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DETERMINATION OF EMISSIONS OF VAPOUR OF FLAMMABLE TECHNICAL LIQUIDS FROM ENTERPRISE FOR THEIR STORING AND DISTRIBUTION AND RATIONAL ADJUSTMENTS OF THEIR BREATHING VALVES

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Abstract

In this study, generally devoted to increasing the level of ecological safety of the exploitation process of reusable reservoirs for storing flammable technical liquids for the enterprise for the storage and distribution of petroleum products as part of the appropriate environmental protection technology, the parameters of such liquids stored in reservoirs of the enterprise, and technical indicators of reservoirs for their storage according to the developed method. Methods for determining the magnitude of the mass hourly emission of vapours of such liquids, caused by the phenomena of small and large breathing of reservoirs, as well as the total emission by both mechanisms, taking into account the daily values of the atmospheric temperature difference and the degree of filling of the reservoir, have been improved and described, and the results of the corresponding computational research. A calculated study of the effectiveness of the use of a breathing valve to reduce the emission of vapours of technical flammable liquids from reservoirs for their storage by the mechanism of small breathing and justification of the choice of setting the tightening of its spring has been carried out. A list of recommendations has been formulated to improve the ecological safety of the exploitation process of reusable reservoirs for storing liquids, the vapours of which are toxic, fire and explosive, greenhouse and energy-intensive pollutants.

Key words: ecological safety, environmental protection technologies, pollutants emission, vapour of technic flammable liquids, large reservoir breathing, small reservoir breathing, breathing valves.

Relevance of the study.

The production process of any enterprise for storage and distribution of petroleum products (ESDPP) is accompanied by emissions of flammable technical liquids (FTL), which are caused by the phenomena of large (LRB) and small (SRB) reservoir breathing, i.e. reusable high-capacity containers, vapours of liquids in which are flammable and explosive, toxic, chemically active, which also are a valuable energy resource and greenhouse substances [1 – 4].

Normatively established indicators of the ecological safety (ES) level of the exploitation process of such high-risk facilities should be achieved on the basis of appropriate methodological support – ecological safety management system (ESMS) [1], the material base of which are environmental protection technologies (EPT) that are chains of executive bodies [3, 4 – 11].

It is known that reusable packaging for such fluents is loaded mechanically by weight and inertia factors, which are steady, shock or oscillating in nature, in itself is a complex and expensive product of high-tech production [4].

It should be noted that this situation is typical at the «retail» level, as in the classifier of ES factors, built on a hierarchical principle and developed in [2], there are both consumption of motor fuel as a non-renewable energy resource and emissions of motor fuel vapour caused by phenomena of SRB and LRB, namely the fuel tank of a vehicle with a reciprocating internal combustion engine (RICE) [1 – 3].

It also should be noted that vehicle with RICE means are the main consumer of FTL stored in such enterprises and a powerful source of environmental pollution by various physical factors – this is a qualitative aspect of the relevance of the topic of this study, they together produce up to 75 % of energy (mechanical and electric) in our country – this is a quantitative aspect of the relevance of the topic of this study [3].

Purpose of the study. Improving approaches to reducing emissions into the environment of a mixture of FTL vapours as a toxic, flammable and explosive, greenhouse and energy-containing pollutant caused by the phenomena of LRB and SRB of ESDPP as reusable packaging.

Problem of the study. Determination of parameters of mass hourly emission of mixture of FTL vapours due to the phenomena of LRB and SRB for their storage as reusable packaging, as well as technical characteristics of the control elements of the executive bodies of the relevant EPT, as well as energy, economic and ecological effects from their use.

Object of the study. ES of exploitation process of reservoirs for storing of FTL of ESDPP.

Subject of the study. Energy, economic and ecological effects from the application of the developed control element of executive bodies of the relevant to the object of the study EPT.

Methods of the study. Analysis of specialized scientific and technical, normative, reference and patent literature, provisions of scientific disciplines «Funda-

mentals of packaging», «Ecological safety management systems», «Environmental protection technologies», «Technical mechanics of liquids and gases», «Fuels and lubricants and technical fluids», «Thermodynamics» and «Metrology», the method of least squares.

Tasks of the study.

1. Analysis of scientific and technical, reference, normative and patent literature and substantiation of the relevance of the research topic.

2. Calculated study of FTL parameters stored in reservoirs of ESDPP and technical indicators of reservoirs for their storage.

3. Improving the method for determining the value of the mass hourly emission of FTL vapours caused by the phenomena of LRB and SRB for their storage and total emission by both mechanisms.

4. Obtaining a set of initial data for calculated study.

5. Obtaining and analysing the results of the calculated study of the values of FTL vapour emissions caused by the phenomena of LRB and SRB for their storage, taking into account the daily values of the difference in atmospheric air temperature and the degree of filling of reservoirs.

6. Carrying out of calculated study of efficiency of application of the respiratory valve for reduction of emissions of FTL vapours from reservoirs for their storage by the SRB mechanism and the substantiation of adjustment of an inhaling of its spring.

7. Formulation of a list of recommendations for increasing the ES level in the exploitation process of reusable reservoirs for storage of FTL.

Scientific novelty of obtained results. For the first time, the approach to determining the technical characteristics of the control device of the executive body of EPT from the emission of a mixture of FTL vapours caused by the phenomena of LRB and SRB for their storage as reusable reservoirs at the ESDPP.

Practical value of obtained results. The obtained results are suitable for ensuring the implementation of their design and organizational part of a higher ES level of exploitation process of reservoirs for storage of petroleum products as reusable containers by eliminating the emission of a mixture of FTL vapours and obtaining appropriate ecological, energy and economic effects.

1. General problem statement and literature analysis

LRB with motor fuel is a phenomenon of emission of motor fuel vapour into the environmental air, which has a volley character, due to the displacement of the gaseous medium from the reservoir with liquid medium when it is fully or partially filled (refuelling) through either an open shut-off valve or a specially adjusted breathing valve [3, 13, 20].

SRB with motor fuel is a phenomenon of emission of motor fuel vapour into the environmental air, which has a volley character, due to cyclical changes in temperature (including daily fluctuations in air temperature and barometric pressure) in the exploitation process of vehicle or its fuel tank, which leads to alternating intensification of processes of evaporation and condensation of motor fuel and the corresponding change in the magnitude of the pressure of its saturated vapour in the re-

servoir, the excess and lack of which is compensated by mass exchange with the environmental air through a properly configured two-way valve in the shut-off body of the reservoir [3, 13, 20].

Losses of oil products during their storage in reservoirs are divided into the following [12]: a) from leaks in leaky housings and loosely closed shut-off bodies of reservoirs and their service pipelines and fittings; b) from mixing at alternating refuelling of different types and grades of oil products in the same reservoir; c) from evaporation when squeezing into the environmental air of steam-air mixture. The phenomena of LRB and SRB are types of loss of oil products during their storage in reservoirs from evaporation. Such losses also include: a) from reservoir ventilation and ejection of oil vapour; b) from the saturation of air over the free surface of the oil product with its vapour [21, 22, 25].

Each of the four types of FTL, stored in large quantities in several reservoirs each [18, 19], forms a layer of saturated vapour over its free surface with a volume equal to the volume of the reservoir above the free surface of the liquid and the mass determined by the excess saturated vapour pressure depending on the liquid temperature [25]. Vapours of FTL, which are stored in the reservoir of the enterprise, released by the mechanisms of LRB and SRB, emitted in the environmental air and constitute the emission of pollutants. Such pollutant, consisting mainly of hydrocarbons of different types – saturated, unsaturated, polycyclic – with the formulas $C_5 - C_{20}$ [12], as well as ethyl alcohol C_2H_5OH [14 – 17].

Environmental pollution of such pollutant must be characterized qualitatively and quantitatively.

Regarding the qualitative aspect of the emission, to provide such a characteristic, we can use the results of determining the value of the dimensionless indicator of relative aggressiveness of such a pollutant in the monograph [2], where it is equated to the value of the fuel component of the complex fuel-ecological criterion of prof. Igor Parsadanov $A_{fv} = 38.4$, which in physical terms is the ratio of the MPC of the k-th pollutant to the MPC of the pollutant, which is selected as the reference, in this case it is taken as carbon monoxide CO [2].

MPC(CO) in the air of the working area is 20 mg/m^3 . That is, it means that the emission of 1 kg/h of motor fuel and motor oil vapours is 38.4 times more dangerous (harmful) than 1 kg/h of CO, or the emission of 1 kg/h of motor fuel and motor oil vapours as a toxic pollutant in its aggressiveness corresponds to the emission of 38.4 kg/h CO [2, 3, 17].

Regarding the quantitative aspect of the emission, to provide such a characteristic, it can be used the traditional approach, namely to choose for this characteristic the magnitude of the mass hourly emission G_{fv} in kg/h , because it is in terms of mass emission that the law of continuity of gaseous fluid flow is fulfilled, since its volume is determined by the dependence of its density on temperature [3, 13]. That is why a complex assessment of pollutant emissions is the product of the above values, which separately characterize the qualitative and quantitative aspects of emissions, ie $A_{fv} \cdot G_{fv}$ in kg/h [1 – 3].

The breathing valve of the reservoir, which automatically eliminates the phenomenon of its SRB in the tra-

ditional way, on the direct course of the shut-off body (i.e. the release of FTL vapour at a positive value of excess pressure in the reservoir) has a spring adjusted to the limit value of excess pressure $\Delta P_{fv+} = 10$ kPa. On the reverse course of the shut-off body (i.e. air intake at a negative value of excess pressure in the reservoir) has a spring adjusted to the limit value of excess pressure $\Delta P_{fv-} = -5$ kPa [2, 3]. The breathing valve of the reservoir, which automatically eliminates the phenomenon of its LRB in the traditional way – release into the system of blowing or directly into the atmosphere, has only a direct course of the shut-off device, i.e. or it is adjusted to the minimum pressure drop, so the value of its resistance can be neglected.

It is assumed that the FTL vapours that leave the cavities of sealed reservoirs for storage in the ESDPP, located above the free surface of liquids, through the breathing valves of reservoirs for both types of breathing, overcoming the forces of the springs of these valves and low hydraulic resistance and periodically flow by self moving into the storage reservoirs of low pressure, mixing with each other and accumulate in them for a period of one day.

2. Analysis of nomenclature of reservoirs and flammable technical liquids under storage in the enterprise

The following types of FTL are stored at the enterprise: a) diesel fuel in 3 identical cylindrical reservoirs; b) gasoline in 5 identical cylindrical reservoirs; c) motor oil in 2 identical cylindrical reservoirs; d) ethanol in 1 cylindrical reservoir [18, 19].

