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ПЕРСПЕКТИВНЫЕ ТЕХНОЛОГИИ УДАЛЕНИЯ И УТИЛИЗАЦИИ СЕРОВОДОРОДА ИЗ МАЗУТА

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Наличие сероводорода в топочном мазуте представляет экологическую опасность, так как при хранении, перекачке и транспортировке сероводород концентрируется в газовой фазе резервуаров, емкостей и цистерн, что при проведении операций слива-налива может привести к превышению его ПДК в воздухе, а также к созданию взрывоопасных смесей. Концентрация H_2S в мазуте, производимом на нефтеперерабатывающих заводах, составляет 20-500 ppm, в то время как в товарном мазуте его содержание ограничивают до 10 ppm. Рассмотрены аналитические методы определения концентрации сероводорода в нефтепродуктах. Представлены промышленные и перспективные технологии снижения содержания H_2S в мазуте, их основные достоинства и недостатки. Показаны возможности низкоэнергетических волновых технологий в облагораживании нефтяного сырья и нефтепродуктов и механизмы действия ультразвука и постоянного магнитного поля на нефтяные дисперсные системы. Извлекаемый из мазута сероводород ни по объемам, ни по концентрации не может быть использован как самостоятельное сырье для переработки в элементную серу в процессе Клауса и представляет собой побочный токсичный продукт. В то же время, сероводородсодержащие отходы могут быть ценным сырьем для получения широкого спектра полезных органических соединений (антиоксиданты, лекарственные препараты, пестициды, фунгициды). В процессах малотоннажной химии актуальны электрохимические процессы. В результате анодной или катодной активации сероводорода (алкантиолов) при комнатной температуре и атмосферном давлении образуется тиильный (алкилтиильный) радикал. Наряду с продуктами тиолирования органических соединений образуются также моно-, ди- и трисульфиды, обладающие более высокой биологической активностью и более низкой токсичностью по сравнению с тиолами. Конкурентноспособность электросинтеза весьма высока, его относят к процессам безотходного производства, так как в основе его заключена экологически ориентированная идея «зеленой химии».

Ключевые слова: сероводород в мазуте, методы анализа сероводорода, удаление сероводорода, волновые технологии, редоксактивация сероводорода, электросинтез

PROMISING TECHNOLOGY FOR REMOVAL AND DISPOSAL OF HYDROGEN SULFIDE FROM FUEL OIL

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The presence of hydrogen sulfide in fuel oil is a danger, since hydrogen sulfide is concentrated in the gas phase of tanks, vessels and tanks truck that when carrying out operations of drainage-fulness can lead to an excess of its MAC in air and to the creation of explosive mixtures. The concentration of H_2S in fuel oil produced at refineries is 20-500 ppm, while its content in commercial fuel is limited to 10 ppm. Analytical methods of definition of concentration of a hydrogen sulfide in oil products are considered. Industrial and promising technologies for reducing H_2S in fuel oil, their main merits and demerits are presented. The possibilities of low-energy wave technologies in the refinement of petroleum and oil products and mechanisms of action of ultrasound and constant magnetic field on oil disperse systems are shown. The hydrogen sulfide extracted from fuel oil neither on volumes, nor on concentration can't be used as independent raw materials for processing into elemental sulfur in the Claus process and is a toxic by-product. At the same time, hydrogen sulfide-containing wastes can serve as valuable raw materials for the production of wide range of useful organic compounds (antioxidants, drugs, pesticides, fungicides) in electrochemical processes. In processes of low-tonnage chemistry, electrochemical processes are relevant. As a result of anode or cathode activation of a hydrogen sulfide (alkanethiols) at ambient temperature and atmospheric pressure the thiyl (alkylthiyl) radical is formed. Along with products of a thiolation of organic compounds are formed also mono - di - and the trisulphides having higher biological activity and lower toxiferous in comparison with thiols. The competitiveness of electrosynthesis is very high, it is considered as processes of waste-free production as at the heart of it ecologically focused idea of "green chemistry" is concluded.

Key words: fuel oil hydrogen sulfide, hydrogen sulfide analysis methods, hydrogen sulfide removal, wave technologies, hydrogen sulfide redox activation, electrosynthesis with alkanethiols

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Continuous deterioration in physical and chemical characteristics of oil, and, exactly, weighting of its composition and increase in a share of sulfur, leads to the fact that the quantity of the rest of atmospheric distillation increases as well as sulfur content in oil products. For deepening of petroleum refining need of complex modernization and development of the industry on the basis of the advanced domestic technologies increases [1]. Removal of sulfur compounds for the purpose of production of marketable oil products is carried out in the course of hydrotreating that leads to formation of large amounts of hydrogen sulfide.

Production of commodity oil products is followed by removal from them sulfur compounds, mainly in the course of hydrotreating that leads to formation of large amounts of hydrogen sulfide. Statistics shows that at oil refining with the content of sulfur of 2-3% with a depth to processing of 80-85% about 30 thousand tons/year of hydrogen sulfide on each one million processed oil are formed on average [2].

In structure of power fuel of Russian Federation the share of furnace fuel oil is rather large. In addition to power generation, fuel oil is used in metallurgy, housing and communal services, in power plants of maritime vessels. In Russia, the share of production of fuel oil in 2018 made more than 50 million t. From them about 70% are sent for export where fuel oil is sent for further processing [3].

