

Conference Paper

The Development of New Methods of Disposal of Processing Sulfur Wastes from a Hydro-carbon Feedstock to various Sulfur Derivatives

Nadezhda Titovna Berberova,* Nadezhda Anatol'evna Pivovarova, Valentina Nikolaevna Storozhenko, Elena Vladimirovna Shinkar', and Ivan Vladimirovich Smolyaninov

Astrakhan State Technical University, Astrakhan, Russia

Abstract

The tendency to reduce the content of sulfur compounds in particular H₂S and low molecular thiols (RSH) in oil products sets the task of their extraction and disposal in order to obtain practically useful sulfur compounds. Hydrogen sulfide and thiols can be extracted from hydrocarbon fractions using N-methylpyrrolidone-as selective solvent. Hydrogen sulfide can be extracted from the residual oil products using a low energy exposure such as ultrasound and a constant magnetic field. The releasing gas is concentrated in N-methylpyrrolidone. Further, hydrogen sulfide and mercaptans can be used in the chemical synthesis of biologically active thioethers containing a catechol fragment. Another way of H₂S and RSH utilization is the chemical adsorption of acidic components by modified polynuclear pivalate (acetate) zinc(II) silica gel. As a result of the interaction of complexes with H₂S and RSH, it is possible to obtain zinc sulfide or zinc thiolates, which can be used in various fields of industry or agriculture. Hydrogen sulfide and thiols can also be applied in the electrochemical or microwaved assisted organic synthesis. This approach is promising from the standpoint of environmental safety of synthesis and low energy costs of the reactions. The SH-functionalization of hydrocarbons (indan, indene, decalin, tetralin, naphthalene and 1,2-dihydronaphthalene) leads to obtain biologically active compounds.

Keywords: hydrogen sulfide, thiols, extraction, N-methylpyrrolidone, ultrasonic and magnetic treatment, microwave, redox activation

Corresponding Author:

Nadezhda Titovna Berberova
 berberova@astu.org

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The increase of environmental requirements for the content of sulfur-containing compounds in oil products, in particular hydrogen sulfide and low molecular weight alkanethiols (RSH), causes an urgent need to develop new and energy-efficient ways of their utilization. The known methods of sulfur waste recovery are resource and energy intensive. The application of these approaches does not lead to the production of practically useful sulfur-containing compounds, and in some cases these wastes are burned or discharged into the atmosphere. The particularly negative impact on the

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environment is typical for the processing of hydrocarbons with a high content of sulfur and hydrogen sulfide.

Currently, there are no methods aimed at using waste (H_2S and RSH) as key reagents in the synthesis of various sulfur compounds. In this study it is proposed for the first time to apply a multitarget approach to the refinement of light hydrocarbon fractions or residual petroleum products (fuel oil), followed by their utilization in practically useful organosulfur compounds (see Figure 1).

