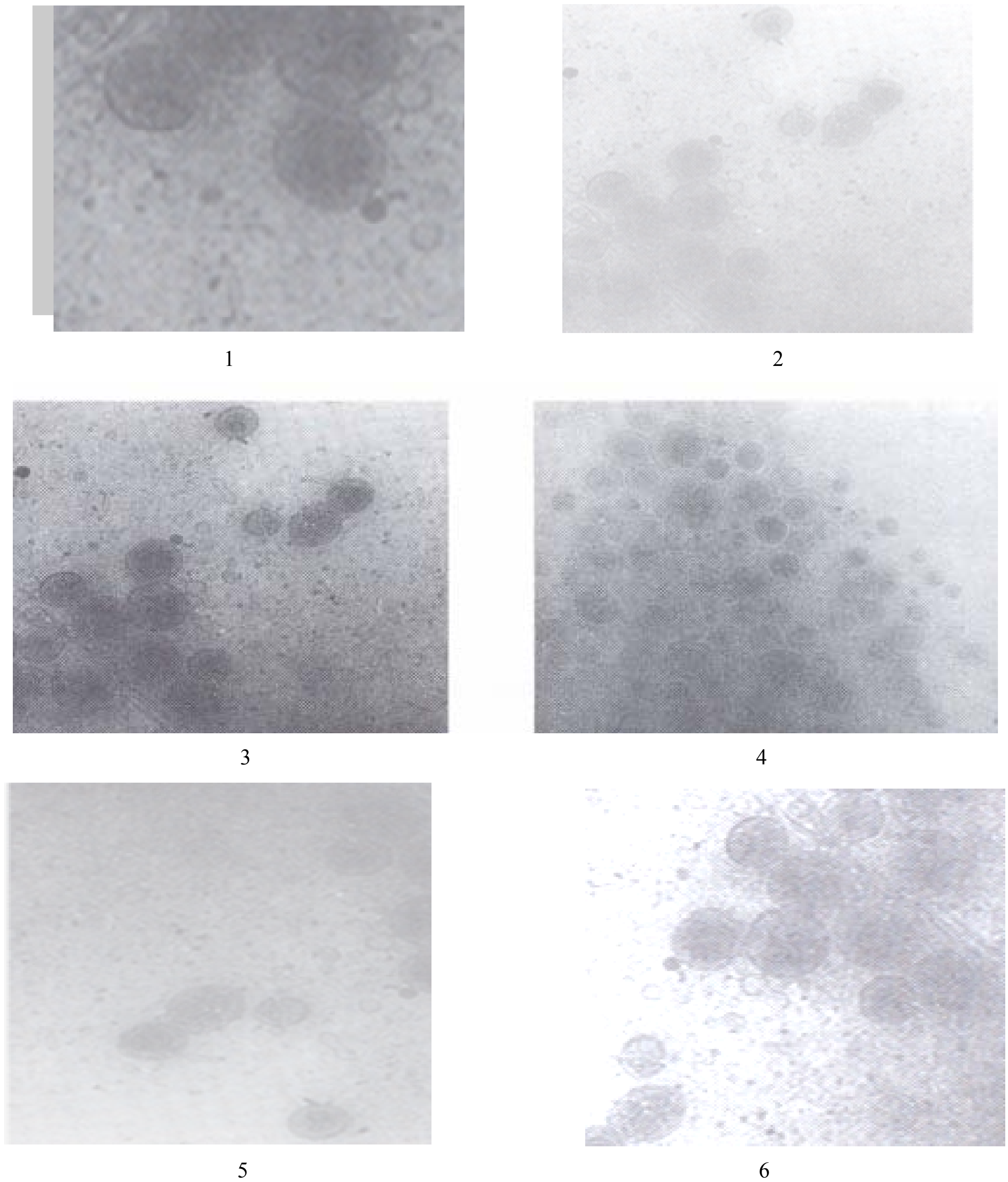


Figure 4 – Electro microscopic images of the soap-alkali emulsion "cotton tar – saponified fatty acid – alkali".
The alkali excess, %: 1 – 10, 2 – 15, 3 – 18, 4 – 20, 5 – 24, 6 – 28

Technological indicators of the soap-alkali emulsion "cotton tar – saponified fatty acid – alkali"

Composition of the emulsion	Indicators of the emulsion at 65^{o}C	
	Density ρ, kg/cm	Viscosity η, cSt
Tar	900	4000
Tar + 15% alkali solution	910	3550
Tar + 15% alkali solution (5% alkali excess)	920	3500
Tar + 15% alkali solution (10% alkali excess)	925	3055
Tar + 15% alkali solution (15% alkali excess)	930	2511
Tar + 15% alkali solution (20% alkali excess)	938	2050
Tar + 15% alkali solution (25% alkali excess)	950	2512