The volume of one cylindrical reservoir for storage of the k-th type of FTL $W(k)$ at the magnitudes of the diameter of the base $D(k)$ (in m) and the height of the forming line $H(k)$ (in m) is determined by formula (1). The maximum total volume of the k-th type of FTL on storage $W(k)_\Sigma$ at number of identical tanks $N(k)$ (in psc) and degree of filling of each $\varepsilon(k)$ (dimensionless value) is defined by formula (2). Data on the geometric parameters of the reservoirs are summarized in Table 1. The maximum total mass of the k-th type of FTL in storage $m(k)_f$ at its density under normal conditions $\rho(k)$ (in kg/m^3) is determined by formula (3). The maximum total chemical energy of the k-th type of FTL in storage

$E(k)$ at the magnitudes of lower heat of combustion $Q(k)$ (in MJ/kg) is determined by formula (4). Data on the physical properties of FTL are summarized in Table 2. The results of the calculation of the mass and chemical energy of the FTL, which are in the fully filled reservoirs of the enterprise, also are summarized in Table 2.

Dimensionless index of relative aggressiveness of vapours of the k-th type of FTL in storage $A(k)$ at magnitudes of average daily MPC of liquid vapours in atmospheric air $MCP_{ad}(k)$ (in mg/m^3) and MPC of reference pollutant ($A(\text{CO}) = 1.0$) $MCP_{ad}(\text{CO}) = 20$ mg/m^3 is determined by simplified formula (5). Data on the magnitudes of index $A(k)$ and its components are summarized in Table 2. The following thermodynamic parameters were taken as normal conditions: barometric pressure $p_0 = 101325$ Pa, air temperature $t_0 = 0$ °C or $T_0 = 273$ K, universal gas constant $R = 8.314$ J/(mol·K). Evaporation of FTL characterizes the temperature dependence of the magnitude of the saturated vapour pressure $p(k)_{sv}$ – a formula of the form (6), the constant coefficients $a(k)$ and $b(k)$ which are reduced to Table 2 and obtained by approximation of tabular data from the source [25].

$$W(k) = \pi \cdot D(k)^2 \cdot H(k) / 4, \text{ m}^3. \tag{1}$$

$$W(k)_\Sigma = W(k) \cdot N(k) \cdot \varepsilon(k), \text{ m}^3. \tag{2}$$

$$m(k)_f = \rho(k) \cdot W(k)_\Sigma, \text{ kg}. \tag{3}$$

$$E(k) = m(k)_f \cdot Q(k) / 1000, \text{ GJ}. \tag{4}$$

$$A(k) = MCP_{ad}(\text{CO}) / MCP_{ad}(k). \tag{5}$$

$$p(k)_{sv} = \exp((t_v(k) - b(k)) / a(k)) \cdot 1000, \text{ Pa}. \tag{6}$$

Table 1 – Data on geometric parameters of reservoirs [18, 19]

Type of k th FTL	Magnitude of parameter				
	N(k)	D(k)	H(k)	W(k)	W(k) _Σ
	psc	m	m	m ³	m ³
DF	3	10	12	942.480	2827.440
BF	5	10	15	1178.100	5890.500
MO	2	5	10	196.350	392.700
EA	1	5	10	196.350	196.350
Total	11	–	–	942.480	2827.440

Table 2 – Some physical properties of flammable technical liquids [17, 20, 25]

Type of k th FTL	Magnitude of parameter							
	$\rho(k)$	$Q(k)$	$m(k)_f$	$E(k)$	$MCP_{ad}(k)$	$A(k)$	$a(k)$	$b(k)$
	kg/m^3	MJ/kg	kg	GJ	mg/m^3	–	–	–
DF	850	42.7	2403324.0	102621.93	300	0.067	53.439	2.500
BF	750	44.0	4417875.0	194386.5	100	0.200	40.935	-91.000
MO	870	41.0	341649.0	14007.609	300	0.067	55.310	75.500
EA	810	27.0	159043.5	4294.1745	1000	0.020	23.945	-17.436
Total	–	–	2403324.0	102621.93	–	–	–	–

3. Method of determining the value of the mass hourly emission of FTL vapours caused by the phenomenon of LRB for their storage

It can be assumed that the period of time between full filling of reservoirs $d(k)$ (in days) $T_{lb}(k) = d(k) \cdot 24$ (per hour) is the same and synchronized for the same name of FTL (k) in storage

and different for different liquids. The magnitudes of these values are summarized in Table 2. It also can be assumed that the new filling of the reservoirs occurs at the degree of filling $\varepsilon(k)_{lb} = 0.1$. Then the volume of vapours of the k-th FTL released during a single reservoir filling due to the manifestation of the phenomenon of LRB, $W(k)_{lb\Sigma}$ is determined by formula

(7), and the total volume $W_{lb\Sigma}$ – by formula (8). So, $W(DF)_{lb\Sigma} = 2544.7 \text{ m}^3$, $W(BF)_{lb\Sigma} = 5301.5 \text{ m}^3$, $W(MO)_{lb\Sigma} = 353.4 \text{ m}^3$, $W(EA)_{lb\Sigma} = 176.7 \text{ m}^3$, a $W_{lb\Sigma} = 8376.3 \text{ m}^3$.

The vapour density of the k-th FTL in the reservoir under normal conditions $\rho(k)_v$ is determined by formula (9) according to the equation of state of an ideal gas for known magnitudes of the molar mass of the k-th FTL $\mu(k)_v$ (in kg/mol). To determine the molar mass of the mixture of FTL vapours in the low pressure reservoir, it should be noted that all types of liquids of petroleum origin are mixtures of different hydrocarbons, mainly normal alkanes (saturated) with the chemical formula C_nH_m , where $m = 2 \cdot n + 2$, with a typical hydrocarbon in gasoline is octane C_8H_{18} , i.e. $n = 8$ and $m = 18$, in the composition of diesel fuel – cetane $C_{16}H_{34}$, i.e. $n = 16$ and $m = 34$, and motor oil – tetracontan $C_{40}H_{82}$, i.e. $n = 40$ and $m = 82$ [3]. Then the molar mass of the hydrocarbon with the chemical formula C_nH_{2n+2} is determined by formula (10). So, $\mu(C_8H_{18}) = 114 \text{ g/mol}$, $\mu(C_{16}H_{34}) = 226 \text{ g/mol}$, $\mu(C_{40}H_{82}) = 562 \text{ g/mol}$ [3]. Then the magnitude of the molar mass is taken as follows: $\mu(DF)_v = 0.226 \text{ kg/mol}$ (for cetane $C_{16}H_{34}$), $\mu(BF)_v = 0.114 \text{ kg/mol}$ (for octane C_8H_{18}), $\mu(MO)_v = 0.562 \text{ kg/mol}$ (for tetragontane $C_{40}H_{82}$), $\mu(EA)_v = 0.046 \text{ kg/mol}$ (for ethanol C_2H_5OH). Hence, we have the following values of density: $\rho(DF)_v = 10.089 \text{ kg/m}^3$, $\rho(BF)_v = 5.089 \text{ kg/m}^3$, $\rho(MO)_v = 25.089 \text{ kg/m}^3$, $\rho(EA)_v = 2.054$.

$$W(k)_{lb\Sigma} = W(k)_{lb\Sigma} \cdot (1 - \varepsilon(k)_{lb}), \text{ m}^3. \quad (7)$$

$$W_{lb\Sigma} = \sum_{k=1}^{k=4} W(k)_{lb\Sigma}, \text{ m}^3. \quad (8)$$

$$\rho(k)_v = \mu(k)_v \cdot p_0 / (R \cdot T_0), \text{ kg/m}^3. \quad (9)$$

$$\mu(C_nH_m) = \mu(C) \cdot n + \mu(H) \cdot m = 12 \cdot n + 1 \cdot m = 12 \cdot n + 1 \cdot (2 \cdot n + 2), \text{ g/mol}. \quad (10)$$

The mass of volley FTL vapour emission caused by the phenomenon of LRB of storage reservoir $m_{lb}(k)$ is determined by formula (11), and the total emission $m_{lb\Sigma}$ – by formula (12). Then we have the following magnitudes of the mass of the volley emission: $m_{lb}(DF) = 25673.7 \text{ kg}$, $m_{lb}(BF) = 26980.1 \text{ kg}$, $m_{lb}(MO) = 8867.1 \text{ kg}$, $m_{lb}(EA) = 362.9 \text{ kg}$ and $m_{lb\Sigma} = 61883.8 \text{ kg}$. The average magnitude of the density of the FTL vapour mixture under normal conditions $\rho(k)_{v\Sigma}$ is determined by formula (13). The value obtained for it is 10.011 kg/m^3 .

The value of the mass hourly emission of FTL vapours caused by the phenomenon of LRB for their

storage, $G_{lb}(k)$ is determined by formula (14), and the total emission $G_{lb\Sigma}$ – by formula (15). Then we have the following values of mass hourly emission: $G_{lb}(DF) = 11.886 \text{ kg/h}$, $G_{lb}(BF) = 12.491 \text{ kg/h}$, $G_{lb}(MO) = 2.053 \text{ kg/h}$, $G_{lb}(EA) = 0.252$ and $G_{lb\Sigma} = 26.681 \text{ kg/h}$.

$$m_{lb}(k) = \rho(k)_v \cdot W(k)_{lb\Sigma}, \text{ kg}. \quad (11)$$

$$m_{lb\Sigma} = \sum_{k=1}^{k=4} m(k)_{lb\Sigma}, \text{ kg/h}. \quad (12)$$

$$\rho(k)_{v\Sigma} = \sum_{k=1}^{k=4} (\rho(k)_v \cdot m(k)_v) / \sum_{k=1}^{k=4} (m(k)_v), \text{ kg/m}^3. \quad (13)$$

$$G_{lb}(k) = m_{lb}(k) / T_{lb}(k), \text{ kg/h}. \quad (14)$$

$$G_{lb\Sigma} = \sum_{k=1}^{k=4} G(k)_{lb\Sigma}, \text{ kg/h}. \quad (15)$$

The average magnitude of the lower heat of combustion of the vapour mixture FTL $Q(k)_{v\Sigma}$ is determined by formula (16). The magnitude obtained for it is 42.9 MJ/kg , because $Q(DF)_v = 42.7 \text{ MJ/kg}$, $Q(BF)_v = 44.0 \text{ MJ/kg}$, $Q(MO)_v = 41.0 \text{ MJ/kg}$, $Q(EA)_v = 42.9 \text{ MJ/kg}$. The amount of chemical energy released with the emission of vapours of the k-th type of FTL $E(k)$ at the magnitudes of the lower heat of combustion $Q(k)_v$ (in MJ/kg) is determined by formula (17). The emission of such chemical energy $e(k)$ is determined by formula (18) or (19).

$$Q(k)_{v\Sigma} = \sum_{k=1}^{k=4} (Q(k)_v \cdot m(k)_v) / \sum_{k=1}^{k=4} (m(k)_v), \text{ MJ/kg}. \quad (16)$$

$$E(k) = m(k)_{lb} \cdot Q(k) / 1000, \text{ GJ}. \quad (17)$$

$$e(k) = G_{lb}(k) \cdot Q(k), \text{ MJ/kg}; \quad (18)$$

$$e(k) = G_{lb}(k) \cdot Q(k) / 3600, \text{ MW}. \quad (19)$$

The magnitude of the reduced mass hourly emission of FTL vapours, from the phenomenon of LRB for their storage, $A(k) \cdot G_{lb}(k)$ is determined by formula (20), and the total emission $\Sigma(A(k) \cdot G_{lb}(k))$ – by the formula (21). The results of calculations by formulas (7) – (21) are summarized in Table 3.

