

DISTRIBUTION OF SULFUR-CONTAINING COMPOUNDS IN  
STREAMS FOR CONCENTRATION OF PROPYLENE

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Production of propylene is increasing steadily all over the world. For example, it increased by approximately 8 times in the USA and Japan from 1965 to 1980 [1]. Many installations for combined refining of type G-43-107 and KT-1 oil are supplemented by installations for concentration of propylene in our country for the more complete utilization of the resources of propylene contained in refinery gases. To produce propylene which satisfies the requirements of GOST 25043-81 for the concentration of sulfur compounds, it is necessary to know the group composition of these compounds and their distribution by technological streams, which will permit selecting the most economical and rational scheme for preparation of the raw material for the propylene concentration installation.

In this respect, the composition of sulfur compounds in propane-propylene fractions (PPF) processed in combined types G-43-107 and KT-1 catalytic cracking installations of the Moscow and Pavlodar Petroleum Processing Plants, and their distribution by fractions in the propylene concentration installation of the Moscow Petroleum Processing Plant, whose principal technological scheme is shown in Fig. 1, was studied. The concentration of sulfur compounds on conversion to elementary sulfur was determined with the improved VNIUS method, which provides for a high precision of the analysis [2].

The studies showed that the concentration of sulfur compounds in PPF is directly dependent on the efficiency of hydrorefining of the raw material from the G-43-107 and KG-1 catalytic cracking installations. The concentration of thiol sulfur in PPF in normal operation of the hydrorefining section is 0.002-0.01 wt. %. The concentration of thiol sulfur in PPF increases to 0.04 wt.% in the hydrorefining section installations, and the concentration of hydrogen sulfide attains 0.01 wt.% in some periods.

The scheme for production of propylene from refinery gases includes sulfur purification and PPF rectification units, and in the case of production of a high grade of propylene, also a finished propylene drying unit. Most of the PPF is eliminated from the sulfur compounds in the sulfur purification unit with an alkaline solution, and the remainder is redistributed between the propylene and propane fractions during rectification. The data on the distribution of sulfur compounds in concentration of propylene in conditions of a poorly and satisfactorily operating hydrorefining section are reported in Table 1: the residual concentration of sulfur in the hydrorefined vacuum distillate is respectively 0.98 and 0.49 wt. %.

The analysis of the operation of the hydrorefining section over one year at the Moscow Petroleum Processing Plant showed that the degree of sulfur purification of the vacuum distillate during satisfactory operation of the hydrorefining section is 60 wt.% and higher, versus 25-28 wt.% in the other cases. For a 60 wt.% degree of purification of the vacuum distillate, the concentration of thiols and carbon oxysulfides in PPF entering for purification is respectively 16-44 and traces, 2.2 ppm, and for a 28 wt.% degree of purification, 83-350 and 6-17 ppm.

The study of the distribution of sulfur compounds between the propylene and propane fractions in the propane column (see Fig. 1) revealed a distinct feature: regardless of the initial concentration of thiol sulfur in the deethanized PPF entering for gas separation, almost 95% of the thiol sulfur is redistributed into the propane fraction (below the propane column). The concentration of thiol sulfur in the propane fraction increases by approximately three times in comparison to the concentration in PPF. Less than 5% of the thiol sulfur goes into the propylene fraction (above the propane column).

TABLE 1.

Stream	Amount, ton/h	Concentration of compounds (on conversion to elementary sulfur)				
		ppm			rel. %	
		N <sub>2</sub> S	RSH	COS	RSH	COS
Concentration of sulfur in hydrorefined raw material: 0.98 wt. % in starting material: 1.36 wt. %						
PPF <sup>1*</sup>	7,730	Absent	114,5	4,3	100	100
Propylene 2 <sup>2*</sup>	6,267	>	5,8	3,88	4,1	87,6
Propane 3 <sup>3*</sup>	1,463	>	580,0	2,3	95,9	12,4

Concentration of sulfur in hydrorefined raw material:  
0.49 wt. %, in starting material: 1.22 wt. %

PPF <sup>1*</sup>	10,07	Traces	28,5	0,95	100	100
Propylene 2 <sup>2*</sup>	7,53	>	2,1	1,2	5,49	93,75
Propane 3 <sup>3*</sup>	2,54	>	107,1	0,3	94,51	6,25

\*Below deethanizer.

<sup>2\*</sup>Above propane column.

<sup>3\*</sup>Below propane column.

