

**REDUCING FUEL LOSSES FROM EVAPORATION.
SELECTION OF THE OPTIMUM SORBENT**

A. F. Aksenov, S. V. Boichenko, A. V. Shvets, and S. V. Ivanov

UDC 661.183+665.6

Sorption of motor fuel vapors by sorbents of different natures is described. The goal is to select the optimum sorbent to prevent fuel losses from evaporation during storage. Industrial medium-pore silica gels KSS-3 and KSS-4 are effective in recovery. Industrial zeolite NaX and SKT activated carbon have high adsorption power, but they are difficult to regenerate due to strong retention of hydrocarbons and secondary catalytic processes. A model of a system for preventing fuel losses from evaporation was created and industrial tests were conducted.

The rational use of hydrocarbon feedstock is a priority direction in energy and resource conservation policy [1, 2]. One stage in the implementation of this policy is attempting to prevent losses of hydrocarbon fuels [1] from evaporation during storage.

TABLE 1

Indexes	Fuel		
	motor gasoline A-76 (GOST 2084)	aviation gasoline (TU 38.5901481-96)	jet fuel (GOST 10227 or GSTU 320.00149943.007)
Distillation, °C			
IBP	41.5	45	150
10 %	53.5	75	162
50 %	87	109	183
90 %	159	150	208
EP	191	183	218
Density at 20°C, kg/m ³	732	746	787
Saturated vapor pressure at 38°C, kPa	62	39.1	2.4
Surface tension, mN/m	23.4	24.4	25.9

National Aviation University. Ukrainian Oil and Gas Academy. L. V. Pisarzhevskii Institute of Physical Chemistry. Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 5, pp. 22 – 27, September – October, 2003.

TABLE 2

Sorbent	Total pore volume, V , cm^3/g	Specific surface S , m^2/g	Average pore radius r , nm
<i>Zeolites</i>			
Clinoptilolite (natural)	–	25	0.38
Synthetic			
NaA	0.15	760	0.4
CaA	0.18	800	0.5
NaX	0.24	1100	0.74
<i>Silica gels</i>			
Fine-pore KSMG	0.37	570	1.3
Medium-pore			
KSS-4	0.75	650	2.5
KSS-3	0.83	520	2.8
Large-pore KSK	0.76 – 0.93	250 – 270	6.1 – 7.5
<i>Carbon sorbents</i>			
SKT	0.83	620	–
Anthracite	0.3	–	–
AG-3	0.83	280	1.2
AR-V	0.52	–	–
BPL	0.95	700	–
SUA	1.22	–	–
Aerogel	0.34	170	–
C-TNB	0.98	–	–
FF	0.88	960	3 – 7
KAU	0.65	–	–

According to the data from analysis of many publications on the rational use of petroleum energy sources, there are no technologies to fully prevent losses of fuels caused by evaporation. To reduce this type of irrevocable losses, it is expedient to improve the “breathing” fixtures of storage tanks.

We investigated the kinetics of adsorption of vapors of different kinds of motor fuels (Table 1) by different sorbents (Table 2). The purpose of these studies was to select the optimum sorbent for industrial systems of prevention of fuel losses from evaporation during shipment and storage.

The selective power of sorbents allows using them in many areas [1, 3, 4]: for absorption of the components of industrial wastes that pollute air and water; for drying natural gas; for regenerating petroleum