$$A(k) \cdot G_{lb}(k) = A(k) \cdot G_{lb}(k), \text{ kg/h}; \quad (20)$$

$$\Sigma(A(k) \cdot G_{lb}(k)) = \sum_{k=1}^{k=4} (A(k) \cdot G_{lb}(k)), \text{ kg/h}. \quad (21)$$

Table 3 – Results of calculated study

Type of k th FTL	Magnitude of parameter									
	$W(k)_{lb\Sigma}$ m ³	$\mu(k)_v$ kg/mole	$\rho(k)_v$ kg/m ³	$m_{lb}(k)$ kg	$G_{lb}(k)$ kg/h	$Q(k)_v$ MJ/kg	$E(k)$ GJ	$e(k)$		$A(k) \cdot G_{lb}(k)$ kg/h
								MJ/h	MW	
DF	2544.696	0.226	10.089	25673.69	11.886	42.7	1096.3	507.5	0.141	0.792
BF	5301.450	0.114	5.089	26980.09	12.491	44.0	1187.1	549.6	0.153	2.498
MO	353.430	0.562	25.089	8867.142	2.053	41.0	363.6	84.2	0.023	0.137
EA	176.715	0.046	2.054	362.8902	0.252	27.0	9.8	6.8	0.002	0.005
Mixture	8376.291	0.224	10.011	61883.82	26.681	42.9	2656.7	1148.1	0.319	3.432

4. Method of determining the value of the mass hourly emission of FTL vapours caused by the phenomenon of SRB for their storage

To obtain the results of calculations that are closer to the real picture of the studied processes, in this study abandoned the following two assumptions [3]:

1. maximum t_{0max} and minimum t_{0min} daily atmospheric air temperature and daily atmospheric air temperature difference Δt_0 have constant magnitudes equal to the average for 2018 year;

2. the degree of filling of the reservoir $\varepsilon(k)$ has one of the three constant magnitude for all reservoirs during the year – 1/4, 1/2 or 3/4.

Therefore, the following additions have been made to the method presented in this study:

1. maximum t_{0max} and minimum t_{0min} daily atmospheric air temperature and daily atmospheric air temperature difference Δt_0 do not have constant magnitudes by days of the month, and for each date have individual magnitudes obtained from meteorological observations for the whole of 2018 from sources [23, 24];

2. the degree of filling of the tank $\varepsilon(k)$ varies linearly between the magnitudes of «fully filled» – 0.999 and «completely emptied» – 0.100 for large reservoirs with fast-consuming liquids (diesel fuel and gasoline) and 0.05 for smaller reservoirs with long-consumed liquids (motor oil and ethanol);

3. the process of filling the reservoir (refuelling) takes place periodically (period $T(k)_{fill}$) and on the dates specified in Table 4.

Table 4 – Tank refuelling schedule [18, 19]

Type of k th FTL	Magnitude of parameter				
	$\varepsilon(k)_{max}$	$\varepsilon(k)_{min}$	$T(k)_{fill} = T_{in}(k)$		Date
	–	–	times per year	days/ hours	
DF	0.999	0.100	3	90/	15/01, 15/04, 15/07, 15/10
BF				2160	
MO		0.050	6	180/	15/01, 15/07
EA				4320	15/01, 15/03, 15/05, 15/07, 15/09, 15/11

The magnitude of the change in FTL vapour pressure in the reservoir caused by the change in evaporation of the liquid with a change in its temperature, $\Delta p_{sv}(k)$ is defined as the difference between the magnitudes of saturated vapour pressure at maximum $p_{sv}(k)_{max}$ and minimum $\Delta p_{sv}(k)_{min}$ air temperature for the current day, i.e. by formula (22), the components of which – by formulas (23) and (24).

$$\Delta p_{sv}(k) = p_{sv}(k)_{max} - \Delta p_{sv}(k)_{min}, \text{ Pa}; \quad (22)$$

$$p_{sv}(k)_{max} = \exp((t_v(k)_{max} - b(k)) / a(k)) \cdot 1000, \text{ Pa}; \quad (23)$$

$$p_{sv}(k)_{min} = \exp((t_v(k)_{min} - b(k)) / a(k)) \cdot 1000, \text{ Pa}. \quad (24)$$

The magnitude of the change in the mass of FTL vapours in the reservoir caused by the change in the evaporation of the liquid with a change in its temperature, $\Delta m_{sv}(k)$ is determined by formula (25), i.e. by the Clapeyron-Mendeleev equation. The magnitude of the FTL vapour mass in the reservoir under normal conditions $m_{sv}(k)_0$ is determined by formula (26), in which the magnitude of the density $\rho(k)_v$ is determined by formula (9). The magnitude of the mass of FTL vapours in the reservoir at a temperature $t_v(k)_{max}$, i.e. at the end of the phase of «exhalation» of SRB $m_{sv}(k)_t$, is defined as the sum of the two previous magnitude – see formula (27).

$$\Delta m_{sv}(k) = \mu(k) \cdot \Delta p_{sv}(k) \cdot W(k)_\Sigma \cdot (1 - \varepsilon(k)) / (R \cdot (t_v(k)_{max} + 237)), \text{ kg}. \quad (25)$$

$$m_{sv}(k)_0 = \rho(k)_v \cdot W(k)_\Sigma \cdot (1 - \varepsilon(k)), \text{ kg}. \quad (26)$$

$$m_{sv}(k)_t = m_{sv}(k)_0 + \Delta m_{sv}(k), \text{ kg}. \quad (27)$$

The magnitude of the FTL vapour pressure in the reservoir at a temperature $t_v(k)_{min}$, i.e. at the beginning of the «exhalation» phase of SRB $p_{sv}(k)_0$ is determined by

formula (28), i.e. by the Clapeyron-Mendeleev equation. The magnitude of the FTL vapour pressure in the reservoir at a temperature $t_v(k)_{max}$, i.e. at the end of the «exhalation» phase of the SRB $p_{sv}(k)_t$ is determined in a similar way by formula (29). The magnitude of the profit of the vapour pressure of FTL in the reservoir, obtained during the implementation of the phase of «exhalation» phase of the SRB $\Delta p_{sv}(k)_t$ is determined by formula (30).

$$p_{sv}(k)_0 = R / \mu(k) / (W(k)_\Sigma \cdot (1 - \varepsilon(k)) \times m_{sv}(k)_0 \cdot (t_v(k)_{min} + 237)), \text{ Pa}. \quad (28)$$

$$p_{sv}(k)_t = R / \mu(k) / (W(k)_\Sigma \cdot (1 - \varepsilon(k)) \times m_{sv}(k)_t \cdot (t_v(k)_{max} + 237)), \text{ Pa}. \quad (29)$$

$$\Delta p_{sv}(k)_t = p_{sv}(k)_t - p_{sv}(k)_0, \text{ Pa}. \quad (30)$$

The magnitude of the mass emission of FTL vapours from the reservoir in the phase of «exhalation» of SRB $m_{sb}(k)$ is determined by formula (31), i.e. by the equation of state of the ideal gas. The total magnitude of the mass emission of vapours of all FTL from the reservoir in the phase of «exhalation» of SRB $m_{sb}(k)_\Sigma$ is determined by formula (32).

$$m_{sb}(k) = \mu(k) \cdot \Delta p_{sv}(k)_t \cdot W(k)_\Sigma \times (1 - \varepsilon(k)) / (R \cdot (t_v(k)_{max} + 237)), \text{ kg}. \quad (31)$$

$$m_{sb}(k)_\Sigma = \sum_{k=1}^{k=4} m_{sb}(k), \text{ kg}. \quad (32)$$

The magnitude of the potential energy effect from the combustion of FTL vapour emissions from the reservoir caused by the phenomenon of SRB $E(k)_{sb}$ is determined by formula (33) taking into account the magnitude of the lower heat of combustion of such a substance

$Q(k)$. The total magnitude of the potential energy effect from the combustion of FTL vapour emissions from the reservoir caused by the phenomenon of SRB $E(\Sigma)_{sb}$ is determined by formula (34).

$$E(k)_{sb} = m_{sb}(k) \cdot Q(k) / 1000, \text{ GJ.} \quad (33)$$

$$E(\Sigma)_{sb} = \sum_{k=1}^{k=4} E(k)_{sb}, \text{ GJ.} \quad (34)$$

The magnitude of the mass hourly emission of FTL vapours from the reservoir caused by the SRB phenomenon, $G_{sb}(k)$ is determined by formula (35) taking into account the magnitude of the duration of the complete cycle (set of successive processes of «exhalation» and «inhalation») of the SRB phenomenon $T_{sb}(k) = 24$ h. The total magnitude of the mass hourly emission of FTL vapours from the reservoir caused by the phenomenon of SRB, $G_{sb}(\Sigma)$ is determined by formula (36).

$$G_{sb}(k) = m_{sb}(k) / T_{sb}(k), \text{ kg/h.} \quad (35)$$

$$G(\Sigma)_{sb} = \sum_{k=1}^{k=4} G(k)_{sb}, \text{ kg/h.} \quad (36)$$

The magnitude of the hourly potential energy effect from the combustion of FTL vapour emissions from the reservoir caused by the SRB phenomenon, $e(k)_{sb}$ is determined by formula (37) or (38) taking into account the magnitude of the lower heat of combustion of such a substance $Q(k)$, and the total magnitudes of $e(\Sigma)_{sb}$ – by formulas (39) and (40).

$$e(k)_{sb} = G_{sb}(k) \cdot Q(k), \text{ MJ/h.} \quad (37)$$

$$e(k)_{sb} = G_{sb}(k) \cdot Q(k) / 3600, \text{ MW.} \quad (38)$$

$$e(\Sigma)_{sb} = \sum_{k=1}^{k=4} e(k)_{sb}, \text{ MJ/h.} \quad (39)$$

$$e(\Sigma)_{sb} = \sum_{k=1}^{k=4} e(k)_{sb} / 3600, \text{ MW.} \quad (40)$$

The above considerations give a result that is easily obtained by applying a different approach based on the disciplines of «Metrology» and «Thermodynamics». This gain of the mass of FTL vapours Δm_{fv} , caused by the physical process of its evaporation with its heating, and can be estimated by formulas (41) – (58). Finally, after the transformations, we have formulas (59) – (61).