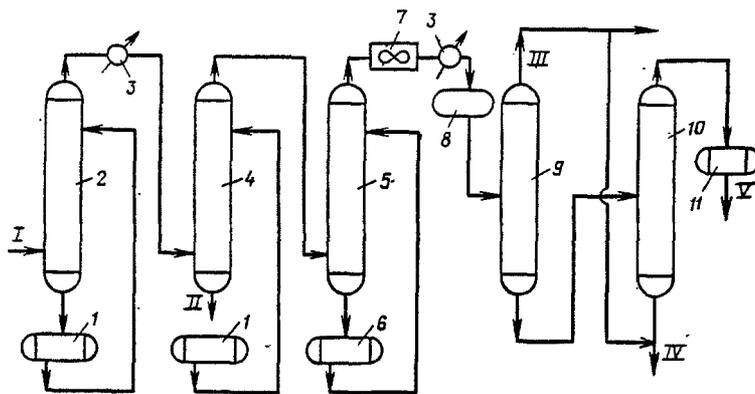


Fig. 1. Diagram of the propylene concentration installation: 1, 6, 11) tanks for solution of alkali, chemically purified water, and propylene; 2, 4) columns for hot and cold alkali refining; 3) cooler; 5) column for washing traces of alkali from PPF; 7) air cooler; 8) intermediate tank for PPF in the liquid phase; 9) deethanizer; 10) propane column; I) PPF; II) spent alkali; III) to gas separation; IV) propane; V) propylene.

Most of the carbon oxysulfide is concentrated in the propylene (bp of 47.7°C) due to its low bp (-50°C) and only an insignificant amount (10-15% of the initial amount) is removed with the propane. The residual concentration of COS in the propane satisfies the Exxon requirements: no greater than 2 ppm [3]. In this case, the probability of total conversion of COS into H<sub>2</sub>S is very low. Propane with this concentration of COS was tested for corrosive aggressiveness (testing on a copper plate).

The data obtained on the composition of contaminants in PPF and the features of the distributions of sulfur in concentration of propylene permit selecting the most rational scheme for purification of the raw material and target fractions of the propylene concentration unit as a fraction of the requirements for the concentration of contaminant compounds. These data were used in developing the technological scheme for the propylene concentration installation at the Permnefteorgsintez Scientific Association.

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## AROMATIZATION OF GASOLINE ON ZINC-MODIFIED ZEOLITE-CONTAINING CATALYSTS

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Modification of ultrahigh-silicon (UHS) zeolites of the ZSM type [1] and UHS zeolite-containing catalysts [2] with gallium and zinc significantly improves their catalytic properties in aromatization of hydrocarbons. However, the effect of the amount of modifying metal has been inadequately studied.

The activity and selectivity of granulated catalysts synthesized by addition of 30% decationized UHS zeolite (Si:Al = 16) to an amorphous aluminosilicate matrix were investigated in the present study. The concentration of zinc was varied within the limits of 0-10 wt.% in the catalyst. Low-octane (65 points, MM) gasoline from thermal cracking (TCG) containing 40% unsaturated hydrocarbons was used as the raw material for aromatization (cycloreforming). The experiment was conducted on a flow-type laboratory setup. The characteristics of the starting TCG and the experimental method are reported in [2].

As the data in Fig. 1 indicate, at moderate temperature (425°C), the maximum changes in the catalytic properties of the samples are observed on addition of the first 0.5 wt.% of zinc: the cracking activity decreases sharply (the yield of gas decreases by ~8%) and the yield of liquid catalyzate increases while coke formation does not change (~3.5%). The concentration of aromatic hydrocarbons in the liquid catalyzate decreases by 10% (Fig. 2), which causes a 3-4-point decrease in its octane number, determined by the calculation method in [3]. The paraffins:olefins ratio decreases sharply in the cracking gases (Fig. 3).

A further increase in the concentration of zinc to 10 wt.% virtually does not alter the properties of the catalysts with respect to the indicated indexes except for the yield of hydrogen, which increases by almost three times (see Fig. 1). The concentration of xylenes increases and the concentration of C<sub>9+</sub> components decreases while the concentration of benzene and toluene remain almost constant in the aromatic compounds formed (Table 1) with an increase in the concentration of zinc in the catalyst. The concentration of unsaturated hydrocarbons in the catalyzate does not exceed 5-8 wt.% in all cases.

The changes in the catalytic properties of the samples established at moderate temperatures of aromatization correlate with the data from IR spectroscopic analysis, which indicate that addition of the first 0.5 wt.% of zinc to UHS zeolite sharply decreases the intensity of the lines at 3600 cm<sup>-1</sup>. These lines characterize the strongly acid hydroxyl groups [4] active in low-temperature transformations of hydrocarbons. An increase in the intensity of the lines at 1455 cm<sup>-1</sup>, assigned to groups with Lewis acidity [5], is simultaneously observed in the IR spectra of pyridine adsorbed on the surface of the zeolite-containing catalyst. When the concentration of zinc is increased to 10 wt. %, the acidity of the catalysts does not change significantly.

When the temperature is increased to 500°C, modification of the catalysts with zinc has almost no effect on the yield of cracking gases and liquid catalyzate (see Fig. 1), but the selectivity of the reactions of aromatization of TCG increases significantly (see Fig. 2). The maximum concentration of aromatic compounds in the catalyzate (~82%) and its octane number (~92) are attained when 5 wt.% zinc is added to the catalyst. The concentration of unsaturated hydrocarbons in the catalyzate does not exceed 3%.

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