

QUANTITATIVE ESTIMATION OF THE HARMFUL EMISSIONS FROM THE TECHNOLOGICAL EQUIPMENT BY THE PROCESSING AND TRANSPORTATION OF PETROLEUM PRODUCTS

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ABSTRACT

The biggest and most significant share in environmental pollution have industry and transport. The main pollutant emitted into the air are: sulfur and nitrogen oxides, carbon monoxide, light hydrocarbons, heavy unburned hydrocarbons, hydrogen sulfide, mercaptans and others. The purpose of this work is to identify emissions from process equipment in petroleum refining. The subject of the proceeding are the so-called diffuse sources of pollution caused by impaired technological regime leaks of devices and communications, lack or inefficient operation of ventilation equipment and more.

Keywords: emissions, hydrocarbons, liquid petroleum products, storage and transportation

INTRODUCTION

Industry and transport have the highest share in environment pollution. In particular, petroleum industry is also one of the sources of air pollution. This is connected mainly with the operations of oil refining and further chemical treatment of the petroleum products [1÷3].

The main pollutants emitted in the air are: sulfur and nitrogen oxides, carbon oxide, light hydrocarbons, unburnt heavy hydrocarbons, hydrogen sulfide, mercaptans,

etc. The quantities of emitted substances vary in wide range depending on the grade of the crude oil processed, the efficiency of the treatment itself and the products obtained [4, 5].

Several authors briefly described in their publications the possibilities for dumping hazardous substances in the atmosphere during the different stages of production, processing and storage of petroleum products [4÷7]:

- Possible sources of emissions of light hydrocarbons and sulfur compounds are also the storage, transportation and processing of crude oil and its products using imperfectly built oil tanks, valves, pumps and the piping connected to them, as well as failures of these elements;
- Distillation installations – hydrocarbons, hydrogen sulfide and mercaptanes are emitted during the refining of different types of petroleum products;
- Catalytic creviceing installations – hydrocarbons, carbon oxide and fine dust are emitted in the air during catalyst regeneration and their removal with chimney gases. The first two contaminants are usually burnt in special furnaces before dumping them in the atmosphere with the waste gases;
- Oil refining installations – by these operations, sediments and various waste waters rich in sulfur compounds are dumped from the surface of which hydrogen sulfide and unpleasantly smelling substances are emitted;
- Bitumen flashing installations – these installations generate unpleasantly smelling substances;
- Flare stacks – all the unused gases in an oil refinery are driven to flare stacks and burnt. This is why the nature of the burnt gases incessantly

changes with respect to both quality and quantity. It is very hard to ensure full burning of these gases without emitting smoke of unburnt particles which, in some cases, is very dense.

The concern for the protection of clean air turned to be a comprehensive and very serious problem of the world and experts from various fields are trying to find a solution. The implementation of efficient engineering solution is related to precise knowledge on the type and concentration of the pollutants present in the air which are determined by different techniques.

In this respect, the aim of the present work is to determine the hazardous emissions from the technological equipment during oil processing, storage and transportation of petroleum products. The objects of the study are the so called diffuse sources of pollution engendered by disturbed technological regime, leaks from devices and infrastructure, lack or inefficient operation of ventilation equipment, etc.

MATERIALS AND METHODS

Formulation of the tasks

The objects of the present study were assumed to be diffuse sources of pollution and namely reactors, tanks and tank cars. Each of these units might be a significant source of pollution contaminating mainly the lowest layers of the atmosphere. The tasks were then formulated as follows:

- Calculation of the emissions of pollutants from the production and processing of petroleum products;

- Calculation of hydrocarbon emissions by the storage of petroleum products:

- Emissions from vessels containing single component liquids;
- Emissions from vessels containing multi-component mixtures liquids.

Description of the methods used

I. Method for calculation of the emissions of pollutants by the production and processing of petroleum products developed by V. M. Elterman.

