



Development of technology for the separation of petroleum acids from distillates

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Abstract

The research on the process of alkalization of naphthenic acids from oil distillates is reflected in the article. In the article, work was done on obtaining a stable emulsion during the alkalization of naphthenic acids. In order to prevent the formation of the resulting emulsion, an alkalization process was carried out in the presence of sodium hydroxide. This process is carried out at a temperature of 100 °C and under pressure. The article mentions various methods of separation from fat fractions.

According to the presented technological scheme, first, the oil fraction is heated to a temperature of 45-55 °C and then to 150-170 °C. The heated fraction is mixed with 1.2-2.5% NaOH solution. The mixture is cleaned of alkaline waste at the temperature of 120-130 °C. The purified distillate is mixed with hot water at the temperature of 60 °C and sent to the precipitator. As a result, the oil distillate obtained from the precipitator is dried with hot air in a drying tank and sent to the commodity department. As a result of the extraction of alkaline waste with a binary solvent (methylethylketone: toluene), petroleum acids with a degree of purity of 95-98% are obtained.

Keywords: alkaline waste, naphthenic acid, oil fractions, binary solvents, oil distillates

Introduction

Naphthenic acids have a complex chemical composition. They are monobasic cyclic acids with carboxyl groups at the end of the side chain. Small molecular naphthenic acids are mainly monobasic derivatives of cyclopentane. They may also contain small amounts of oil acids. Naphthenic acids obtained from high molecular weight fractions are dominated by bicyclic and polycyclic acids. The amount of naphthenic acids in oils can vary from 0.003% to 3%. The density of naphthenic acids varies between 0.94-1.6 g/cm³ in a very large interval.

The refractive index of naphthenic acids depends on the ratio of C and H elements. While the refractive index of natural naphthenic acids is 1.42-1.43, for synthetic naphthenic acids (C10-C22) this number is 1.49, for aliphatic hydrocarbons it is 1.28, for asphaltenes it is from 1.39 to 1.47, and for phenols it is above 1.50.

During oil refining, naphthenic acids are unevenly distributed in oil distillates and are mainly concentrated in oil distillates. Release of fuel and oil distillates from naphthenic acids is carried out in refineries by treating them with an aqueous solution of sodium hydroxide. Here, these acids are dissolved by the formation of aqueous solutions of naphthenic acid salts or alkaline wastes, as it is called in factory practice. "Crude" naphthenic acids or acidols are obtained as a result of the complete decomposition of alkaline wastes using mineral acids. With the exception of sodium salts of naphthenic acids, a certain amount of hydrocarbons can usually be found in alkaline wastes.

The content of naphthenic acids in Azerbaijani oils varies in the range of 0.1-1.67% (by mass). The research works conducted by a number of authors provide information on the separation and simultaneous purification of naphthenic acids in "May 28" oil fields. It was determined that up to 0.45% (by mass) of naftenic acids were collected in the oil obtained from "May 28" oil fields. As is known, the main mass of naphthenic acids is collected in the main fractions of oil. Therefore, the studied oil is first separated into

separate fractions and the amount of naphthenic acids contained in them is determined. Kerosene and gasoil fractions boiling at 200-240 °C and 240-350 °C are separated from oil. Naphthenic acids are separated in the form of sodium salts from the indicated distillation fractions with the help of 5% NaOH solution, and then these salts are decomposed using 15% sulfuric acid solution. The naphthenic acids are then extracted into light gasoline. Alkalization of distillation fractions and decomposition of alkaline residues with acid is carried out in a test facility according to the mentioned industrial method. As a result, the yield of naphthenic acids separated from the distillation fractions was determined to be 2.4% (by mass) in the kerosene fraction and 2.2% (by mass) in the gasoil fraction. The extraction of naphthenic acids from petroleum products is determined by the intermittent purification method. This method is considered the simplest, but not economical and time-consuming. Refining of oil products is carried out by both semi-continuous and continuous methods. Various chemical compounds are used for the separation of naphthenic acids.

Various methods are used to purify petroleum products from sulfur-containing compounds. Oils are divided into different classifications according to the amount of sulfur they contain. It is based on the removal of organic sulfur compounds through desulfurization methods. Also, methods of selective removal of organic sulfur compounds with simultaneous purification of oil fractions are analyzed in detail. In the presented article, the scheme of purification of petroleum acids from oil distillates with alkali is given [1-8].

Experimental part

It is obtained by continuous emulsion during the alkalization process of naphthenic acids from oil distillates. In order to prevent the formation of an emulsion, the alkalization process is carried out under pressure at a temperature of 100 °C in the presence of sodium hydroxide. A plant for alkalizing oil distillates is shown below.

The oil fraction is heated to 45-55 °C by the pump (1) in the "tube-in-tube" type heat exchanger due to the heat of the distillate coming from the precipitator (8). It then enters the tube furnace (3). The excess pressure in the furnace is 0.6-1.0 MPa. Here, the raw material is heated to 150-170 °C and sent to the mixer (4). At the same time, 1.2-2.5% NaOH solution is supplied to the mixer (4) through the pump. The mixture is fed to the precipitator (5), where it is cleaned of alkaline waste at 120-130 °C. The obtained distillate is sent to the second mixer (7) and mixed with hot water at a temperature of 60 °C. The mixture is then fed to a precipitator (8). The distillate, freed from naphthenic acids, is dried with hot air in the dryer tank (11) by giving its heat to the raw materials through the heat exchanger (2) at 90-100 °C and is sent to the commodity department through the pump (12). The alkaline wastes obtained from the pressure alkalization of oil distillates contain 4.5-10.5% sodium naphthenates, 6.5-8.5% unsaponifiable matter, and 83-87% water.