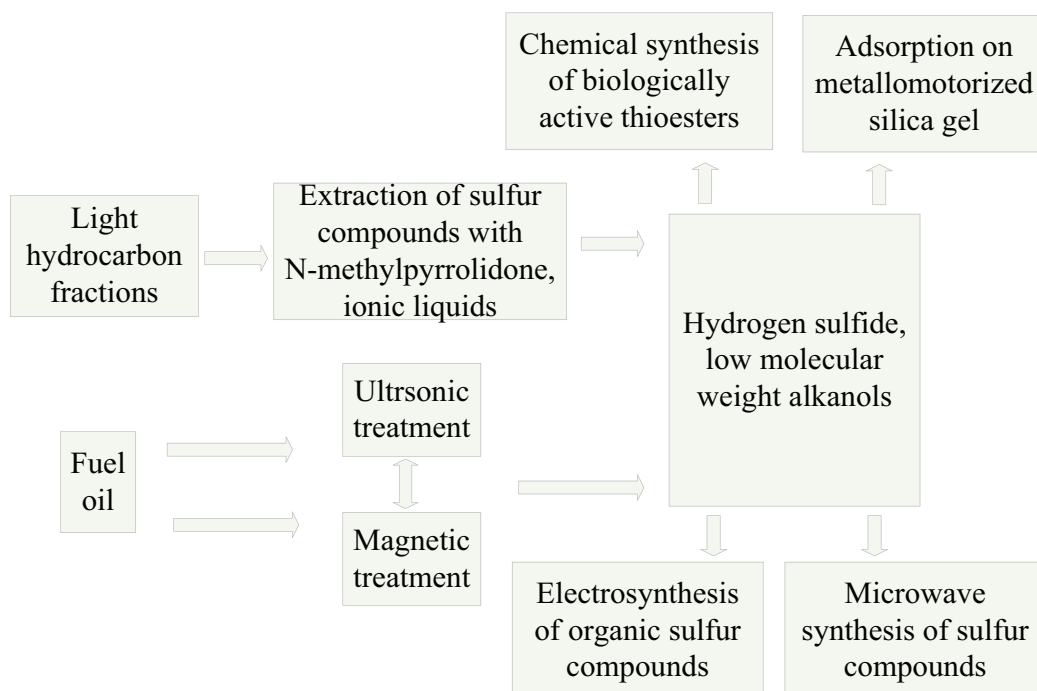


Figure 1: The scheme of disposal of recoverable sulfur waste.

Recently, the promising methods of sulfur removal include the solvent extraction processes. At this stage of research, we have been studied the extraction of various sulfur-containing compounds from the petroleum and condensate raw materials using solutions based on N-methylpyrrolidone. On the example of the model mixture the selectivity of the solvent with respect to different classes of organic sulfur compounds: thiols, mono-, di- and trisulfides is shown. The solvent has the greatest affinity to aromatic sulfur compounds. The degree of extraction (α , %) increases in the range from mono- to di- and trisulfides. In the case of aliphatic thiols, there is a decrease of the degree of extraction with elongation of the hydrocarbon group in thiols (see Table 1).

For light gasoline fractions BP-90°C and BP-120°C the optimal parameters of extraction with mixtures based on N-methylpyrrolidone using co-solvents (water, dimethyl carbonate, glycerin, phenol) were established: temperature 35°C, solvent – raw material

ratio 1:1. Among the considered solvent combinations, the mixture containing 5% wt. dimethyl carbonate showed the highest efficiency with respect to sulfur compounds.

TABLE 1: The degree of extraction of organic sulfur compounds in single-stage extraction from the model mixture.

Compound	α , %	Compound	α , %
$(C_6H_5)_2S_3$	98,0	$C_5H_{11}SH$	71,6
C_4H_4S	83,5	$C_6H_{11}SH$	70,3
C_6H_5SH	81,0	C_5H_9SH	69,6
C_3H_7SH	76,9	$C_6H_{13}SH$	68,7
$(C_6H_{11})_2S_3$	75,9	$(C_4H_9)_2S$	60,2
$C_6H_5CH_2SH$	75,5	$C_7H_{15}SH$	66,2
C_4H_9SH	73,4	$(C_4H_9)_2S$	48,6

At the same time, the highest yield of raffinate at moderate total sulfur content was observed for the water-containing solvent (5% wt.). In this case, the multi-stage extraction of sulfur components from gasoline fractions allowed reducing the content of organic sulfur compounds by 7–10 times (0.0187 and 0.006 % wt.).