$$\Delta m_{fv} = (\partial m_{fv} / \partial T_{fv}) \cdot \Delta T_{fv}, \text{ kg,} \quad (41)$$

$$m_{fv} = \mu_{fv} \cdot p_{fv}(T_{fv}) \cdot V_{fv} / (R \cdot T_{fv}), \text{ kg,} \quad (42)$$

$$\partial m_{fv} / \partial T_{fv} = \partial / \partial T_{fv} (\mu_{fv} \cdot p_{fv}(T_{fv}) \cdot V_{fv} / (R \cdot T_{fv})) = \mu_{fv} \cdot V_{fv} / R \cdot (\partial / \partial T (p_{fv}(T_{fv}) / T_{fv})), \text{ kg/K,} \quad (43)$$

$$(u / v) = (u \cdot v - u \cdot v) / v^2, u = p_{fv}(T_{fv}), v = T_{fv}, \quad (44)$$

$$p_{fv}(T_{fv}) = p_{fv0} + \Delta p_{fv}(T_{fv})_t + \Delta p_{fv}(T_{fv})_v, \text{ Pa,} \quad (45)$$

$$p_{fv0} = m_{fv0} / \mu_{fv} \cdot R \cdot T_{fv0} / V_{fv0} = 101325 \text{ Pa,} \quad (46)$$

$$T_{fv0} = 273 \text{ K, } R = 8.314 \text{ J/(mol}\cdot\text{K),} \quad (47)$$

$$m_{fv0} = \mu_{fv} \cdot p_{fv0} \cdot V_{fv0} / (R \cdot T_{fv0}), \text{ kg,} \quad (48)$$

$$\rho_{fv0} = \mu_{fv} \cdot p_{fv0} / (R \cdot T_{fv0}), \text{ kg/m}^3, \quad (49)$$

$$\Delta p_{fv}(T_{fv})_t = (\partial p_{fv} / \partial T_{fv}) \cdot \Delta T_{fv}, \text{ Pa,} \quad (50)$$

$$\partial p_{fv} / \partial T_{fv} = m_{fv0} / \mu_{fv} \cdot R / V_{fv0}, \text{ Pa/K,} \quad (51)$$

$$\Delta p_{fv}(T_{fv})_v = p_{sv}(T_{fv}) - p_{sv}(T_0), \text{ Pa,} \quad (52)$$

$$p_{sv}(T_0) = \exp((t_{fv0} - a(k)) / b(k)) \cdot 10^3 = \text{const, Pa,} \quad (53)$$

$$p_{sv}(T_{fv}) = \exp((t_{fv} - a(k)) / b(k)) \cdot 10^3 = \text{const, Pa,} \quad (53)$$

$$= \exp((T_{fv} - 273 - a(k)) / b(k)) \cdot 10^3 = \text{const, Pa,} \quad (53)$$

$$= \exp w(k) \cdot 10^3, \text{ Pa, } a(k) = \text{const, } b(k) = \text{const,} \quad (54)$$

$$w(k) = ((T_{fv} - 273 - a(k)) / b(k)), \quad (54)$$

$$u = \partial p_{fv}(T_{fv}) / \partial T_{fv} = \partial / \partial T_{fv} (p_{fv0} + \Delta p_{fv}(T_{fv})_t + \Delta p_{fv}(T_{fv})_v) = \partial / \partial T_{fv} ((m_{fv0} / \mu_{fv} \cdot R \cdot T_{fv0} / V_{fv0}) + (\partial p_{fv} / \partial T_{fv}) \cdot \Delta T_{fv} + (p_{sv}(T_{fv}) - p_{sv}(T_{fv0}))) = \partial / \partial T_{fv} ((m_{fv0} / \mu_{fv} \cdot R \cdot T_{fv0} / V_{fv0}) + (m_{fv0} / \mu_{fv} \cdot R / V_{fv0}) \cdot (T_{fv} - T_{fv0}) + 10^3 \cdot (\exp((T_{fv} - 273 - a(k)) / b(k))) - \exp((T_{fv0} - 273 - a(k)) / b(k)))) = \partial / \partial T_{fv} (101325 + (\rho_{fv0} / \mu_{fv} \cdot 8.314) \cdot (T_{fv} - 273) + 10^3 \cdot (\exp((T_{fv} - 273 - a(k)) / b(k))) - \exp((273 - 273 - a(k)) / b(k)))) = \partial / \partial T_{fv} ((\rho_{fv0} / \mu_{fv} \cdot 8.314) \cdot T_{fv} + 10^3 \cdot \exp((T_{fv} - 273 - a(k)) / b(k))) = \partial / \partial T_{fv} ((\rho_{fv0} / \mu_{fv} \cdot 8.314) \cdot T_{fv}) + \partial / \partial T_{fv} (10^3 \cdot \exp((T_{fv} - 273 - a(k)) / b(k))) = m_{fv0} / \mu_{fv} \cdot R / V_{fv0} + 10^3 \cdot \partial / \partial T_{fv} (\exp w(k)) = m_{fv0} / \mu_{fv} \cdot R / V_{fv0} + 10^3 \cdot \exp w(k) \cdot \partial / \partial T_{fv} (w(k)) = m_{fv0} / \mu_{fv} \cdot R / V_{fv0} + 10^3 \cdot \exp w(k) \cdot \partial / \partial T_{fv} (((T_{fv} - 273 - a(k)) / b(k)) = m_{fv0} / \mu_{fv} \cdot R / V_{fv0} + 10^3 \cdot \exp(((T_{fv} - 273 - a(k)) / b(k)) \cdot 1 / b(k)), \quad (55)$$

$$(\exp w(k)) = \exp w(k) \cdot w(k), v = \partial T_{fv} / \partial T_{fv} = 1, \quad (56)$$

$$w = \partial / \partial T_{fv} ((T_{fv} - 273 - a(k)) / b(k)) = 1 / b(k), \quad (56)$$

$$\Delta T_{fv} = (\Delta t_{air} + 273) - T_{fv0} = \Delta t_{air}, \text{ K,} \quad (57)$$

$$V_{fv} = (1 - \varepsilon) \cdot N(k) \cdot W(k), \text{ m}^3, \quad (58)$$

$$\varepsilon = 1/4; 1/2; 3/4 = \text{const,} \quad (58)$$

$$\partial m_{fv} / \partial T_{fv} = \mu_{fv} \cdot (1 - \varepsilon) \cdot N(k) \cdot W(k) / (b(k) \cdot R \cdot T_{fv}) \times \exp((T_{fv} - 273 - a(k)) / b(k)), \text{ kg/K,} \quad (59)$$

$$\Delta m_{fv} = \mu_{fv} \cdot (1 - \varepsilon) \cdot N(k) \cdot W(k) / (b(k) \cdot R \cdot T_{fv}) \times \exp((T_{fv} - 273 - a(k)) / b(k)) \cdot (\Delta t_{air} + 273), \text{ kg,} \quad (60)$$

$$G_{fv}(k)_S = (\mu_{fv} \cdot (1 - \varepsilon) \cdot N(k) \cdot W(k) / (b(k) \cdot R \cdot T_{fv}) \times \exp((T_{fv} - 273 - a(k)) / b(k)) \times (\Delta t_{air} + 273)) / T_{colls}, \text{ kg/h.} \quad (61)$$

$$\times (\Delta t_{air} + 273)) / T_{colls}, \text{ kg/h.} \quad (61)$$

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$$\times (\Delta t_{air} + 273)) / T_{colls}, \text{ kg/h.} \quad (61)$$

The magnitude of the hourly potential energy effect from the combustion of FTL vapour emissions from the reservoir caused by the phenomena of LRB and SRB, $e(k)_\Sigma$ is determined by formula (67) or formula (68) taking into account the magnitude of the lower heat of combustion of such substance $Q(k)$, and total the magnitude of $e(\Sigma)_\Sigma$ is by formulas (69) and (70).

$$e(k)_\Sigma = G_\Sigma(k) \cdot Q(k), \text{ MJ/h.} \quad (67)$$

$$e(k)_\Sigma = G_\Sigma(k) \cdot Q(k) / 3600, \text{ MW.} \quad (68)$$

$$e(\Sigma)_\Sigma = \sum_{k=1}^{k=4} e(k)_\Sigma, \text{ MJ/h.} \quad (69)$$

$$e(\Sigma)_\Sigma = \sum_{k=1}^{k=4} e(k)_\Sigma / 3600, \text{ MW.} \quad (70)$$

The magnitude of the reduced mass hourly emission of FTL vapours from the reservoir caused by the SRB phenomenon, $A(k) \cdot G_{sb}(k)$ is determined by formula (71), and the total emission $\Sigma(A(k) \cdot G_{sb}(k))$ – by the formula (72). The magnitude of the reduced mass hourly emission of FTL vapours from the reservoir caused by the phenomena of LRB and SRB, $A(k) \cdot G_\Sigma(k)$ is determined by formula (73), and the total emission $\Sigma(A(k) \cdot G_{sb}(k))$ – by the formula (74).

$$A(k) \cdot G_{sb}(k) = A(k) \cdot G_{sb}(k), \text{ kg/h.} \quad (71)$$

$$\Sigma(A(k) \cdot G_{sb}(k)) = \sum_{k=1}^{k=4} (A(k) \cdot G_{sb}(k)), \text{ kg/h.} \quad (72)$$

$$A(k) \cdot G_\Sigma(k) = A(k) \cdot G_\Sigma(k), \text{ kg/h.} \quad (73)$$

$$\Sigma(A(k) \cdot G_\Sigma(k)) = \sum_{k=1}^{k=4} (A(k) \cdot G_\Sigma(k)), \text{ kg/h.} \quad (74)$$

6. Obtaining a set of initial data for calculated study

To implement the proposed and improved approach to determining the magnitudes of the mass hourly emission of FTL vapours by the SRB mechanism, information is needed on the evaporation rates of these FTL and the magnitude of the daily temperature difference as the driving force of such process.

Such information is shown in Fig. 1 – 3, the graphs on them are described by formulas (75) – (77) [3, 25], whence after transformations we have formulas (78) – (80). The magnitude of the average monthly daily temperature difference can be approximated by a polynomial of the 2nd degree [3, 23, 24] – formula (81). For ethanol, formula (82) was obtained.

$$t(\text{MO}) = 55.310 \cdot \ln(p_{sv}(\text{MO})) + 75.5; \quad (75)$$

$$R^2 = 0.973, \text{ }^\circ\text{C,}$$

$$t(\text{DF}) = 53.439 \cdot \ln(p_{sv}(\text{DF})) + 2.5; R^2 = 0.978, \text{ }^\circ\text{C,} \quad (76)$$

$$t(\text{BF}) = 40.935 \cdot \ln(p_{sv}(\text{BF})) - 91.0; R^2 = 0.934, \text{ }^\circ\text{C,} \quad (77)$$

$$p_{sv}(\text{MO}) = \exp((t(\text{MO}) - 75.5) / 55.310), \text{ kPa,} \quad (78)$$

$$p_{sv}(\text{DF}) = \exp((t(\text{DF}) - 2.5) / 53.439), \text{ kPa,} \quad (79)$$

$$p_{sv}(\text{BF}) = \exp((t(\text{BF}) + 91.0) / 40.935), \text{ kPa.} \quad (80)$$

$$\Delta t_{air} = -3.608 \cdot 10^{-4} \cdot d^2 + 1.342 \cdot 10^{-1} \cdot d, \quad (81)$$

$$R^2 = 0.851, \text{ }^\circ\text{C.}$$

$$p_{sv}(\text{EA}) = \exp((t(\text{EA}) + 17.4) / 23.9), \text{ kPa.} \quad (82)$$

7. Results of the calculated study and their analysis

Figure 4 shows the distributions of the magnitudes of mass hourly FTL vapour emissions of all types $G(k)_{sb}$ and total $G(\Sigma)_{sb}$ emissions by days of the most (February – a) and least (June – b) productive months of 2019, as well as the magnitudes of temperature difference atmospheric air Δt_0 in Kharkiv. It shows that the nature of the change in the magnitudes of $G(k)_{sb}$ and $G(\Sigma)_{sb}$ on the days of the months of the year repeats the change in the magnitudes of Δt_0 and depends little on the magnitudes of $\varepsilon(k)$.

