

Oil production from local oil

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Abstract. Acids in oil are one of the raw materials needed to prevent corrosion in the oil industry, as well as raw materials needed for the extraction of oil. In this case, the fractions of the oil acids are first separated and the oils in the various cyclic compounds are extracted from them. Oil acids are widely used in the most important sectors of the economy; The annual industrial demand for naphthenic acids is several times higher than their production. Despite the sharp deficit, a large part of the oil acids were lost in the refineries. Therefore, research on the discovery of sources of petroleum acids is urgent, and it is necessary to study the detailed composition of natural oil acids, which are separated from the high fat content in them.

1 Introduction

The general formula of naphthenic acids $C_nH_{2n+z}O_2$ can be defined as a mixture of cyclic, aromatic and linear monocarboxylic acids present in oil, where n indicates the number of carbon atoms and z is due to the presence of hydrogen. Cyclic or aromatic groups, the value of z can be a negative integer or zero [1].

Pure naphthenic acid is an important raw material in the chemical industry. Two-thirds of the produced naphthenic acid is converted into metal salts as various additives, such as wood preservatives, paint dryers, lubricants and fuel additives [2]. The acidity of petroleum is expressed in terms of total acid number (UAC). The KOH required to neutralize the total acids in 1 g of oil is expressed in milligrams. Crude oils with an acidity of more than 0.5 mg KOH / g are considered to have corrosion properties of oil refineries [3,4].

Heavy oils with high concentrations of NC are usually classified as low-quality oil and are sold at a lower price. The presence of high concentrations of naphthenic acid in oil reduces the service life of equipment used in exploration and refining processes, often due to corrosion. In order to improve the quality and reduce the price of such oil, it is very important to remove NC compounds from it. It is known that catalytic methods are more

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effective than all the existing physical and chemical methods, and their effectiveness depends on the firing temperature of the catalyst, as well as the surface area of the catalyst [5].

Naphthenic acid (NC), a mixture of alicyclic carboxylic acid and saturated aliphatic acid, is a component of heavy crude oil and the acidity of heavy crude oil depends on them [6]. Caustic washing and mixing of heavy acid crude oil with conventional crude oil use two traditional methods to remove NC from heavy crude oil. The disadvantages of the mixing method are its low efficiency, which removes about 2-3% [7], and as a result, NC is often not completely removed from the mixture, and is often used as a corrosion softener.

In the literature, methods of deoxidation include catalytic methods, non-catalytic methods [8, 9]. Thermal decomposition, which is an example of a non-catalytic cracking method, has been shown to be ineffective in reducing the acidity of heavy crude oil [10]. Typically, temperatures above 400 ° C are used. This offers thermal cracking of heavy crude oil, which leads to the formation of coke [6]. The catalytic decarboxylation process [11, 16] has been used as an alternative to non-catalytic methods for the removal of naphthenic acids (NA) from heavy crude oil. On the other hand, polymeric compounds that exhibit basic properties can be used to neutralize NC. Although this method requires the use of expensive neutralizing agents that are difficult to recover from deoxidized products.

The esterification process was used to remove NC from heavy crude oil. NCs react with alcohol to form esters [12]. Metal oxides and carboxylates have been used successfully to remove NCs from heavy crude oils using esterification at reaction temperatures between 250 and 350 ° C [13 - 15].

2 Results and discussions

It is known that naphthenic acids are an integral part of the oxygen content of petroleum, so the study of the quality and composition of oils should be considered in the following three areas:

the first is a general study of oil and gas condensates; second - the creation of catalysts for the oil refining industry and petrochemical synthesis; the third is to improve the adsorption quality of petroleum products and the adsorption separation of complex natural and technical mixtures.

The first direction is characterized by the study of oil, oil and gas condensates and gas condensates of Uzbek fields by determining the group and individual hydrocarbon content.

It is known that the oils of Southern Uzbekistan belong to heavy resin oils, which contain large amounts of sulfur and nitrogen, and insignificant amounts of light fractions.

