FORECASTING EVAPORATION OF MOTOR FUELS UNDER LONG TERM STORAGE

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Elements of a method for forecasting the evaporation of motor fuels under long-term storage are presented based on physical and statistical modeling of the fuel evaporation process in storage facilities. The novel method can be used to obtain prompt forecast estimates necessary for making informed decisions on long-term fuel storage with minimal resource consumption. Provided examples of motor fuel evaporation forecasts confirm the advantages of the proposed method.

Keywords*: motor fuels, motor gasoline, evaporation, evaporation process, modeling, forecasting, fuel storage.*

The long-term storage of motor fuels is accompanied by a change in their quantity, which is associated, first of all, with their natural loss (evaporation). In addition to the thermodynamic instability of its components, the decrease in the quantity of stored gasoline can be described in terms of storage conditions (climatic factors, the technical condition of storage facilities, their equipment with means for reducing evaporation losses, reservoir "turnover", storage duration, etc.) [1-3].

At present, in order to predict the evaporation of motor fuels under long-term storage conditions, expert methods are used based either on the results of evaluating the indicators of fuel properties (fractional composition, saturated vapor pressure, maximum vapor lock index, etc.) under laboratory conditions, or on the

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results of statistical processing of experimental data about changes in the mass of fuel stored in different climatic zones and facility types [4].

Analysis of the evaporation characteristics of fuel, in particular motor gasoline (saturated vapor pressure, fractional composition, maximum vapor lock index), established by the Technical Regulations of the Customs Union 013/2011, GOST R 51105, GOST R 51866 and GOST 32513, identifies challenges in forecasting fuel evaporation during long-term storage. This is largely due to the regulatory requirements and standardization documents being focused mainly on ensuring the necessary operational parameters for internal combustion engines (warm-up time, acceleration capability, wear, efficiency, prevention of vapor locks in the power system, etc.). Additionally, the classification of the fuel evaporation adopted in the standards (for example, in GOST 32513) lacks specificity. When analyzing the evaporation of contemporary Russian-made gasolines according to their component composition, special attention should be paid to the content of low-boiling components (butane-butylene and pentane fractions, ethers, etc.), since an increase in the content of these components can significantly affect the tendency of gasoline to evaporation losses.

Difficulties in the quantitative forecasting of the fuel evaporation under conditions of long-term storage using laboratory methods according to GOST 17799, ASTM D 86, GOST ISO 3405, GOST R 53707, GOST 1756, GOST EN 13016-1, GOST 28781, GOST 31874, GOST 33157, ASTM D 323, ASTM D 4953, ASTM D 5191, as well as other methods [5, 6], are due to the weak correlation between the actual loss of oil products, in particular gasoline, due to evaporation under real storage conditions with the fractional composition and saturated vapor pressure parameters [7]. In addition, contemporary laboratory methods do not accurately simulate the process of fuel evaporation in reservoirs or fully account for the storage conditions and design features of storage facilities. As a result, the forecasting of the tendency of fuels to losses from evaporation tends be carried out indirectly on the principle of "more or less".

The conventional approach to forecasting fuel evaporation, based on a passive experiment (observation) under actual storage conditions, is associated with long-term data collection (fuels can be stored for up to 5 years or more depending on the climatic zone), which requires a large amount of experimental material and significant storage costs. Moreover, this approach does not take into account the influence of many factors whose contribution is very difficult to evaluate during testing in storage facilities (reservoir failure, losses from leaks, spills, etc.).

Taking into account the abovementioned shortcomings of the known technical solutions for forecasting the evaporation of motor fuels, a method is proposed based on obtaining forecasting information on fuel evaporation under storage conditions according to the results of modeling the evaporation process in a physical reservoir model [8].

The physical model is implemented in the form of an experimental installation incorporating reservoir models, fuel mass meters, units of fuel supply, registration and control, operation, parameter processing, and visualization [9]. In the experimental installation, the "mechanism" of the fuel evaporation process remains the same as in the reservoir, while the conditions for the implementation of the evaporation process in the model and in the reservoir are functionally similar to each other.

