

Systems for Sulphur Extraction and Recovery of Its Wastes in Industry

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Abstract

New efficient systems are considered for dissolving of sulphur, including its deposits in industrial communications. New ways for recovery of industrial wastes of sulphur are suggested to yield multinomenclature sulphur-organic compounds with the totality of useful properties following the unified technology.

INTRODUCTION

In relation to putting into operation the gas fields rich in hydrogen sulphide and mercaptans, the by-product sulphur production increases and the problem of its deposits removing in wells and pipelines, as well as in industrial communications, becomes acute [1]. Commonly used solvents for sulphur – trichloroethylene, tetrachloroethylene, oil-processing products (AR-1, EBPh, PS) – are characterized by a low efficiency and require elevated temperature [2]. Sulphur is more efficiently dissolved by systems based on dialkyldisulphides [3, 4]. Main obstacle, which restrains their widespread use, lies in the problem of sulphur regeneration from solutions obtained. In addition, the dialkyldisulphides used feature a stable unpleasant smell, which removal requires the special chemical treatment of equipment. The reagents in use are rather expensive.

In dissolving the elemental sulphur, use has also been made of bases, metalloorganic compounds and hydrides of metals. The majority of these methods are of pure preparative importance because of their technologically inef-

ficient nature, laborious implementing, high prices of source reagents. And with the use of alkalis, sulphur dissolving is carried out under violent conditions at high temperatures (up to 100 °C) and is accompanied by considerable oxidation of sulphur [5]. Development of more efficient methods of elemental sulphur dissolving would allow, on the one hand, to recover sulphur when dissolved in the pipelines and industrial communications, and on the other, to obtain on the basis of sulphur solutions the multi-nomenclature sulphur-organic compounds with the totality of useful properties following the unified technology.

RESULTS AND DISCUSSION

We suggested systems of several types for quick sulfur dissolving, with the base-reducing media used for activation of elemental sulphur. That makes for quick and complete dissolving of sulphur at room temperature even with warming-up effect. Resulting aqueous solutions of sulphur are stable in storage, and on their dilution with water most of dissolved sulphur is released of them.

Previously we determined that elemental sulphur is readily activated in hydrazinehydrate – alkali system to form polysulfide anions, which allows these systems to be used for quick and complete dissolving of sulphur [6]. In the process, however, alkali is the corrosive constituent of the system. It was also found that the same efficient activation of elemental sulphur is achieved in hydrazinehydrate – organic amines systems. As the last ones mentioned, there have been tested primary, secondary, and tertiary amines – monoethanolamine, morpholine, triethylamine, and triethanolamine, and pure hydrazinehydrate [7].

Sulphur reacts with hydrazinehydrate with a warming-up and violent release of hydrogen sulphide and ammonia, which condense at the reactor outlet as $(\text{NH}_4)^+\text{HS}^-$ [8]. Reaction of sulphur with hydrazinehydrate – alkali or hydrazinehydrate – amine system starts at room temperature and proceeds exothermally, warming the reaction body up to 60–65 °C. As this takes place, the release of gas decreases and the maximum amount of dissolved sulphur in-

creases (Table 1). This amount depends on the nature of applied amine, its concentration in the hydrazinehydrate solution and is as much as 700–1344 g per 1 l of hydrazinehydrate. As mole fraction of amine increases from 5 to 50 %, the effect of maximum sulphur dissolving grows up about half again, the primary amines being more active than secondary ones and then on to tertiary ones.

The best results are available for hydrazinehydrate – alkali systems and hydrazinehydrate – monoethanolamin system. Alkylamines themselves react with sulphur to give hydropolysulfides or thioamides only on heating or in the presence of catalysts [9]. And only the interaction with sulphur of such an activated amine as benzylamine proceeds at room temperature and results in benzylammonium polysulphides. However, the joint action of sulphur and hydrogen sulphide on alkylamines is accompanied by formation of corresponding polysulfides [10–12].

