

CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

Liquid-Phase Adding of Mercaptans to Olefins in the Presence of a Heterogeneous Catalyst Based on Cu₂O

Kh. E. Kharlampidi^a, R. M. Akhmadullin^b, *, A. A. Sirotkin^a, and A. G. Akhmadullina^b

^aKazan National Research Technological University, Kazan, 420015 Russia

^bNTTs AhmadullinS Science and Technology, Kazan, 420139 Russia

*e-mail: ahmadullinr@gmail.com

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Abstract—The reaction from adding *tert*-dodecyl mercaptan to octene-1 in the presence of a heterogeneous catalyst based on copper(I) oxide and an aqueous solution of an alkali is studied, and the formation of organic sulfides is confirmed. The first order of the reaction with respect to *tert*-dodecyl mercaptan and potassium hydroxide is found. The effect of the nature and concentration of aqueous solutions of alkalis is studied. The apparent energy of activation of 9.24 ± 0.55 kJ/mol and a preexponential factor of 0.576 ± 0.035 min⁻¹ are calculated. The possibility of demercaptanizing the straight-run kerosene fraction based on the given reaction is confirmed on a continuous laboratory unit.

Keywords: demercaptanization, *tert*-dodecyl mercaptan, octene-1, straight-run kerosene fraction, organic sulfide, heterogeneous catalyst, copper(I) oxide, aviation fuel

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INTRODUCTION

A characteristic of the last decade is the increased recovery and processing of hydrocarbon feedstock (HCF) with growing concentrations of mercaptans and total sulfur [1, 2]. Due to the increased recovery of high-sulfur petroleums, the problems of removing sulfur compounds (including mercaptans) with elevated corrosion activity [3], toxicity, fetid odor, and capacity for poisoning catalysts [4], accelerating the wear of the process equipment and petroleum and gas pipelines, and inflicting environmental damage [5], are highly relevant. On the other hand, the high chemical activity of mercaptans allows us to remove them from HCF in a number of ways under milder conditions, compared to other sulfur compounds [6, 7].

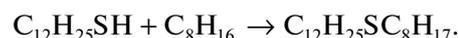
The familiar [6] technology of the caustic demercaptanization of the kerosene fraction used in global practice to obtain aviation fuel includes oxidizing mercaptans in the liquid hydrocarbon phase to dialkyl sulfides at 40–60°C and up to 1.0 MPa with atmospheric oxygen in the presence of phthalocyanine catalysts supported on a carbon substrate.

The use of catalysts with substrates based on polyolefins [7] that are stable under the process conditions [8] in the caustic demercaptanization of kerosene fractions is also possible. The use of atmospheric oxygen in the described technologies reduces the safety of the process, while its excess results in overoxidation of the kerosene fraction, and thus a drop in its thermo-oxi-

dative stability, which is strictly regulated according to GOST 10227–2013.

Literature sources describe the interaction between mercaptans and olefins according to the conjugated Michael addition reaction catalyzed by bases or nucleophiles [9, 10], which proceeds against the Markovnikov rule with the formation of corrosion-inactive and thermally stable organic sulfides. Complexes based on copper(I) are familiar catalysts [11, 12].

In this work, we studied the possibility of conducting the caustic demercaptanization of HCF according to model reaction (1) of adding *tert*-dodecyl mercaptan to octene-1 in the straight-run kerosene fraction using a heterogeneous catalyst based on Cu₂O and an aqueous solution of an alkali in an oxygen-free medium. The choice of mercaptan is justified by the need for maximally reducing the side oxidation reaction with residual oxygen that is due to the branched structure and high molecular weight of *tert*-dodecyl mercaptan:



EXPERIMENTAL

Preparing the Catalyst

The catalyst was prepared according to the procedure described in [13]. The concentration of the catalyst component in polyethylene is expressed by the figure specified with a hyphen after the oxide formula, so

Cu₂O-40 is a catalyst with a copper(I) content of 40 wt %. KAZPELEN high-pressure polyethylene 15313 003 (GOST 16337–77) was used as the polymer substrate. The Cu₂O-40 heterogeneous catalyst was cubes with a face size of 2 × 2 mm; 1.0 g of the heterogeneous catalyst consists of 65 cubes.

Reagents

Our reagents were primary reference fuel grade isooctane (GOST 12433–83), chemically pure grade octene-1 (TU 6-09-14-1994–78); *tert*-dodecyl mercaptan CAS 25103-58-6; potassium hydroxide (GOST 24363–80); technical grade argon in cylinders (GOST 10157–79); and technical grade oxygen (GOST 5583–78).