Based on the classical evaporation indicator concepts [10], the average mass evaporation rate (W_{ev}, kg/m²h) is taken to represent the mass of fuel (M_n, kg) evaporated from the surface (S, m²) during time period (τ, h):

$$W_{ev} = \frac{M_n}{S\tau} \tag{1}$$

When forecasting the level of fuel evaporation, it is advisable to rely on mathematical models of the evaporation process that take into account the conditions reproducing mass transfer in the reservoir. Since the exact form of possible models is unknown, it is proposed to interpret the relationships between the composition of fuels, the conditions of their storage in reservoirs, and the W_{ev} evaporation rate as multifactorial nonlinear regression models having the form:

$$W_{ev} = G(x_1, ..., x_k) = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} \sum_{j=1}^{k} b_{ij} x_i x_j + \sum_{j=1}^{k} b_{ij} x_i^2 + \varepsilon \tag{2}$$

where x_i are the coded variables of forecasting factors, $(i = 1, k)$, defined as $x_i = (X_i^{nat} - X_{i_0}^{nat})/\Delta X_i^{nat}$; X_i^{nat} are the values of factors in natural variables; $X_{i_0}^{nat}$ is the central coordinate of the experiment (zero level) according to i-th factor $X_{i_0}^{nat} = 0.5(X_{i_{max}}^{nat} + X_{i_{min}}^{nat})$; ΔX_i^{nat} is the half-interval of change in i-th factor in experiment $\Delta X_i^{nat} = 0.5(X_{i_{max}}^{nat} - X_{i_{min}}^{i})$; $X_{i_{max}}^{nat}$ and $X_{i_{min}}^{i}$ are the upper and lower levels of factor variation, respectively; b_0, b_i, b_{ij}, b_{ii} are the regression coefficients; k is the number of factors; ε is the experimental error. The calculation of the parameters of the model (2) was carried out according to the following formulas [11]:

$$b_0 = \bar{y}_0; b_i = A\{iy\}; b_{ij} = D\{ijy\};$$

$$b_{ii} = B\{iiy\} + C\sum_{i=1}^{k}\{iiy\} - \frac{\bar{y}_0}{2}; \bar{y}_0 = \left(\sum_{u_0=1}^{n_0} y_{u_0}\right) n_0^{-1}; \tag{3}$$

$$\{iy\} = \sum_{u=1}^{N} x_{iu} y_u; \{ijy\} = \sum_{u=1}^{N} x_{iu} x_{ju} y_u; \{iiy\} = \sum_{u=1}^{N} x_{iu}^2 y_u$$

where N is the number of experiments in the experimental plan; u is the experiment number.

In accordance with the proposed methodology, the forecast (potential) tendency of fuels to evaporation losses is characterized by an $Int(W_{ev})$ (kg/m²·h) aggregated indicator (integral estimate) of evaporation. In this case, an assumption is made about the uniformity of the distribution of the fuel storage conditions over the
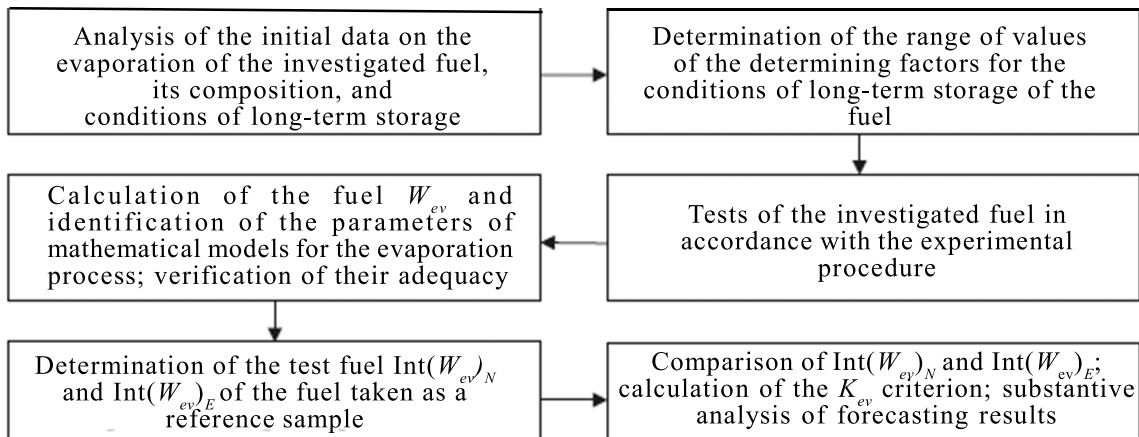

Fig.1. Algorithm for forecasting the level of motor fuel evaporation.

