PETROLEUM AND GAS PROCESSING

THERMAL STABILITY OF ORGANIC SULFUR COMPOUNDS
IN ORENBURG GAS CONDENSATE

A. M. Mazgarov, A. F. Fakhriev,
A. V. Neyaglov, and I. Kh. Gizatullina

The increased production and processing of high-sulfur crude oils and gas condensates is demanding a thorough study of the composition and thermal stability of the organic sulfur compounds present in these materials. It was established in [1, 2] that many organic sulfur compounds are lower in thermal stability than hydrocarbons. When subjected to heating in the petroleum refining process, they undergo various conversions, liberating considerable quantities of hydrogen sulfide and mercaptans, corroding equipment, and having an adverse effect on quality of the petroleum products.

In the present article, we are presenting material from a study of the thermal stability of organic sulfur compounds present in Orenburg gas condensate. The thermal of the organic sulfur compounds was investigated in a flow-type laboratory unit with a contact time of approximately 20 sec, at atmospheric pressure, over a temperature range of 150-500°C. The reactor of this unit consisted of a glass tube with a diameter of 10 mm and a length of 550 mm, within which there was placed a rod made of St. 3 [mild] steel with a diameter of 4 mm and a length of 260 mm. The annular space between the glass tube and the rod formed the reaction zone. The reactor was mounted in a tubular furnace with a stable temperature field that was measured by means of a Chromel—Alumel thermocouple and a PP-63 potentiometer. The temperature in the furnace was held to within ±5°C by means of a laboratory autotransformer. The condensate used as feedstock was supplied to the reactor by a Model M-304 metering pump. The condesate after passing through the reactor was cooled in a water cooler, and the liquid products were collected in a snow-cooled trap. The gaseous products that were evolved upon heating the condensate were carried off by a stream of nitrogen to two series-connected Drechsel models, each containing 50 ml of a 10% aqueous potassium hydroxide solution to absorb the hydrogen sulfide and low-boiling mercaptans.

The group composition of the organic sulfur compounds was determined by potentiometric titration in a PH-121 instrument [3, 4]. The results of these experiments are presented in Table 1.

As can be seen from Table 1 and Fig. 1, the 40-65% of the sulfur compounds in the Orenburg condensate are mercaptans. It is known [1, 2] that mercaptans are the least thermally stable of the organic sulfur compounds, and hence we may except considerable decomposition of mercaptans in high-temperature processing of the condensate. And indeed, when the condensate

TABLE 1. Thermal Stability of Organic
Sulfur Compounds in Orenburg Condensate

Test temperature, °C	Sulfur content, wt. % on condensates						
	H_2S	S_{RSH}	S_{RSR}	S_{RSSR}	S	$S_{unident}$	ΣS
20	None	0,8226	0,3212	0,0461		0,0901	1,28
150	"	0,8188	0,3144	0,0431	"	0,1037	1,28
200	"	0,8099	0,3250	0,0366	"	0,1085	1,28
250	Trace	0,7860	0,3210	0,0386	"	0,1344	1,28
275	0,0005	0,7771	0,3210	0,0460	"	0,1354	1,28
300	0,0020	0,7678	0,3267	0,0459	"	0,1376	1,28
350	0,0041	0,7665	9,3300	0,0423	Trace	0,1371	1,28
400	0,0225	0,6753	0,3316	0,0402	0,0001	0,2103	1,28
450	0,0863	0,5039	0,3117	0,0446	0,0115	0,3220	1,28
500	0,2145	0,4095	0,2825	0,0303	0,0236	0,3196	1,28
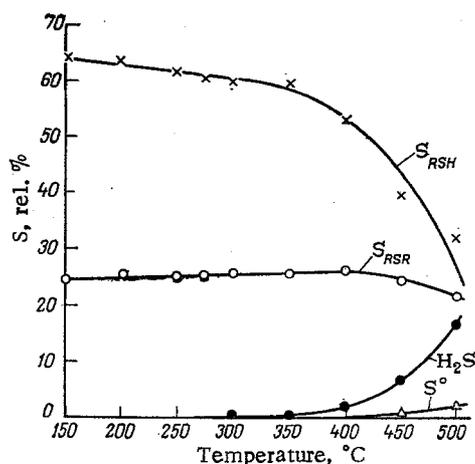
Fig. 1 Group composition of sulfur
compounds in Orenburg condensate as a
function of heating temperature.

was heated to 250°C or higher, we found a considerable decrease in the concentration of mercaptan sulfur, and hydrogen sulfide appeared in the gaseous reaction products. The content of disulfide sulfur in the condensate did not change significantly. When the condensate was heated to 400°C, there was a slight increase in the content of sulfide sulfur, but at still higher temperatures it dropped off to 0.2825% by weight. The quantity of unidentified sulfur (thiophenes and resins) began to increase even at 200°C. Heating of the condensate apparently forms thermally stable cyclic sulfur compounds and resins, as evidenced by the gradual change in color of the reaction products from light yellow to brown.