The presence of hydrogen sulfide, as well as methyl- and ethylmercaptans is typical for both straight-run fuel oils obtained from high-sulfur oil or gas condensate, and for the residual products of secondary processes of processing of high-sulfur raw materials. The concentration of H_2S in fuel oil produced in Russia at oil and gas processing plants ranges from 20 to 500 ppm [4].

The appearance of hydrogen sulfide and volatile mercaptans in straight-run fuel oils is due to the peculiarities of the technology of distillation of high-sulfur raw materials (oils and gas condensates). By settlement path with use of the constants of phase equilibrium determined by Wynn's nomogram it is established that at concentration of a hydrogen sulfide in a feed stock of 100-170 mg/dm^3 (0.15 MPa, 350 °C) its content in fuel oil will be 9-15 mg/dm^3 [5].

Emergence of a secondary hydrogen sulfide in fuel oil is bound to the fact that for suppression of hydrochloric and hydrosulfuric corrosion of an equipment the aqueous solution of caustic soda is entered into a raw stream of installations of atmospheric distillation. As a result of neutralization of a hydrogen sulfide and mercaptans caustic soda forms sulfide and hydrosulphide which are toxiferous and in processes of storage, transportation and use of furnace fuel oil is exposed to hydrolysis with formation of a hydrogen sulfide [6-7].

In addition, a hydrogen sulfide is formed as a result of a thermolysis of various sulfur compounds of raw materials at its heating on installation of distillation to 320-360 °C. Under the terms of a vapor-liquid equilibria at process parameters of work of nutritious section and a cube of an atmospheric column it inevitably remains in a liquid phase even in a distillation residue of a column – straight-run fuel oil [5].

Problems of technological, ecological and economic character at further processing and use of fuel oil are caused even by insignificant amount of hydrogen sulfide.

These include problems associated with high corrosion aggressiveness of sulfur compounds: corrosion of exposed in contact with the oil surface process equipment, tanks, valves, pipelines, railway tanks, nodes, burners and furnaces for burning fuel oil. The intensity of hydrogen sulfide corrosion in the gas phase formed in fuel oil storage tanks and fuel oil tanks truck is high [8].

The main problem is the threat to security as the H_2S which is contained in fuel oil at storage, pumping and transportation concentrates in a gas phase of tanks, vessels and tanks truck that can lead to creation of explosive concentration and also to excess of its MAC in air. H_2S concentration in the gas phase can be one or two orders of magnitude higher than the initial concentration in the fuel. So, 1 mg/kg of hydrogen sulfide in fuel oil can result in concentration already at the level of 80-1000 mg/kg of H_2S in a gas phase in a tight tank. It creates threat to security to health and life of the personnel which are carrying out draining drainage and filling operations. Besides, hydrogen sulfide and mercaptans have a strong unpleasant smell which is already felt at a concentration of 0.012-0.03 mg/m^3 [9].

All this causes need of imposition of the restriction on hydrogen sulfide content in fuel oil. According to Technical regulations of EEU of TR CU 013/2011 hydrogen sulfide content in fuel oil should not exceed 10 ppm. And for the fuel oil intended for export to the European countries the norm no more than 2 ppm is established [4].

Methods of determination of content of hydrogen sulfide in oil and oil products can be classified depending on: estimates of the obtained measuring information on qualitative and quantitative; aggregate state of the analyzed substance – gaseous or liquid; fractional, component composition of analyte – in oil, gas condensate, gasoline, fuel oil, etc.; essence of a method of obtaining result of measurement – chemical; physical and physico-chemical; time of receipt of information – on express methods, laboratory, straight-line flow method.

To qualitative the method of determination of content of hydrogen sulfide in fuel oil which was used when the lack of a hydrogen sulfide was the regulatory requirement to fuel oil in accordance with GOST 10585-75 is. This method consists in translation of the hydrogen sulfide dissolved in oil product in sodium sulfide by means of processing by alkali, the subsequent its separation and decomposition by the hydrochloric acid. The allocated couples check for presence of a hydrogen sulfide by means of the indicator paper impregnated with lead acetate. The resulting lead sulfide causes a darkening of the indicator paper and indicates the presence of hydrogen sulfide in fuel oil.

Final information in the analysis on contents H_2S is determination of its concentration in liquid oil product. However, the analysis is in most cases carried out in a gas phase. Sample preparation provides replacement dissolved in an oilstock or oil product of a hydrogen sulfide and the subsequent analysis of a gas phase by this or that method.

The analyzed substance – fractional and component composition, has significant effect on the applied procedures, essence of a method, accuracy of the received results, etc. So, determination of content of hydrogen sulfide in dark oil products, in residual fuels becomes significantly complicated because of the increased density, viscosity, hardening temperature. As a rule, in such cases the sample preparation consisting in heating and/or dissolution of test of heavy oil product is applied. It can lead to increase in an error of result. In general the essence of methods of definition of H_2S in a gas phase, in easy or heavy petroleum and oil products is similar in many cases.

On the essence the applied methods of the analysis of concentration of hydrogen sulfide are very various: chemical (titrimetric, extraction, colorimetric, indicator); physical – spectrophotometric, chromatographic and physico-chemical (electrochemical – a cyclic voltammetry, electrometric titration, etc.).

