

COMBINED SCHEME FOR DEMERCAPTIZATION OF LIGHT FRACTIONS FROM CRUDE
OILS AND GAS CONDENSATES OF THE CASPIAN DEPRESSION

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Crude oils and gas condensates of the Caspian Depression are distinguished by uniquely high contents of mercaptans, mostly concentrated in the head distillate fractions. Mercaptans are low in thermal stability, and hence hydrogen sulfide is evolved when these fractions are heated [1]. Data on the contents of total and mercaptan sulfur in the light fractions of crude oils and condensates from different fields (Table 1) show the following [1-5]: Desulfurization of the IBP-62°C fraction comes down to removal of hydrogen sulfide and mercaptans. This has been proven in processing Orenburg condensate at the Industrial Association "Salavatnefteorgsintez" [6].

With a separate process to demercaptize the Zhanazhol and Tengiz crude oils, it is also possible to solve the problem of producing diesel fuel with a maximum of 0.5% total sulfur. Since these crudes will be processed in the Orsk and Gur'ev refineries, where there is no capacity for hydrotreating diesel fuels, there is an urgent need for the development of a combined scheme to demercaptize light products. Moreover, since these refineries do not have any Claus units, it is necessary to burn the large amounts of hydrogen sulfide obtained in amine treatment of gases from the primary distillation units and hydrogen-rich gas (HRG) in reforming units.

Processing the Zhanazhol and Tengiz crudes involves increases in the quantity of hydrogen sulfide, both in the gases from primary distillation and in the HRG. Therefore, the combined processing scheme should include a section for processing hydrogen sulfide into elemental sulfur by the VNIUS-6 method [7], which is more efficient than the Claus process for handling relatively small quantities of hydrogen sulfide (6000 to 10,000 tonnes per year).

Semicommercial tests have been run in sections for demercaptizing IBP-62°C and diesel fuel cuts at the Orsk refinery, which had begun to receive Zhanazhol crude oil for processing in mixture with other crudes (Émba, Kenkiyak). The treatment consists essentially of liquid-phase oxidation of organic sulfur compounds by atmospheric oxygen in the presence of homogeneous phthalocyanine catalysts.

The flow plan of the unit for demercaptizing light products is shown in Fig. 1. A process known as DMT was developed for demercaptization of the diesel fuel; the treatment of the IBP-62°C cut was performed in accordance with the VNIUS-12 technology [6], which is used at the Industrial Association "Salavatnefteorgsintez" and has been incorporated in the processing scheme of the Astrakhan gas processing plant.

TABLE 1

| Petroleum crude | Total sulfur, wt. % | | | | | Mercaptan sulfur, wt. % | | | | |
|-----------------|---------------------|------------------|--------|---------|---------|-------------------------|------------------|--------|---------|---------|
| | in oil or cond. | in fraction (°C) | | | | in oil or cond. | in fraction (°C) | | | |
| | | H. K.—62 | 28—180 | 160—250 | 180—350 | | H. K.—62 | 28—180 | 160—250 | 180—350 |
| Condensate | | | | | | | | | | |
| Astrakhan | 1.38 | 0.5 | 0.43 | 0.5 | 1.5 | 0.38 | 0.4 | 0.25 | 0.32 | 0.19 |
| Orenburg | 1.00 | 1.05 | 0.9 | — | — | 0.7 | 0.85 | 0.6 | — | — |
| Karachaganak | 0.67 | 0.5 | 0.4 | 0.36 | 0.66 | 0.16 | 0.3 | 0.25 | 0.16 | 0.17 |
| Crude Oil | | | | | | | | | | |
| Zhanazhol | 0.47 | 0.6 | 0.3 | 0.36 | 0.37 | 0.18 | 0.56 | 0.23 | 0.17 | 0.13 |
| Tengiz | 0.76 | 0.31 | 0.28 | 0.25 | 0.48 | 0.11 | 0.3 | 0.068 | 0.06 | 0.038 |

All-Union Scientific-Research Institute of Hydrocarbon Feedstocks (VNIUS). Industrial Association "Orsknefteorgsintez." Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 11, pp. 21-23, November, 1987.