Table 1

Variation levels	Factors		
	Fuel temperature, T, °C	Leakage coefficient, K_l	Filling factor, K_f
Main level "0"	35	0.5	0.6
Upper level "+1"	50	1.0	0.9
Lower level "-1"	20	0	0.3
Variation step	15	0.5	0.3
Code designations	x_1	x_2	x_3

storage time period. It is straightforward to compare the values of integral estimates according to the K_{ev} evaporation criterion and the ratio of the $\text{Int}(W_{ev})_N$ evaporation integral estimate of the investigated fuel to the $\text{Int}(W_{ev})_E$ integral estimate obtained for the fuel taken as a standard (reference sample):

$$K_{ev} = \text{Int}\left(W_{vap}\right)_N \left[\text{Int}\left(W_{vap}\right)_E\right]^{-1} = \left[\underbrace{\int dx_1 ... \int dx_k}_{D} G_N\left(x_1, ..., x_k\right)\right]\left[\underbrace{\int dx_1 ... \int dx_k}_{D} G_E\left(x_1, ..., x_k\right)\right]^{-1} \quad (4)$$

where $G_N(x_1, ..., x_k)$ and $G_E(x_1, ..., x_k)$ are the integrands of the form (2), depending on k determining factors; D is the domain of integration of the G_N and G_E functions, specified in the form of a hypercube by the boundaries of the variation intervals of the x_i factors (in this case, -1, +1) $i = 1, ..., k$.

Taken together, models of the evaporation process of the form (2), integral estimates, and the evaporation criteria for fuels make it possible to predict fuel evaporation losses during long-term storage in accordance with the algorithm schematically shown in Fig.1.

The numerical criteria and integral fuel evaporation estimates allow a generalized characteristic of the fuel evaporation dynamics in various reservoirs to be obtained in order to evaluate the relative degree of "superiority" of one fuel over another.

The variation range of determining factors for the conditions of model fuel storage was selected based on the analysis of the accumulated statistics of their actual values in the conditions of real storage. The levels and step of variation of the factors are presented in Table 1.

The range of fuel temperature variation (x_i) covers the most probable temperatures of fuel stored under different climatic regions (for example, in a temperate climate – 20°C – the lower level (-1); in a very hot dry climate – 50°C – the upper level (+1)). The lower level $K_l(x_2 = 0)$ characterizes the possible leakage of reservoir, the main level $K_l(x_2 = 0.5)$ – the operation of the breathing valve ($P_i > 2000$ Pa), the upper level $K_l(x_2 = 1)$ – the operation of the reservoir safety valve ($P_i > 4000$ Pa). The lower level $K_f(x_3 = 0.3)$ characterizes the volume of non-draining residue in the reservoir; the main level $K_f(x_3 = 0.6)$ – filling the reservoir by 60% of its capacity; the upper level $K_f(x_3 = 0.9)$ – filling the reservoir to 90% with fuel, taking into account its thermal expansion.

A quantitative expression of mutually independent forecasting estimates of the influence of evaporation process factors taking the numerical form of the mathematical model coefficients (2) can be obtained from the results of studying the response surface in the physical model of the fuel storage reservoir. Taking into account

Table 2

Gasoline sample number	alkylate	reforming gasoline	cracking gasoline	isomerate	isopentane fraction	MTBE	straight-run gas-condensate gasoline (35-140°C)
			Component composition of gasoline samples, wt.%				
1	17	63	20	-	-	-	-
2	10	58	25	-	-	2	5
3	-	40	18	10	9	9	14