Figure 5 shows the distributions of the average monthly magnitudes of the mass hourly emission of FTL vapours of all types caused by the phenomenon of SRB $G(k)_{sb}$ (a), LRB $G(\Sigma)_{lb}$ (b) and total emission $G(\Sigma)_\Sigma$ (c), by months 2019. In Fig. 5 shows that the nature of the change in the total magnitudes of $G(k)_{sb}$, $G(\Sigma)_{lb}$ and $G(\Sigma)_\Sigma$ over the months of the year repeats the change in the average monthly magnitudes of Δt_0 and to a lesser extent depends on the magnitudes of $\varepsilon(k)$. The magnitudes of $G(\text{DF})_{sb}$ varies from 6.3 (February) to 32.9 (June) kg/h, the magnitudes of $G(\text{BF})_{sb}$ – from 9.7 (February) to 64.9 (June) kg/h, magnitudes of $G(\text{MO})_{sb}$ – from 1.1 (February) to 14.3 (June) kg/h, magnitudes of $G(\text{EA})_{sb}$ – from 0.2 (February) to 0.5 (June) kg/h, and the total emission of $G(\Sigma)_{sb}$ – from 17.2 (February) to 112.6 (June) kg/h. The magnitudes of $G(k)_{sb}$ is constant by days of months and months of the year (this is a feature of the method presented in the study) and is $G(\text{DF})_{lb} = 11.9$ kg/h, $G(\text{BF})_{lb} = 12.5$ kg/h, $G(\text{MO})_{lb} = 2.1$ kg/h, $G(\text{EA})_{lb} = 0.3$ kg/h. The total emission $G(k)_\Sigma$, i.e. the sum of $G(k)_{sb}$ and $G(k)_{lb}$ for the vapour mixture of all combustible liquids varies from 43.9 (February) to 139.3 (June) kg/h.

Figure 6 illustrates the distributions of the average monthly magnitudes of energy $e(k)_\Sigma$ (a) and ecological $A(k) \cdot G(\Sigma)_\Sigma$ (b) effects of vapours of FTL of all kinds and total emissions caused by the sum of the phenomena of SRB and LRB for the months of 2019. It shows that the nature of the change in the total magnitudes of $e(k)_\Sigma$ and $A(k) \cdot G(\Sigma)_\Sigma$ over the months of the year repeats the change in the magnitudes of $G(k)_\Sigma$. The magnitudes of $e(\Sigma)_\Sigma$ varies from 0.526 (February) to 1.669 (June) MW, and the value of $A(k) \cdot G(\Sigma)_\Sigma$ – from 5.8 (February) to 19.6 (June) kg/h.

Fig. 7,a – 7,e presents the ratio of maximum, average and minimum annual magnitudes of FTL emissions of all types and total emissions, as well as the annual energy effect for 2019. It shows that the minimum annual magnitudes of mass hourly emissions of all types of FTL under the SRB mechanism less than such magnitudes for LRB; the average annual magnitudes are the opposite, and the maximum ones are many times higher.

Fig. 7,f shows the ratio of the magnitudes of the maximum annual mass hourly emissions of FTL vapours of all types and total emissions caused by the phenomenon of SRB and LRB for 2019. It shows that the relative contribution of emissions under the SRB mechanism in total emissions for different FTL is not the same, so in particular, it is 73.4 % for diesel fuel, 83.9 % for gasoline, 87.4 % for motor oil, 71.9 % for ethanol, and 80.9 % in general.

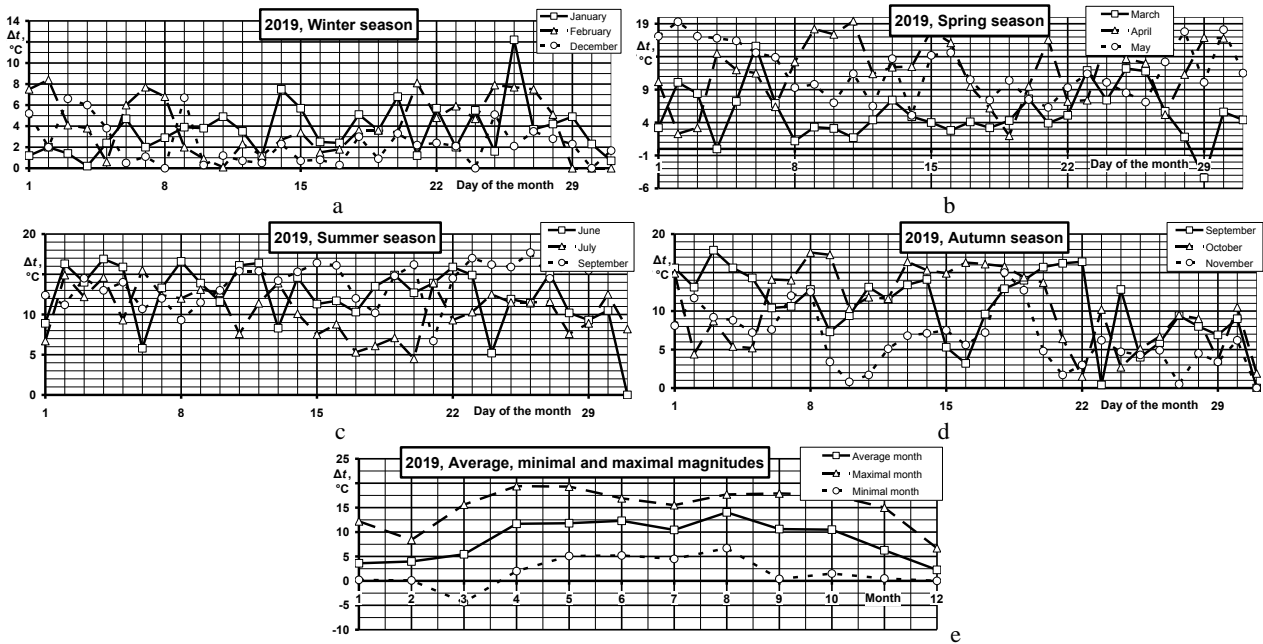


Figure 1 – Distribution of atmospheric temperature difference magnitudes in Kharkiv by days of months in 2019 (a – d) and distribution of minimum, average and maximum magnitudes of atmospheric air temperature difference in Kharkiv by months in 2019 (e) (according to from sources [23, 24])

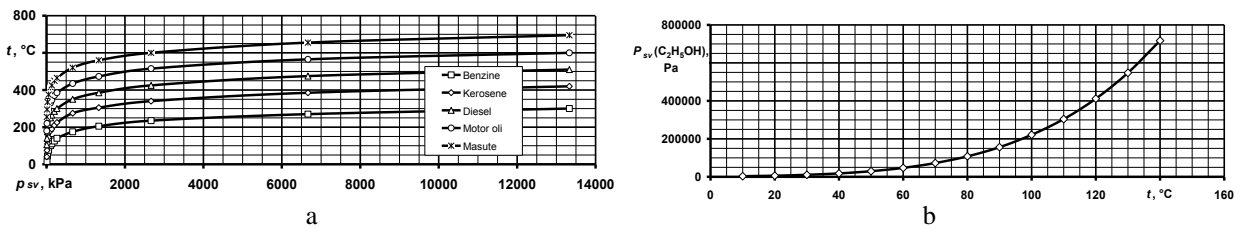


Figure 2 – Nomograms of saturated vapour pressure of petroleum products (a) and ethanol (b) (obtained on the basis of data from the source [25])

The magnitude of the economic effect from the utilization of diverted and accumulated vapours of the k-th type of FTL by burning $F(k)$ is determined by formula (83) taking into account the unit price of the reference FTL (in this case – diesel fuel) $P_M(DF)$ in \$/kg and the ratio the calorific value of the k-th type of FTL $Q(k)$ in MJ/kg and the calorific value of the reference FTL $Q(DF)$. The magnitude of $P_M(DF)$ in \$/kg is determined by the known magnitudes of the unit price of fuel volume $P_W(DF)$ in \$/m³ and its density $\rho(DF) = 0.840$ kg/l (see formula (84)). The unit price of fuel volume $P_W(DF)$ USD in \$/m³ is currently determined taking into account the unit price of fuel volume $P_W(DF)_{UAH}$ in UAH/m³ (currently, i.e. as of September 17, 2020, $P_W(DF)_{UAH} = 22.0 \cdot 103$ UAH/l) and the official exchange rate of the Ukrainian hryvnia to the US dollar $ExR(UAH/USD)$ in UAH/USD of the National Bank of Ukraine (currently, i.e. as of September 17, 2020, $ExR(UAH/USD) = 28.120$ UAH/USD). The magnitude of the total economic effect from the utilization of a mixture of diverted and accumulated vapours of FTL by burning $F(\Sigma)$ is determined by formula (85). To take into account the phenomenon of inflation, the value of $F(\Sigma)$ and its components $F(k)$ should be divided by the ratio of the magnitudes of CPI indexes for the US dollar

for the current $CRI_{USD}(2020) = 256$ and base $CRI_{USD}(1984) = 100$ periods – formula (86) [26].

$$F(k) = P_M(DF) \cdot G(k) \cdot Q(k) / Q(DF), \text{ \$/h.} \quad (83)$$

$$P_M(DF) = P_W(DF)_{USD} \cdot \rho(DF) = P_M(DF)_{UAH} / ExR(UAH/USD) \cdot \rho(DF) = 22.0 / 28.120 \cdot 0.840 = 0.657, \text{ \$/kg.} \quad (84)$$

$$F(\Sigma) = \sum_{k=1}^{k=4} F(k), \text{ \$/h.} \quad (85)$$

$$F(k)_{CPI} = F(k) / (CPI_{USD}(2020) / CPI_{USD}(1984)) = F(k) / 2.56, \text{ \$/h.} \quad (86)$$

Fig. 8 contains the ratio of the magnitudes of the maximum annual mass hourly emissions of FTL vapours of all types in the structure of total emissions (a), emissions under the mechanism of SRB (b) and LRB (c). It shows that for all types of emissions the predominant component is gasoline vapour – 57.6 % for SRB, 46.8 % – for LRB and 55.5 % in total emissions. In second place are diesel fuel vapours – 29.2 % for SRB, 44.5 % – for LRB and 32.1 % in total emissions. The situation with engine oil vapours is as follows: 12.6 % for SRB, 7.7 % for LRB and 11.7 % in total emissions. For ethanol vapours: 0.6 % for SRB, 0.9 % for LRB and 0.6 % for total emissions.