Time of obtaining result of the analysis depends on a goal and influences the choice of a method – the analysis in stationary conditions in laboratories, automatic flow analysis of the substance or an express method by means of the portable or stationary device. In the latter case, the procedure is simplified and the time for obtaining the analysis result is reduced, but the accuracy of the result is decreased.

One of the first quantitative methods of the analysis is based on infusion of a hydrogen sulfide in solution of chloride cadmium. The examinee oil product is stirred up in a dividing funnel with a slightly acidified solution of chloride cadmium and then settling and drain a water layer. The formed sulfide of cadmium can be an iodometry or potentiometric titration, weighing of a deposit etc. Shortcomings of a method are the considerable volume of test fuel sample, need of filtering of extract therefore cadmium sulfide losses are possible [10]. An essential bad point is use and formation of toxic salts of cadmium, need of their utilization.

According to the IP 399 standard and similar GOST 32505 and GOST P 53716, a hydrogen sulfide blow from fuel oil test by nitrogen, free of oxygen, in alkaline suspension of a hydroxide of cadmium. Cadmium sulfide is determined in the form of methylene blue, formed in the presence of a strong acid solution of N,N-dimethyl-1,4-phenylenediamindihydrochloride and iron (II) chloride on the spectrophotometer at the wavelength of 670 nm. As salts of cadmium constitute danger because of the toxicity, the standard allows replacement them on a zinc acetate dihydrate. This method is intend for concentration of hydrogen sulfide in fuel oil from 0.5 to 30 ppm. When determining concentration of hydrogen sulfide in fuel oil and its components by a technique of IP 399 of an error of definition can arise because of difficulties in ensuring stability of an exit of products at synthesis of methylene blue; the strong preventing influences of easily oxidized components, a narrow interval of linearity of the calibration schedule; insufficient purity of nitrogen; difficulties in selection of small tests.

Spectrophotometric methods continue to be improved both in gas, and in a liquid phase. At the maintenance of H_2S from 0 to 150 ppm in a wide interval of pressure and temperatures authors of [11] suggest to use a multivariate optical computing technique (MOC) in the ultraviolet range. The relative accuracy of a method of 3.3%. SpectraSensors TDLAS technology method implemented by ASTM WK52082 shows high speed, stable work, reliability [12].

With the help of cadmium salts and iodometric titration, hydrogen sulfide is determined in heavy oil products [13].

MM titrimetric method 1404-85 is developed according to requirements of the MOBIL company for determination of amount of hydrogen sulfide in residual fuels in the range from 0.5 to 200 ppm. The titrimetric technique differs in the fact that the hydrogen sulfide which is forced out from fuel and turned into sulfide of cadmium is oxidized solution of the periodat of potassium, and the excess of iodine is titrated by sodium thiosulphate (reverse iodometric titration). When implementing this method, determination errors may occur due to the instability of the nitrogen bubbling rate of the absorber series; with the need to use as a solvent toluene, which reduces the viscosity of petroleum products and, as a consequence, increases the rate of separation from the sample H_2S; with insufficient mixing of the sample in the container; with insufficient purity of nitrogen passed through the absorbers (especially clean nitrogen is preferred); with difficulties encountered in the purification of absorbers from cadmium sulfide residues.

The IP 570 standard and GOST 33198 similar to it describes a method of determination of content of hydrogen sulfide in residual oil fuels and ship fuel oil by means of the automatic analyzer in the range of concentration from 0 to 50 mg/kg. The essence of a method consists in dissolution of small volume of a sample in basic oil-thinner and heating of the received solution. Through a cell with a sample the purified air which then comes to the electrochemical sensor is passed. The amount of the air which passed through the sensor is measured by the mass flowmeter, and the detector measures hydrogen sulfide content. The lack of a method is that there are strong interfere influences of the polar components poisoning the sensor.

With use of the automatic analyzer by method of fast liquid-phase extraction define the maintenance of H_2S in distillate and residual oil products (such as, ship fuel, naval or fuel oil) and also in petroleum crudes and a wastage of the oil processing plants in the range of concentration of 0.4-200 mg/kg (ASTM D7621). For exercise of this method it is necessary to eliminate the disturbing influence of mercaptans and alkylsulfides, also to carry out test at the established equilibrium of content of hydrogen sulfide in a vapor and liquid phase.

Colorimetric methods of determination of content of H_2S used in the analysis of petroleum of the Middle East in combination with membrane technologies. An initial stage – extraction of hydrogen sulfide in a steam phase with the subsequent analysis on a colorimetric tape. Tests showed high sensitivity and reliability of the method [14]. Suggest to use also the colorimetric sensor – a disposable plate with the sensing reagents-dyes applied on it. The plate contains more than 30 points for different concentration of a hydrogen sulfide from 1 to 50 ppm. The analyzed gas is mixed with the damp nitrogen. Time of the analysis is less than 30 min. Note reliability and low cost of the method [15].

The chromatographic method can be applied both to gas, and to a liquid phase. And it does not demand preliminary replacement or extraction of hydrogen sulfide from relatively light liquids, such, as oil, gas condensates, light oil products. The method considered in [16] is intended for petroleum with the concentration of H_2S from 1.1 to 500 ppm. Division takes place on two columns, one to a dimethyl siloxane phase, another – on porous layer open tubular (PLOT) which hydrogen sulfide separates from other easy sulphurous substance. It use chemiluminescence detector.

