

REVIEWS

MERCAPTANS FROM GAS CONDENSATES AND CRUDE OILS

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Industrial separation schemes are described, and promising areas of application of mercaptans from gas condensate and kerosene distillates of medium-sulfur crude oils are noted. The fields of mercaptan-containing gas condensates and crude oils in regions confined to the Caspian Sea basin opened up with the development of deep drilling technology. Many of these fields have been industrially exploited in the Astrakhan' regions of the Russian Federation, Kazakhstan, and Uzbekistan. Production of Markovo crude oil in the Irkutsk region with a uniquely high mercaptan content has begun. Production of heavy carbonaceous crudes containing up to 50-80 ppm methyl- and ethylmercaptans is increasing at high rates in the region between the Volga and the Urals.

With the increase in production of mercaptan-containing gas condensates and crude oils, it became possible to extract and use natural mercaptans – new chemical stock for independent applications – in the economy.

We would like to acquaint the reader with industrial methods of production and areas of application of natural mercaptans.

MERCAPTAN COMPOUNDS IN CRUDE OILS AND GAS CONDENSATES

Mercaptans are not found in many West Siberian crude oils. Crudes from the Ural-Volga region are also distinguished by a low content and sometimes the total absence of these compounds [1]. Of the crudes from this region, only the high-sulfur crude from the Ishmael field (up to 0.3 wt. %) and Kuibyshev region (up to 0.45 wt. % mercaptan sulfur) contain the most mercaptans.

An exception is crude from the Markovo field in East Siberia, as it has a high mercaptan content. Another feature of this crude is the absence of elemental, sulfide, and disulfide sulfur. For a total sulfur content of 0.96-1.08%, the share of mercaptan sulfur is 0.5-0.7%. The organosulfur compounds in Markovo crude oil are thus basically mercaptans and thiophenes.

Gas condensates and Caspian Sea bottom land have a high mercaptan content [2]. The composition of total and mercaptan sulfur in these gas condensates and crudes and the concentration of methyl- and ethylmercaptans, of the greatest interest for the needs of the economy, are reported in Table 1 [3].

Most of the sulfur in almost all cuts is mercaptan sulfur. Tengiz crude and Karachaganak gas condensate contain 350 and 427 ppm C₁-C₂ mercaptans after stabilization. As a consequence, the gas condensate and oil fields in the Caspian Sea bottom lands are a reliable source of lower mercaptans.

According to the published data, the content of macromolecular mercaptans of tertiary structure, *tert*-dodecylmercaptan in particular, is important in 200-300°C kerosene cuts of some crudes and condensates [4]. The content of total, mercaptan, and sulfide sulfur in these cuts of a number of crudes is reported in Table 2.

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TABLE 1

Feedstock	Sulfur content, wt. %					Content, ppm	
	in feedstock	in cut, °C				methylmercaptan	ethylmercaptan
		IBP-62	28-180	160-250	180-350		
Gas condensate							
Astrakhan	1.38/0.38	0.5/0.4	0.43/0.25	0.5/0.32	1.5/0.19	10	160
Orenburg	1/0.7	1.05/0.85	0.9/0.6	—	—	5	400
Karachaganak	0.67/0.16	0.5/0.3	0.4/0.25	0.36/0.16	0.66/0.17	22	405
Crude oil							
Zhanazhol	0.47/0.18	0.6/0.56	0.3/0.23	0.36/0.17	0.37/0.13	12	63
Tengiz	0.76/0.11	0.31/0.3	0.28/0.068	0.25/0.06	0.48/0.038	150	200
Note. In the numerator: total sulfur content; in the denominator: mercaptan sulfur content							

TABLE 2

Sulfur	Content (%) in 200-300°C cut of crude oil			
	Staroishimbai	Terekli	Vvedenov	Markovo
Total	1.48	1.22	1.46	0.81
Mercaptan	0.25	0.28	0.51	0.34
Sulfide	0.72	0.81	0.89	—