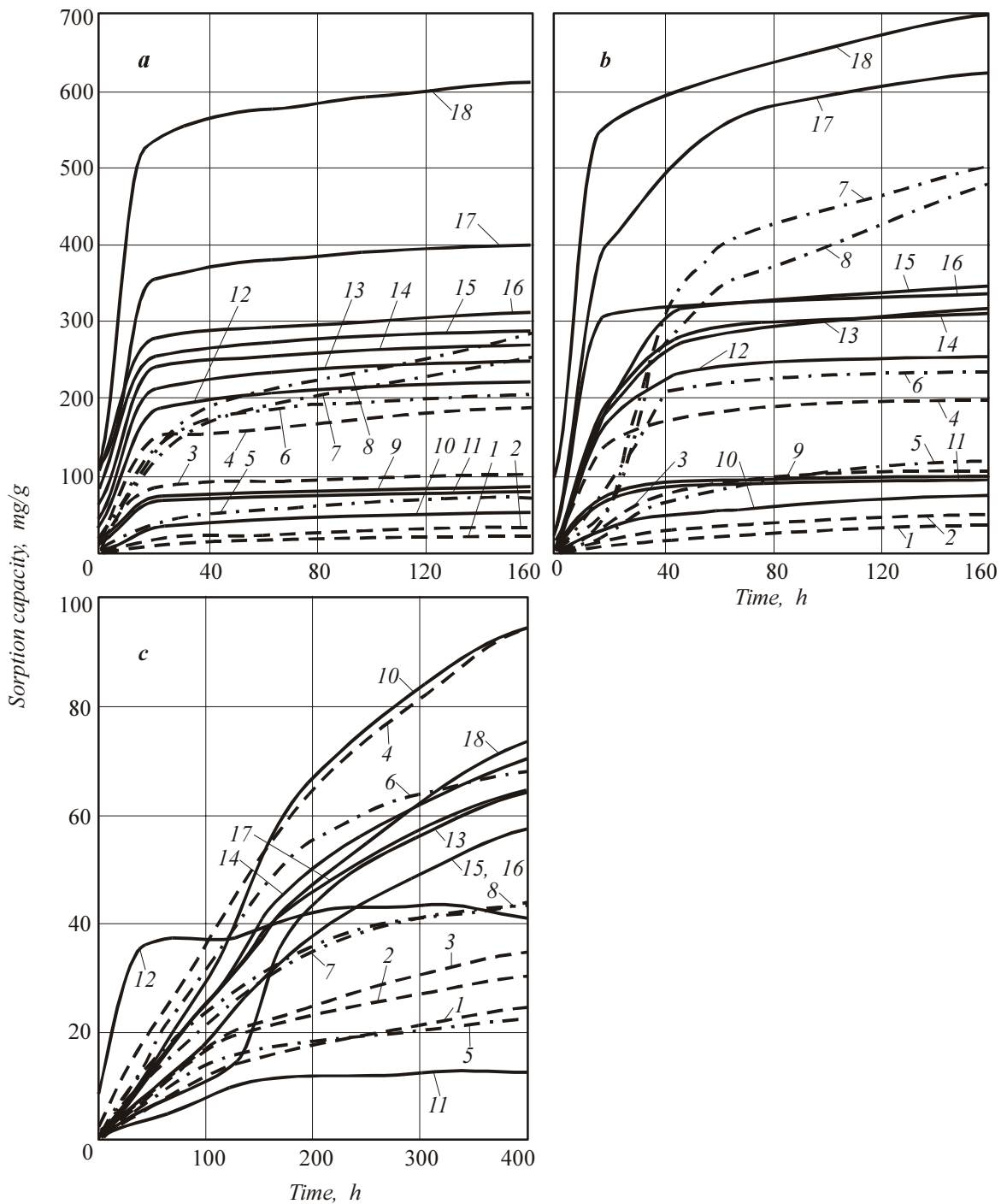


Fig. 1. Kinetics of adsorption of vapors of automotive gasoline (a), aviation gasoline (b), and jet fuel (c) by different sorbents: ---: zeolites: 1) clinoptilolite; 2) NaA; 3) CaA; 4) NaX; -.-.-: silica gels: 5) KSK; 6) KSMG; 7) KSS-3; 8) KSS-4; —: carbon: 9) anthracite; 10) FF; 11) Aerogel; 12) AR-V; 13) AG-3; 14) SKT; 15) BPL; 16) KAU; 17) C-TNB; 18) SUA.

fuels and oils; for treating liquids and gases; for analyzing the quality of gas, fuels, and lubricants by physicochemical methods, in particular, by chromatography; for removing and regenerating valuable substances and solvents; for separating valuable substances in catalytic processes, in particular, oil and gas refining and petrochemistry.