Reaction between *tert*-Dodecyl Mercaptan and Octene-1

The reaction between *tert*-dodecyl mercaptan and octene-1 was conducted in a medium of isooctane inside a 150-mL glass three-neck cylindrical reactor: 2.5 to 20.0 mL of an aqueous solution of potassium or sodium hydroxide, 0.064 mol (10.0 mL) of octene-1, and 40 mL of isooctane were charged into the reactor, the concentration of *tert*-dodecyl mercaptan in the hydrocarbon phase was varied from 0.003125 to 0.0625 mol/L, and 1–5 g of heterogeneous Cu₂O-40 catalyst was used. Argon was fed from the cylinder to the reaction solution at a velocity of 100 h⁻¹. Argon from the reactor was removed to the atmosphere through a reflux water condenser. The solution in the reactor was stirred at a speed of 1400 rpm. The temperature of the reaction solution was kept in the range of 40–80°C using a temperature-controlled magnetic stirrer. The quantitative concentration of mercaptans was determined via potentiometric titration according to GOST 22985-2017.

Oxidation of *tert*-Dodecyl Mercaptan

The oxidation of *tert*-dodecyl mercaptan was conducted under the conditions of the previous reaction while replacing argon with air.

The reaction products were isolated by separating the hydrocarbon part from the heterogeneous catalyst and alkaline solution with subsequent evaporation of the isooctane.

Combination Scattering Spectra (Raman Spectroscopy)

The combination scattering spectra were recorded on a Vertex 70 Fourier-transform IR spectrometer equipped with a RAM II Raman accessory (Bruker, Germany).

RESULTS AND DISCUSSION

It was preliminarily found that the rate of the process did not depend on the speed of the stirrer above 1200 rpm. Subsequent experiments were performed at the stirrer speeds of 1400 rpm.

The Raman spectrum of the product of the reaction of *tert*-dodecyl mercaptan and octene-1 in an oxygen atmosphere (Fig. 1a) was characterized by bands of disulfide (S–S) and sulfide (C–S) at 515 and 747 cm⁻¹, respectively. The band of disulfide disappeared when there was no oxygen (Fig. 1b), and the reaction product retained only the band of organic sulfide (C–S) at 747 cm⁻¹. Our data reliably indicate the formation of organic sulfide in the oxygen-free medium during interaction between *tert*-dodecyl mercaptan and octene-1 in the presence of a Cu₂O-40 heterogeneous catalyst and an alkaline solution.

The order of the liquid-phase reaction with respect to *tert*-dodecyl mercaptan with octene-1 in the presence of a heterogeneous catalyst based on Cu₂O and an alkaline solution was found differentially at different initial concentrations of *tert*-dodecyl mercaptan. Figure 2 shows how the concentration of *tert*-dodecyl mercaptan changes during the reaction; the inset shows the logarithmic dependence of the initial rate of the change in the amount of *tert*-dodecyl mercaptan on its initial concentration. As is seen, this last dependence is linear, and its slope ratio is 1.0369. The reaction is thus of the first order in relation to *tert*-dodecyl mercaptan.

Our study of the effect the nature of alkaline solutions with a concentration of 2.77 mol/L showed that the rate of the reaction upon adding *tert*-dodecyl mercaptan to octene-1 at 1.2 × 10⁻³ mol L⁻¹ min⁻¹ in the presence of an aqueous solution of potassium hydroxide was more than that of 8.0 × 10⁻⁴ mol L⁻¹ min⁻¹ in the presence of an aqueous solution of sodium hydroxide. The higher reaction rate in the presence of potassium hydroxide was apparently due to the higher constant of dissociation of potassium hydroxide, compared to sodium hydroxide. This raised the concentration of OH⁻ ions in the solution and thus the basicity, affecting the rate of the given reaction [9].

An increase in the rate of the reaction of addition of *tert*-dodecyl mercaptan to octene-1 was observed upon raising the concentration of the aqueous solutions of potassium hydroxide from 1.95 to 13.48 mol/L (Fig. 3), due to the increased polarization of the S–H bond of mercaptan at the stronger concentration of the aqueous solution of KOH.

