

STUDY ON ELIMINATION OF MERCAPTANS FROM JET FUELS WITH CALCIUM OXIDE

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(Received April 18, 1967)

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A great part of the world's petroleum production contains sulphur compounds. Formerly, high sulphur content petroleum and petroleum products were in fact utilized where their sulphur content was not detrimental. New oil fields recently discovered furnish oils of high sulphur content and it is now imperative that such types of oil be processed. Even during storage as well as during processing, sulphurous oils cause corrosion damages, but it is their use as motor fuels that is the most disadvantageous. A number of new problems arises with the processing of these crudes. In Hungary this question arose with the exploitation of the Nagylengyel oil field, and answers to it were sought for by the personnel of the Research Institute for Petroleum and Natural Gas (MÁFKI), and by the Department of Chemical Technology [1, 2, 3].

In fuels for jet propulsion engines, in these special types of petroleum, it is very important that mercaptan content should be below 0.005 per cent, or 50 p.p.m. To achieve this, a sorbent was sought for, with the help of which a motor fuel that corresponds to standard specifications could be produced in an economical way. Mercaptans are conspicuous among the organic sulphur compounds present in petroleum and petroleum products. Mercaptans can already be detected in the crudes, but can be formed as decomposition products in an atmospheric distillation. According to REID [4], generally, mercaptans of the alkenes in the $C_1 \dots C_4$ range occur in petroleum fractions; to a higher proportion: ethyl mercaptan. Depending on the origin of the crudes, long-chain and cyclic mercaptans also occur in them.

The presence of mercaptans in motor fuels is very noxious: on account of their active hydrogen they are rather corrosive. This corrosive action is damaging all along from processing to consumption. Sulphur content in benzines reduces their octane rating, and when such benzines are treated with tetra-ethyl-lead their sensitivity to lead is increased.

Besides these effects, sulphur compounds may cause colouration, and may assist the formation of resinous compounds [5]. Mercaptans are catalyst poisons and shorten the useful life by the cracking of catalysts.

Possibilities for the removal of mercaptans

The methods for the removal of mercaptans can be physical or chemical. In the case of physical methods selectivity and efficiency are important. *Solvent extraction* is extensively mentioned in the literature, but purification by *distillation* or by *azeotropic distillation* is also feasible.

Sorption is an important method for the removal of mercaptans. Primarily, this is a physical process but is accompanied, generally, by phenomena of *chemisorption*. For this purpose diatomaceous earth, activated alumina, or silica gels are used.

On aluminium silicates hydrogen sulphide and olefin are formed from mercaptan. The desulphuration effect of alumina is a function of its iron oxide and aluminium oxide content [6].

Sorptive and catalytic sorptive desulphuration methods are the Gray process, the Perco desulphuration and the Houdry process [7].

Desulphuration with calcium oxide, the subject of this paper, is mentioned in the literature. In a patent by BENSON [8] the oil is desulphurated with the aid of lime, this being mixed with the oil in cold or at boiling point, and then treated with overheated steam. According to DUBBS [9], calcium hydroxide-hydrosulphide is used; this being formed in the oil from calcium hydroxide, water and hydrogen sulphide. Desulphuration according to CROSBY and CAMEY [10] is carried out in a 2...5 per cent suspension at low pressure, then the oil is treated with a sodium hydroxide solution of 15...30 °Bé. SCHAAFSMA [11] contacted the oil vapour with calcium oxide or with calcium hydroxide, to remove mercaptans. Studies of MAMEDLI [12] reveal that without a catalyst calcium carbonate containing calcium oxide does not reduce the sulphur content of oils because hydrogen sulphide dissolved in the oil is formed from mercaptans. This hydrogen sulphide, however, can be removed by aqueous washing. When a catalyst is added, aqueous washing does not diminish sulphur content because this is bound by the catalyst, mainly in the form of elementary sulphur. Pure calcium oxide is not effective for the first step, i.e. for the formation of hydrogen sulphide. Temperature was round about 300 °C. Mercaptans can be removed effectively by chemical means and at high degrees of selectivity.