The kinetics of sorption of fuels was investigated on previously calcined sorbents (silica gels and carbons at 210°C, zeolites at 400°C) in closed desiccators at saturated vapor pressure and room temperature: automotive and aviation gasolines for 7 days, JF jet fuel for 16 days.

As Fig. 1a-c shows, the sorption kinetics and maximum sorption of gasoline and jet fuel vapors by different sorbents differ strongly. As expected, the jet fuel was less volatile: even very active sorbents sorbed a maximum of 10 wt. % of its vapors over a long time. The saturated vapor pressure of the more volatile automotive gasoline causes them to be sorbed by the more active sorbents to a greater degree: 35-60 wt. % after a relatively short time. In the case of aviation fuel, the limiting saturation of the individual sorbents attained 40-75 wt. %.

Important differences were observed in the properties of the sorbents and with respect to the same adsorbate. Of the zeolites studied, relatively more automotive gasoline vapors were adsorbed quickly by NaX (approximately 20 wt. %, or 200 mg/g). The other zeolites exhibited much lower absorption power, and clinoptilolite almost did not absorb the vapors of this fuel.

Of the silica gels studied, medium-pore KSS-3 and KSS-4 had the highest power for absorption of automotive gasoline vapors: the maximum sorption capacity attained 25-30%. KSMG silica gel absorbed