Differential processing of the kinetic curves of the change in the amount of *tert*-dodecyl mercaptan at different concentrations of potassium hydroxide showed that the dependence of the logarithm of the initial rate of the change in the amount of *tert*-dodecyl mercaptan on the logarithm of the concentration of potassium hydroxide lg [KOH] was a line with a slope

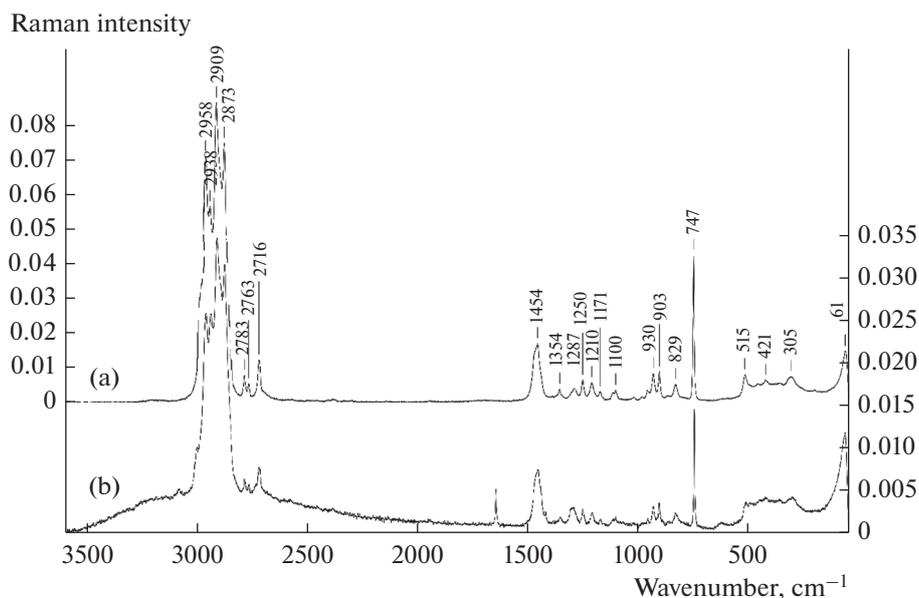


Fig. 1. Raman spectra of the product of the reaction between *tert*-dodecyl mercaptan and octene-1 in (a) with and (b) without oxygen.

ratio of 0.7399 (Fig. 4). The reaction is approximately of the first order, in relation to potassium hydroxide.

The reaction from adding *tert*-dodecyl mercaptan to octene-1 proceeds at the surface of the interfacial boundary between the aqueous solution of the alkali and the heterogeneous surface of the catalyst; however, the reaction rate constant was determined by the

change in the volumetric concentrations of the reacting substances, due to which the energy of activation of the given reaction refers to the apparent energy.

The apparent energy of activation of the considered reaction was calculated using the Arrhenius equation in the external kinetic region in the range of 40–80°C at a concentration of *tert*-dodecyl mercaptan in a

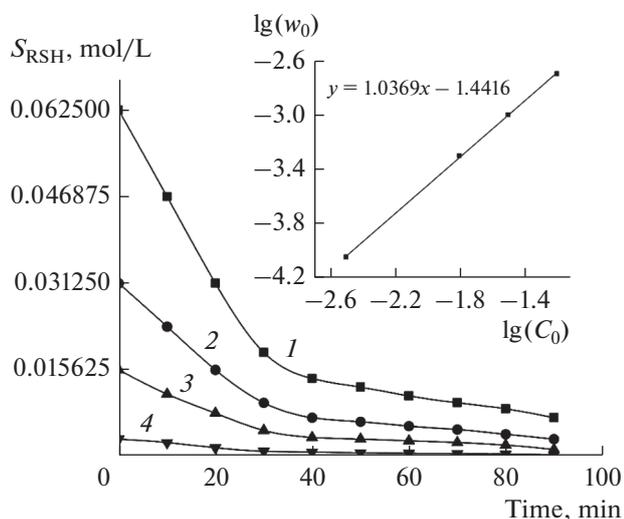


Fig. 2. Kinetic curves of the change in the amount of *tert*-dodecyl mercaptan at different initial concentrations: (1) 0.0625, (2) 0.03125, (3) 0.01563, and (4) 0.00313 mol/L. Reaction temperature, 80°C; 0.064 mol of octene-1; 5.0 mL of an aqueous solution of potassium hydroxide (13.48 mol/L); 5 g of Cu₂O-40 catalyst; velocity of argon feed, 100 h⁻¹. Inset: logarithmic dependence of the initial rate of the change in the amount of *tert*-dodecyl mercaptan on its initial concentration.