1. Determination of the amount of harmful substances released from equipment operating under pressure:

To solve this problem, the coefficient of non-hermeticity (m) was employed, the non-exceeding of which guarantees the hermeticity of the equipment and its proper operation. Thus, the emissions of pollutants can be calculated with precision high enough for practical purposes and predict the contamination of the ground atmospheric air.

The amount of gas leaked from the equipment per unit time is:

$$G = \frac{Gi - Gf}{\tau} = \frac{1}{\tau} \left(\frac{Pi \cdot V}{R \cdot Ti} - \frac{Pf \cdot V}{R \cdot Tf} \right) \quad (1),$$

where:

G – the amount of gas leaked by the equipment, kg/h;

V – volume of the gaseous and vapor-air phases within the equipment, m^3 ;

R – gas constant for the working medium, $J/(kg \cdot K)$.

Assuming $T_i = T_f = T$, the expression is transformed to:

$$G = \frac{\Delta P \cdot V}{\tau \cdot R \cdot T_i} \quad (2)$$

Multiplying the numerator and denominator by P_i and using the dependence of the coefficient of non-hermeticity (m) we obtain:

$$G = m \frac{P_i}{R \cdot T} \cdot V \quad (3)$$

According the characteristic gas equation

$\rho_i = \frac{P_i}{R \cdot T}$. Substituting in eq. (3) we obtain:

$$G = m \cdot \rho_i \cdot V \quad (4)$$

Formula (4) allows determining the amount of gas leaked by the equipment only in the cases when the hermeticity tests are carried out with gases the temperature of which is the same as the one the gases will have under working conditions in the equipment.

For pressures higher than 200 kPa, the determination was performed using the formula:

$$G = 3600 f \psi_{max} \frac{P}{\sqrt{RT}} \quad (5)$$

F – total area of the crevice, m^2 ;
 Ψ - coefficient (for two-atom gases $\psi_{max} = 2,14$);

For three- and four-atom gases $\psi_{max} = 2,05m^{1/2}/s$;

It was experimentally established by the hermeticity tests that the pressure in the equipment decreases by an exponential law: $P_f = P_i \cdot \exp(-a\tau)$, where a is a constant depending on the degree of hermeticity of the equipment.

Taking into account the change of pressure within the equipment during the test the amount of gas leaked for 1 hour will be:

$$G = 3600f\psi_{max} \frac{Pi}{\sqrt{RT}} \int_0^1 \exp(-a\tau) d\tau \quad (6)$$

After some transformations, the following expression was obtained for the total area of the crevice:

$$f = \frac{m \cdot V}{3600\psi_{max}\sqrt{Rt \cdot Tt}} \quad (7)$$

Substituting the area in (6), it becomes:

$$G = \frac{m \cdot V \cdot P}{\sqrt{RtTt} \cdot \sqrt{RpTp}} \quad (8)$$

If the tests are carried out at temperature $T_t=293K$, $R_t=R_B=286,6 J/(kg.K)$ and these values are used in eq.(8), and the gas constant of the working gas is expressed by

its molecular weight and the pressure P is taken in Pa, we obtain:

$$G = 1,2 \cdot 10^{-4} \cdot \eta \cdot m \cdot V \cdot P \cdot \sqrt{\frac{Mp}{Tp}} \quad (9),$$

where η is coefficient of reserve with values ranging from 1,5 to 2,0.

For gaseous and vapor-air mixtures, the amount of each gas or vapor leaked from the equipment (kg/h) is:

$$G_k = i_k \cdot G \quad (10),$$

where i_k is the portion of gas or vapor in the mixture and G is the total amount of leaked gas calculated by formula (9).

2. Determination of the amount of harmful substances leaked from technological equipment operating under vacuum:

A piece of equipment containing toxic medium under vacuum up to 1000 Pa is also considered to be a source of air pollution.