As the detector use also flame and photometric, allowing to analyze concentration of H_2S, also methyl- and ethylmercaptan in petroleum and gas condensate in a wide interval according to the Russian GOST 50802 standard. The method is characterized by high sensitivity and accuracy.

Quantitatively, the content of hydrogen sulfide, methyl- and ethylmercaptans is determined at the Astrakhan GPP using GOST R 50802 adapted for fuel oil. Gas chromatographic method approved by VNIIM Institute for Metrology named of Mendeleev. The oil product sample is pre-diluted with toluene and divided into a capillary column with a methylsiloxane liquid phase with the registration of hydrogen sulfide, methyl and ethylmercaptans leaving the chromatographic column by a flame photometric detector (PFD) and the calculation of the measurement results by absolute calibration. For analysis, use the program "Agilent ChemStation", allowing you to create a method of analysis – a set of parameters required to perform a chromatograph analysis according to the analytical task. The method is a set of control tables in which the values of the parameters corresponding to the analysis are specified. The range of measured concentrations varies from 0.0002% up to 0.03% by weight.

The study of the hydrogen sulfide content in petroleum products is also carried out using the method of cyclic voltammetry, which is based on the ability of molecules to electrochemical oxidation in organic media (acetonitrile, methylene chloride, dimethylformamide) to the corresponding cation radical. This electrochemical analysis method consists of applying a cyclic voltage sweep to an electrochemical cell and measuring the current as a function of the applied potential. Cyclic voltammograms are recorded in a three-electrode cell without a diaphragm with a working volume of 5 mm^2, at a potential sweep rate of 0.5 V/s. A stationary platinum electrode is used as a working electrode ($S = 3.14\ mm^2$). The reference electrode is silver-chloride saturated with a waterproof diaphragm. The auxiliary electrode is a platinum wire with a diameter of 2 mm. As a background electrolyte of tetrabutylammonium perchlorate 0.1 M (99.9%) and sodium perchlorate [17].

The combined method of definition of H_2S in the range of 2-20 ppm for residual fuels combining a cyclic voltammetry and the paper analytical device is offered by authors of [18]. With the help of the modified processing method by wax of the paper analytical device forms hydrophobic zones and hydrophilic channels. Zones with a sample and electrolyte are connected to a working nickel electrode, an auxiliary platinum and chlorsilver electrode of comparison. The procedure includes preliminary microextraction of hydrogen sulfide alkaline solution. Then sulphidic ions get to an analytical zone at +0.45 V.

The express method of content of hydrogen sulfide in liquid oil products consists in application of an aspirator with indicator tubes. Use of the special syringe-desorber allows to bubble the studied product before full replacement with the subsequent analysis in an indicator tube. Range of the measured concentration of hydrogen sulfide is from 3.3 to 66 ppm. The given error makes no more than 5% of the relative [19].

It should be noted that now for commodity furnace fuel oil the quantitative determination of content of hydrogen sulfide is carried out according to TR CU 013/2011 and apply only the following standards: GOST P 53716, GOST 32505, IP 570 and GOST 33198.

To reduce the content of hydrogen sulfide in fuel oil, technological methods are used, which are conventionally divided into two large groups: technologies based on physical and chemical methods.

The physical methods of ennobling include Stripping, blowing out or degassing. The first technology to remove hydrogen sulfide from petroleum products introduced in Russia was steam Stripping.

All stream of commodity fuel oil, or its components with the maximum content of hydrogen sulfide comes to an upper of the column equipped with wipers; in a cube steam moves, from a bottom of a column there is a purified fuel oil, the top product is condensed with formation of acid water [20].

However, such simplicity leads to a number of negative consequences which to overcome not easy. Fuel oil enters from the plants where it is cooled to 150 °C, and steam stripping process by steam demands more high temperature – higher than 200 °C in order to avoid fuel oil flood. It involves need of heating and a energy consumption. The dissolved hydrogen sulfide completely is removed from fuel oil, however during its finding in the cube of a column a secondary hydrogen sulfide is formed of sulfur compound which begin to decay with formation of H_2S (up to 10 ppm). Providing an acceptable ecological situation requires construction of an additional column on utilization of acid water [20-21].

These problems can be avoided by using another desorbing agent for degassing hydrogen sulfide from fuel oil – inert gas, in particular nitrogen, or light hydrocarbon gases. Process is carried out in the desorber, supplied with the wipers or in rectification columns containing up to 20 perfect plates with a pressure of 0.1-0.3 MPa and temperature providing low viscosity of fuel oil. But aren't higher temperatures of the beginning of decomposition of sulfur compounds of the cleaned fractions, a volume ratio of blow-down gas to raw materials – 1-25:1 Supplies fuel oil and blow-down gas a countercurrent in a top and bottom part of a column respectively. Residual content of hydrogen sulfide doesn't exceed 2 ppm [22].

Stripping of heavy oil products by medium-boiling oil fractions with boiling limits in the range of 180-400 °C, which do not contain sulfur compounds, allows to remove hydrogen sulfide almost completely. The process is carried out in a steam column at a pressure of up to 25 kPa, cooling the bottoms in two stages. The consumption of desorbing agent is from 3 to 35%. To create a vacuum in the steam column-desorber, a water ring pump is usually used, in which an aqueous solution of monoethanolamine or diethanolamine is used as the working fluid [21, 23].