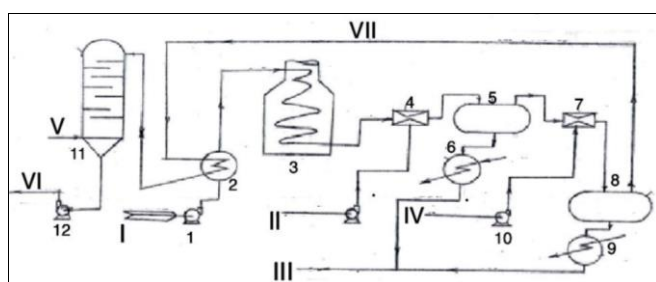


Fig 1: Alkali purification of oil fractions

1, 10, 12 – pumps; 2, 6, 9 – heat exchanger; 3- tube furnace; 4, 7 – mixer; 5, 8 – precipitating, 11- drying tank.
I - raw material; II – NaOH (1.2-2.5%); III – alkaline waste; IV – hot water; V – hot air; VI – purified distillate; VII – oil distillate.

The method of operation of this specified device was improved by academician R. H. Ismayilov and L. N. Furman. Alkalization of oil distillates is carried out using 10-12% diesel alkali waste. Sea water plays the role of an electrolyte here, preventing the formation of an emulsion. A good separation of phases is observed with an increase in the extraction coefficient of naphthenic acids. It also allows you to get quality oil without washing with water after alkaline treatment. For this reason, purification of naphthenic acids from these mixtures is of great importance.

Results and discussion

One of the existing industrial methods for separating petroleum acids from fractions is to treat them with an aqueous solution of sodium hydroxide.



Naphthenic acids dissolve in water by reacting with sodium alkali. In factory practice, this is called "alkaline waste". In addition to sodium salts, alkaline waste contains hydrocarbons, phenols, tar and other substances. In addition, when the concentration of alkali and the molecular mass of naphthenic acids are high, the amount of unsaponifiable matter in them is also high. Alkaline waste obtained from refining of oil distillates, distilled naphthenic acids and oil acidol were used in the research work. At the same time, ethyl alcohol and hexane were used as solvents. Alkaline

waste is decomposed with the help of sulfuric acid, which is a mineral acid. As a result, crude naphthenic acids (acidols) are obtained. The following table shows the physical and chemical properties of alkaline waste.

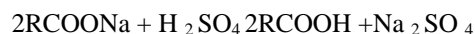


Table 1: Physico-chemical properties of alkaline waste of oil fraction

Indicators	Oi fraction
Amount of naphthenic acids in alkaline waste, % (by mass)	10.5
Acid number of the organic part, mg KOH/g	88
Amount of naphthenic acids in alkaline waste, % (by mass)	6.5
Acid number of pure naphthenic acids, mg KOH/g	167.2
Amount of non-saponifiable matter in alkaline waste, % (by mass)	4.6
Amount of naphthenic acids in the organic part, % (by mass)	52
The amount of unsaponifiables in the organic part, % (by mass)	48.2
Molecular mass of naphthenic acids	335
Amount of NaOH, % (by mass):	
freely	0.85
related	1.60
Total alkalinity, % (by mass)	2.45

The amount of neutral hydrocarbons captured by the sodium salt of naphthenic acids increases as their molecular weight increases. C6 -C10 aliphatic and naphthenic acids predominate in oil distillates. The amount of hydrocarbons in the alkaline waste separated from kerosene distillates is 30-40% and some tar-asphalt substances and phenols. Alkaline waste obtained from oil fractions contains up to 55-60% hydrocarbons and a small amount of tar-asphalt substances and phenols. Most of these acids must be removed from those mixtures. The high amount of non-saponifiable components of naphthenic acids, as well as the fact that technical naphthenic acids have a bad color, limits their wide use in the national economy and petrochemical synthesis. For this, the regeneration of NaOH from naphthenic acids, the separation and use of neutral hydrocarbons, and the development of technology for the separation of phenols are of particular importance. As mentioned above, during the separation of high molecular weight naphthenic acids contained in oil fractions from oils, they take with them a large amount of unsaponifiable substances. The above-mentioned mixtures prevent the use of high-molecular acids and naphthenic acids in a wide field of application. Thus, more effective ways to purify both low-molecular and high-molecular naphthenic acids should be found. As a result of the conducted research, it should be noted that high purity naphthenic acids can be obtained by cleaning oil fractions from alkaline waste.

Conclusions

1. Purification of high molecular weight naphthenic acids from neutral hydrocarbons and physicochemical properties of oil distillates were studied.
2. The non-saponifiable substances present in acidols are mainly concentrated in the oil fractions and only 3-13% are naphthenic acids.

3. By mixing alkaline waste with a binary solvent (methylethylketone: toluene) in a ratio of 1:1 for 8-10 minutes as a result of extraction at a temperature of 40 °C, petroleum acids with a degree of purity of 95-98% are obtained.

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