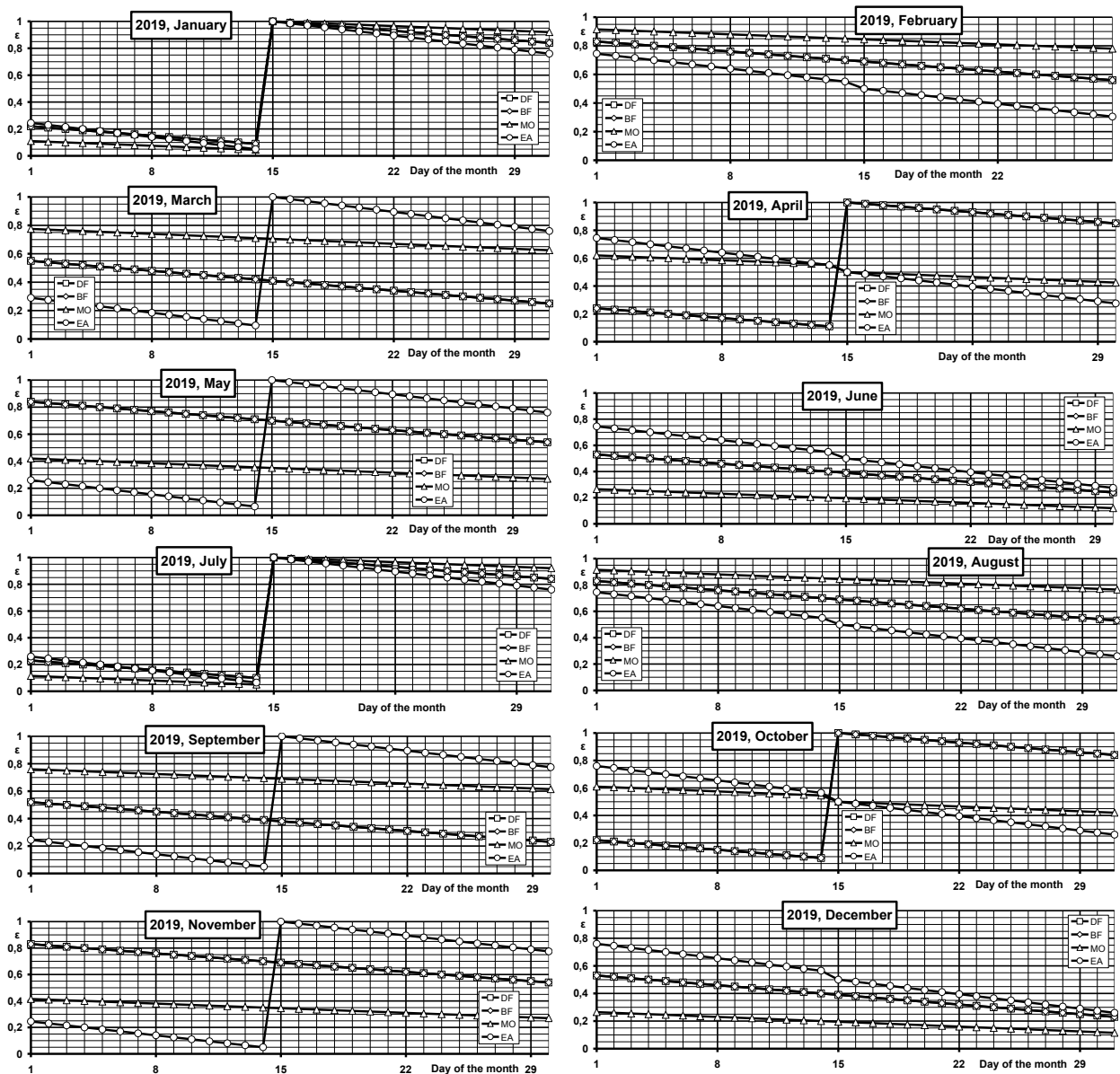


Figure 3 – Distribution of magnitudes of the degree of filling of reservoir $\epsilon(k)$ by days of months in 2019

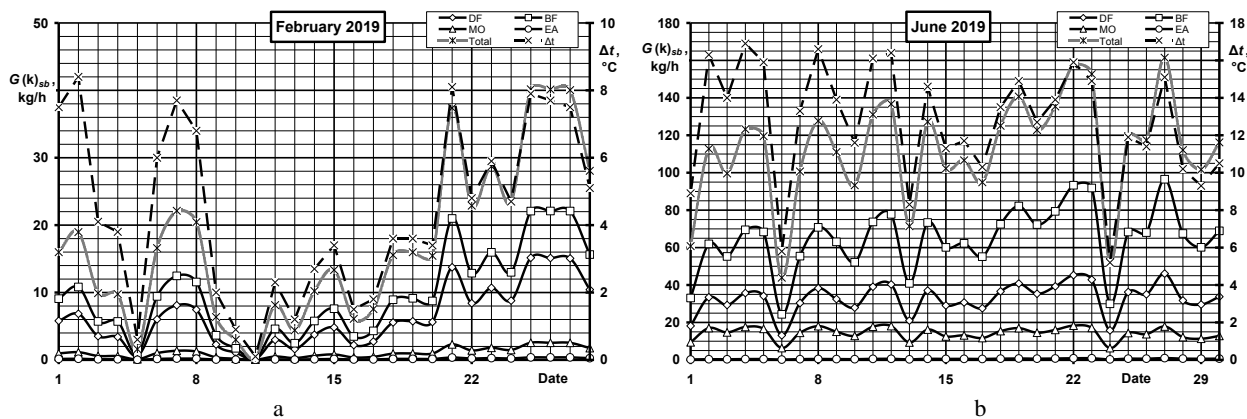


Figure 4 – Distributions of magnitudes of mass hourly emissions of vapours of FTL of all types $G(k)_{sb}$ and total emissions $G(\Sigma)_{sb}$ by days of the most (February – a) and least (June – b) productive months of 2019, as well as the magnitudes of difference atmospheric air temperature Δt_0 in Kharkiv

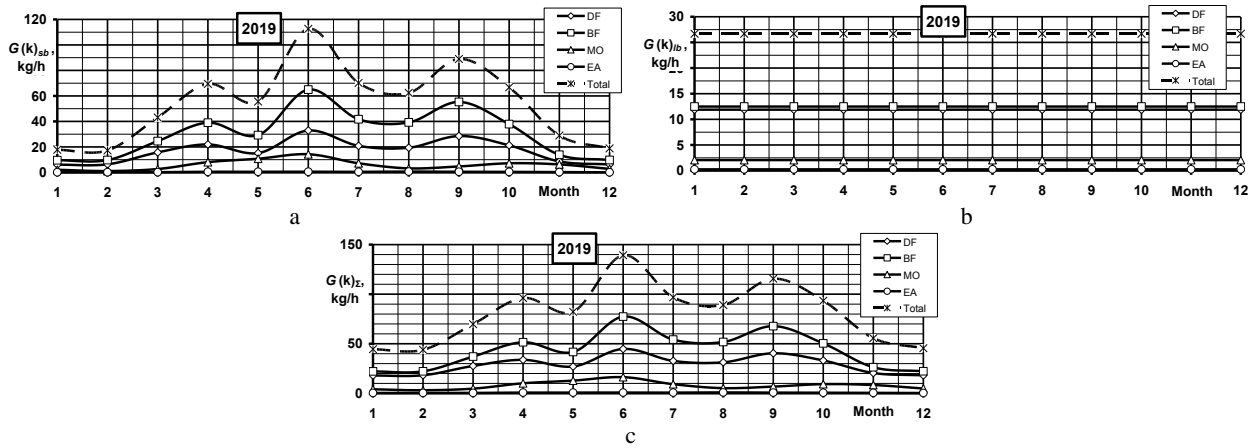


Figure 5 – Distributions of average monthly magnitudes of mass hourly emission of vapours of FTL of all types caused by the phenomenon of SRB $G(k)_{sb}$ (a), LRB $G(k)_{lb}$ (b) and total emission $G(\Sigma)_{\Sigma}$ (c), by months of 2019

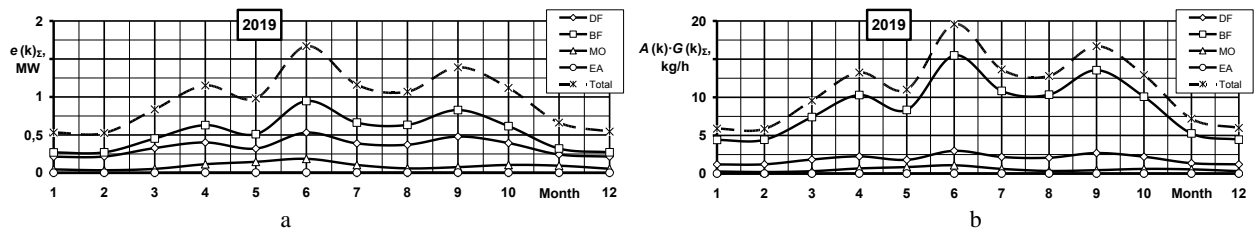


Figure 6 – Distributions of average monthly magnitudes of energy $e(k)_{\Sigma}$ (a) and ecological $A(k) \cdot G(k)_{\Sigma}$ (b) effects from vapours of FTL of all types and total emissions caused by the sum of phenomena of SRB and LRB by months 2019