Through *hydrogenation at elevated pressure*, i.e. hydrocracking, hydrorefining, destructive hydrogenation, various degrees of desulphuration can be achieved. Mercaptans can be completely decomposed to saturated hydrocarbons and hydrogen sulphide.

By *oxidation*, mercaptans are converted into disulphides or sulphonic acids. *Metal oxides* produce mercaptides which are easily crystallized. From hydrocarbons in the vapour phase mercaptans can be eliminated with the aid of sodium oxide [13].

Experimental

First, a study of the thermodynamics and reaction kinetics pertaining to the reactions that occur in the reactor, was undertaken in order to form an idea about the possibilities open from a technological point of view. Subsequently, the technological experiments were carried out for the special method for the removal, with the aid of a calcium oxide sorbent, the mercaptans from petroleum. In this paper it is proposed to deal with questions of technology only. A special petroleum fraction (type TSZ-1) of the Szőny Refinery of the Komáromi Kőolajipari Co. was used in our experiments. This fraction serves as the fuel for jet engines; its characteristics are listed in Table 1. The mercaptan content of this fraction was changed in the course

Table 1

Characteristics of the petroleum fraction used in this study

Density, d_4^{20}	0.779
B.p. at the beginning	146 °C
10 per cent distilled at	158 °C
50 per cent distilled at	171 °C
90 per cent distilled at	204 °C
98 per cent distilled at	236 °C
B.p. at the end of distillation	245 °C
Acidity, mg KOH per 100 ml	0.8
Turbidity point	6.3 °C
Viscosity at 20 °C	1.27 cSt
Flash point	39 °C
Mercaptans, per cent by weight	0.004
Total sulphur, per cent by weight	0.21

of the experiments by the addition of various quantities of ethyl mercaptan n-octyl-mercaptan and thiophenol, respectively.

A favourable feature of the *calcium oxide* used in our experiments was its high sorptive capacity. Because of its high sensitivity to moisture and air, the *builder's white lime* was kept in a glass powder bottle closed with a ground glass stopper.

The calcium oxide grains of sizes between 6 and 8 mm, 3 and 6 mm, and 1 and 3 mm, respectively, were used after removal of dust by screening. In technical experiments mainly burnt lime of 3 to 6 mm grain sizes was used; some characteristics are the following: average weight, $7.23 \cdot 10^{-2}$ g per grain, average volume, $2.39 \cdot 10^{-1}$ cm³ per grain.

Also *limestone* from Dorog was used in our experiments; 5 per cent was the maximum content of all mineral components besides calcium carbonate, thus it was sufficiently homogeneous for industrial utilization.

The *n*-octyl-mercaptan, $C_8H_{17}SH$, was synthesized at the University of Chemical Industry, Veszprém. It was 93 per cent pure.

Ethyl-mercaptan, C_2H_5SH , we obtained from the Komáromi Kőolajipari Co., the purity was 95 per cent.

The apparatus for the experiments envisaged allowed the study of the several parameters under dynamic conditions. To a certain degree this apparatus is like the laboratory one used in the OD process for the desulphuration of benzines with sodium oxide.