Production of synthetic mercaptans, methyl- and *tert*-dodecylmercaptans in particular, has been widely developed abroad. Methylmercaptan is synthesized from methanol and hydrogen sulfide in the presence of aluminum oxide. It is primarily used as stock for production of a substitute for the natural methionine contained in fish meal [5].

tert-Dodecylmercaptan is obtained from propylene tetramer and hydrogen sulfide in the presence of aluminum chloride and used as a molecular weight regulator for different polymer materials [6]. The largest manufacturers of these mercaptans are the American companies Penwalt Corp. (plants in the US, Holland, and Japan) and Phillips Petroleum Co. (plants in the US and Belgium, as well as the French company Atochem [7]. According to the estimates of American and European experts, the synthetic mercaptan production volume in developed countries is greater than 150,000 tons/year. Western Europe's share is approximately 30% of this amount. The annual increase in production is approximately 7% [8]. As indicated above, due to the large reserves of unique mercaptan-containing feedstock, Russia can use it to manufacture mercaptans.

SEPARATION OF LOW-MOLECULAR-WEIGHT MERCAPTANS FROM GAS CONDENSATE.

AREAS OF APPLICATION

Extraction of mercaptans from condensate is based on alkaline extraction with subsequent thermal regeneration of the alkali. The process scheme for production of low-molecular-weight mercaptans from stable gas condensate is shown in Fig. 1 [9]. After stabilization, the condensate is fed in from underneath the extractor and an aqueous solution of alkali goes in at the top. The extractor is a hollow cylindrical unit with valve trays. All of the trays have a spillover device.

The mercaptans react with the alkali in the extractor with formation of sodium mercaptides dissolved in water. The mixture goes into tank 2 where the alkali solution containing sodium mercaptides goes through a

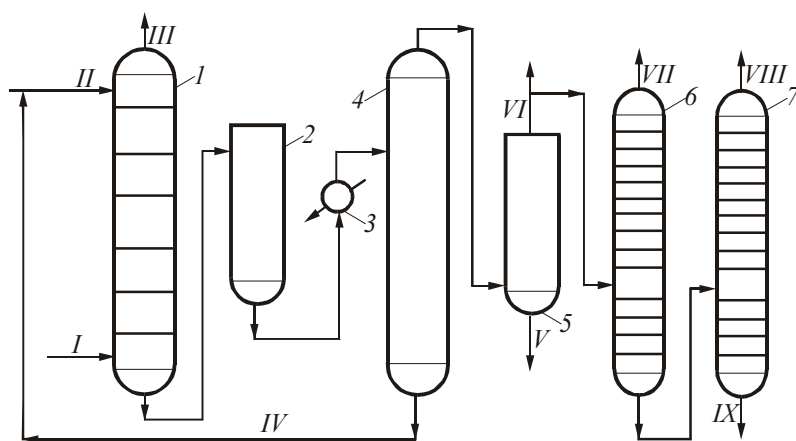


Fig. 1. Process diagram of extraction of lower mercaptans from gas condensate: 1) extractor; 2, 5) tanks for alkali with mercaptides and mixture of mercaptans; 3) steam heater; 4) regenerator; 6, 7) fractionation towers; I) stable condensate; II, IV) fresh and regenerated alkali; III) treated stable condensate; V) water for treatment; VI) mixture of natural mercaptans; VII) methylmercaptan; VIII) ethylmercaptan; IX) residue.

heater to a regeneration tower after clarification of hydrocarbon condensate. By heating the solution, the sodium mercaptides decompose into mercaptans and free alkali in this tower.

Mercaptans and water vapors going in at the top of the regenerator are condensed and poured into tank 5, where they are separated into two layers: lower: aqueous, and upper: mixture of mercaptans. The highest degree (65-72%) of extraction of mercaptans is attained with a 2.5:1 ratio of condensate to alkali and is a weak function of the concentration of alkali within the limits of 1.5-10 wt. %.