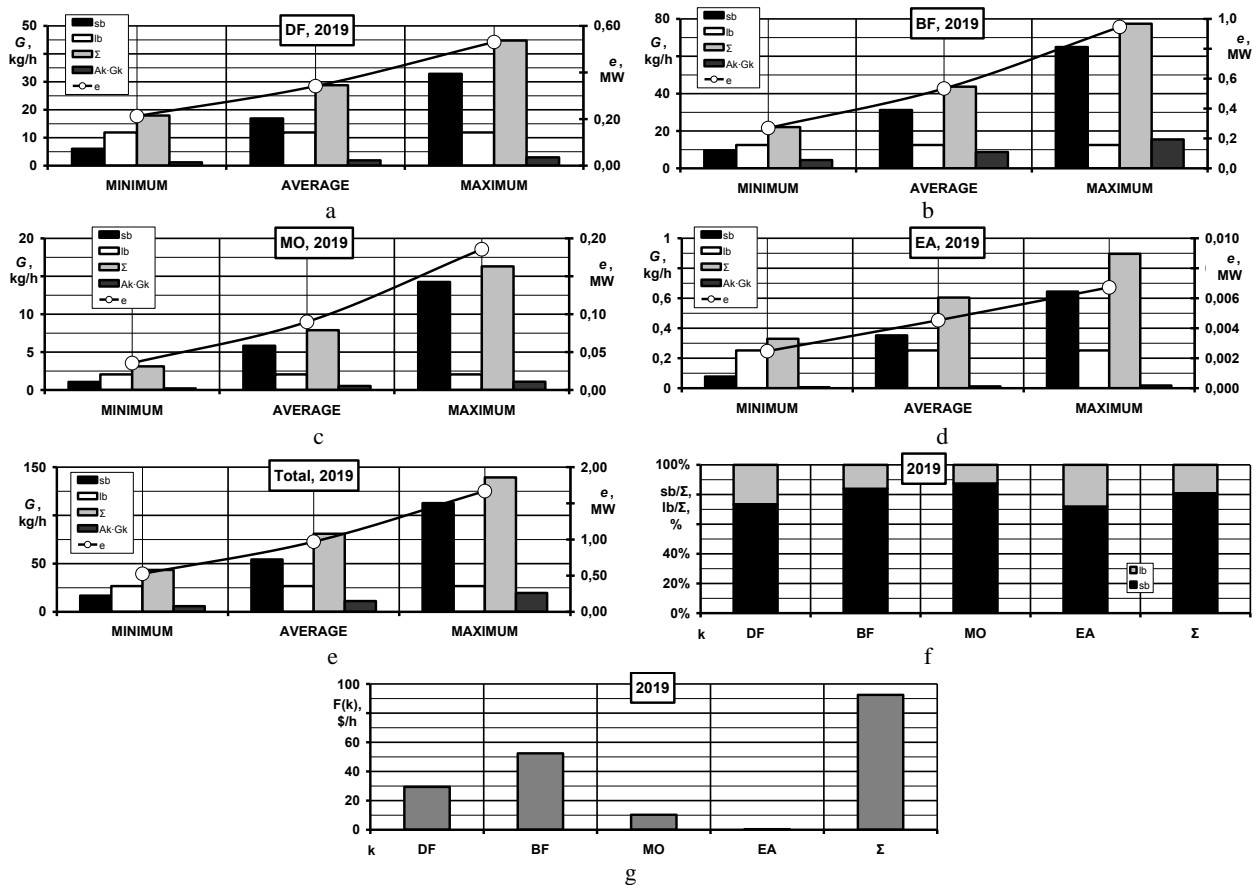


Figure 7 – Ratio of maximum, average and minimum annual magnitudes of FTL emissions of all types and total emissions, as well as the annual energy effect for 2019 (a – e), ratio of the magnitudes of the maximum annual mass hourly emissions of FTL vapours of all types and total emissions caused by the phenomenon of SRB and LRB for 2019 (f), ratio of the magnitudes of the maximum annual mass hourly emissions of FTL vapours of all types and total emissions caused by the phenomenon of SRB and LRB in 2019 (g)

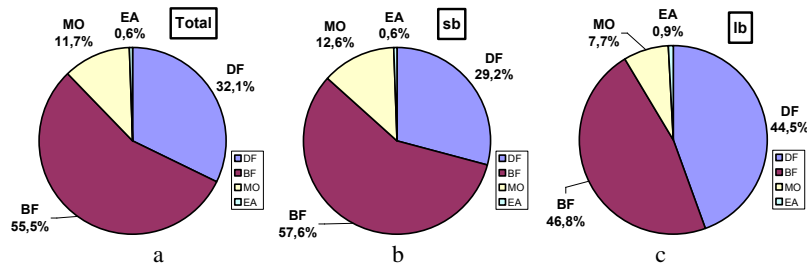


Figure 8 – Ratio of the magnitudes of the maximum annual mass hourly emissions of FTL vapours of all types in the structure of total emissions (a), emissions under the mechanism of SRB (b) and LRB (c)

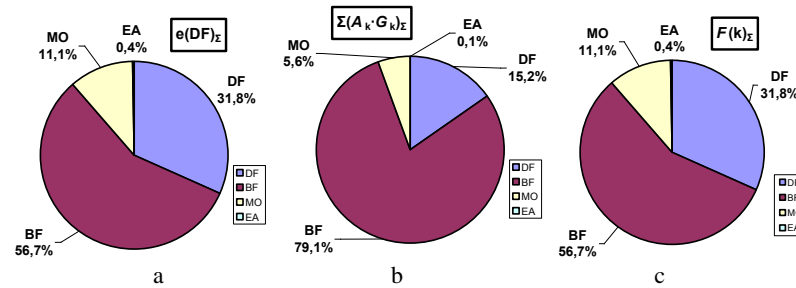


Figure 9 – Ratio of the magnitudes of energy (a), ecological (b) and economic (c) effects of FTL vapour emissions of all types in the structure of the cumulative effect

Figure 9 shows the ratio of the magnitudes of energy (a), ecological (b) and economic (c) effects of FTL vapour emissions of all types in the structure of the cumulative effect. Figure 9 shows that the part of gasoline vapours in the total energy effect, eco-effect and economic effect is 56.7, 79.1 and 31.8 % respectively, diesel fuel vapours – 31.8, 15.2, 56.7 %, motor oil vapours – 11.1, 5.6 and 11.1 %, and ethanol – 0.4, 0.1 and 0.4 %.

Fig. 7,g shows the ratio of the magnitudes of the maximum annual mass hourly emissions of FTL vapours of all types and total emissions caused by the phenomenon of SRB and LRB in 2019. At Fig. 7,g it can be seen that this cost is 29.41 \$/h for diesel fuel, 52.43 \$/h for gasoline, 10.29 \$/h for motor oil and 0.37 \$/h for ethanol, and in general – 92.50 \$/h.

8. Method and results of the calculated study of the effectiveness of using of the breathing valve and the rationale magnitude of adjustment the tension of its spring

Since the spring of the reservoir's breathing valve can be adjusted to different magnitudes of the limit back pressure in it $\Delta p(k)_{fv}$, and the force corresponding to such pressure magnitudes loads all valve elements with mechanical forces, mostly stationary and long-term, it makes sense, firstly, to obtain rational magnitude of such a adjustment, and secondly, to find the correlations between the magnitude of the atmospheric air temperature difference Δt_0 and the emission magnitude $G_{sb}(\Sigma)$, as well as the magnitude of the pressure $\Delta p(k)_{fv}$.

If the breathing valve of the reservoir is set to the limit magnitude of the excess vapour pressure of the FTL in it $\Delta p(k)_{fv}$ (in Pa), then the secondary driving force of the volley of liquid vapour will be the pressure $\Delta p(k)_{op}$, determined by formula (87) (see formula (30)).

$$\Delta p(k)_{op} = \Delta p(k)_i - \Delta p(k)_{fv}, \text{ Pa.} \tag{87}$$

If the value of $\Delta p(k)_{op}$ is positive, i.e. $\Delta p(k)_{op} > 0 \text{ Pa}$, then and only then there is a volley emission of FTL vapours from the reservoir, due to the phenomenon of SRB. If $\Delta p(k)_{op} \leq 0 \text{ Pa}$, then the emission does not occur, and the FTL vapours remains in the reservoir and is under pressure $\Delta p(k)_i$.

The mass of the volley emission is the value determined by formula (87), which is converted by formula (31). The parameters of the variants of this calculation study are summarized in Table 5.

$$m_{sb}(k) = \mu(k) \cdot \Delta p(k)_{op} \cdot W(k)_{\Sigma} \times (1 - \varepsilon(k)) / (R \cdot (t_v(k)_{\max} + 237)), \text{ kg.} \tag{88}$$

The magnitudes of mass hourly emissions $G_{sb}(k)$, energy $e_{sb}(k)$ and ecological $A(k) \cdot G_{sb}(k)$ effects are determined by formulas (35) – (40), respectively.

Table 5 – parameters of the variants of the calculation study

Variant			Parameter	
No.	Title	Sign.	lb	sb
1	Basic	A	+	$\Delta P_{fv} = 0 \text{ kPa}$
2	Small 1	B	-	$\Delta P_{fv} = 0 \text{ kPa}$
3	Small 2	C	-	$\Delta P_{fv} = 1 \text{ kPa}$
4	Small 3	D	-	$\Delta P_{fv} = 2.5 \text{ kPa}$
5	Small 4	E	-	$\Delta P_{fv} = 5 \text{ kPa}$
6	Best	F	-	$\Delta P_{fv} = 10 \text{ kPa}$

Figure 10 shows the dependences of the magnitudes of the mass hourly emission of FTL vapours $G_{sb}(k)$ depending on the adjustment of the spring of the breathing valve $\Delta p(k)_{fv}$ for the least (a – February) and most (b – June) productive month of 2019.

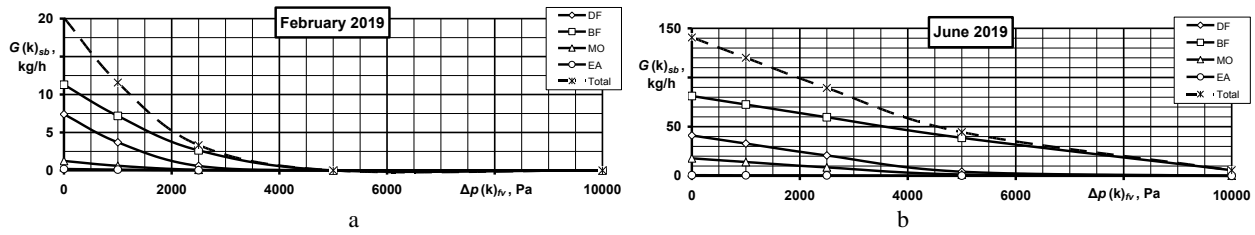


Figure 10 – Dependences of the magnitudes of the mass hourly emission of FTL vapours $G_{sb}(k)$ depending on the adjustment of the spring of the breathing valve $\Delta p(k)_{fv}$ for the least (a – February) and most (b – June) productive month of 2019

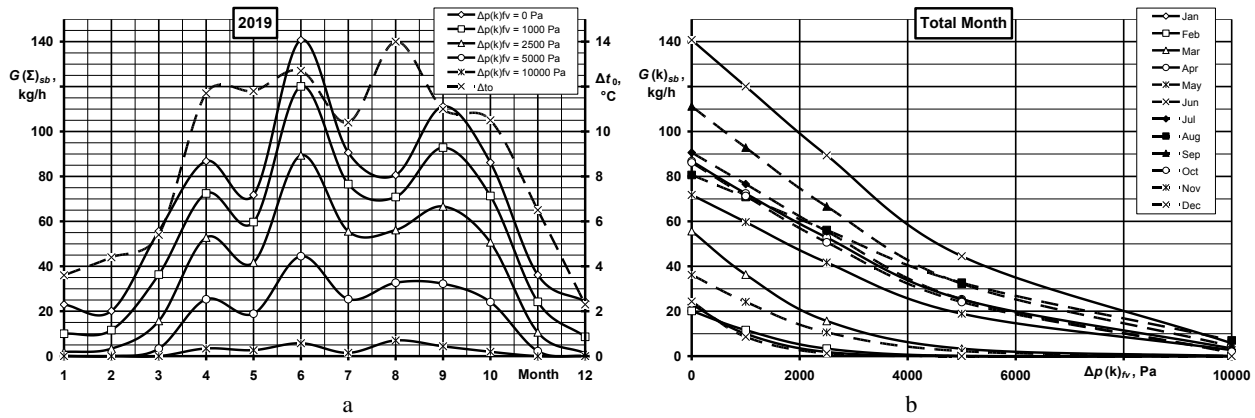


Figure 11 – Dependences of the magnitudes of the total mass hourly emission of FTL vapours $G_{sb}(\Sigma)$ depending on the adjustment of the spring of the breathing valve $\Delta p(k)_{fv}$, as well as the average monthly magnitudes of the daily temperature difference Δt_0 by months of 2019 (a) and also dependences of the total magnitudes of the mass hourly emission of FTL vapours $G_{sb}(k)$ depending on the adjustment of the spring of the breathing valve $\Delta p(k)_{fv}$ for the months of 2019 (b)

It shows that the magnitudes mass hourly emission $G_{sb}(k)$ for different types of FTL decreases with increasing limit value of the pressure to which the breathing valve spring is adjust, such dependences are nonlinear, and zero emission $G_{sb}(k)$ is achieved for different types of FTL at different valve spring adjustment, and different for different months (i.e., different magnitudes of the average monthly temperature difference).