Development and introduction of technology in production: a) determination of naphthenic acids in raw materials by titration in the presence of binary compounds indicator; b) treatment of alkaline wastes using binary solvents; c) obtaining a secondary plasticizer based on selective cleaning products (protected by RU patent) for oils for polyvinyl chloride compositions; d) A schematic diagram of naphthenic acid production has been developed. A fundamental technological scheme has been developed that has been tested in the industrial environment: b) production of copper naphthenate on the basis of alkaline wastes and copper sulfate and calcium (magnesium) naphthenate by treatment of alkaline wastes with hard water; c) the use of heavy metal naphthenates as a pigment and binder plasticizer in the production of asphalt concrete during construction and repair work on highways.

The following possibilities have been created: a) PVC stabilizers - the use of petroleum acids as heavy metal resins; b) increase the plasticity of the extract to selectively purify the modification of important functions; c) separation of petroleum acids from waste using acrylic (methacrylic), production of deodorized diesel naphthenic acids; e) adsorption fraction of naphthenic acids.

Alkaline wastes are sodium salts of naphthenic acids, which are among the commercial products produced by industry. Soapy naphtha are sodium salts of naphthenic acids, which are obtained in the process of washing the solar fractions of kerosene, gasoline and oil.

Naphthenic acids are separated from aqueous solutions of sodium salts by strong mixing with mineral acids for 1-2 hours. The process of separating naphthenic acids takes place in several stages and the naphthenic acid itself turns out to be dirty and requires cleaning. To simplify the process of separation of naphthenic acids from aqueous solutions of sodium salts, we obtain a product by treating an aqueous solution of soap naphthene with organic compounds at a temperature of 333-383 K, and then separating the layer containing the resulting mixture. Acrylic or (methacrylic) acid was used as the organic compound. Processing was carried out in the presence of ammonium carbonate in the presence of the molar ratio of acid and ammonium carbonate 1: 0.25 - 1: 1, as well as hydrogen peroxide obtained in the amount of 0.1-0.5 mass.

The alkaline wastes used had the following parameters: sodium naphthenate - 1-4%, sodium hydroxide - 0.4%, diesel fuel - up to 1%, water - 84-97%. In the proposed process, an alkaline medium in the presence of an oxidizing agent is used to obtain polyacrylates of water-soluble polyelectrolytes.

Uzbek oils are mainly divided into non-acidic oils: their acidity ranges from 0.10 to 0.45 mg KOH / g. We assume that the amount of KOH used to neutralize naphthenic acids is equal to the content of naphthenic acids. If we accept that k.m. If Uzbek oil is 0.1 mg KOH / g, calculations show that if the Fergana refinery is fully loaded with oil, the naphthenic acid yield will be 600 tons per year. It is a major raw material base for the production of naphthenic acid, which is in short supply in Uzbekistan. Based on the needs of many sectors of the economy, we have conducted extensive experiments at oil refineries in the CIS countries to refine naphthenic acid resources in various ways. (240 to 260 mg KOH / g) (Table 1).

Table 1. General information on naphthenic acid resources for 11 oil refineries

N	FACTORIES	Amount of naphthenic acids, g / l		
		Tons Acidity, KOH / g	Tons Acidity, KOH / g 240-260 mg	Tons Acidity, KOH / g 240-260 mg
1.	Komsomolsk -Amurs	1118	238	796
2.	Khabarovsk	540	234	123
3.	Lvov	240	220	31
4.	Grozny	250	218	30
5.	Batumi	500	222	200
6.	Krasnodar	2720	218	640
7.	NGZ named after AG	170000	222	7700
8.	New Baku	7000	218	3000
9.	Krasnovodsk	800	220	140
10.	Altiriq	60	–	30
11.	Fergana	880	221	290
	Total:	31218		13370

The high content of acrylic (methacrylic) acid accelerates the separation and polymerization process of naphthenic acid and accelerates the isolation process of naphthenic

acids. Thus, according to the method we propose, the polymerization of acrylic (methacrylic) acid, the separation of naphthenic acids, the purification of alkaline wastewater, and the production of polyelectrolyte solutions occur simultaneously. The proposed method is waste-free because the top layer containing naphthenic acid remains the bottom layer after separation, which is a 5-15% viscous aqueous solution of the polyelectrolyte. It is an ampholytic polyelectrolyte of the polyacrylamide type. Naphthenic acid is obtained with 99% yield according to the following scheme.