Table 3

| Model coefficients	Motor fuels					Components						
	regular-92 gasoline (sample No. 1)	regular-92 gasoline (sample No. 2)	regular-92 gasoline (sample No. 3)	TS-1 fuel	DT-Z-K5 fuel	alkylate	reforming gasoline	cracking gasoline	isomerate	isopentane fraction	methyl tert-butyl ether	straight-run gas-condensate gasoline
b_0	2.25	2.77	4.80	0.18	0.15	1.76	2.57	3.05	7.05	9.58	9.56	7.32
b_1	0.97	1.19	2.29	0.08	0.06	0.81	1.13	1.33	3.47	4.05	4.54	3.83
b_2	-0.40	-0.49	-0.73	-0.03	-0.03	-0.29	-0.43	-0.50	-1.02	-1.36	-1.29	-1.09
b_3	-0.56	-0.70	-1.36	-0.05	-0.04	-0.49	-0.66	-0.77	-2.18	-2.78	-2.98	-2.20
b_{12}	-0.22	-0.29	-0.66	-0.02	-0.02	-0.18	-0.27	-0.30	-0.88	-1.31	-1.06	-1.00
b_{13}	0.21	0.26	0.16	0.02	0.02	0.10	0.27	0.30	0.43	0.24	0.54	0.15
b_{23}	0	0	0	0	0	0	0	-0.03	-0.04	-0.10	-0.06	0
b_{11}	0	0	0.12	0	0	0.06	0.05	0.04	0.05	0.05	0	0
b_{22}	-0.43	-0.51	-1.01	-0.03	-0.03	-0.34	-0.50	-0.60	-1.48	-2.34	-2.10	-1.41
b_{33}	-0.40	-0.49	-0.68	-0.03	-0.02	-0.28	-0.40	-0.50	-1.01	-1.09	-1.31	-1.23
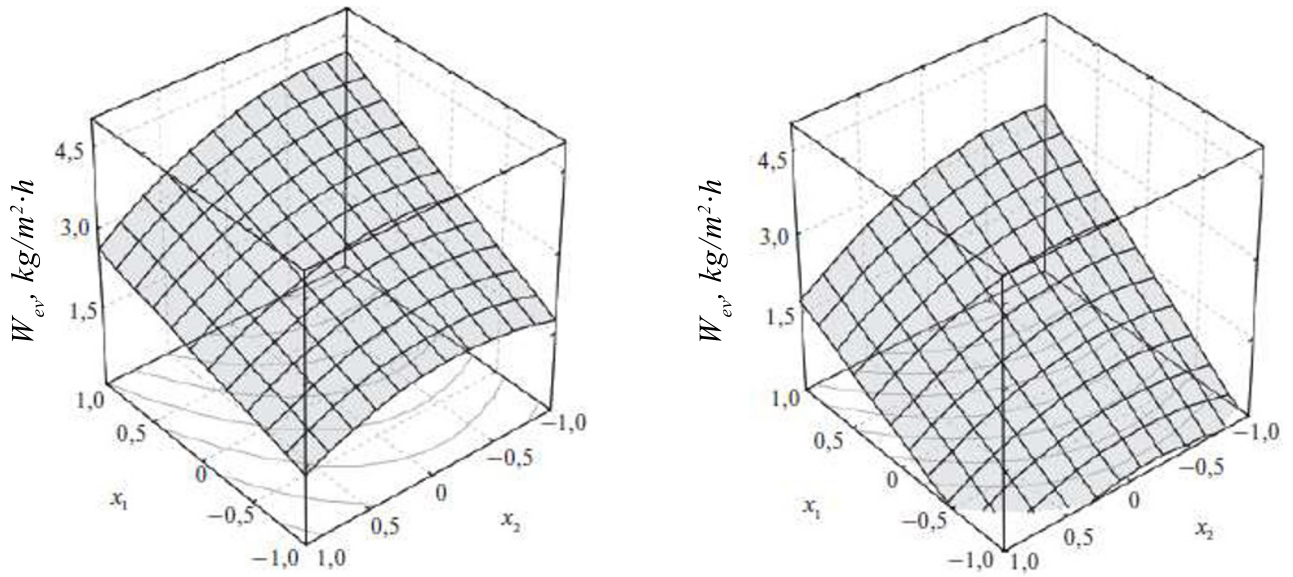
Fig. 2. Dependence of the W_{ev} forecasted values for Regular-92 gasoline (sample No. 2) on the evaporation temperature (x_1) and leakage coefficient (x_2) at the values of the filling factor (x_3): a) at the lower level (-1), b) at the upper level (+1).
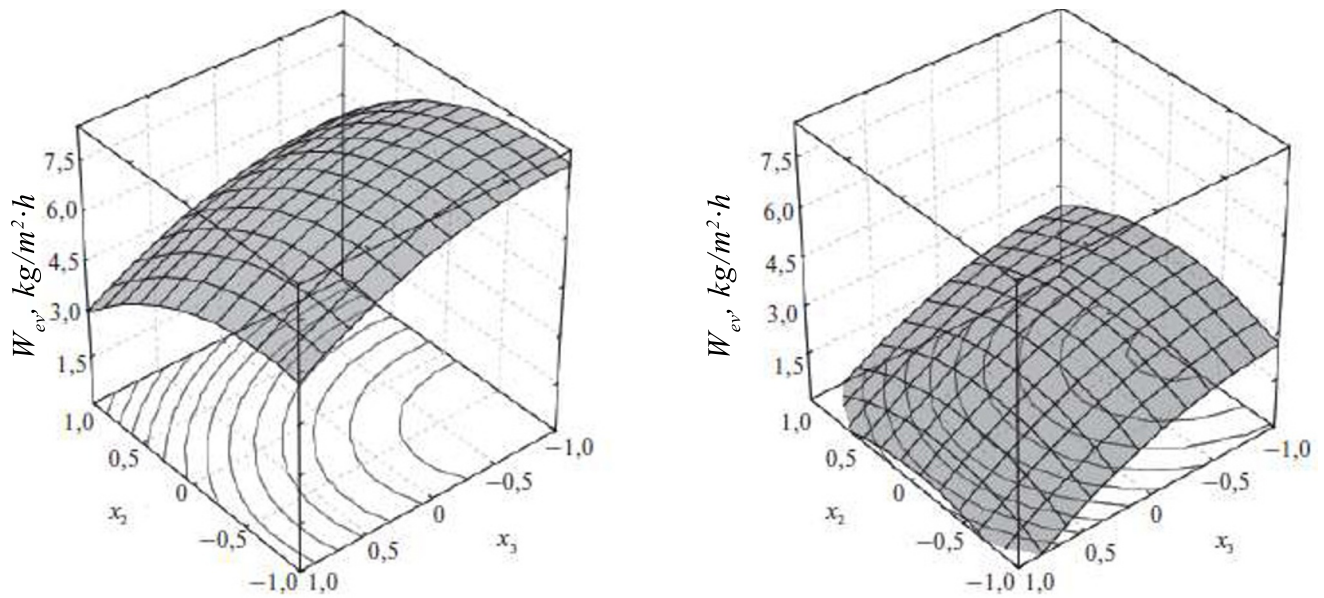