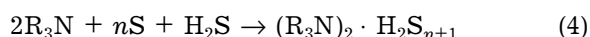
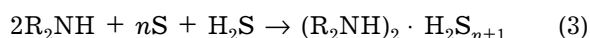
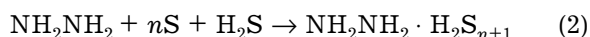
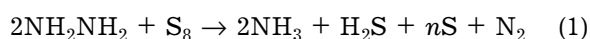
In this connection, the mechanism of sulphur activation in hydrazinehydrate – amine

TABLE 1

Reactions of sulphur and hydrazinehydrate (50 ml) – base system

Base	Proportion hydrazinehydrate : base		Amount of dissolved sulphur	
	mol	% mass	mol	g/l
KOH	1.0:0.05	94:6	1.0	640
KOH	1.0:0.1	90:10	1.31	840
KOH	1.0:0.2	82:18	1.47	940
KOH	1.0:0.5	72:28	1.95	1248
KOH	2.0:0.5	78:22	5.05	1510
NaOH	1.0:0.1	93:7	1.10	704
NaOH	1.0:0.2	86:14	1.30	840
NaOH	1.0:0.3	81:19	1.70	1088
NaOH	1.0:0.5	72:28	1.95	1248
NaOH	2.0:0.5	83:17	5.04	1500
Triethylamine	1:0.05	91.0:9.0	1.1	700
»	1:0.1	83.0:17.0	1.3	830
»	1:0.2	71.0:29.0	1.35	860
»	1:0.5	50.0:50.0	1.5	960
Triethanolamine	1:0.1	77.0:23.0	1.25	800
»	1:0.5	40.0:60.0	1.5	960
Morpholine	1:0.1	85.0:15.0	1.35	860
»	1:0.5	53.0:47.0	1.75	1120
Monoethanolamine	1:0.1	89.0:11.0	1.5	960
»	1:0.5	62.0:38.0	2.1	1344

system is most likely due to primary nucleophilic attack of S_8 by hydrazine followed by opening of sulphur ring and release of hydrogen sulphide and ammonia. Subsequent interaction of sulphur and hydrogen sulphide with hydrazinehydrate or amines results in stable ammonium and hydrazonium polysulphides ($n = 6-8$):



If sulphur reacts only with hydrazinehydrate, then (1) and (2) models are realized to form predominantly ammonia and hydrogen sulphide. In the presence of amine, (3) and (4) models are realized. At low concentrations of amine, more sulphur dissolves in the systems suggested than in hydrazinehydrate – alkali systems [6].

Maximum sulphur dissolving in hydrazinehydrate – alkali or hydrazinehydrate – amine systems results in saturated aqueous solutions of polysulphides, dark-red in colour, which are stable in storage under ordinary conditions. On dilution with water, sulphur solutions eliminate sulphur, which separates out by fractionation of water suspensions.

Systems developed for sulphur activation are noted for their high technological and economical features (reducing agent – hydrazinehydrate, base – sodium hydroxide, organic amines – commercial products), and are also ecologically secure, since hydrazinehydrate, in reduction-oxidation reactions with sulphur, turns into water and nitrogen. Hydrazinehydrate is commonly taken in excess to sulphur, even though its aqueous solutions are used. An excess hydrazine promotes further chemical reactions in solutions obtained. With amines used as a base, the systems suggested for elemental sulphur activation do not cause the corrosion of metal surfaces and may be used to advantage for cleaning of various communications from sulphur in its manufacture and application. Methods of sulfur dissolving in suggested systems are approbated at pilot production conditions in Irkutsk Institute of

Chemistry, SB RAS, preproduction lots of sulphur solutions are produced, which are stable in storage and are able to eliminate sulphur on dilution with water.