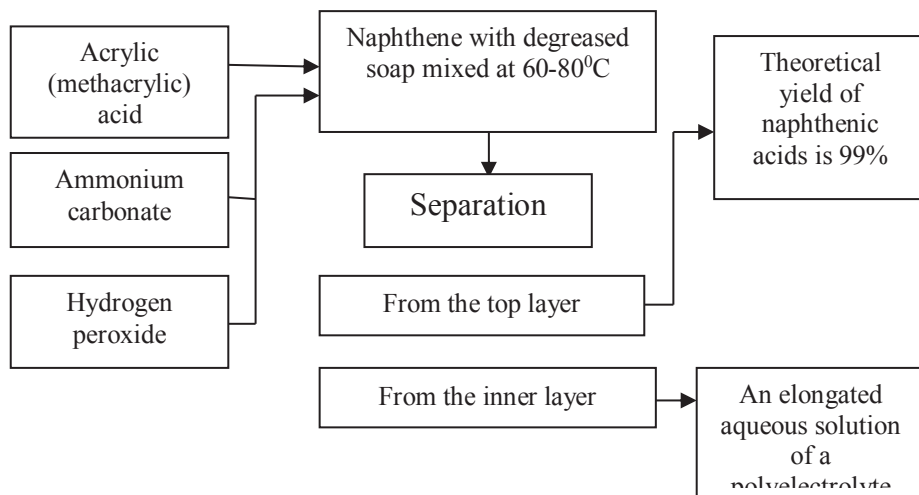


Fig. 1. Naphthenic acid obtained with 99% yield

This method is easy to implement and makes problems such as separating naphthenic acids at least 96-99% from k.m. The production of 230 mg KOH / g of very rare polyelectrolytes allows to reduce and save energy resources, return wastewater to production and, most importantly, simplify the method of separating naphthenic acids from alkaline wastes.

This section of the dissertation describes the selection of adsorbents for the purification of naphthenic acids from resins and other compounds, adsorption separation of technical naphthenic acids, the possibility of using adsorbents, active centers, adsorption of adsorbents from solutions on their static and dynamic capacities for naphthenic acids.

The use of adsorbents and adsorption methods allows not only to obtain naphthenic acids of a certain degree of purity, but also to determine their individual composition.

Adsorbents used for the separation of naphthenic acids should be selective compared to naphthenic acids, have a high adsorption capacity and do not react chemically with the substances under analysis, have a large specific surface area and porous volume, providing a sufficiently high activity. should be. In selective adsorption in the purification of naphthenic acids and their isolation, the granules have a sufficiently high thermal stability and mechanical strength, which allows them to be regenerated without significantly changing the activity of the adsorbent.

Adsorption purification of naphthenic acids from resinous components was performed using adsorption chromatography. Strongly based anion exchange resins amberlay IRE-400 and freshly prepared AB-16 and AB-17 were used, with a total dynamic exchange capacity of 14,70,19,22 and 13,05 (mass), respectively. The capacitance, size and total values of some anion exchange resins (fatty and naphthenic acids) and kerosene are given in Table 2.

Table 2. A Dynamic capacity of anion exchange resins

Sorbate	Until the jump	Full
AB-16-OH form		
Baku naphthenic acids	11,60	19,22
N — my acid	8,00	32,06
N — valeric acid	6,00	14,75
Iso — valeric acid	6,00	14,21
Caprylic acid	7,92	21,02
Pelargonic acid	0,00	---
Kerosene	0,00	---
AB-17-OH form		
Boku naften kislotalari	8,00	13,05
H—valerian kislota	10,00	15,65
Kerosin	0,00	---
Amberlay IRA-400		
Baku naphthenic acids	8,00	14,7

Apparently, anion exchange resins are not as active as kerosene. It has the highest capacity for naphthenic acids in the form of anion exchange resin AB-16-OH (up to 32%).

Thus, anion exchange resins are suitable for the purification and separation of naphthenic acids. However, they are difficult to find and regenerate, only active in the form of freshly prepared OH.

Thus, the process of adsorption purification of naphthenic acids using column chromatography is accompanied by an ion exchange reaction between the acid proton and the adsorbent cation.

In the case of physical adsorption, they can be almost completely desorbed with a mixture of acetone-benzene (in this case, α -fractions), in which case naphthenic acids are well soluble. Naphthenes, on the other hand, are strongly retained by adsorbents of naphthenic acids formed in adsorbents under the action of coordination unsaturated metal atoms and acid anions, and are not desorbed by the acetone-benzene mixture. They can be separated only in the second stage of desorption, in which a more polar solvent - aqueous alcohol - in this case separates the α -fraction.