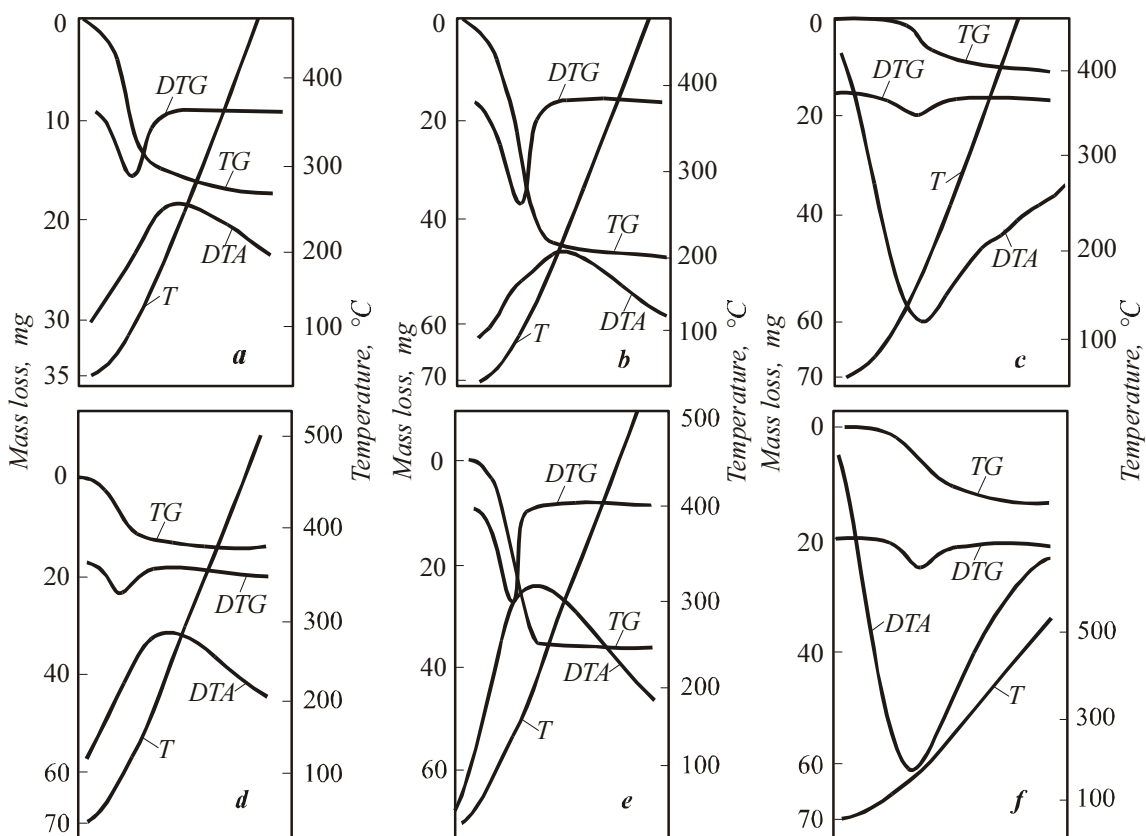


Fig. 2. Results of thermogravimetry of medium-pore silica gels after adsorption of automotive gasoline (a, d), aviation gasoline (b, e), and jet fuel (c, f) vapors: a, b) KSS-3, sample $m = 182$ and 242.2 mg, scale division ratio: $DTG = 1/5$, $DTA = 1/10$, heating rate $c = 10^\circ\text{C}/\text{min}$, medium: helium; c) same, $m = 210.5$ mg, $DTG = 1/5$, $DTA = 1/3$, $c = 10^\circ\text{C}/\text{min}$, medium: argon; d, e) KSS-4, $m = 146.5$ and 187.5 mg, $DTG = 1/5$, $DTA = 1/10$, $c = 10^\circ\text{C}/\text{min}$, medium: helium; f) same, $m = 243.8$ mg, $DTG = 1/5$, $DTA = 1/3$, $c = 10^\circ\text{C}/\text{min}$, medium: argon.

gasoline vapors more rapidly, but its maximum sorption capacity was lower. KSK exhibited much lower activity in this case.

Of the carbon sorbents, three groups can be distinguished based on the sorption capacity. The first group has two kinds of special bead carbon: SUA and C-TNB. A very high sorption rate and fuel vapor maximum sorption capacity, attaining 40-60 wt. %, are characteristic of them.

The second group includes a number of industrial and special carbon substances: BPL, SKT, AR-V, AG-3, KAU. They are characterized by a relatively high sorption rate, have a maximum sorption capacity of 22-32 wt. %, and in contrast to the sorbents in the first group, are relatively widely available and inexpensive (except for KAU).

The third group includes FF, anthracite, and aerogel (unactivated) sorbents, which are characterized by a relatively low sorption rate and maximum sorption capacity (under 10 wt. %).

In the case of aviation gasoline, the above tendency persists, but the limiting values of the sorption capacity for vapors of this fuel are 3-10% higher and attain 50 wt. % for medium-pore silica gels KSS-4 and KSS-3.

In contrast to gasolines, the lowest amount of adsorbed fractions is characteristic of jet fuel due to the low saturated vapor pressure. For most sorbents, the sorption kinetic curves do not go out to saturation, i.e., their maximum sorption capacity is not attained even after 16 days.

Elimination of adsorbed fuel fractions – desorption – was investigated in inert medium (helium or argon) by thermogravimetry on a MOM OD-102 derivatograph. The results (Figs. 2 and 3) indicate that medium-pore silica gels KSS-3 and KSS-4 are the most promising for sorption recovery of fuel vapors.