Fig. 3. Dependence of the forecasted values of W_{ev} for Regular-92 gasoline (sample No. 3) on the leakage coefficient (x_2) and the filling factor (x_3) at the values of evaporation temperature: a) at the lower level (-1), b) at the upper level (+1).

the requirements for efficiency according to the optimality criteria D and E, as well as a high degree of orthogonality and rotatability of the experiment matrix, the forecast of fuel W_2 was performed using the Box-Behnken three-level experimental plan for three factors [11, 12].

The results of testing the method for forecasting evaporation are provided below on the example of motor fuels widely used in technology and subject to long-term storage for state needs: samples of
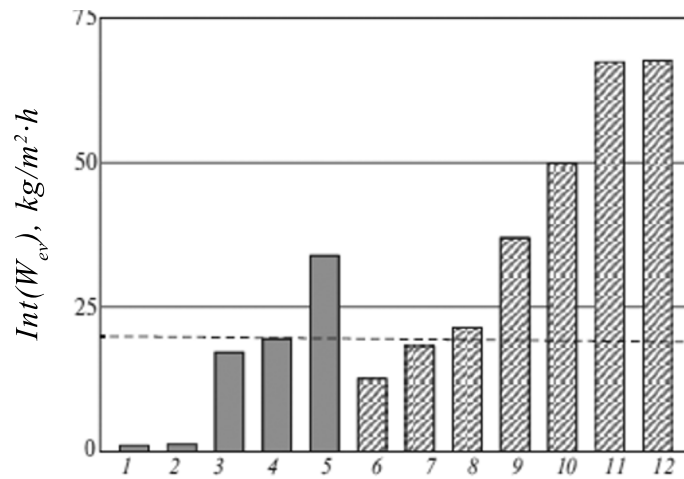
Fig. 4. Int(W_{ev}) integral estimates of evaporation rate for motor fuels and their components; the dashed line denotes the level of evaporation of the fuel taken as a reference sample (standard): 1) DT-Z-K5; 2)TS-1; 3) Regular-92 (sample No. 1); 4) Regular-92 (sample No. 2); 5) Regular-92 (sample No. 3); 6) alkylate; 7) reforming gasoline; 8) catalytic cracking gasoline; 9) straight-run gasoline; 10) isomerate; 11) MTBE; 12) isopentane fraction.

Regular-92 automobile gasoline (GOST R 51105) of various component composition (Table 2); TS-1 fuel for jet engines (GOST 10227); DT-Z-K5 diesel fuel (GOST 32511). In order to obtain forecast estimates of the effect of gasoline components on the level of their evaporation, studies were carried out with various components currently involved in industrial production: alkylate, reforming gasoline, catalytic cracking gasoline, isomerate, isopentane fraction, methyl tert-butyl ether (MTBE), straight-run gas-condensate gasoline (35–140°C).

The values of coefficients for mathematical models (2) of the fuel evaporation process presented in Table 3 were calculated according to the experimental data on the evaporation rate W_{ev} of motor fuels and their components according to the formulas (3).

The duration of each test stage comprised 240 minutes. Quality evaluation of the approximation of experimental results by functions of the form (2) according to Fisher's criterion demonstrated the obtained mathematical models (see Table 3) to adequately describe the process of fuel evaporation in the reservoir. For example, for Regular-92 automobile gasoline (sample No. 1), the model of the evaporation process has the form:

$$W_{ev} = 2.25 + 0.97x_1 - 0.40x_2 - 0.56x_3 - 0.22x_1x_2 + 0.21x_1x_3 - 0.43x_2^2 - 0.40x_3^2 \qquad (5)$$

Based on the analysis of mathematical forecasting models (see Table 3), it is straightforward to obtain information on the amount of fuel evaporation losses under conditions corresponding to interlevel factor values (between levels of "+1" and "0" or "−1" and "0"). For example, let us assume, that the evaporation rate W_{ev} of Regular-92 automobile gasoline (sample no. 2) is to be determined under the following test conditions: the fuel evaporation temperature is 30°C ($x_1 = -0.33$); an intermediate level of connection of the reservoir with the atmosphere is set by the pressure regulation device ($x_2 = 0.5$); the reservoir is filled with fuel to 50% of its capacity ($x_3 = -0.33$).

Table 4

Integral estimate and evaporation criterion	Motor fuel				
	regular-92 gasoline			TS-1	DT-Z-K5
	sample No. 1	sample No. 2	sample No. 3		
$Int(W_{ev})$	17.22	19.52	33.94	1.28	1.07
K	0.88	1.00	1.74	0.07	0.05

Table 5

Sample No.	"Weighted" $Int(W_{ev})$ of experimental gasoline components, kg/m²·h							$Int(W_{ev})$ of gasoline, kg/m²·h	
	alkylate	reforming gasoline	cracking gasoline	isomerate	isopentane fraction	MTBE	straight-run gas-condensate gasoline (35-140°C)	according to experimental results	according to calculation results
1	2.14	11.53	4.30	-	-	-	-	17.22	17.97
2	1.25	10.63	5.37	-	-	1.36	1.84	19.52	20.45
3	-	7.32	3.87	4.99	6.09	6.06	5.18	33.94	33.51

The model of the evaporation process for Regular-92 automobile gasoline (sample No. 2) takes the form:

$$W_{ev} = 2.77 + 1.19x_1 - 0.49x_2 - 0.70x_3 - 0.29x_1x_2 + 0.26x_1x_3 - 0.51x_2^2 - 0.49x_3^2 \qquad (6)$$

By substituting the coded values of the storage conditions into the obtained expression (6), the W_{ev} of the Regular-92 automobile gasoline (sample No. 2) is obtained equal to 2.26 kg/m²·h.