The regenerated alkali solution at the bottom of the regenerator goes to the extractor after cooling as a mercaptan extractant. The purified stable condensate at the top of the extractor goes to the commercial product farm. The mixture of mercaptans at the top of the regenerator goes into tank 5, is removed from the unit after settling and is used as a fuel gas odorant. If necessary, this mixture can easily be separated into individual products by fractionation.

The 99.5% pure commercial ethylmercaptan resources at Orenburg Gas Processing Plant (GPP) are estimated at 10,000 tons/year [10]. It can be used for production of pesticides (Etafos) and herbicides (Sutana, Kotofora, and Eptana) [11]. Methylmercaptan can be used as feedstock for production of synthetic methionine a valuable substitute for natural methionine $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$.

In all industrial methods of synthesis of methionine, methylmercaptan is added at the double bond to acrolein with formation of 3-methylthiopropionaldehyde in the first stage. This stage can be organized directly at the plant manufacturing natural methylmercaptan, eliminating shipment of toxic mercaptan with a strong unpleasant odor.

Unfortunately, methylmercaptan is irrationally used at gas processing plants. At Orenburg GPP, after alkali removal of sulfur-containing compounds from the propane-butane fraction, the alkali is regenerated, and the products of regeneration containing 80-85% methylmercaptan and 20-15% ethylmercaptan are burned in elemental sulfur production furnaces [12]. No qualified use has been found for the method of extracting lower mercaptans from natural gas by low-temperature absorption of gas condensate cuts [13].

Production of synthetic methionine and a number of pesticides and herbicides from natural mercaptans can thus be organized in Russia.

Another use of mercaptans separated by alkali extraction is for catalytic oxidation of alkali solutions of mercaptides to disulfides in the presence of cobalt and vanadium phthalocyanine complexes [14]. The mercaptans are extracted from the feedstock with a solution of alkali in which the catalyst is dissolved.

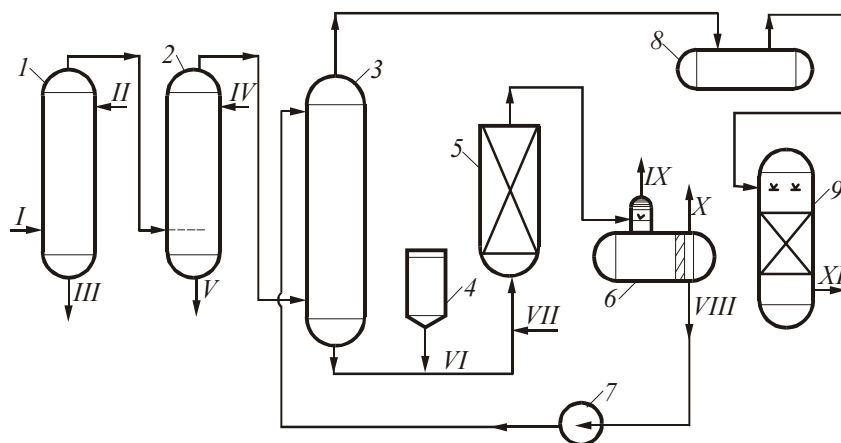


Fig. 2. Diagram of the plant for demercaptization of liquefied gases with simultaneous production of disulfides: 1, 2) towers for removal of hydrogen sulfide and alkali washing; 3) extractor; 4) tank with catalyst; 5) oxidation tower; 6, 8) sulfide and alkali sedimentation tanks; 7) pump; 9) sand filter; I) liquefied gas; II) amine; III) amine for regeneration; IV, V, VIII) fresh, spent, and circulating alkali; VI) addition of catalyst; VII) air for oxidation; IX) blown gas for combustion; X) disulfides; XI) treated liquefied gas.