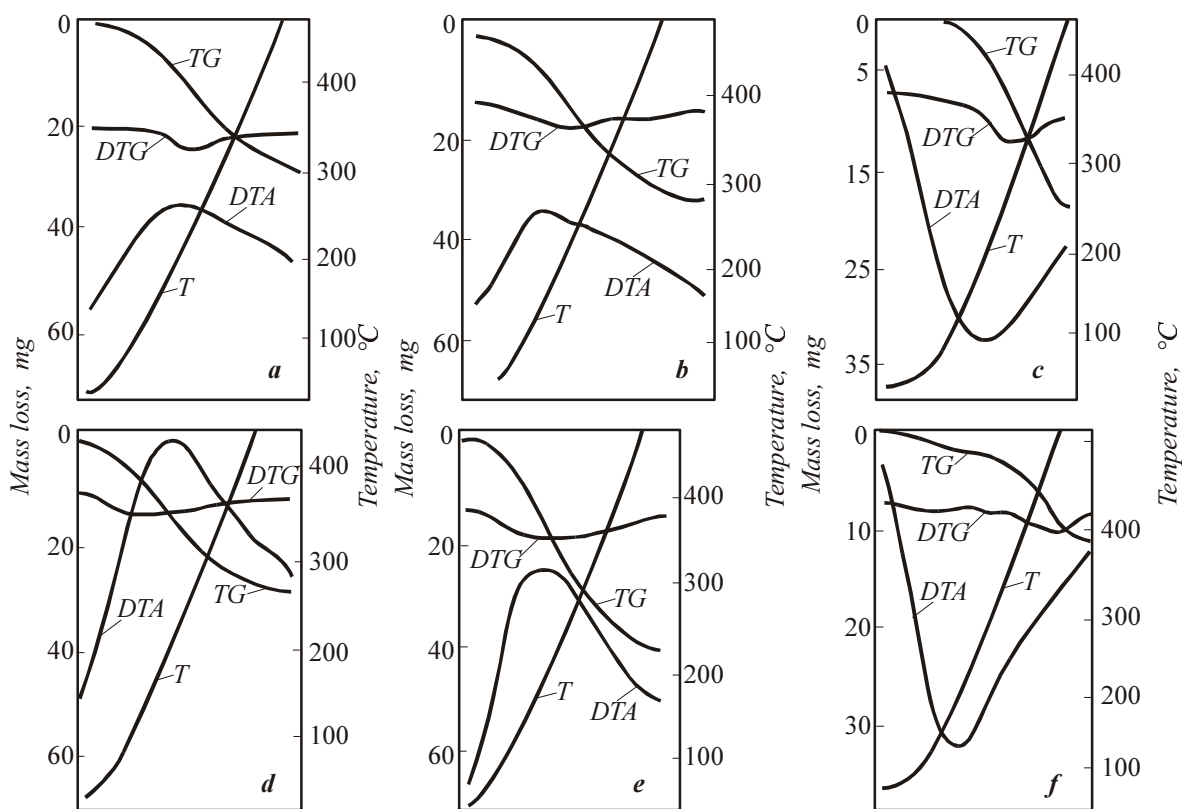


Fig. 3. Results of thermogravimetry of sorbents after adsorption of automotive gasoline (a, d), aviation gasoline (b, e), and jet fuel (c, f) vapors: a, b) zeolite NaX, $m = 203$ and 218 mg, $DTG = 1/5$, $DTA = 1/3$, $c = 10^\circ\text{C}/\text{min}$, medium: helium; c) same, $m = 259.2$ mg, $DTG = 1/5$, $DTA = 1/3$, $c = 10^\circ\text{C}/\text{min}$, medium: argon; d, e) SKT activated carbon, $m = 183$ and 228.3 mg, $DTG = 1/5$, $DTA = 1/10$, $c = 10^\circ\text{C}/\text{min}$, medium: helium; f) same, $m = 217.8$ mg, $DTG = 1/5$, $DTA = 1/3$, $c = 10^\circ\text{C}/\text{min}$, medium: argon.

Elimination of the adsorbed gasoline fractions begins at 20°C and is completed at 210°C. The maximum desorption rate is observed in the 90-105°C temperature range, as seen with the initial (*TG*) and differential (*DTG*) weight loss curves.

Aviation gasoline vapors are adsorbed and removed by silica gels in much higher quantities (18.3-19.6 wt. %) than the low-molecular-weight fractions of automotive gasoline (8.5-8.7 wt. %). We can hypothesize that this is due to the different volatility, i.e., different hydrocarbon composition, of these fuels and correspondingly the different character of equilibrium sorption-desorption processes.