Forecasting models of the form (2) visualize multidimensional relationships between the fuel W_{ev} and storage conditions. For example, Figs. 2 and 3 show 3D dependences of the W_{ev} forecasted values for two Regular-92 gasoline samples on the determining factors of the evaporation process.

The figures clearly show how significantly the forecasted values of evaporation levels differ: when the composition of Regular-92 gasoline changes (samples No. 2 or No. 3, see Table 2), depending on the levels (lower or upper) of the reservoir filling factor (see Fig. 2) and temperature (see Fig. 3), under the simultaneous varying of two factors of x_1 and x_2 (see Fig. 2) and x_2 and x_3 (see Fig.3).

Generalized forecasting estimates of their tendency to evaporation losses were obtained by calculating the Int(W_{ev}) values of motor fuels and components using the formula (3). Additionally, according to the criterion K_{ev}, the superiority in terms of evaporation of one fuel (component) above the other in the following row is identified.

For fuels:
DT-Z-K5 < TS-1 < Regular-92 (sample No. 1) < Regular-92 (sample No. 2) < Regular-92 (sample No. 3).

For components:
alkylate < reforming gasoline < catalytic cracking gasoline < straight-run gasoline < isomerate < MTBE< isopentane fraction (Fig. 4).

The forecasted values of the criteria and evaporation integral estimates for the investigated fuels presented in Table 4 provide a useful new characteristic of the variability of the fuel evaporation dynamics in the reservoir in the entire given range of variation of the process determining factors, as well as showing the relative "advantages" of one fuel over others.

The comparison of the K_{ev} criterion values for motor fuels (see Table 4) with the value of the reference criterion (Regular-92 gasoline, sample No. 2) ensures the forecasting tendency of fuels to evaporation losses during storage to be established and the evaporation level of the selected fuel for comparison with others.

Using the calculated values of the integral estimates Int(W_{ev}) for the fuel components, the evaporation estimate Int(W_{ev}) of the fuel with a probability of more than 95% can be reliably forecasted by the sum of "weighted" integral evaporation estimates of the components making up the fuel (Table 5). The difference between the values of the Int(W_{ev}) integral evaporation estimates of gasoline obtained by calculation and experiment does not exceed 5% at a confidence level of 0.95.

The necessary reliability verification of the forecasted results was carried out according to the correspondence between the results obtained under non-stationary conditions of the physical model and natural conditions of long-term fuel storage. Statistical studies have shown the presence of a stable linear relationship between modeled test results and long-term fuel storage conditions for state needs (the correlation coefficient reaches 0.90-0.95 with a confidence level of 0.95).

Forecasting the evaporation of fuels using the proposed method has benefits in terms of the reduced probability of erroneous decision-making in long-term storage of fuels with a low level of physical stability. For example, if the gasoline under long-term storage meets the requirements of GOST 32513-2013, but has a evaporation level of 1.5 times higher than that of gasoline taken as a standard for the given storage conditions,

then the forecasted evaporation losses in the RVS-5000 vertical ground reservoir in climatic region II$_5$ during the year can amount to more than 14,000 kg. At the same time, the loss of gasoline with satisfactory physical stability under the same storage conditions will not exceed 9,300 kg.

Thus, timely operational forecasting of the fuel evaporation level at the stage of making decisions on the possibility of long-term storage serves to prevent an increase in annual evaporation losses (for gasoline in the RVS-5000 reservoir – more than 4500 kg) and ensure both the adoption of scientifically grounded decisions on placing fuels for long-term storage and their compliance during storage with the requirements established by the state customer.

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