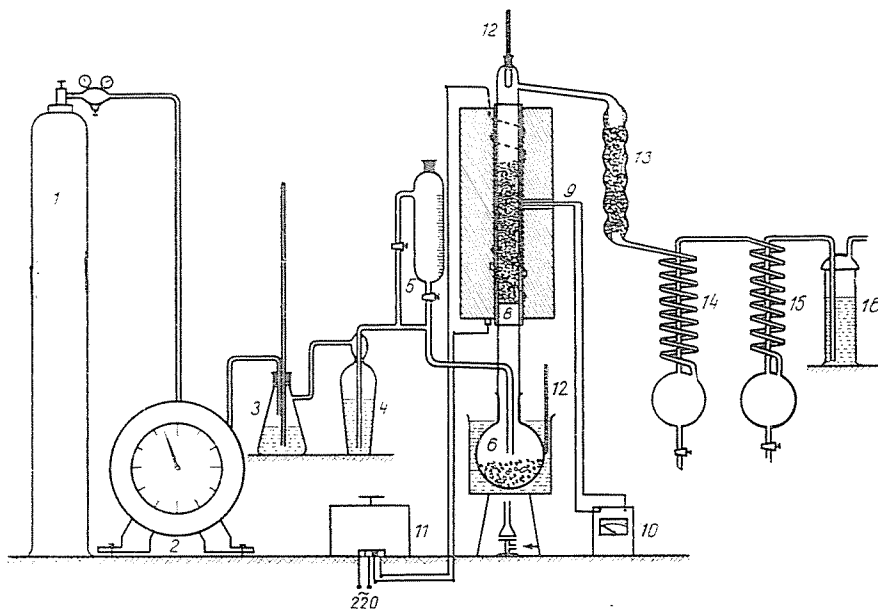


Fig. 1. Apparatus for the technological experiments. 1. Nitrogen gas cylinder. 2. Gas meter. 3. Pressure equalizer. 4. Sulphuric acid scrubber. 5. Dosage burette. 6. Evaporation flask. 7. Oil bath. 8. Lagged glass column with controllable heating, in a porcelain cylinder. 9. Iron-constantan thermocouple. 10. Temperature indicator. 11. Variable transformer. 12. Thermometers. 13. Column, filled with Raschig rings. 14, 15. Air coolers. 16. Scrubber

Fig. 1 shows the principle of the construction. Through a reducing valve inert gas is taken from flask (1) and, passing the meter (2), it is directed into the bubble-tube provided with a safety pipe (3). Herefrom the gas stream passes the sulphuric acid washer (4) and enters the evaporation flask (6) partly filled with Raschig rings. Upon the Raschig rings, kept at $260^{\circ}C$, the petroleum is fed through a burette (5). The mixture of petroleum vapour and nitrogen gas ascends from the evaporator into the reactor tube (8) placed vertically and filled to 53 cm of its length with burnt lime, therefrom the hydrocarbon vapours are led into the small column (13) filled with Raschig rings; the external surface of this column is slightly corrugated. The petroleum vapours partially condensed in column (13) are finally condensed in the condensers (14) and (15) in series, cooled by air. Tail gases are vented after

an aqueous wash in scrubber (16). At the upper end of the reactor tube, a little further from the heated section, a thermometer is inserted through a ground glass sleeve. The reactor is cylindrical, lagged with asbestos and mineral wool, enclosed in an aluminium sheath, and placed in a porcelain oven the heating of which is done by resistance wires wound on the superficies. Directly connected to it is the iron-constantan thermo-couple (9) the leads of which are attached to the variable transformer (11) and the thermometer instrument (10). The evaporator flask is heated with the oil-bath thermostat (7) and a gas flame, a lubricating oil of flash point higher than

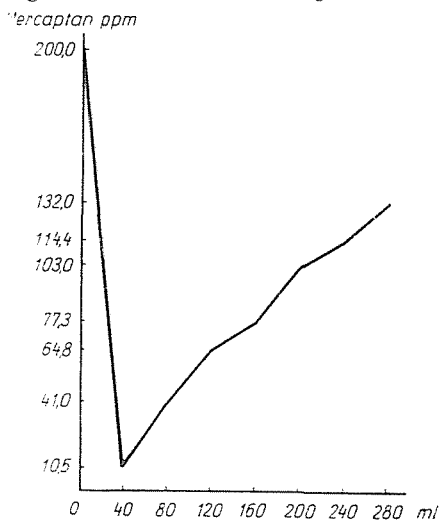


Fig. 2. Elimination of mercaptan from a petroleum fraction admixed with *n*-octyl-mercaptan, through treatment on a calcium oxide column at 300 °C. Temperature 300 °C. Grain-diameter CaO 3—6 mm. Mercaptan content of the sample 200 ppm. Feed rate 0.36 l/h

300 °C serves as the heat transfer medium. The non-heated connecting links are lagged carefully with asbestos in order to minimize losses due to cooling. Tinted water was placed into the bubble tube, thus the level of the liquid in the capillary could be clearly observed. The reactor tube, 63 cm long and of 2.7 cm i.d. has a grating at its lower end for the support of the filling.