The similar way of steam stripping of fuel oil by medium boiling fractions differing in division of a stream in a desorber and the organization of a countercurrent of a cube residue with a reduced pressure of 0.08-0.26 atm is given in [24].

The advantage of physical methods is that they do not use expensive reagents, do not form acid or alkaline effluents, and in the product the total sulfur content is reduced due to the removed hydrogen sulfide and mercaptans. The disadvantage is the need to install additional distillation and Stripping columns, desorbers, related technological equipment, blocks of utilization of acid water. It demands additional floor spaces, an expense of the denuding agents. Electricity consumption, fuels and waters increases. Utilization of hydrogen sulfide-containing gases is obligatory. Often this problem is solved by extraction of a hydrogen sulfide and the direction it in a stream of acid gas on installations of production of element sulfur on Klaus's technology if that is available in the scheme of the plant. It, in turn, causes requirements to composition of gas and efficiency of installation for ensuring its profitability.

Chemical methods consist in processing of oil and oil products the reagents interacting with hydrogen sulfide. As absorbers and converters use the various substances containing formaldehyde, amines, their derivatives, triazine derivatives, acrolein, hydrogen peroxide, methanol, compounds of the dioxazine series [25-35]. Absorbers are substances that bind hydrogen sulfide into reversible compounds that can decompose with the release of free hydrogen sulfide, and neutralizers are substances that form strong chemical bonds [25].

The most often used combinations of components of absorbers are: water and formaldehyde in various ratios; formaldehyde and methanol; amines; carbamide, dialdehydes, triazine derivants. The specific consumption of absorbers varies in the wide range: from 1.5 to 20 g/g of H_2S depending on an absorbing capacity and activity of reagent [31]. In absorption of a hydrogen sulfide reagents on the basis of triazines which resultant of reaction has the covalent binding "carbon-sulfur" have the greatest activity. Triazines interact with H_2S with formation of rather stable compounds soluble in fuel oil which can be exposed to heating to 350 °C [31,32]. The chemistry of interaction of additive on the basis of triazine with a hydrogen sulfide looks thus [25]:

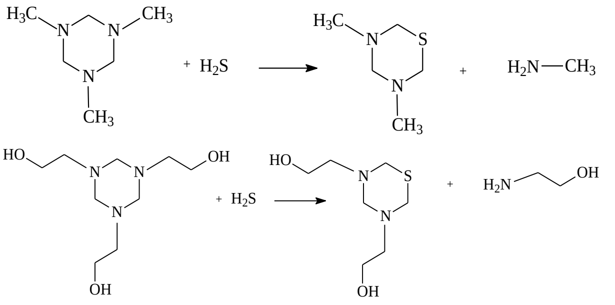

Fig. 1. Chemistry of the interaction of triazines with hydrogen sulfide molecule

Рис. 1. Химия взаимодействия триазинов с молекулой сероводорода

The first triazine reacts mainly with the addition of one molecule of hydrogen sulfide. The second triazine, due to the presence of the polar hydroxyl group, shifting the electron density, is able to react with two molecules of hydrogen sulfide, and under favorable conditions – even with three:

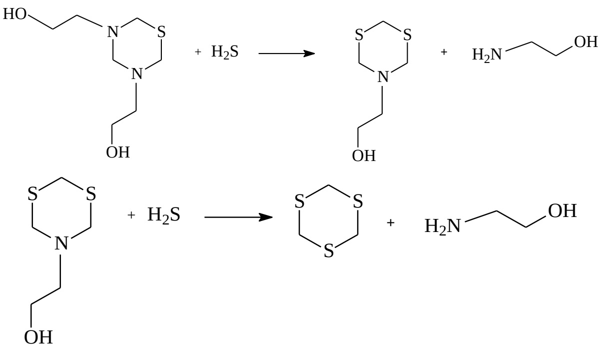

Fig. 2. Chemistry of the sequential interaction of triazines with two or three hydrogen sulfide molecules

Рис. 2. Химия последовательного взаимодействия триазинов с двумя или тремя молекулами сероводорода

Thus, additives based on triazines having radicals-CH_2-CH_2-OH, at equal molar concentration of the main substance will always be more effective. According to the authors, BASF was the first to use such triazines [20].

Authors [34] consider that use of chemical absorbers – one their effective ways of a solution of the problem of presence of a hydrogen sulfide at fuel oil. In certain cases enter the substances capable into their structure simultaneously to have a dispersing ability, to inhibit processes of corrosion and to suppress the growth of sulfate-reducing bacteria [35].

Absorbers and neutralizers bind hydrogen sulfide to the formation of non-volatile sulfur compounds. They are often toxic, flammable, corrodent and has an unpleasant smell. They can lead to precipitation and sediment. Aqueous solutions of some of them have a high alkaline pH, and the water contained in them can worsen the boiler fuel index for content of water-soluble acids and alkalis. The efficiency level of some absorbers is unstable. Many absorbers and neutralizers have a very high cost. The content of total sulfur in the commodity product as a result of the interaction of absorbers is not reduced. Further combustion of the fuel produces additional amounts of carbon dioxide, polluting the environment. Finally, their influence on the quality and safety of commercial fuel oil has not been sufficiently investigated. In addition, additives sometimes lead to the formation of loose deposits and an increase in fuel consumption [4, 9, 36].