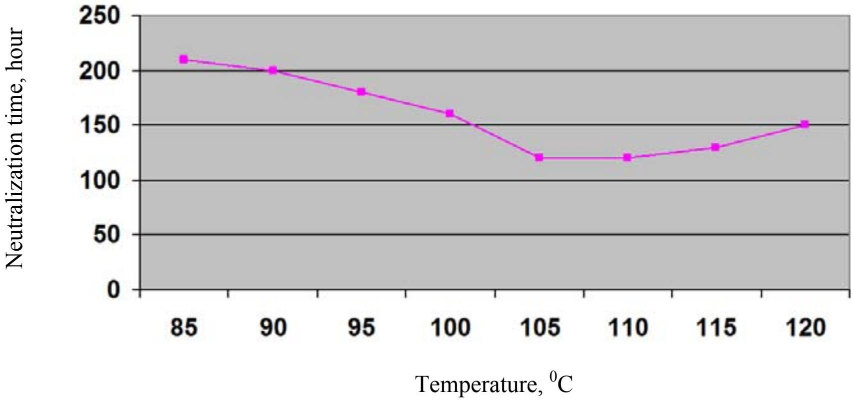


Figure 5 – The effect of temperature on the tar neutralization process duration.
Conditions: the effective alkali solution concentration corresponds to 15%,
the alkali excess – 20%, the saponified tar additive amount – 10%

To accelerate the emulsification process, a part of the saponified tar from the previous feed can be introduced into the initial reaction mixture. In continuous technologies, this additive can be easily implemented by recycling a part of the reaction mixture leaving the reactor. The authors studied how the saponified tar additive amount affects the time of the neutralization process in terms of the crude fatty acid initial content.

Conclusions. Thus, on the basis of the carried out experimental studies, the most favorable mode of saponification (neutralization) of the tar's fatty acids was determined, which subsequently provides the highest yield. The fatty acids are subsequently separated in the form of associates and individual molecules, the process as a whole follows the model of nonstationary convective diffusion with the introduction of concentration-dependent transfer coefficient. The increase in temperature has a favorable effect on the saponification process of the tar's fatty acids to a certain value, however, at higher temperatures, by increasing the rate of the reverse reaction, the saponification rate decreases. The obtained experimental data show that the cotton oil fatty acid distillation tars can be considered a valuable raw material of free fatty acids in order to obtain on their basis surface-active non-ionic substances used in the complex preparation of oil.

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МАҚТА ГУДРОНЫНАН БОС МАЙЛЫ ҚЫШҚЫЛДАРДЫҢ БӨЛІНУІ

Аннотация. Берілген мақалада технологиялық факторлардың мұнайды сусыздандыру процесінде қолданылатын жаңа беттік белсенді заттардың синтездеу технологиясын әзірлеуге қажетті мақта гудрондарының майлы қышқылдарының сабындану процесіне әсерін зерттеу нәтижелері келтірілген.

Сілті (натрий гидроксиді) концентрациясын таңдауды негіздеу және бейтараптандыру процесінің тиімді режимдерін анықтау үшін «гудрон-бейтараптандырушы реагент» жүйесінің «қайнау» уақытына тәуелді сілтінің минимал қажетті концентрациясын анықтау әдістемесі қолданылған. Алынған мәліметтер негізінде сілті ерітіндісінің тиімді концентрациясы 8-15% сәйкестігі анықталған, бұл кезде сілтінің артық мөлшері «қайнау» уақытына әсер етпейді. Нақты шарттарда ерітіндідегі натрий гидроксиді концентрациясынан гидроксильді санның өзгеру тәуелділігі алынған, мұнда сілті ерітіндісінің концентрациясы артқан кезде сабындану дәрежесіде артатындығы көрсетілген, алайда концентрацияның белгілі бір мәніне дейін ғана. Температураның бейтараптандыру процесінің ұзақтығына әсері орнатылған. Майлы қышқылдардың мұнайгаз саласының әртүрлі салаларында өз қолданысын тапқан құнды және қолжетімді шикізат болып табылатындығы көрсетілген, сондықтан оларды қалдықтардан, оның ішінде дистилляцияның мақта гудрондарынан 65% мөлшермен бөліп алу мақсатқа сай және экономикалық негізделген.

Түйін сөздер: майлы қышқылдар, сабындану, мұнай, госсипол, деэмульгатор, қайнау, тұтқырлық, сілті, гидроксильді сан, сусыздандыру, реагент, эмульсия.

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ВЫДЕЛЕНИЕ СВОБОДНЫХ ЖИРНЫХ КИСЛОТ ИЗ ХЛОПКОВОГО ГУДРОНА

Аннотация. В данной статье приведены результаты исследования влияния технологических факторов на процесс омыления жирных кислот хлопковых гудронов, необходимые для разработки технологии синтеза новых поверхностно-активных веществ, используемых в процессах обезвоживания нефти.

Для обоснования выбора концентрации щелочи (гидроксида натрия) и определения эффективных режимов процесса нейтрализации использована методика определения минимально необходимой концентрации щелочи в зависимости от времени «закипания» системы «гудрон – омыляемый реагент». На основе полученных данных сделан вывод о том, что эффективная концентрация раствора щелочи соответствует 8-15%, при этом количество избытка щелочи не оказывает влияния на время «закипания». Получена зависимость изменения гидроксильного числа от концентрации гидроксида натрия в растворе, в реальных условиях, где показано, что при повышении концентрации раствора щелочи повышается степень омыления, но только до определенного значения концентрации. Установлено влияние температуры на продолжительность процесса нейтрализации. Показано, что жирные кислоты являются ценным и достаточно доступным сырьем, находящие свое применение в самых различных областях нефтегазовой отрасли, поэтому их извлечение из отходов, а именно, из хлопковых гудронов дистилляции, с содержанием их до 65%, является целесообразным и экономически обоснованным.

Ключевые слова: жирные кислоты, омыление, нефть, госсипол, деэмульгатор, скипание, вязкость, щелочь, гидроксильное число, обезвоживание, реагент, эмульсия.

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