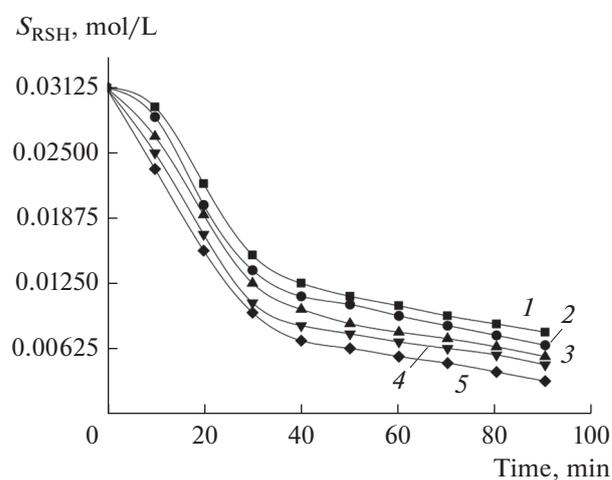


Fig. 3. Kinetic curves of the change in the amount of *tert*-dodecyl mercaptan on the concentration of the solution of potassium hydroxide: (1) 1.95, (2) 4.24, (3) 6.90, (4) 9.97, and (5) 13.48 mol/L. Reaction temperature, 80°C; concentration of *tert*-dodecyl mercaptan, 0.03125 mol/L; 0.064 mol of octene-1; 5.0 mL of an aqueous solution of potassium hydroxide; 5 g of Cu₂O-40 catalyst; velocity of the argon feed, 100 h⁻¹.

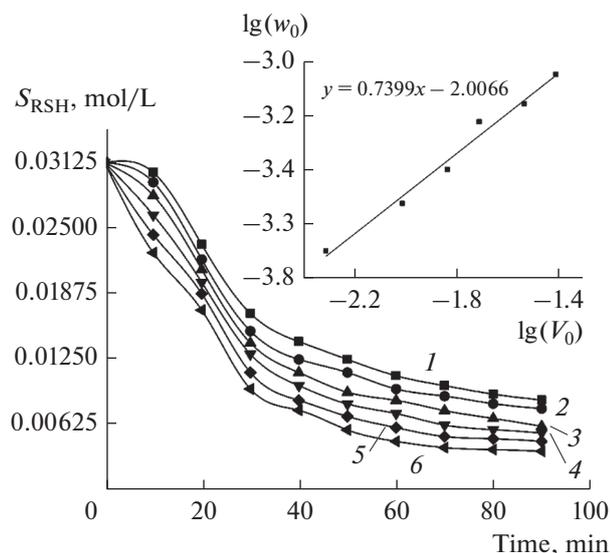


Fig. 4. Kinetic curves of the change in the concentration of *tert*-dodecyl mercaptan on the amount of the solution of potassium hydroxide: (1) 2.5, (2) 5.0, (3) 7.5, (4) 10.0, (5) 15.0, and (6) 20.0 mL. Reaction temperature, 80°C; concentration of *tert*-dodecyl mercaptan, 0.03125 mol/L; 0.064 mol of octene-1; concentration of the aqueous solution of potassium hydroxide, 1.95 mol/L; 5 g of Cu₂O-40 catalyst; velocity of the argon feed, 100 h⁻¹. Inset: logarithmic dependence of the initial rate of the change in the amount of *tert*-dodecyl mercaptan on the concentration of potassium hydroxide.

hydrocarbon phase of 0.03125 mol/L; 0.064 mol of octene-1; 40.0 mL of isoctane; 5.0 mL of a 13.48 mol/L aqueous solution of potassium hydroxide; and 5 g of Cu₂O catalyst at an argon feed velocity

of 100 h⁻¹ is 9.24 ± 0.55 kJ/mol. The value of the pre-exponential factor is 0.576 ± 0.035 min⁻¹. The design equation for calculating the rate of the reaction from the catalytic addition of dodecyl mercaptan to octene-1 in the presence of Cu₂O in an alkaline medium is

$$v = 0.576 \exp(9240/RT) [C_{12}H_{25}SH] \times [OH^-] [C_8H_{16}]^x [Cu_2O]^y,$$

where R is the universal gas constant, 8.314 J mol⁻¹ K⁻¹; T is temperature, K; and x and y are the orders of the reaction with respect to octene-1 and Cu₂O, respectively.