Technical solution on increase in effectiveness of oil refining from hydrogen sulfide and mercaptans due to use of the technology based on combination of physical and chemical methods of impact on initial oil is offered in [37]. The essence is that at the first stage of cleaning the physical method is used for removal of the main amount of hydrogen sulfide and mercaptans, and at the second stage residual amounts of sulfur compounds connect in the chemical way with the purpose of bringing quality of naphtha to requirements of the standard.

To chemical methods of neutralization of H_2S should include the ozonolysis. Removal of hydrogen sulfide occurs in the ozonation reaction to sulfur dioxide and water. The implementation of this method requires relatively simple technological equipment, low temperatures and an ozone production unit [38].

Oxidative methods of hydrogen sulfide removal are implemented in the presence of catalytic complexes containing metals such as iron, cobalt. For example, sulfur-containing substances are oxidized to the corresponding sulphone by the oxidizing system H_2O_2-CH_3COOH-$FeSO_4$ [39].

Low-energy wave technologies – a constant magnetic field of low strength, low-frequency electric and ultrasonic fields intensively investigate in recent years and put into practice. Numerous examples show that their impact on hydrocarbon raw materials allows to improve considerably indicators of many processes of oil processing [40]. Among them there are processes on removal of sulfur compounds, distillation of mild components and gases in solution.

For ultra-deep desulfurization of fuels with the help of ultrasound (28 kHz, 0.408 W/cm^2) intensify oxidizing translation processes of sulfur compounds in sulfones which extract then polar solvents with effectiveness up to 99% [41, 42]. Ultrasonic methods of decrease in content of sulfur compounds in petroleum, mixes of oil products, residual fuels and an oil wastage are developed [43, 44].

The mechanism of action of ultrasound on oil disperse systems lies in the fact that large associates of molecules (supramolecular formations, tori, crystallites, etc.) are crushed and reduced in size [45, 46]. These changes favors to processes of refining or upgrading of petroleum and oil products, including heavy.

A constant magnetic field (induction 0.15-0.23 T, linear flow rate up to 0.01 m/s) during vacuum distillation of hydrocarbon residues causes an increase in the yield of distillates by 2-6% by volume. And the effect is greater, the heavier the residue. For pretreatment raw materials initial boiling point of residues was 10-60 °C lower than the no pretreatment raw materials, than for the raw depending on its structure [47]. At atmospheric distillation of gas condensate pretreatment processed in a magnetic field the yield of light distillates increased by 7-10%. At the same time the quality of products increased: octane value of gasoline fraction grew by seven points, the viscosity of diesel fraction and the coking behavior of the residue decreased [48].

The action of a constant magnetic field on the flow of crude oil intensifies the process of dehydration and desalting. In the combination of a constant magnetic field with a demulsifier, the dehydration depth is 98-99% [49].

The effect of a constant magnetic field on the above effects in oil dispersed systems is associated with the presence of unpaired spins in molecules. Paramagnetism of petroleum products, estimated by the number of paramagnetic centers, varies from 10^{15} for the gasoline fraction to 10^{18}-10^{20} spin/g for fuel oils and tar oils [50]. Paramagnetic molecules (their unpaired spins) are oriented in the external magnetic field in the direction of the field vector. In a constant magnetic field, this leads to a change in the mutual positioning of molecules due to turns, deformation of associates with the loss of part of the outer layers and their transition to a dispersion medium. As a result of such restructuring, there is a more ordered strongly correlated organization of the dispersed structure with smaller particle sizes of the dispersed phase.

The process can be accompanied by an increase in the amount of the dispersed phase passing through the free-radical process of homolysis of molecules of resins and asphaltenes having weak bonds between large fragments [50]. It is known that after exposure to a constant magnetic field (induction of 0.225 T) in dynamic mode on straight-run oil and gas condensate residues, the number of paramagnetic centers in the treated samples increases by 1.1-1.3 times in comparison with the initial ones depending on the nature of the residue [51].

Application of influences by ultrasound and the constant magnetic field allows at small energy consumptions for generation of ultrasound and an electromagnetic field (for permanent magnets consumption of the electric power is absent) targeted to transform oil disperse systems for obtaining required effect. At the same time low-energy influence on hydrocarbon raw materials and oil products ultrasound and a constant magnetic field answer environmental challenges of the present: are reagentless, don't make a wastage and don't pose a threat for health and human life and a surrounding medium [47].

The directions of processing of a hydrogen sulfide, the mercaptans and other toxic and aggressive light sulfur compounds extracted from an oilstock or oil products (including processes of blowing out, desulphurization and hydrotreating) decide by their quantity, structure and combinations on other processes. Most often acid hydrogen sulfide-containing gases, utilize by Claus's method where they receive element sulfur with conversion from 94 to 99.9%. This process is considered now the most universal since allows to reduce considerably emission of pollutants in a surrounding medium and to minimize risk of a stop of plant and dumping of hydrogen sulfide-containing gas on a torch [52].

The main disadvantages of the Claus process in a two-stage direct-flow scheme are a low degree of conversion of hydrogen sulfide into elemental sulfur (94-96%), limited by the thermodynamic equilibrium of the reversible reaction of the interaction of H_2S and SO_2. To increase the conversion of H_2S into sulfur, an additional catalytic stage of post-treatment from three reactors, more efficient catalysts are used, which allows increasing the conversion to 99.9%, but complicates and increases the cost of the technology [53, 54]. The specific capital investment, cost of sulfur and cost-effectiveness of the Claus process depend on the concentration of H_2S in acid gas. Thus, the cost of processing acid gas containing 50% H_2S is one quarter higher than the cost of processing gas containing 90% H_2S [55].