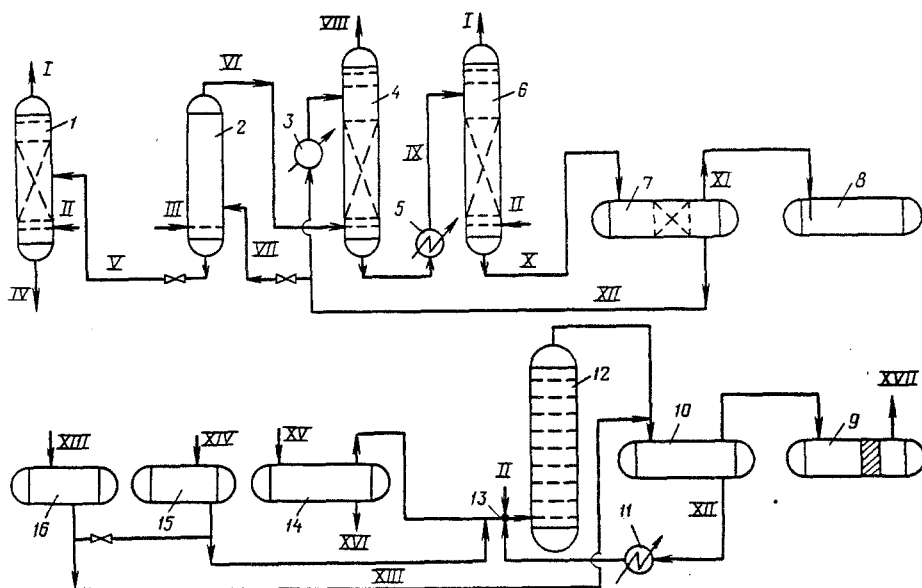


Fig. 1. Combined flow plan for demercaptization of light products at Orsk refinery: I) to furnace; II) air; III) IBP-62°C cut (RH + H₂S + RSH); IV) sour caustic waste (Na₂SO₄, Na₂S₂O₃) to biological treatment; V) sour caustic waste (Na₂S); VI) IBP-62°C cut, freed of hydrogen sulfide; VII) 6% NaOH solution; VIII) treated IBP-62°C cut; IX) catalyst complex with mercaptans; X) catalyst complex with disulfides; XI) disulfides; XII) purified catalyst complex; XIII) concentrated sodium hydroxide; XIV) aqueous caustic solution from stabilizer; XV) diesel fuel to treating; XVI) naphthenic acids; XVII) treated diesel fuel.

Winter-grade diesel fuel (0.17% total sulfur, 0.07% mercaptan sulfur) under a pressure of 0.2-0.5 MPa enters the tank 14, where the naphthenic acids are removed by treatment with a 2-5% aqueous sodium hydroxide solution. The treated diesel fuel is pumped at a pressure of 1-2 MPa to the mixing manifold 13, where it is mixed with circulating catalyst-fuel complex (CFC:DF = 1:1-5), compressed air supplied at 2 MPa, and an aqueous caustic solution from the stabilizer, fed by means of a metering pump (up to 160 liters/h) from the tank 15.

The quantity of atmospheric oxygen fed to the reactor is twice the stoichiometric amount. The pressure in the reactor is maintained at a level to give complete dissolution of the air in the liquid phase. The mixture is fed through a distributing manifold to the reactor 12, where the mercaptans are oxidized to disulfides at a temperature of 50-60°C. The reactor is a column with shower-type sieve trays. The mixture from the top of the reactor passes into the separator 10, where the diesel fuel separates from the CFC; the latter is pumped through the heat exchanger 11 and back to the reactor. The diesel fuel with disulfides from the top of the separator 10 passes into the separator 9, where drops of CFC are removed from the fuel.