To confirm the possibility of practical application of the reaction of adding mercaptans to olefins, we performed a study on the straight-run kerosene fraction from OOO LUKOIL-Nizhegorodnefteorgsintez with a concentration of the initial mercaptan sulfur of 113.0 ppm and a concentration of natural olefins of 2 wt %. It was found (Fig. 5) that the rate of demercaptanization of the straight-run kerosene fraction grows along with the temperature and the concentration and amount of the alkaline solution, as when conducting the model reaction.

Experiments on the demercaptanization of the kerosene fraction were performed on the continuous laboratory unit presented in Fig. 6. The kerosene fraction was fed from the receiving flask to the top part of heated column plug-flow reactor 1 by peristaltic pump 6 at a flow rate of 300 to 520 mL/h. An inert gas, argon, was fed into flask 10 in a continuous mode at a velocity of 100 h⁻¹. The reaction temperature was maintained in a range of 50–54°C. Also, an alkaline solution with a concentration of 13.48 mol/L (promoter) was fed to

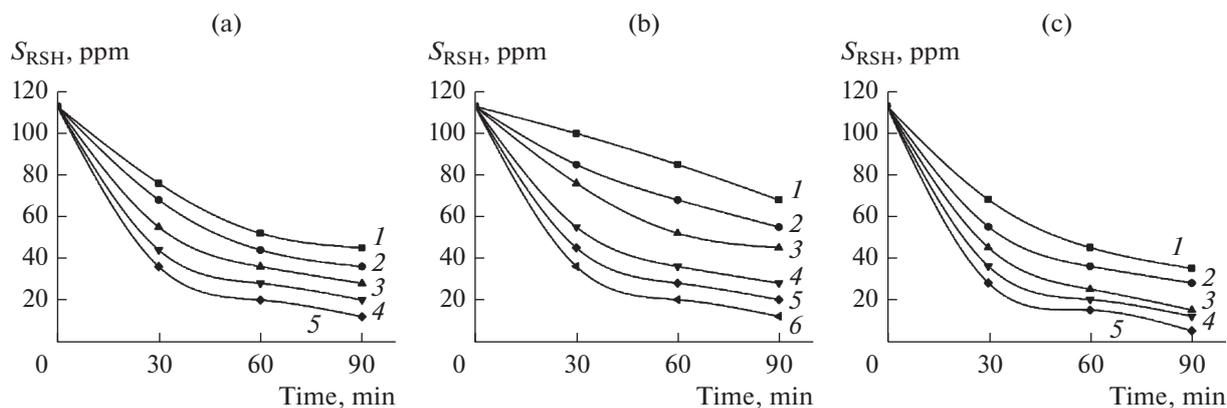


Fig. 5. Volume of the kerosene fraction, 100.0 mL; weight of Cu₂O-40 catalyst, 10 g; concentration of the mercaptan fraction, 113.0 ppm; velocity of the argon feed, 100 h⁻¹. (a) Kinetic curves of the change in the amount of mercaptan sulfur on the concentration of the solution of potassium hydroxide in the straight-run kerosene fraction: (1) 1.95, (2) 4.24, (3) 6.90, (4) 9.97, and (5) 13.48 mol/L. Reaction temperature, 80°C; 5.0 mL of the aqueous solution of potassium hydroxide. (b) Kinetic curves of the change in the concentration of mercaptan sulfur on the amount of the solution of potassium hydroxide in the straight-run kerosene fraction: (1) 1.0, (2) 3.0, (3) 5.0, (4) 10.0, (5) 20.0, and (6) 25.0 mL. Reaction temperature, 80°C; aqueous solution of potassium hydroxide with a concentration of 1.95 mol/L. (c) Kinetic curves of the change in the concentration of mercaptan sulfur on temperature in the straight-run kerosene fraction: (1) 50, (2) 60, (3) 70, (4) 80, and (5) 90°C. 25 mL of an aqueous solution of potassium hydroxide with a concentration of 1.95 mol/L.