Sulphur solutions obtained in base-reduction systems provided a basis for development of further technologies for production of usable sulphur-organic compounds:

1) obtaining of dialkylpolysulphides as sulphuring agents in the manufacture of oil hydrorefining catalysts;

2) synthesis of thiocol on alkylation of sulphur solutions by alkane dihalides;

3) synthesis of alkanedithiols on the basis of thiocol;

4) synthesis of higher dialkylsulphides as extractants of noble metals;

5) use of dialkylpolysulphides to yield synthetic thiophene.

Suggested technologies for sulphur-organic compounds production on the basis of sulphur solutions do not involve organic solvent resources, thus their realization is free of solvent recuperation stages and organic sewage. It is also free of noxious gas release. Sulphur solutions themselves with definite proportions of source reagents appeared to be efficient catalysts in delignification of wood in alkali processing of cellulose [13, 14].

Suggested methods of synthesis for a number of sulphur-organic products are substantially studied in experiments.

Dialkylpolysulphides synthesis

Dialkylpolysulphides are sulphuring agents in the manufacture of oil hydrorefining catalysts. To enhance the parameters of commercial catalysts it is necessary to activate them prior to their use by transforming of catalyst active metals into highly dispersed sulphide forms of a certain structure. Most efficient for catalyst activation appeared to be dialkylpolysulphides, which advantage over the other reagents lies in the fact that they are low-volatile, feature low toxicity, low temperature of thermocatalytic decomposition, are favourable for attainment of high catalytic activity. At present, oil refining plants of Russia own 119 blocks and units for hydrorefining and

hydrocracking, which contain 3540 t of catalyst. With an inter-regeneration period of 2 years, demand for sulphuring agent amounts to 170 t recalculated to sulphur.

The problem of dialkylpolysulphides synthesis by conventional methods lies in the fact that they are based on sodium sulphide reaction with sulphur in the aqueous-alcohol media followed by alkylation of the obtained sodium polysulphides by alkyl halides (occurs at 100–120 °C). These methods are of little technological efficiency and are expensive, since sulphur is appreciably oxidized to sulphates and being lost. In addition, to alkylate sodium polysulphides, the only adequate agents are highly priced alkylbromides or alkyl iodides.

By means of technologically efficient systems for sulphur dissolving, conditions are developed for alkylation of sulphur solutions by lower alkylhalides to form dialkylpolysulphides. Synthesis of dialkylpolysulphides occurs on the basis of elemental sulphur, sodium hydroxide, and reducing agent in aqueous media at atmospheric pressure and room temperature (preparing of sodium polysulphides) followed by alkylation by appropriate alkylchloride also at room temperature. The presence of an excess hydrazine promotes activation of polysulphide anions in the reactions with alkylchlorides. The yield of highly pure dialkylpolysulphides is nearly quantitative. The reducing agent in use is acceptable from the ecological point of view, since in the course of synthesis and sewage recovery, it turns only into water and nitrogen [15].

Conditions are developed for alkylation of sulphur solutions by higher alkylhalides, which leads to higher dialkylpolysulfides, being extractants of noble metals (dioctylsulphide).

Production of synthetic thiophene

Thiophene is more important intermediate product of commercial organic chemistry and raw material for production of pesticides, preparations, semiconductor materials, modifiers for oils and fuels, low-temperature oils for refrigerator setups, and hydraulic liquids. Silicon-organic monomers on the basis of thiophene are used for obtaining of silicon-orga-

nic surface-active substances, in particular, the foam stabilizer KEP-7 applied for fabrication of fireproof polyurethane foam highly competitive in its properties with best available foreign foam stabilizers. Foam stabilizer KEP-7 is also efficient as surface-active dope in production of top-quality galvanic coatings.