On contact of an aqueous solution of alkali containing mercaptans in the form of sodium mercaptides with atmospheric oxygen, the mercaptans are converted into disulfides which are separated, and the aqueous solution of alkali with the catalyst dissolved in it is sent for extraction again. This method is the basis of removal of mercaptans from liquefied gases with simultaneous production of disulfide concentrate [15].

The process scheme is shown in Fig. 2. The feedstock is fed into tower 1, where hydrogen sulfide is removed in countercurrent with amine. Preliminary removal of hydrogen sulfide residues is conducted in tower 2 with an alkali. The product, free of hydrogen sulfide, and at a temperature of 15-35°C, goes into the extractor where it is in contact with a moving countercurrent with a catalyst complex in the ratio of 3:1. The catalyst complex is obtained by dissolving the catalyst (0.3-0.5 kg) periodically fed from tank 4 in 10-20% caustic soda solution (1000 kg).

On contact with the catalyst complex, the mercaptans are transformed into mercaptides and pass into the alkaline phase. The product, free of mercaptans, enters sedimentation tank 8 for separation of the alkali solution and passes through a sand filter into the commercial product farm.

The mercaptide-saturated catalyst complex goes into tower 5, and air is delivered for oxidative regeneration. The contact time of the catalyst complex with the air is a minimum of 5 min. The regenerated complex from the tower goes into sedimentation tank 6 for separation of disulfides and is then pumped back into the system. The disulfides are insoluble in the catalyst complex and are separated by simple sedimentation.

The described process has the following drawbacks.

- The spent alkali solution containing the catalyst – cobalt phthalocyanine complexes – is periodically taken out of the plant and mixed with plant sulfur-alkali wastewaters with a very undesirable cobalt ion content.
- When an alkali solution of a homogeneous catalyst is used, it is necessary to very accurately proportion the oxygen for oxidation of the mercaptans and regeneration of the catalyst. With an excess of oxygen in the alkali solution, the mercaptans are oxidized into disulfides in the stage of extraction of the mercaptans with subsequent repeated extraction of disulfides into the treated hydrocarbons. It is undesirable for disulfides to enter the hydrocarbon fraction in which the total sulfur content is limited. With an oxygen deficit, some of the catalyst is not regenerated so that the efficiency of the treatment decreases.
- Important fluctuations in the initial concentration of mercaptans at the plants make it difficult to control the temperature and air flow rate in the regenerator.

To eliminate these drawbacks, the process has been perfected in a number of plants [16]. The mercaptan-containing alkali solution began to be regenerated with a catalyst on a solid support. Entry of metal

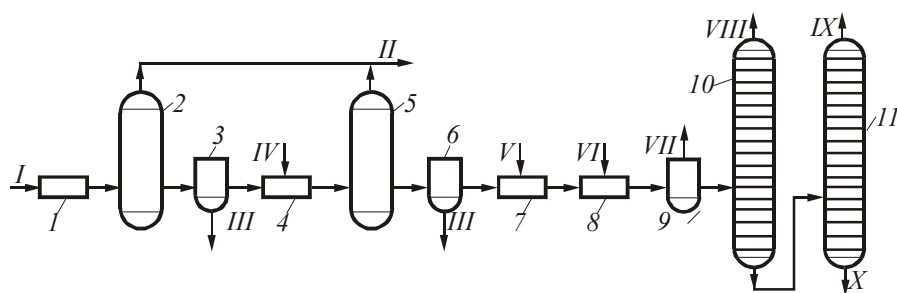


Fig. 3. Industrial scheme for separation of mercaptan concentrate from the kerosene cut: 1) knothole mixer; 2, 5) stage I and II contactor towers–sedimentation tanks; 3, 6) stage I and II collectors; 4) stage II mixer; 7, 8) mixers for washing out isopentane and for breaking up the emulsion; 9) mercaptide layer sedimentation tank; 10) alcohol distillation tower; 11) mercaptan stripping tower; I) feedstock (kerosene cut, alkali, alcohol); II) spent kerosene cut; III) spent alkali; IV) kerosene cut in stage II; V, VII) fresh and spent isopentane; VI) water; VIII) spent alcohol; IX) mercaptan concentrate; X) residue after stripping.

phthalocyanines with the spent alkali solution into the plant wastewaters was totally eliminated in this way, and the lifetime of the catalyst was increased by 10-12 times.