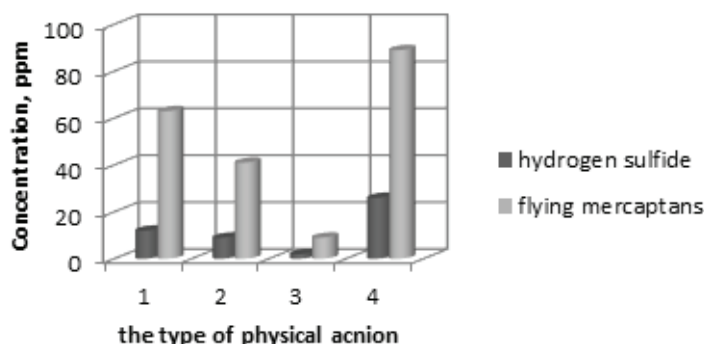
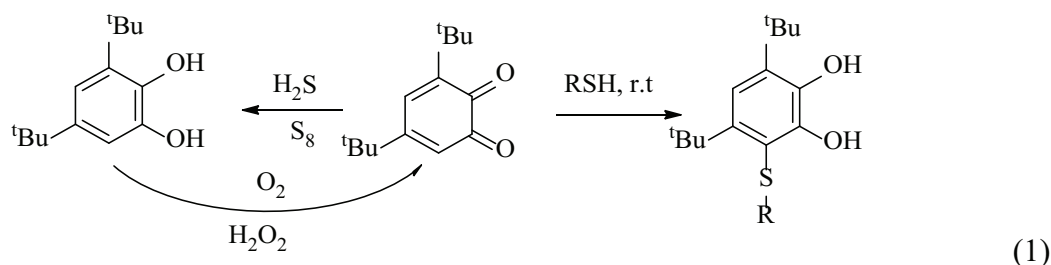


Figure 2: The dependence of the concentration of sulfur components extracted from fuel oil on the type of physical action: 1 – ultrasound, 2 – a constant magnetic field, 3 – a combination of ultrasound and magnetic field; 4 – before treatment.

To intensify the process of extraction of dissolved hydrogen sulfide and low molecular weight thiols from fuel oil, it has been proposed to use ultrasonic and magnetic treatment. The fuel oil flow at a temperature of 60–80 ° C was exposed to ultrasound at a frequency of 20–60 kHz and/or a constant magnetic field with an induction of 0.05–0.3 T. In case of low-energy wave effects, the structure of oil disperse systems changes, resulting in increased efficiency of H_2S and RSH separation (see Figure 2).

The most promising approach is the combination of ultrasonic and magnetic impacts, as the content of hydrogen sulfide and thiols (methyl- and ethylthiols) in fuel oil is reduced by 9–10 times compared to the data obtained before treatment.

As a result of various methods of extraction of H_2S and RSH from hydrocarbon mixtures, a solution of these components in N-methylpyrrolidone or their mixture in a gaseous state is formed. In the first case, it is proposed to direct the concentrate separated from the extract of selective purification for use in the chemical synthesis of biologically active thioethers [1] containing a catechol fragment (scheme 1).



The interaction of low molecular weight thiols with a soft organic oxidizer – 3,5-di-*tert*-butyl-*o*-benzoquinone leads to thioethers with the yield up to 94 %. In the reaction of quinone with hydrogen sulfide sulfur is formed. Sterically hindered catechols are easily regenerated by air oxygen to allow use their oxidized form repeatedly.

The second approach of the further use of a mixture of acidic components is the chemical adsorption of H_2S and RSH on silica modified by polynuclear zinc(II) carboxylates (pivalate or acetate). In the study the effect of ultrasound exposure of different duration on the diffusion of zinc(II) carboxylates into the porous structure of the carrier was analyzed. The process of desulfurization of the model mixture (isooctan + hydrogen sulfide) was also studied.

Using UV-visible spectroscopy and flame atomic adsorption spectrometry methods, it was found that ultrasonic action contributes to an increase in the diffusion rate of zinc pivalate(II) by ≈ 1.5 times compared to zinc acetate(II). The concentration of hydrogen sulfide (100 ppm, isooctane) decreased to 25 ppm after adsorption purification by the data of energy dispersive X-ray fluorescence spectrometry. The experimental data were confirmed by quantum chemical calculations (DFT method, basis of 6-31G(d)/ B3LYP). The results of thermal effect calculations (ΔH) of different pathway of the reactions of metal pivalates (d-elements) with methantiole (H_2S) indicate the absence of energy difficulty of binding transformations ($\Delta H = -176 - (-361)$ kJ/mol). It has shown that the interaction of complexes with H_2S and RSH could lead to obtain zinc sulfide or thiolates, which can be used as potential anti-tick agents in various fields of industry or agriculture [2].