This is additionally confirmed by our data [5] on the capacity of silica gels to sorb individual hydrocarbons from the vapor phase [5]. In addition, these results indicate the necessity of additionally studying the effect of the hydrocarbon composition of fuels on the absorption capacity of silica gels.

The jet fuel fractions are adsorbed and removed by the silica gels in much smaller amounts (4.8-4.9%) and at higher temperatures (40-310°C) due to its low saturated vapor pressure. The maximum desorption rate was observed at 132-146°C.

Gasoline fractions are desorbed in the amount of 14.5 wt. % from NaX zeolite molecular sieve in a wide range of temperatures, from 20 to 500°C and higher (see Fig. 3a-c). This process can arbitrarily be divided into two stages: with maximum desorption rates at 230 and 435°C; the weight losses were 10.6-11.1 and 3.5-3.9%.

The shift in the temperature of removal of adsorbed fractions to high temperatures in comparison to the temperatures for silica gels could be due to joining of comparatively small pores and the presence of strong acid sites. Secondary catalytic transformations of hydrocarbons into aromatic and other compounds take place on these sites, especially in the second stage of removal at 435°C.

Jet fuel fractions are desorbed from zeolite NaX in much more important amounts (7.7 wt. %) at high temperatures (above 500°C) with the maximum rate at 282°C and desorption is accompanied by secondary processes.

SKT carbon sorbent exhibits a comparatively high capacity to absorb vapors of these fuels: 10.5-17.9 wt. % (see Fig. 3d-f) due to the affinity of its carbon surface to their hydrocarbon fractions of different molecular weight.

For this reason, removal of adsorbed gasoline cuts from it is difficult in comparison to their removal from silica gels and takes place in a wide temperature region (above 500°C) with the maximum rate: at 150°C for automotive gasoline, at 220°C for aviation fuels enriched with hydrocarbons of higher molecular weight.

Adsorbed fractions of jet fuel are removed from the pores of SKT in two distinct stages: with the maximum rate at 88 and 462°C: weight losses of 0.9 and 9.6 wt. %. This can hypothetically be attributed to a certain distribution of the different fractions of this fuel in the pores or different locations in the sorbents. The second stage of desorption with a maximum at a higher temperature (462°C) is accompanied by secondary catalytic processes.

The study of the effect of the carrier gas (medium) on the character of desorption showed that the process takes place with an exothermic heat effect (*DTA* curves) in helium and with an endothermic effect in argon.

According to the findings of the laboratory studies, the medium pore industrial silica gels KSS-3 and KSS-4 can be used as effective adsorbents for recovering vapors of the investigated fuels. The differences in their absorption capacity for fuel vapors with different distillation curves are most probably due to the tendency of these fuels to evaporate (volatility).

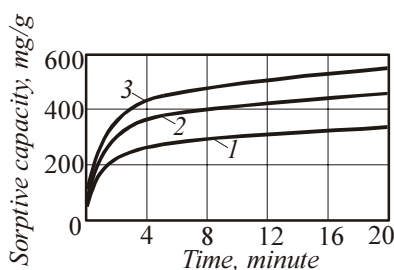


Fig. 4. Change in the sorption capacity of silica gels for automotive gasoline vapors in conditions of modeling large tank “breathing”: 1) large-pore KSK; 2) fine-pore KSMG; 3) medium-pore KSS-4.