212 g of calcium oxide, grain sizes 3 to 6 mm, was filled into the reactor tube. Temperature was 300 °C, resp. 400 °C. Experiments with burnt lime, grain sizes 6 to 8 mm, were also carried out. Space velocity too was varied in the experiments. 40 ml samples of the hydrocarbon that passed the reactor and condensed were tested according to the specifications of the relevant GOST (U.S.S.R.) Standard. *n*-Octyl-mercaptan, ethyl-mercaptan and thiophenol were added to the petroleum samples to raise mercaptan content. In most of the experiments petroleum with added *n*-octyl-mercaptan was used.

Results are presented in diagrams, the abscissae marking the volume, in ml, of the sample, with the p.p.m. concentrations of mercaptan found

marked on the ordinate. The origin is the mercaptan content of the untreated sample. *Fig. 2* shows results of experiments at 300 °C; the corresponding data are listed in *Table 2*.

Table 2

Reduction at 300 °C of the mercaptan content of a petroleum fraction to which n-octyl-mercaptan had been added

Quantity, ml	0	40	80	120	160	200	240	280
Mercaptan, p.p.m.	200	10.55	41	64.8	77.3	103	114.4	132

The graph shows that at 300 °C calcium oxide does not eliminate sulphur to a sufficient degree: in the second step the sample tested contained more than the allowed 50 p.p.m. of mercaptan, there was no colouration of the column. In view of this, further experiments were carried out at 400 °C, and

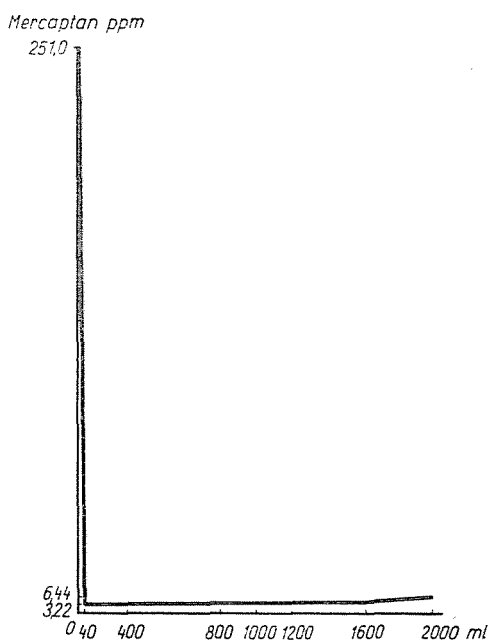


Fig. 3. Elimination of mercaptan from a petroleum fraction admixed with n-octyl-mercaptan, through treatment on a calcium oxide column at 400 °C. — Temperature 400 °C. Grain-diameter CaO 3–6 mm. Mercaptan content of the sample 251 p.p.m. Feed rate 0.55 l/h

a few at 500 °C. In the latter some cracking of the petroleum was perceivable. Therefore 400 °C was chosen as the temperature for subsequent experiments. *Fig. 3* presents the results of experiments at 400 °C, data are collected in *Table 3*.

Table 3

Reduction at 400 °C of the mercaptan content of a petroleum fraction to which n-octyl-mercaptan had been added

Quantity, ml	0	40	500	800	1000	1200	1600	2000
Mercaptan, p.p.m.	116	2.51	3.22	3.22	3.22	3.22	3.22	6.44

Experiments at 400 °C gave very good results; even in the 50th raffinate not more than 6.5 p.p.m. of mercaptan was detected. The calcium oxide column had a similar effect when petroleum containing ethyl-mercaptan instead of n-octyl-mercaptan was treated. The lower third of the column became slightly grey, the middle third intensively so, turning black, the upper third was of a lighter grey again. This colour change is due to carbon separated from the mercaptan and deposited in the reactor.