The use of a solid catalyst only in a special reactor eliminated its contact with the treated product in the extractor and consequently prevented oxidation of mercaptan sulfur and contamination of the treated product with disulfides in this equipment.

In demercaptanization of the propane-butane fraction by these method, the mercaptan sulfur content in the feedstock decreases to 3 ppm; the mixture of disulfides obtained has the following composition, wt. % [17]: 47-49 dimethyl disulfide, 26-28 methylethyl disulfide, 24-26 diethyl disulfide.

The disulfide concentrate is used as an odorant for natural gas and for sulfurizing of cobalt- and nickel–molybdenum catalysts for many petroleum refining processes and in agrochemistry [18]. In addition, individual disulfides are obtained and used for production of dialkyl polysulfides, medical products, dyes, and in pesticide production [19].

SEPARATION OF MERCAPTANS FROM CRUDE OIL KEROSENE CUTS

Kerosene cuts with IBP of 190-200 and EP of 290-300°C containing a minimum of 0.25% mercaptan sulfur are used for separation of mercaptans. Mercaptans are separated by alkali extraction using booster additives for completeness of extraction. Methanol [20] and ethanol [21] have shown good results as additives to the alkali.

The feedstock is treated with an extracting solution of 50% caustic soda in alcohol (1:2) taken in the ratio of 1:8. Distillation of the alcohol from the extract phase increases the mercaptan sulfur content in the concentrate to 10-11.5 wt. %. The extract phase is washed with isopentane to remove entrained hydrocarbons so that the mercaptan sulfur content in the final product attains 15-15.3 wt. %. The yield of mercaptan concentration is 2.5-3% in feedstock [22].

A diagram of separation of mercaptans from the kerosene cut is shown in Fig. 3. The feedstock is the kerosene cut and the ethanol and alkali are fed into stage I knothole mixer and the mixture then goes into a sedimentation tank to separate the extract and raffinate phases. The extract phase enters stage I collector where it is separated. The lower layer – the alkali layer – is removed from the system, and the upper mercaptide layer, which is a mixture of mercaptides, alcohol, alkali, and entrained hydrocarbons, goes to the stage II mixer where it is mixed with a new portion of the kerosene cut. The mixture then enters the sedimentation tank and then the stage II extract phase collector where it is separated into alkali and mercaptide phases. After sedimentation, the alkali layer is removed from the system, and the mercaptide layer initially enters mixer 7 for washing out the entrained hydrocarbons with isopentane and then to mixer 8, fed with water to break up the emulsion formed in mixer 7.

The hydrocarbon-free mercaptides and isopentane from mixer 8 go into sedimentation tank 9 and the isopentane is removed from the plant, while the mercaptide phase enters tower 10 for distillation of the alcohol. The mercaptides are simultaneously hydrolyzed into mercaptans in the tower. The mercaptans from tower 10 enter tower 11 and the pure product (mercaptans) is distilled off at the top to the finished product farm and the residue is taken out from the bottom.

The mercaptans obtained are colorless and have the following physicochemical characteristics: cutpoints, °C (pressure, kPa): 43 (1.5)-100 (1); density at 20°C, kg/m³: 889.1; refractive index at 20°C: 1.4840; mol. wt.: 179; sulfur content, wt. %: total 16.2, mercaptan 15.2.

Rubbers and their vulcanizates obtained in regulation of the molecular weight of the polymers with *tert*-dodecyl mercaptan and mercaptans of petroleum origin are characterized by identical plastic and physicomechanical properties, as the studies showed [23].

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