Due to the dependence of micellarization concentration on high-molecular-weight naphthenic acid solutions in cyclohexane, assumed to be thermodynamically stable systems, the thermal effects and micellarization energy of this process were proposed by calculating micellarization in anhydrous media and described by some equations used for water resources. This Narmetova G.R. and Azimova M. can be seen in the example of the dispersion of saturated oxidized bitumen in benzene. The enthalpy (Hm), free energy (Gm) and entropy (Sm) of the micelle were calculated based on the linear relationship of the logarithm of the micelle formation concentration to the temperature. These values are given below in Table 3:

Table 3. The enthalpy (Hm), free energy (Gm) and entropy (Sm) of the micelle calculated based on the linear relationship of the logarithm of the micelle formation concentration to the temperature

Temp.	MKK, mol/litr	KDJ, mol	KDJ, mol	Dj, mol
290	0,010		11,48	67,1
295	0,011	30,56	11,44	66,2
300	0,013		11,20	65,8

It can be seen that the heat of formation of micelles is much higher, which is primarily due to the dimerization of high-molecular-weight naphthenic acid molecules. In the process, the free energy of micellarization decreases with increasing temperature. The entropy of micelles also decreases due to the restriction of the free movement of molecules in the association, although the intensity of Brownian motion increases with increasing temperature.

Based on the above data, the transition of complex structural compounds from one form to another with increasing temperature occurs at a relatively high concentration of the solution. Activation of the viscous flow energy of the solution before and after the critical concentration of micelles (MCC) is 22.6 and 27.9 kJ / mol. The higher the MKK value, the higher the test temperature. This indicates that the size of the bonded group of molecules is greater than the sum of the volumes of the individual molecules included in the group, which also includes the intermolecular space. In the experiment, the complex structure of high-molecular-weight naphthenic acid dispersions decreases with desolvation, which leads to a decrease in viscosity, while the constant acting gravitational forces (cohesion) between high-molecular-weight naphthenic acid molecules are maintained with increasing temperature. Consequently, an increase in the solution temperature leads to an increase in the molecular solution area: the MCC shifts towards increasing the concentration of the naphthenic acid solution in the cyclohexane. As the concentration increases, the ratio of dispersion interactions between the hydrocarbon parts of naphthenic acid molecules increases.

Thus, as a result of intermolecular interactions between structural-kinetic units of the solute (molecules, ions and their associations) in cyclohexane solutions of naphthenic acids, complex structural units (MTB), micelles and other supramolecular formations are formed in solution. Iadi. The number and volume of these supramolecular derivatives of naphthenic acids are manifested by changes in the temperature and concentration of the solution.

In the process of percolation purification of kerosene naphthenic acids with aluminosilicate catalysts and silochrome C-80, very pure naphthenic acids of 20-28 and k.m 305-312 mg KOH / g (original 299 mg KOH / g and more than 170 colorants) are obtained. After desorption of the acetone-benzene mixture with acetone enriched in hydrochloric acid, the activity of the sorbent is well restored. Pink bentonite activated with Tagansky acid was very effective for bleaching dark paraffin naphthenic acids.

Based on the experiments, a schematic diagram of the production of light and deodorized naphthenic acids was developed on the basis of combining the process of partial (80%) separation of acidolides of Fergana fuel. recommended for use.

The yield of light-colored (21) acids is k.m. 307 mg KOH / g is an average of 75%. Phenols are extracted along with some weak non-soapy acids due to lack of alkali. After the solvent is pumped, the residue is added to the k.m. Less than 100 mg of KOH / g, with a pungent odor of 20%, yields about 22% of acids with phenols. The absence of phenols in light-colored naphthenic acids and the presence of black residues were confirmed by IR spectroscopy.

3 Conclusion

The effect of experimental concentration and temperature on the flow of intermolecular interactions with changes in the viscosity of solutions of naphthenic acids was found in a polar solvent (cyclohexane) by studying the values of the concentration of naphthenic acid solutions. For the first time, a new adsorbent was synthesized under the conditional name - SiO₂ - NK naphthenic acid silicate modulus is introduced into an aqueous solution of liquid glass with a solution of 3.3 acetone, which is very porous due to the presence of sorbent. Increased selectivity relative to those of high molecular weight.

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