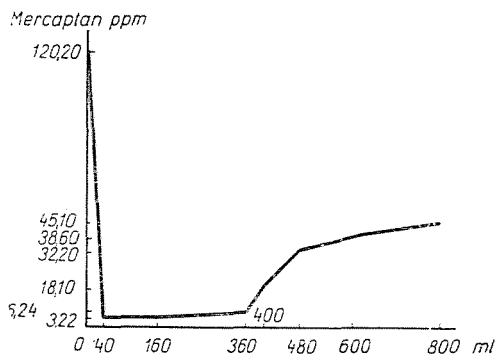


Fig. 4. Elimination of mercaptan from a petroleum fraction admixed with thiophenol, through treatment on a calcium oxide column at 400 °C. Temperature 400 °C. Grain-diameter CaO 3—6 mm. Mercaptan content of the sample 116 p.p.m. Feed rate 0.55 l/h

Fig. 4 shows the result obtained at 400 °C with a petroleum fraction to which thiophenol was admixed; relevant data are collected in Table 4.

Table 4

Reduction at 400 °C of the mercaptan content of a petroleum fraction to which thiophenol had been added

Quantity, ml	0	40	160	360	400	480	600	800
Mercaptan, p.p.m.	120.2	3.22	3.22	6.24	16.1	32.2	38.6	45.1

The graph shows that thiophenol is not bound by calcium oxide in the same degree as are ethyl- and n-octyl-mercaptan. However, thiophenol is seldom present in petroleum products, so this method is quite adequate for the desulphuration of petroleum fractions.

From the point of view of economics, the useful life of the sorbent is of decisive importance. If the mercaptan content of 40 to 50 parts by weight of petroleum, referred to sorbent weight used, can be kept at the allowed limit then it is not worthwhile regenerating the caustic lime spent in the process and this greatly simplifies this technology. Experiments to test the adsorptive capacity were carried out with petroleum containing an added quantity of n-octyl-mercaptan, and as Fig. 5 and values in Table 5 show,

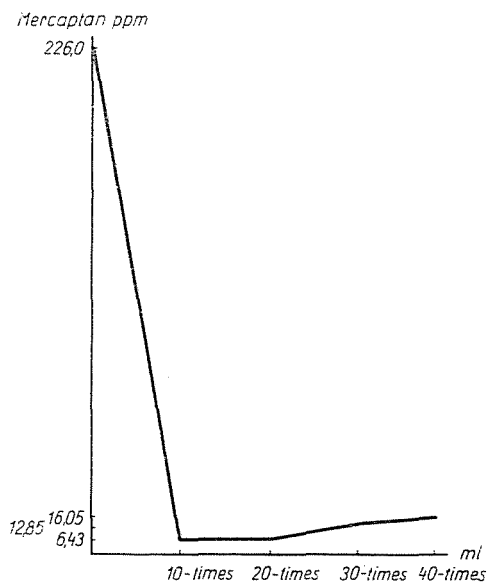


Fig. 5. Sorption capacity of calcium oxide. Temperature 400 °C. Grain-diameter CaO 3—6 mm. Mercaptan content of the sample 226 p.p.m. Feed rate 0.44 l/h

at 400 °C and 0.55 litre per hour feed rate, 40 parts petroleum per part of sorbent could be treated in such a way that still only 16 p.p.m., i.e. about one third of the allowed 50 p.p.m. mercaptan could be detected in the sweetened product.

Table 5

Testing of sorptive capacity

Ratio of CaO to petroleum treated	1 : 10	1 : 20	1 : 30	1 : 40
Mercaptan, p.p.m.	6.43	6.43	12.85	16.05

The petroleum treated on the calcium oxide column was tested according to Hungarian Standard Specifications. Referred to the initial substance, b.p. of the raffinate at the beginning and at the end of distillation was lower by 20 °C, its viscosity was less by 0.02 cSt, its acid number was zero.

Experiments with the calcium oxide column showed that with this sorbent the mercaptan content of special petroleum fractions could be reduced to very low levels. On this basis experiments were carried out to elucidate whether natural limestones have a similar effect.