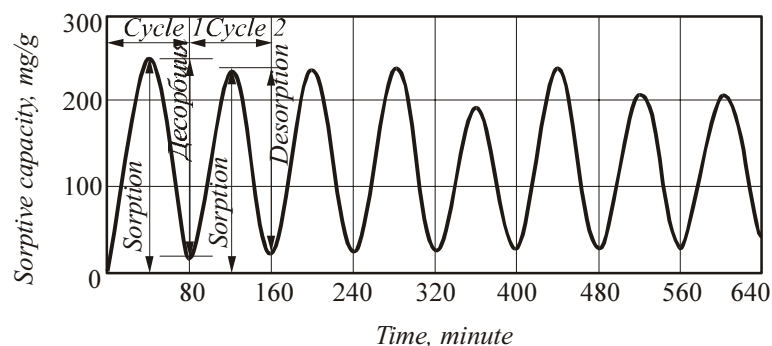


Fig. 5. Graph of operation of NGBV using medium-pore KSS-4 silica gel.

They exhibit the highest activity with respect to aviation gasoline. Industrial zeolite NaX and SKT activated carbon sorbents have a high absorption capacity for vapors of these fuels but are almost unsuitable for recovery of these vapors due to their strong retention in the pore structure and the occurrence of secondary catalytic processes.

To prevent natural losses of hydrocarbon fuels in tank farms, great attention has been focused on improving the “breathing” and protective equipment in the tanks. It was found that approximately 400 kg of gasoline evaporates from a ground tank with a capacity of 50 m³ during a year of storage at 20°C, even with a good “breather”, and 150 kg evaporates from a buried or half-buried tank.

In consideration of the above results and an analysis of the methods and ways of preventing fuel losses from evaporation [1, 3-4], we developed a laboratory model of a new generation breather valve (NGBV). The physical processes of vapor adsorption and condensation by thermoelectric cooling were combined in it [6].

This model was tested during determination of: the absorption capacity of the sorbent for minor and major “breathing” of the tank; its “life” cycle; the operating parameters of the thermoelectric module for regeneration of the sorbent and condensation of the fuel vapors; the efficiency of the system for prevention of fuel losses from evaporation in a set of sorption and thermoelectric processes.

According to the data obtained for fine-pore (KSMG), medium-pore (KSS-4), and large-pore (KSK) silica gels: in dynamic and static conditions of modeling large and small “breathing” of a tank (Fig. 4), the average sorption capacity of the first of 21-cycle major “breathing” of a model tank was 406.95 mg/g, 483.86 mg/g for the second, and 290.76 mg/g for the third.

In 300 cycles of modeling the operations of intake and feed of A-76 automotive gasoline, the absorption capacity and efficiency of desorption for KSS-4 medium-pore silica gel were constant: 150-210 mg/g and 86-93% (Fig. 5). In the 9th annual turnover of the tanks, the lifetime of the sorbent in the “breather” valve was approximately 30 months.

The urgency and practical value of the results obtained are because of the possibility of solving such important problems as:

- increasing the efficiency of use of hydrocarbon fuels due to prevention of evaporation losses;
- preservation of the quality of commercial motor fuels;
- ensuring reliable operation of equipment;
- decreasing the technogenic load on the environment in use of fuel by industry.

The efficiency of medium-pore industrial KSS-3 and KSS-4 silica gels in recovery of motor fuel vapors and the process system for prevention of fuel losses from evaporation based on them was thus demonstrated.

We would like to thank Prof. M. A. Al'tshuler for his valuable advice and recommendations in preparing this article.

REFERENCES

1. S. V. Boichenko, *Rational Use of Hydrocarbon Fuels* [in Russian], NAU, Kiev (2001).
2. M. P. Kovalko and S. P. Denisyuk, *Saving Energy “ a Priority Direction in Ukraine Government Policy* [in Russian], UEZ, Kiev (1998).

3. S. V. Boichenko and O. V. Boichenko, *Probl. Obsh. Energet.*, No. 3, 57-59 (2000).
4. S. Brunauer, *The Adsorption of Gases and Vapors*, Vol. 1, Princeton University Press, Princeton, N. J. (1945).
5. S. V. Boichenko, A. V. Shvets, and A. N. Lastovets, *Avtomatika, Avtomatizatsiya, Elektrotekhn. Kompleksy Sistemy*, No. 1, 92-99 (2002).
6. Ukraine Patent No. 37813 A.