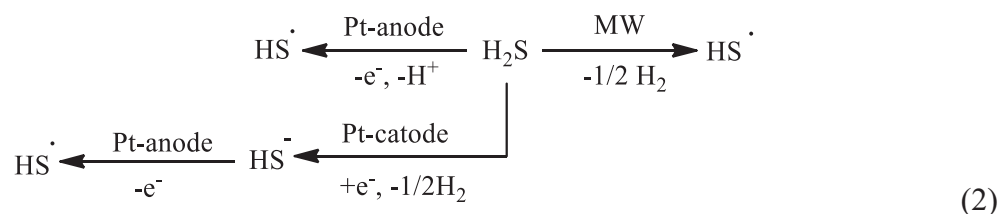
An alternative pathway to use the extracted gaseous waste (hydrogen sulfide and thiols) is electrochemical or microwave activation of these compounds in organic solvents. This approach is promising from the standpoint of environmental safety and low energy consumption.

In the work the synthesis of the practically useful thio-derivatives of hydrocarbons (RH): indane (I), indene (II), decalin (III), tetralin(IV), naphthalene (V) and dihydronaphthalene (VI) has been performed under activation of H₂S.

As a rule, the functionalization of the inert compounds occurs in the reactions with H₂S under rather severe conditions such as photolysis, thermolysis or radiolysis. Catalytic methods of C-H bond activation in hydrocarbons are complicated by the need to use expensive metal-containing catalysts, the presence of stages of separation and regeneration of the catalyst. We have developed effective methods of redox and microwave activation of H₂S extracted from fuel oil in the reactions with hydrocarbons (I-VI).

The relevance of the involvement of H₂S in organic synthesis based on RH (I-VI) is determined by the results of computer prediction of the potential biological activity of thiolation products of initial compounds using the program PASS. Calculations with a high probability indicate the possibility of application of the products SH-functionalization, as promoters of renal function and drugs for the treatment of phobic disorders.