Experimental conditions and apparatus were those just described, results are presented in Fig. 6 and Table 6.

Table 6

Reduction of the mercaptan content of a special petroleum fraction with calcium carbonate

Quantity, ml	0	50	100	150	200
Mercaptan, p.p.m.	198	15.34	51.8	63.16	81.84

Fig. 6 shows that, in contrast to calcium oxide, limestone is much less effective, and that great losses occur through cracking shown also by the colouration of the product. A great part of the petroleum leaving the reactor appears as a fog which does not precipitate but passes through the air-cooled tubes. The divergent behaviour of the two sorbents might be explained as follows. Dur-

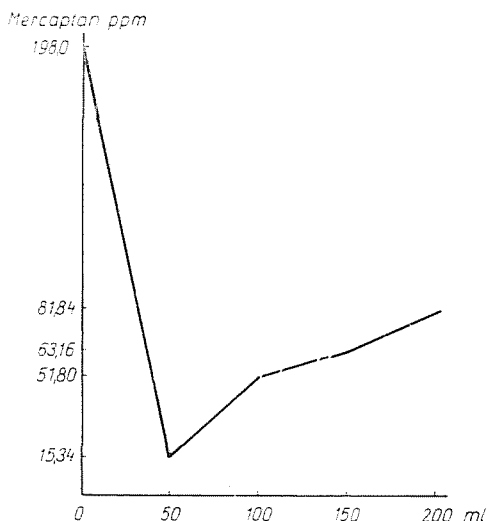
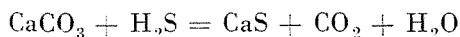


Fig. 6. Elimination of mercaptan with calcium carbonate. Temperature 400 °C. Grain-diameter CaCO_3 3–6 mm. Mercaptan content of the sample 198 p.p.m. Feed rate 0.55 l/h

ing lime-burning carbon dioxide is given off and the structure of the product is much less compact, so that calcium oxide has a much greater surface on which to react with the mercaptans. On the other hand, the normal affinity, at 700 °K, of the reaction



is 1.7 Kcal per mole, approximately, and, considering that in the gas phase hydrogen sulphide is present at a low partial pressure, this reaction can proceed only to a small extent. That some sulphur is bound might be ascribed to the formation of the intermediary where sulphur is present in part together with hydrogen. 0.003 atm is the equilibrium partial pressure of carbon dioxide above calcium carbonate at 700 °K and this means that some calcium oxide

may be formed and makes the elimination of sulphur to a certain measure possible. Our technological experiments carried out with calcium oxide might be evaluated as follows:

a) Experiments have shown that calcium oxide grains of 3 to 6 mm diameter, heated to 400 °C, reduce the mercaptan content of ten times its weight of a petroleum containing 226 p.p.m. n-octyl-mercaptan to 6.5 p.p.m., and even after 40 parts by weight of this petroleum is passed through the calcium oxide column this value rises but to 16 p.p.m., still far below the tolerance limit set for jet engine fuels.

b) Elimination of mercaptans is 98.6 per cent efficient in the first 50 ml, 97.2 per cent efficient for a quantity (by weight) ten times that of the sorbent, and 92.9 per cent at a 1 : 40 weight ratio of sorbent to petroleum treated.

c) Elimination of mercaptan is exclusively due to the sorption effect of the calcium oxide.

d) In the experiments a feed rate of 0.55 litres per hour seemed adequate; nitrogen was passed at a rate of 180 litres per minute.

e) Loss of petroleum is between 0.5 and 1.0 per cent.

f) Optimum temperature of operation is 400 °C.

g) No sorption of mercaptans by calcium carbonate was observed, thus this substance is unsuitable for the sweetening process discussed.

Summary

In this study, a method for the elimination of mercaptans from a special petroleum fraction destined for use as a jet propulsion fuel was tested. It was found that calcium oxide at 400 °C is suitable since it retains an effectiveness of 92.9 per cent even after forty times its weight of the petroleum fraction has been passed through.

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