Commonly synthesis of thiophene based on sulphur-organic compounds is performed by two ways – catalytic or thermal. The development of catalytic methods is blocked by lacking of sufficiently stable catalysts, therefore, thermal methods of thiophene synthesis from sulphur-organic compounds hold much promise. Thermal methods of thiophene synthesis are based on acetylene co-pyrolisis of lower dialkylpolysulphides or disulphide oil (mixture of disulphides, %: 25 Me₂S₂, 25 Et₂S₂, 50 MeS₂Et₂) [16, 17]. Hence, the co-pyrolisis of dimethyl- or diethylpolysulphides with acetylene (470–520 °C) produces thiophene in yield up to 60 %. Gas-phase reaction of dibutyldisulphide and acetylene (400 °C) results in thiophene, the yield of which may be as much as 70 %, but in the process, the yield of benzene increases to 25 %. Thiophene is readily available from reaction mixtures by rectification (standard columns). By-products and gases are easily recovered (hydrogen, hydrogen sulphide, methylmercaptan, carbon disulphide, thienothiophene, benzothiophene and hydrocarbons C₁–C₄).

As of now, technological regulative has been prepared for thiophene production at pilot setup and required data are obtained for development work. The process modification conditions have been developed to enhance the thiophene yield up to 80 % and method selectivity up to 95 %. The developed process of thiophene production is economically feasible when included in the general technology of sulphur-rich oil and natural gas processing. Substantial promises in realization thereby stem from the possibility of the wastes recovery. Sulphide-alkali runoffs taking away 36.5 % of sulphur may be used for disulphides production. Separated in the process of distillation, lower dialkylsulphides may be used as malodorants for domestic gas or as a raw material at the same setup. High-boiling sulphur-rich remainders in circumstances of oil-refining plants may go for bitu-

men production, since compounds of this sort have practically no effect on its properties if not enhancing them.

It is important for Russia to obtain low-cost domestic thiophene and to develop diversity of manufactures with its use, as well as to exclude import of thiophene and products around it (medicinal preparations and other). Besides, there exist foreign needs for thiophene, which can be met through export of thiophene or products around it.

Synthesis of thiocols and alkanedithiols

Conditions are developed for alkylation of sulphur solutions in found systems by dialkyl-dihalides to form thiocols. Thiocols are produced by reaction of alkanedihalides with Na_2S_2 or K_2S_2 generated from elemental sulphur and alkali in aqueous hydrazinehydrate [18, 19]. Thiocols represented syntons for producing of alkanedithiols and alkanepolythiols from simple industrial products. The method is based on S-S bond reduction of appropriate poly(alkyl-endisulphides)(thiocols) in hydrazinehydrate – base system. Polymer dissolving in hydrazinehydrate – base system occurs smoothly when slightly heated and goes to completion over a period of 1 h at 80–90 °C. Alkanedithiols are separated on slight acidification (0 °C) of obtained dithiolate anions [18].

1,2,3-Propanetrithiol synthesis has been performed on the basis of such ready available source reagents as sulphur and 1,2,3-trichloropropane. Reaction of the last mentioned with sulphur solutions in $\text{NaOH} - \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} - \text{H}_2\text{O}$ system results in disulfide thiocol in nearly quantitative yield. Reducing splitting of thiocol by alkali solution of hydrazinehydrate followed by acidification with hydrochloric acid produces trithioglycerol, which yield exceeds 60 %. The synthesis may be performed in one reactor.

CONCLUSION

All necessary reagents for sulphur dissolving are in commercial production (sodium hydroxide and hydrazinehydrate). Ecological aspect is due to simplicity and harmlessness of clean-

ing technology for pipelines and industrial communications from elemental sulphur, the freedom from noxious gas release and organic sewage. Developed on the basis of sulphur solutions, technologies of sulphur-organic products manufacture are based on low-cost raw materials, high yield of target products, the potentialities for recovery of wastes, ecological security of suggested processes. Domestic chemical products obtained may substitute import raw materials in the manufacture of medicinal preparations, polymers, extractants, semiconductors etc., and also may be exported.

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