In multistage, a resource- and energy-intensive technology of receiving sulfur for Claus's method the significant amount of the dioxide of sulfur which is thrown out in a surrounding medium even when keeping ecological standards is inevitably formed. So, for example, at productivity on sulfur of 200 t/day with conversion level of H_2S in sulfur of 95%, about 3.2 thousand t/year of SO_2 are released into the atmosphere. Besides in process a large amount of solid waste (dead catalysts) is formed [56, 57].

The world production of element sulfur from gaseous by-products of refining at oil gas-processing plants reaches 64 million t/year. It is known that demand for element sulfur in the world market often exceeds supply. The cost of commodity sulfur is quite high, and its prices sometimes fall below the cost.

Therefore, the urgent task is to develop new effective technologies that would allow, on the one hand, to completely utilize hydrogen sulfide gas with minimal emissions of sulfur-containing substances into the atmosphere, and, on the other hand, to expand the range of products for processing hydrogen sulfide and other sulfur-containing compounds. To such processes, allowing to process hydrogen sulfide with additional useful product – hydrogen, are radio-lysis, electrolysis, photochemical and thermal dissociation, plasma-chemical dissociation, each of which to some extent has a negative impact on the environment [2]. The main disadvantages of these processes are high energy intensity, or radiation hazard, or low conversion, as well as the requirements for the concentration of hydrogen sulfide in the feed gas. A byproduct of most processes is element sulfur.

Processing of a sulfurous wastage as valuable raw materials for receiving a range of the useful organic compounds (pesticides, fungicides, antioxidants) is a relevant task [58, 59]. Recently the modern production of various products of petrochemical processing is directed, first of all, to a solution of the problem of environmental protection. The ecologically favorable alternate technological processes are economic in comparison with traditional technologies. This results from the fact that harmful and dangerous materials are almost completely utilized during process. Due to their conclusion from a production cycle total material inputs considerably decrease since expenses on transportation and processing of toxic materials considerably decrease.

The growing demand for new materials, especially medicines, determines the modern approach of organic synthesis – the development of fundamentally convenient, economically and technologically sound, environmentally safe and competitive methods of practically important organic compounds synthesis. The environmentally friendly idea of “green chemistry” (atom-economy, rejection of the use of catalysts and protective groups, single-reactor synthesis and complexity, ease of execution) is preferred when developing new technological processes [60, 61]. The competitiveness of electrosynthesis is rather high. Electrochemical reactions belong to the processes of waste-free production, since the role of the oxidizer and reducing agent is performed by the most “pure” reagent – the electron.

At present, electrochemical, catalytic, and electrocatalytic syntheses belong to the methods of "green chemistry", which are modern and quite promising [58, 59]. Electrochemical processes are especially relevant for receiving products of the low-tonnage chemistry demanding the soft conditions of synthesis, for example, of perfumery and medicinal substances [60]. In this regard, the alternate way of use of a sulfur-containing gaseous wastage – the hydrogen sulfide and thiols extracted from various fractions of hydrocarbon raw materials and fuel oil is their use in electrosynthesis by electrochemical activation in organic solvents [61-63]. As a result redox activation, usually, considerably increases reactivity of compounds or the fissile intermediats from mother compounds are generated that allows to simplify their participation in organic synthesis [60].

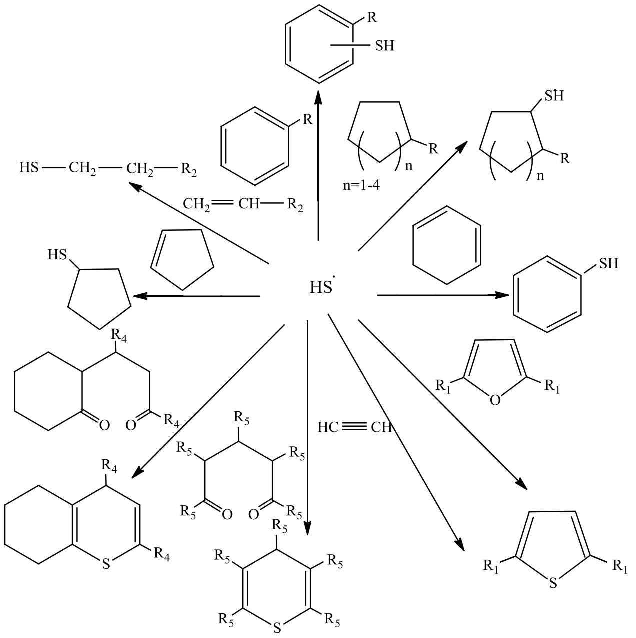

Fig. 3. The use of thiyl radical in reactions with organic compounds to obtain various sulfur derivatives under mild conditions
Рис. 3. Использование тиильного радикала в реакциях с органическими соединениями для получения различных производных серы в мягких условиях

It is expedient to carry out electrosynthesis in those cases if from cheap and available raw materials to which carry hydrogen sulfide and alkanethiols it is possible to receive more complex and almost significant organic compounds (for example, organic polysulfides). It makes sense to apply electrochemical approach to synthesis of compounds if it is possible to carry out single-stage process and at the same time to increase its selectivity on a main product and also to use in case it provides safer carrying out process in terms of environmental protection and when chemical methods of synthesis of compounds are remote.