On the basis of the data presented in Table 1, we can state that, when the condensate is heated to 350–400°C, the formation of hydrogen sulfide takes place mainly through decomposition of mercaptans in accordance with the reaction [2]

$$2RSH \xrightarrow{T} RSR + H_2S.$$
(1)

When the condensate was heated to temperatures above 400°C, the hydrogen sulfide was apparently formed through the decomposition of not only mercaptans, but also sulfides and disulfides. In addition to the hydrogen sulfide, some elemental sulfur was also observed after heating at these temperatures (see Table 1); i.e., the condensate product contains all three groups of "active sulfur."

Under commercial conditions, the condensate is subjected to the action of high temperatures for longer periods. In order to determine the influence of condensate heating time on the thermal stability of the organic sulfur compounds, we carried out experiments in a 1-liter stainless steel autoclave at temperatures of 200 and 250°C, with a period of 3 h at each temperature. The results from analysis of the product show that, when the condensate was heated for this long period, hydrogen sulfide evolution began even at 200°C. When this condensate was fractionated in the AGFU [automated gas fractionation unit] of the Salavat Petrochemical Combine (still temperature 270–300°C), up to 0.3% hydrogen sulfide by weight was found in the stabilizer head; as a consequence, corrosion of lines and condensers was observed. Corrosion of the lines was also observed in the still section of the K-25 fractionating tower, due to the high concentration of low-molecular-weight mercaptans, which are also corrosive at high temperatures when water is present [5]

In the processing of high-sulfur Orenburg condensate, in order to avoid the evolution of hydrogen sulfide, it must not be heated above 200°C. In the interest of preventing corrosion of equipment, the condensate must be thoroughly dehydrated and demercaptized before processing.

Here we should keep in view that the lower aliphatic mercaptans that are obtained in the demercaptization of the Orenburg condensate may find use as odorants, oxidation inhibitors, etc. [6].

TABLE 2. Results From Study of Thermal Stability of Dialkyl Disulfides

Test temperature, °C	Sulfur content, wt.% on feedstock			
	H_2S	S_{RSH}	S_{RSR}	S_{RSSR}
20	None	0,0024	0,0048	10,500
150	"	0,0032	0,0049	10,4990
200	"	0,0032	0,0052	10,4970
250	"	0,0033	0,0058	10,4960
300	"	0,0244	0,0059	10,4520
350	Trace	0,1526	0,0097	10,1890
375	0,0351	0,0070	0,0486	8,3300
400	0,3075	2,0909	0,0510	5,6000

In treating the wide cut of light hydrocarbons (WCLH) from the Orenburg Gas Processing Plant to remove mercaptans by the method given in [7], the corresponding dialkyl disulfides are obtained as a byproduct; these are washed out of the catalyst complex by a hexane or naphtha cut, in the form of a disulfide oil. A certain part of the disulfides gets into the WCLH and proceeds to the gas separation section, where it may be subjected to local overheating to high temperatures (200-300°C) and decomposition of the disulfides. In view of the stringent requirements on quality of the end products from the gas fractionation unit with respect to the content of sulfur compounds, it is necessary to establish the threshhold of thermal stability of the disulfides. In these experiments we used a disulfide oil from the WCLH demercaptization unit of the Salavat Petrochemical Combine. The disulfide oil consists of a straight-run naphtha cut containing dissolved dialkyl disulfides; the content of disulfide sulfur is 10.5% by weight. The disulfide sulfur represents dimethyl, diethyl, and dipropyl disulfides in a 34/50/16 ratio. In addition to the disulfides, the oil contain small amounts of mercaptan, sulfide, and thiophene sulfur, which were present in the original naphtha before its use in washing the catalyst complex. The thermal stability of the dialkyl disulfides was investigated in the flow-type unit described previously (residence time $\tau=20$ sec). The results of these experiments are shown in Table 2.

As can be seen from Table 2, decomposition of the disulfides with the evolution of hydrogen sulfide and mercaptans began at 350°C; significant evolution of hydrogen sulfide was observed at temperatures of 375°C and above. The hydrogen sulfide formation apparently occurred through decomposition of part of the mercaptans that are formed in accordance with reaction (1). This view is supported by the fact that at temperatures above 375°C we found an increase in the concentration of sulfide sulfur. Moreover, at temperatures of 400°C and higher, hydrogen sulfide was also formed by direct decomposition of disulfides, for example, in accordance with the reaction [8]:

$$CH_3SSCH_3 \xrightarrow{T} CH_2=CH_2+S+H_2S. \tag{2}$$

As the heating temperature was increased, the color of the disulfide oil changed from light yellow (300°C) to dark brown (400°C). At temperatures of 350°C and higher, resinous substances were deposited on the inner surface of the reactor, and at 400°C we found solid products that were quite insoluable in organic solvents such as acetone, benzene, and dichloroethane. Elemental analysis of the resins indicated the presence of sulfur, carbon, and hydrogen. The sulfur-containing resin is formed from a thioaldehyde that is produced by the decomposition of disulfides in accordance with the reaction [8]:

$$CH_3SSCH_3 \xrightarrow{T} CH_3SH+CH_2=S. \tag{3}$$

The thioaldehydes are unstable; they polymerize rapidly, forming trimers and compounds of higher molecular weight [8].

On the basis of the data obtained in this study, we can conclude that low-molecular-weight dialkyl disulfides are rather high in thermal stability, and that a disulfide-containing feedstock can be used in a TsGFU [central gas fractionating unit] to produce valuable products, specifically, C_3-C_5 hydrocarbons that will meet Grade A requirements.

1. M. G. Rudenko and V. N Gromova, Dokl. Akad. Nauk SSSR, 31, No. 2, 207 (1951).*
2. R. D. Obolentsev, Yu. E. Nikitin, et al., in: Chemistry of Organic Sulfur Compounds Presnet in.Petroleum Crudes and Products [in Russian], Vol. 8, Vysshaya Shkola, Moscow (1968), pp. 163, 250.
3. A. G. Akhmadullina, A. M. Mazgarov, et al., Neftepererab. Neftekhim. (Moscow), No. 9, 38 (1976).
4. A. M. Mazgarov, A. V. Neyaglov, et al., Neftepererab. Neftekhim. (Moscow), No. 10, 24 (1975).
5. A. A. Gureev, T. I. Krivova, et al., Chemistry of Organic Sulfur Compounds Present in Petroleum Crudes and Products [in Russian], Vol. 8, Vysshaya Shkola, Moscow (1968), pp. 542, 546.
6. Ya. B. Chertkov and V. G. Spirkin, Sulfur and Oxygen Compounds in Petroleum Distillates [in Russian], Khimiya, Moscow (1971), p. 51.
7. A. M. Mazgarov, A. V. Neyaglov, et al., Khim. Tekhnol. Topl. Masel, No. 12, 6 (1976).
8. Kh. I. Areshidze and M. K. Gadzhiev, Catalytic Conversions of Organic Sulfur Compounds on Aluminosilicates [in Russian], Metsniereba, Tbilisi (1974), p. 95.

*As in Russian original; volume and year are inconsistent — Translator.

INFLUENCE OF FEEDSTOCK ORIGIN AND DISTILLATION
RANGE ON YIELD AND SULFUR CONTENT OF COKE

É. Yu. Oganesova and E. V. Smidovich

Along with recently published studies directed toward the reduction of sulfur content in coke by heat treatment [1], information is being reported on the production of coke with lower sulfur contents by the use of selected medium-sulfur feedstocks that have been appropriately pretreated [2, 3].

In this article we are presenting results from a study of the coking characteristics of medium-sulfur feedstocks from various sources and with various distillation ranges, to obtain data on the coke yield and on the sulfur content of the coke.

The feedstocks used in this work were (a) straight-run residues from mixed Romashkino crudes distilling above 350, 450, and 500°C; (b) residues from a catalytic gas oil produced from

TABLE 1. Physicochemical Properties of Coker Feedstocks

	Residues from mixed Romashkino crudes, distilling above			Residues from catalytic gas oil, distilling above			Residues from thermal gas oil, distilling above		
	350°C	450°C	500°C	350°C	400°C	450°C	350 C	400°C	450°C
Yield of residue on original feedstock, mass%	48,0	30,5	20,4	87,0	41,5	14,3	95,1	58,1	28,1
Density ρ_4^{20}	0,9627	0,9976	1,0184	1,0037	1,0451	1,1356	1,0845	1,1467	1,2073
Sulfur content, mass %	2,38	2,93	3,23	2,39	2,40	2,33	3,09	3,36	3,82
Hydrocarbon group composition, mass%									
Paraffinic/naphthenic	24,7	19,1	17,2	26,7	22,5	10,9	6,4	4,6	2,0
Aromatic									
light	13,9	10,2	8,5	4,0	3,9	3,2	2,5	1,2	0,8
medium	23,3	18,9	15,3	4,5	3,2	2,8	4,5	1,6	1,4
heavy	22,7	28,9	31,6	60,2	64,5	71,3	72,0	70,3	59,5
Resins	9,5	13,3	14,6	3,6	4,9	6,0	5,0	4,7	3,7
Asphaltenes	5,9	9,6	12,5	1,0	1,9	5,8	9,1	17,6	32,6