For coagulation of the CFC drops, the separator 9 has a bed of Panchenkov packing or activated carbon. From this separator, the treated fuel flows by gravity to the commercial product tank 5 ($S_m \leq 0.005\%$, $S_t = 0.17\%$). Thus, the DMT process does not change the content of total sulfur in the fuel, merely converting the corrosive mercaptans into inert, thermally stable disulfides. This means that the DMT process can be used only in treating fuels with a maximum total sulfur content of 0.5%.

The caustic content in the CFC is lowered from 30% to 10-15% by dilution with the water of reaction; this dilute CFC from the separator 10 is directed to the section of the unit treating the IBP-62°C cut, and the required quantity of concentrated sodium hydroxide solution is pumped into the separator 10 from the tank 16.

The IBP-62°C cut ($S_t = 0.6\%$, $S_m = 0.56\%$, $S_{H_2S} = 0.03\%$) is fed to the vessel 2, where the hydrogen sulfide is removed in the form of sodium sulfide by the spent CFC (sodium hydroxide content 5-6%). The hydrogen sulfide-free IBP-62°C cut passes into the extractor 4.

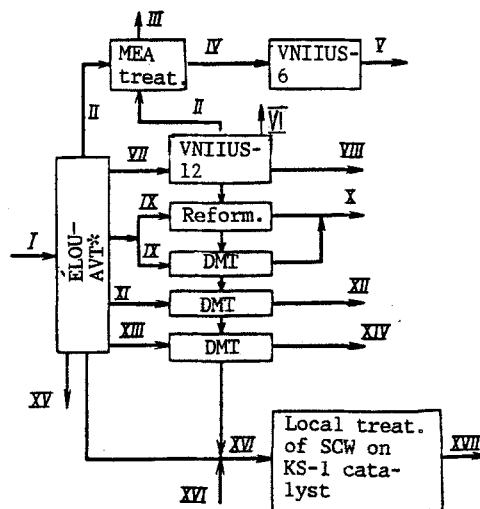


Fig. 2. Block diagram of VNIUS process for demercaptization of gas condensates and crude oils of the Caspian Depression: I) crude; II) hydrocarbon gas and hydrogen sulfide; III) purified gas; IV) hydrogen sulfide; V) elemental sulfur; VI) dialkyl disulfides; VII) IBP-62°C cut; VIII) same, after treatment (RSH \leq 0.003%, Σ S \leq 0.015%); IX) naphtha cut; X) commercial gasoline; XI) kerosine cut; XII) same, after treatment (RSH \leq 0.005%, Σ S \leq 0.25%); XIII) diesel fuel cut; XIV) same, after treatment (RSH \leq 0.01%, Σ S \leq 0.5%); XV) boiler fuel; XVI) sour caustic waste; XVII) same, to biological treatment.

*Electric desalting unit and atmospheric-vacuum tubestill unit (but the text indicates that the tubestill unit is atmospheric pressure only) - Translator.

The catalyst complex is pumped into the top of the extractor at a ratio CFC:RH from 1:5 to 1:10, after precooling to 40°C in the heat exchanger 5. The continuous phase in the extractor is the CFC, which contains 0.003-0.01% DSFK,* 6-15% sodium hydroxide, 1% diethylene glycol, and water. In the extractor, the mercaptans are converted to mercaptides and pass into the caustic phase. The treated IBP-62°C from the top of the extractor 4 is routed to the commercial product tank farm ($S_m = \leq 0.003\%$, S_{H_2S} , none, $S_t \leq 0.015\%$).

The mercaptide-saturated CFC, at 40-50°C, passes into the regenerator column 6. The calculated quantity of air at a pressure of 0.3-0.5 MPa is fed into the still of this column. The caustic is regenerated in the column 6. The spent air from the top of the column passes into the vent system for flaring. The catalyst complex with disulfides passes from the bottom of the column into the separator 7, where the disulfides are separated from the regenerated CFC. The upper layer of disulfides from the separator passes into the tank 8 and from there to storage; the lower CFC layer is recycled through the cooler 3 to the extractor 4.