Earlier [64-71], a wide range of organic compounds was studied for carrying out reactions of their S-functionalization with the participation of hydrogen sulfide.

The effectiveness of the method of utilization of sulfur waste (hydrogen sulfide and low molecular weight alkanethiols) into practically useful products of S-functionalization of hydrocarbons is ensured by the use of redox activation of sulfur-containing reagents. As a result of the anodic or cathodic activation of hydrogen sulfide (alkanethiols) at room temperature and atmospheric pressure, a thiyl (alkylthiyl) radical is formed.

$$H_2S \xrightarrow{-e} H_2S^{\cdot+} \longrightarrow HS^{\cdot} + H^+$$

$$H_2S \xrightarrow[Pt,\ CH_2Cl_2]{+e} 1/2H_2 + HS^-$$

$$HS^- \xrightarrow[Pt,\ CH_2Cl_2]{-e} HS^{\cdot}$$

Fig. 4. Redox transformations of hydrogen sulfide in organic solvents on platinum electrodes with the formation of a thiyl radical
Рис. 4. Окислительно-восстановительные превращения сероводорода в органических растворителях на платиновых электродах с образованием тиильного радикала

For generation of such radicals, as a rule, use conditions of a photolysis, a thermolysis, a radiolysis, or carry out catalytic reactions. For example, to obtain thiols, sulfides and disulfides based on cycloalkanes, alkyl substituted peroxides are used as initiators of radical transformations [72].

Interest in organosulfur compounds is caused by their broad application in various fields of the industry and agriculture. They have high biological activity and are targeted used in organic synthesis, for receiving dyes, antioxidants, medicines, stabilizers of fuels, lubricating oils, polymers and pesticides. Various sulfur-containing alicyclic and heterocyclic compounds have antibacterial, antimicrobial, antiviral activity. Many of them affect to the lipid peroxidation and to the free radical oxidation of oxygen with the formation of its active forms. Thus, these compounds are involved in the biochemical process, which ensures the normal functioning of the body and prevents the development of oxidative stress [73]. The special attention is drawn by the polysufhides which are of great interest to pharmaceutical industry in a type of use as potential antifungal, antihistamine, antitubercular, antibacterial and antineoplastic medicinal preparations [74, 75].

Recently a relevant problem of organic chemistry is improvement of the existing ways of synthesis of organic derivants of sulfur. It is caused by «rigid» conditions of the traditional synthetic approaches necessary for generation the thiyl and the alkylthiyl of radicals.

Energy-saving electrochemical synthesis of organic compounds, which has recently gained widespread recognition in industry, can compete with many catalytic, thermal or photochemical methods [76]. In many cases it becomes an irreplaceable method of exercise of target reaction with high selectivity in the path redox transformations of reagent or substrate and also for processing of cheap and available types of raw materials for the purpose of receiving products of high degree of purity.

When conducting electrosynthesis based on hydrogen sulfide and alkanthiols, along with the products of the thiolation of organic compounds, mono-, di-, and trisulfides are also formed, which have a higher biological activity and are less toxic than thiols.

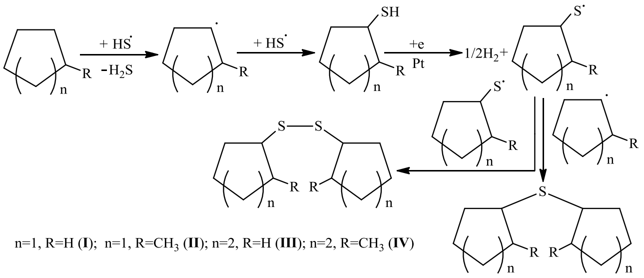

Fig. 5. Synthesis of organic sulfur compounds by thiolation of cycloalkanes with the participation of a thiyl radical
Рис. 5. Синтез органических соединений серы путем тиолирования циклоалканов с участием тиильного радикала

The ability to dispose of sulfur waste in organic sulfur derivatives by redox activation of hydrogen sulfide and alkanethiols demonstrates the promise of further research in this direction. Expansion of the spectrum of organic compounds and the involvement of bicyclic hydrocarbons (indane, indene, decalin, tetralin, etc.) in electrosynthesis will make it possible to obtain thioderivatives based on them at room temperature and atmospheric pressure.

The production capacity of these products is comparable to the volume of recoverable hydrogen sulfide gases from residual fuels in the purification process. Thus, for typical installations of primary processing of gas condensate or oil with a capacity of 3-6 million t/year, the amount of «excess» hydrogen sulfide in fuel oil is from 5 to 30 t/year. Hydrogen sulfide extracted by physical methods neither by volume nor by concentration cannot be used as a raw material for processing into elemental sulfur and in the process of bringing fuel oil to regulatory requirements is a by-product and toxic waste.

Thus, an important scientific and practical task is to develop the basics of energy-efficient technology of extraction, utilization and processing of toxic and aggressive hydrogen sulfide-containing waste generated in the oil and gas processing industry, in particular when cleaning residual fuels, into valuable products with useful properties using the approaches of "green chemistry" and wave methods.

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