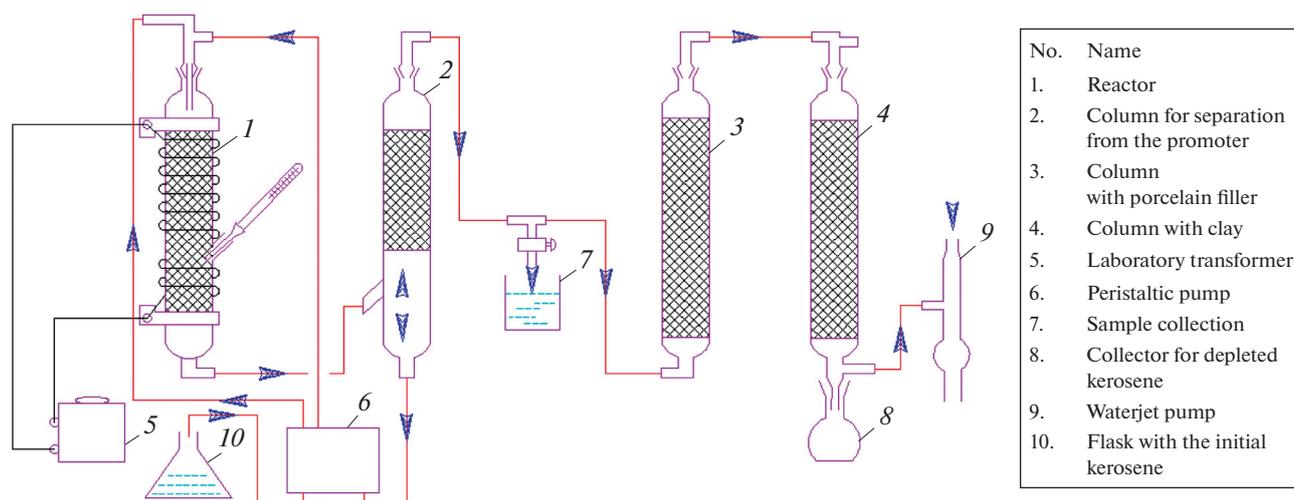


Fig. 6. Scheme of the continuous laboratory unit for the demercaptanization of the kerosene fraction: (1) reactor, (2) column for separation from the promoter, (3) column with a porcelain filler, (4) column with clay, (5) laboratory transformer, (6) peristaltic pump, (7) sample collection, (8) collector for depleted kerosene, (9) waterjet pump, (10) flask with the initial kerosene. Volume of reactor 1, 300 mL; amount of heterogeneous catalyst, 30 g; volume of column 2, 300 mL; volume of column 3, 400 mL; volume of column 4, 400 mL.

the top part of reactor 1 from the bottom part of column for the separation of the aqueous solution of potassium hydroxide 2 by pump 6. The kerosene fraction and the alkaline solution travel from the top to the bottom of reactor 1 through a bed of a heterogeneous catalyst based on Cu_2O , over the surface of which the addition of mercaptans to olefins proceeds. The demercaptanized kerosene fraction and the alkaline solution from the bottom part of reactor 1 enters column 2 equipped with a metallic coalescer (a grid). The settled kerosene fraction from the top part of column 2 enters column 3 with a porcelain filler (D_{balls} of 3–4 mm). At the final stage, the kerosene fraction undergoes final adsorption purification in column 4 filled with bentonite clay. Finally, the kerosene fraction purified

of mercaptan sulfur is forwarded to collector 8, from which a sample is collected for analysis.

As is seen from the data in Table 1, the mode of demercaptanization with a flow rate of the kerosene fraction not exceeding 400 mL/h at 50 to 54°C ensures a stable residual concentration of mercaptan sulfur of 0.0011–0.0019 wt % in the kerosene fraction.

The results from a test of thermo-oxidative stability according to GOST R 52954–2013 (experiment 10) showed that for the straight-run kerosene fraction subjected to demercaptanization in the continuous mode, the pressure differential on the filter reached 9 mmHg over 150 min at a limit of no more than 25 mmHg, and the color index of the deposits on the tube was less than 1 point at a limit of no more than 3 points.

Table 1. Effect of the velocity of feeding the kerosene fraction on the demercaptanization of the kerosene fraction in the presence of a heterogeneous catalyst based on Cu_2O and an aqueous solution of potassium hydroxide

Experiment	Flow rate, mL/h	t , °C	S_{RSH} , wt %
limit for TS-1 fuel:			No more than 0.003
1	520	53	0.0025
2	480	53	0.0025
3	380	53	0.0019
4	400	54	0.0017
5	390	50	0.0019
6	300	52	0.0018
7	300	53	0.0011
8	300	50	0.0015
9	300	52	0.0016

CONCLUSIONS

The proposed demercaptanization of the kerosene fraction [13] by adding *tert*-dodecyl mercaptan to octene-1 in the presence of an alkaline solution of KOH and a Cu₂O-40 catalyst ensures the required depth of demercaptanization of the straight-run kerosene fraction to the residual concentration of mercaptan sulfur (no more than 30 ppm) and thermo-oxidative stability required by GOST 10227–2013 for TS-1 aviation fuel.

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