The composition of the disulfides obtained at the Orsk refinery is as follows (% by weight): dimethyl disulfide 4.4, methyl ethyl disulfide 34.2, diethyl disulfide 57.7, others 3.7. These disulfides have been tested as inhibitors of coke formation in hydrocarbon pyrolysis and as a solvent for the extraction of elemental sulfur; they were found to be highly effective in these applications [8, 9].

The spent CFC after treating the IBP-62°C cut is periodically withdrawn from the system into the tank 2, where it is reused in treating the feed for hydrogen sulfide removal. After complete saturation with hydrogen sulfide in the tank 2, the spent CFC is taken off periodically to the vessel 1 for oxidative treatment to detoxify sour caustic waste (SCW). This vessel receives sour caustic wastes from the entire refinery.

*Initialism not identified in this article; probably refers to the phthalocyanine catalyst - Translator.

The local treatment of the sour caustic wastes consists of oxidation of toxic sodium sulfide and hydrosulfide by atmospheric oxygen in the presence of a heterogeneous phthalocyanine catalyst on a polymeric base (KS-1) to sodium sulfate and thiosulfate at a temperature of 60-80°C and a pressure of 0.1-0.5 MPa. This process is being carried out successfully at the Moscow refinery and the Novokuibyshev Petrochemical Combine [10].

The catalyst used for these processes (VNIIUS-12, DMT, and detoxification of SCW) is an inexpensive and readily available material based on cobalt phthalocyanine (specification TU 014-38-75). Since the catalyst complex can be reused many times, the catalyst consumption in treating 1 tonne of feed is no more than 1 g, with sodium hydroxide 100 g.

At the Gur'ev refinery and at the Industrial Association "Groznefteorgsintez," plans are being made for processing Tengiz crude. Since the Gur'ev refinery does not have any fuel hydrotreating capacity and does not have a Claus unit, and since major capital investment would be required for the construction of the traditional group of units for processing medium-sulfur crudes (fuel hydrotreating, SCW carbonization, Claus process), it will be more desirable to introduce the combined process technology of VNIIUS, which is shown schematically in Fig. 2.

The primary distillation of the crude is performed in existing ÉLOU-AT units (electric desalting unit and atmospheric tubestill unit). The ÉLOU wastewater, containing dissolved hydrogen sulfide and mercaptans, passes to the unit for local treatment of SCW on KS-1 catalyst. The IBP-62°C cut passes to the VNIIUS-12 unit, where it is treated to remove hydrogen sulfide and mercaptans, obtaining disulfides. The diesel fuel and part of the naphtha fractions are demercaptized in DMT units. Part of the naphtha is used as reformer feed. The hydrogen sulfide obtained in amine treatment of the dry gas from the AT and the reformer gas is converted to elemental sulfur in a VNIIUS-6 unit [7].

The VNIIUS-6 process is essentially an oxidation of hydrogen sulfide by atmospheric oxygen at 35-50°C in an aqueous alkaline medium (pH 7.5-9) in the presence of a homogeneous catalyst based on chelate complexes of iron with Trilon B. All components of the catalyst complex are commercially produced materials. In the VNIIUS-6 process, in contrast to the Claus process, the hydrogen sulfide is 100% converted (85% in the Claus process) and colloidal sulfur is obtained, suitable for agricultural applications as a fungicide and acaricide (for control of plant diseases and pests).

The introduction of these processes will give a reduction of the overall costs to the economy (calculated on the basis of processing 1 tonne of crude) amounting to 5.5%, including a reduction of capital investment by a factor of 3.6. The total savings from introduction of these processes in a refinery with a nominal capacity of 6 million tonnes per year will be about 11 million rubles per year, including a saving of capital investment amounting to 14.5 million rubles. This is an indication of the high level of economic efficiency of the combined scheme for demercaptization of hydrocarbon feeds.

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