Fig. 11,a shows the dependences of the magnitudes of the total mass hourly emission of FTL vapours $G_{sb}(\Sigma)$ depending on the adjustment of the spring of the breathing valve $\Delta p(k)_{fv}$, as well as the average monthly magnitudes of the daily temperature difference Δt_0 by months of 2019. It shows that despite to the fact that they repeat in the form of graphics in Fig. 5,c, however, the correlation between the magnitudes of emission $G_{sb}(\Sigma)$ and the daily temperature difference Δt_0 is less pronounced, which is explained by the effect of changing the magnitude of the degree of filling of the reservoir $\epsilon(k)$.

Fig. 12 shows the dependences of the absolute and relative magnitudes of the total annual mass hourly emission of FTL vapours $G_{sb}(\Sigma)$ depending on the adjustment of the breathing valve spring $\Delta p(k)_{fv}$. It shows that such dependences are almost linear. Thus, adjustment the spring of the breathing valve to the magnitude of $\Delta p(k)_{fv} = 1.0$ kPa reduces the total average annual mass emission of FTL vapours by 21.3 %, by

2.5 kPa – by 46.5 %, by 5.0 kPa – at 74.9 %, and at 10 kPa – at 96.8 %.

Fig. 11, b shows the dependences of the total magnitudes of the mass hourly emission of FTL vapours $G_{sb}(k)$ depending on the adjustment of the spring of the breathing valve $\Delta p(k)_{fv}$ for the months of 2019. In Fig. 11,b as in Fig. 10, it is seen that the zero total vapour emission of FTL $G_{sb}(\Sigma)$ is achieved for different months with different adjustments of the valve spring.

Therefore, from the above it is clear that there is a correlation between the magnitude of the total average monthly mass hourly emission of FTL vapours by the SRB mechanism for their storage $G_{sb}(\Sigma)$ and the average monthly magnitude of the daily difference in atmospheric air temperature Δt_0 . There is also such a relationship between the limit magnitude of the adjustment of the spring of the breathing valve, at which the zero magnitude of the emission $G_{sb}(\Sigma)$ is reached, and the magnitude of the temperature difference Δt_0 . Such dependences are illustrated in Fig. 13, and are described by the method of least squares by formulas (89) and (90) which is the main result of this study. Fig. 13 shows that the obtained correlations are linear, pass through the origin and increase with increasing argument.

$$G_{sb}(k) = 7.960 \cdot \Delta t_0, \text{ kg/h; } R^2 = 0.725. \quad (89)$$

$$\Delta p(k)_{fv} = 1028.9 \cdot \Delta t_0, \text{ Pa; } R^2 = 0.887. \quad (90)$$

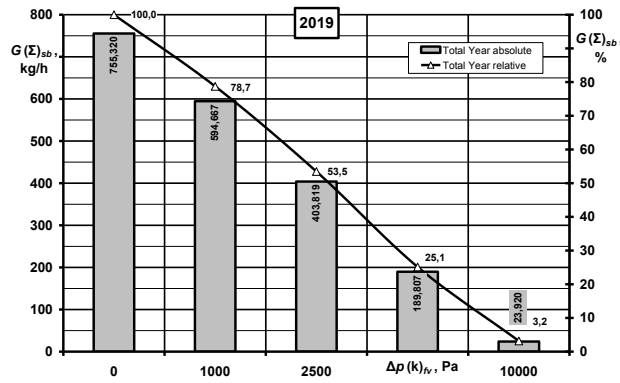


Figure 12 – Dependences of the absolute and relative magnitudes of the total annual mass hourly emission of FTL vapours $G_{sb}(\Sigma)$ depending on the adjustment of the breathing valve spring $\Delta p(k)_{fv}$.

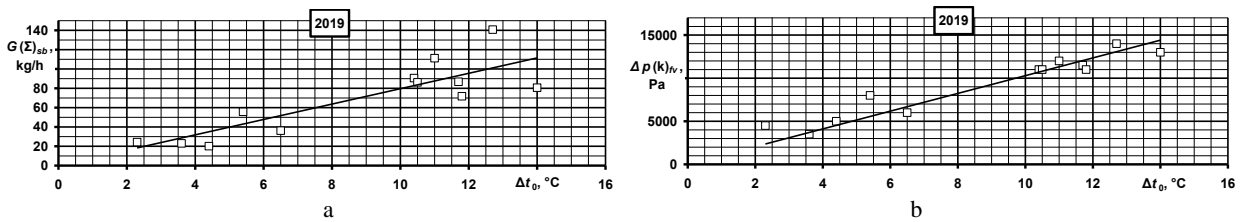


Figure 13 – Correlation between the magnitude of atmospheric air temperature difference Δt_0 and the emission magnitude $G_{sb}(\Sigma)$ (a) and also between the magnitude of pressure $\Delta p(k)_{fv}$ (b)

In connection with the above, we can formulate the following *list of recommendations* for improving the ES level of exploitation process of reusable reservoirs for storage of FTL:

1. All reservoirs for storage of FTL should be equipped with systems of removal, clearing, cooling, accumulation of their vapours which emission is caused by the phenomena of SRB and LRB as such pollutant is toxic, flammable and explosive substance, greenhouse gas, and also is a valuable energy resource.

2. It is proposed to use a breathing valve to remove FTL vapours caused as a phenomenon of SRB, with adjustable in the magnitude of the average daily temperature difference of the atmospheric air force of the shut-off spring to prevent premature failure of its structural elements and increase its service life.

3. It is proposed to use the same breathing valve to remove FTL vapours caused by both the SRB and LRB phenomena. For this purpose it is rational to equip such valve with a spring, the tightening force of which is adjustable, and during the process of filling the reservoir with a new portion of FTL, the threshold magnitude of the tightening force should be set as low as possible, preferably zero.

4. For reservoirs of all four types of FTL it is recommended to use breathing valves of the same design and size, which will simplify the management, maintenance and repair of such unified bodies, for which it is also desirable to adjust the spring tension depending on the type of FTL, i.e. its physical properties.

5. To reduce the emission magnitudes by the SRB mechanism, it is rational to reduce the heating of the reservoirs from air and direct sunlight by placing it below ground level and/or under canopy.

Conclusions

Thus, in this study, which is generally devoted to increasing the ES level of the exploitation process of reusable packaging for storage of FTL for ESDPP as part of the relevant EPT, the following main results were obtained.

1. The scientific and technical, reference, normative and patent literature was analysed and the relevance of the research topic is substantiated.

2. The parameters of the FTL stored in the reservoirs of ESDPP and the technical parameters of the reservoirs for their storage according to the developed method was estimated.

3. The methods of determining the magnitude of the mass hourly emission of FTL vapours caused by the phenomena of SRB and LRB, as well as the total emission by both mechanisms are improved and described.

4. A set of initial data for calculated study was obtained, analysed and illustrated.

5. The results of calculated study of the magnitudes of mass hourly emission of FTL vapours caused by the phenomena of SRB and LRB, taking into account the daily magnitudes of the difference in atmospheric air temperature and the degree of filling of the reservoirs was obtained, illustrated and analysed.

6. The calculated study of efficiency of application of the breathing valve for reduction of emissions of FTL vapours from reservoirs for their storage under the SRB mechanism and the substantiation of adjustment of a tightening of its spring was carried out. A list of recommendations for increasing the ES level in the exploitation process of reusable containers for storage of FTL was formed.

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Conflicts of Interest.

None of the authors have any potential conflicts of interest associated with this present study.

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ВИЗНАЧЕННЯ ВИКИДІВ ПАРІВ ГОРЮЧИХ ТЕХНІЧНИХ РІДИН З РЕЗЕРВУАРІВ ПІДПРИЄМСТВА З ЇХ ЗБЕРІГАННЯ І ДИСТРИБУЦІЇ ТА РАЦІОНАЛЬНИХ НАЛАШТУВАНЬ ЗАПІРНИХ ОРГАНІВ ЇХ ДИХАЛЬНИХ КЛАПАНІВ

У даному дослідженні, в цілому присвяченому підвищенню рівня екологічної безпеки процесу експлуатації багаторазової тари для зберігання горючих технічних рідин для підприємства зі зберігання та дистрибуції нафтопродуктів як частини відповідної технології захисту навколишнього середовища, розрахунково оцінено параметри таких рідин, що перебувають на зберіганні у резервуарах підприємства, та технічні показники резервуарів для їх зберігання за розробленою методикою. Вдосконалено і описано методики визначення значення масового годинного викиду парів таких рідин, спричинених явищами малого і великого дихання резервуарів, а також сумарного викиду за обома механізмами з урахуванням щоденних значень перепаду температури атмосферного повітря та ступеня наповненості резервуара, а також отримано, проаналізовано і проілюстровано результати відповідного розрахункового дослідження. Здійснено розрахункове дослідження ефективності застосування дихального клапану для зменшення викидів парів технічних рідин з резервуарів для їх зберігання за механізмом малого дихання та обґрунтування налаштування затяжки його пружини. Сформульовано список рекомендацій щодо підвищення рівня екологічної безпеки процесу експлуатації багаторазової тари для зберігання рідин, пари яких є токсичним, пожежо- вивухонебезпечним, парниковим і енерговмісним поллютантом.

Ключові слова: екологічна безпека, технології захисту навколишнього середовища, викиди поллютантів, пара технічних горючих рідин, велике дихання резервуару, мале дихання резервуару, дихальний клапан.

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