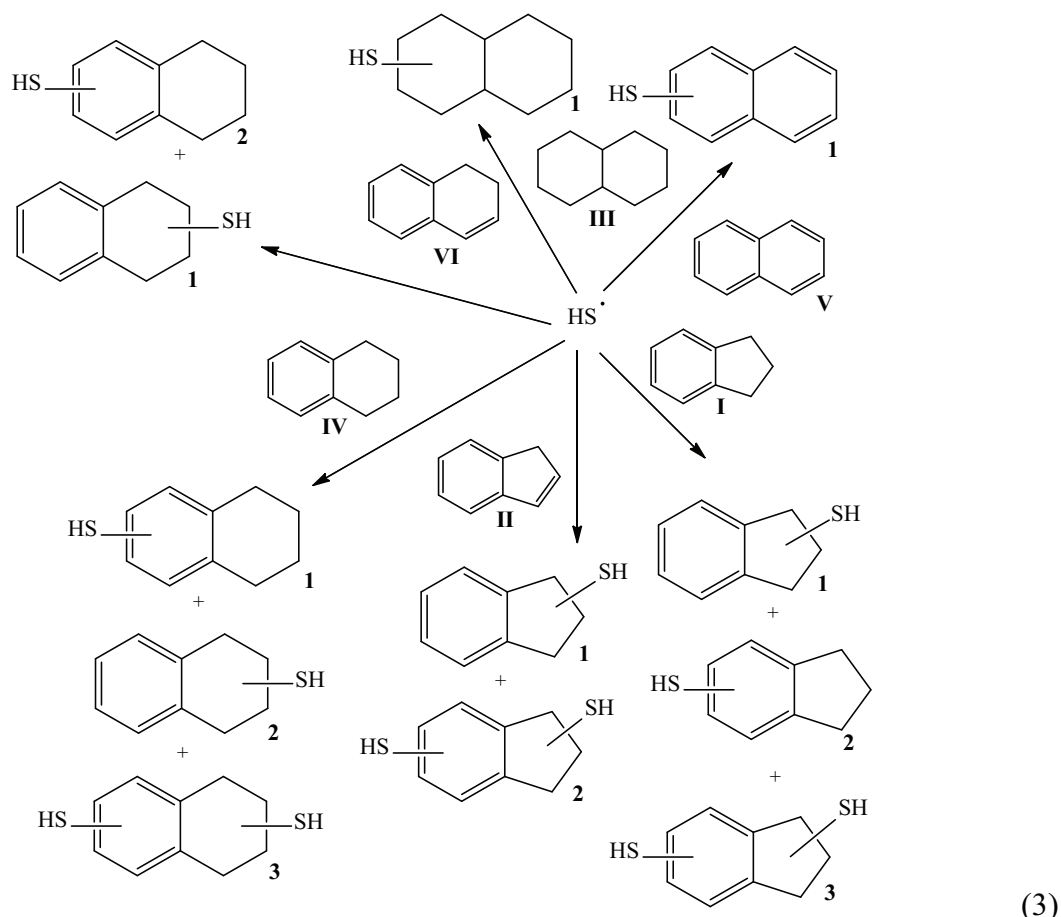
Previously, we have successfully carried out the electrochemical and microwave synthesis of organosulfur derivatives of aromatic compounds, cycloalkenes, cycloalkanes (C₅-C₈) with the participant of H₂S as sulfurizing agent [3–5]. In the paper we propose two methods of redox- H₂S activation (anodic or cathodic) in the reactions with compounds I-VI. One-electron oxidation of H₂S to an unstable radical cation leads to the formation of a thiyl radical. The cathodic activation of H₂S to thiyl radical is characterized by minimizing the bayside transformation of the reagent into inorganic sulfanes (H₂S_n, n=2-8) and sulfur. The thiyl radical is generated as a result of homolysis of the S-H bond under microwave conditions (scheme 2).



Depending on the structure of hydrocarbons, two types of reactions are possible. The first mode is the addition of a thiyl radical to a multiple bond (II, VI), the second is the substitution of a hydrogen atom in an aromatic ring (I, IV, V) or an alicyclic (I, III, IV) fragment (scheme 3).

As a result of the reactions, mainly the products of thiolation of compounds I-VI were obtained, the yield (24-78 %) of compounds varies depending on the method of reagent activation, the duration of synthesis and the structure of hydrocarbons. The formation of dehydroaromatization products for compounds I, II, VI, VI is possible under conditions

of anodic activation of H_2S . The corresponding disulfides were obtained as secondary products of thiols transformations.



Thus, an environmentally safe process of purification of hydrocarbon media from toxic and corrosive waste (hydrogen sulfide and low molecular weight thiols) has been developed. New approaches to utilization of sulfur components based on energy- and resource-saving physical impacts such as ultrasound, magnetic treatment, electric current and microwave irradiation are proposed. The high efficiency of the use of mild organic oxidizers providing utilization of thiols to biologically active thioethers was confirmed.

The expediency of the combined action of ultrasound and magnetic treatment for desulfurization of fuel oil is established. Along with adsorption purification of light hydrocarbon fractions by N-methylpyrrolidone extraction, the prospects of using the method of chemical adsorption of sulfur components on silica gel promoted by zinc(II) carboxylates are shown. The proposed methods of redox and microwave activation of hydrogen sulfide allowed to involve H_2S in the synthesis of practically useful organosulfur derivatives in the mild conditions. This method of H_2S recovery is an alternative to the currently known processes of chemical technology, in which hydrogen sulfide

is considered as an undesirable impurity in hydrocarbon fuels or raw material for the production of sulfur.

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