V. M. Elterman considered the process of molecular diffusion into an air flow passing through the non-hermetic parts of equipment walls. According to him, the following formula can be used for such calculations:

$$G = F \cdot \vartheta \cdot C_0 \cdot \exp\left(-\frac{\vartheta_a}{D}\right) \quad (11)$$

The flow in the crevice tunnel is laminar. Taking into account the characteristic profile of such a flow, Elterman derived a formula for calculation of the amounts of harmful substances (g/s) released by the equipment:

If the inner part of the penetrating pores is a tunnel with cross-section close to circle, then:

$$G = \frac{f \cdot C_0 \cdot D^2}{\vartheta_m \cdot a^2} \quad (12)$$

If the inner part of the penetrating pores is a tunnel with cross section of highly flattened rectangle, then:

$$G = \frac{1}{2} \cdot \frac{f \cdot C_0 \cdot D^2}{\vartheta_m \cdot a^2} \quad (13)$$

The following denotations were used in the latter two expressions:

F – total area of the crevice, m²;

C₀ – concentration of the harmful gas in the equipment, g/m³;

D – coefficient of diffusion of the gas in the air, m²/s;

ϑ_m – flow velocity along tunnel axis, m/s;

a – average length of the tunnels of the penetrating pores, m.

Since the average velocity of a laminar flow in round tunnel is $\vartheta = \frac{1}{2} \vartheta_m$ and in rectangular

ones $\vartheta = \frac{2}{3} \vartheta_m$, the substitution in formulae (12) and (13) gives:

$$G = \frac{1}{2} \cdot \frac{f \cdot C_0 \cdot D^2}{\vartheta \cdot a^2} = \frac{C_0 \cdot f^2 \cdot D^2}{2 \cdot L \cdot a^2} \quad (14)$$

$$G = \frac{1}{3} \cdot \frac{f \cdot C_0 \cdot D^2}{\vartheta \cdot a^2} = \frac{C_0}{3 \cdot L} \cdot \left(\frac{f \cdot D}{a} \right)^2 \quad (15),$$

where **L=f·ϑ** is the quantity of air drawn into the equipment, m³/s.

Formula (14) can be rewritten:

$$G = \frac{1}{2} \cdot \frac{C_0 \cdot f \cdot \vartheta}{Pe^2} \quad (16),$$

where **Pe** = $\frac{\vartheta \cdot a}{D}$ is the criterion of Peclet.

Simple testing would not provide opportunities to determine the area of crevice cross-section and the average length of the penetrating pore tunnels.

Two kinds of tests are necessary to determine the amount of gases released – aerodynamic one by which the amount of air drawn into the equipment depending on the vacuum and a direct measurement of the concentrations of the individual harmful substances present in the equipment.

II. Method for calculation of the emissions of harmful substances by the production and processing of petroleum products developed by the Voeikov Main Geophysical Observatory

The emissions of gases and vapors (kg/h) leaked from devices, reactors and columns is calculated by the formula:

$$\Pi = 0,037(1011PV)^{0,8} \cdot \sqrt{\frac{M_v}{T}} \quad (17),$$

where:

P – pressure in the piece of equipment, GPa;

V – its volume, m³;

M_v – average molecular weight of the vapors of the petroleum products, g/mol;

T – average temperature within the equipment, K.

1. Calculation of the emissions from vessels containing single component liquids:

The amount of pollutants emitted in the air (kg/h) from tanks due to evaporation is calculated by the formula:

$$\Pi = 4,46 \cdot V_T \cdot P_s(38) \cdot M_v \cdot (K_{5C} + K_{5H}) \cdot (K_6 \cdot K_7(1 - \eta)) \cdot 10^{-9} \quad (18),$$

where:

V_T – volume of the liquid in the tank throughout the year, m³/year;

M_v – molecular weight of the vapors of the liquid, g/mol;

η – efficiency coefficient of the tank gas catcher;

K_{5C}, K_{5H} – correcting coefficients depending on the pressure of saturated vapor **P_s(38)** and the temperature of the gas-filled space **T** in cold and warm times of the year;

K₆ – correcting coefficient for the pressure of the saturated vapor which is determined from tabular data;

K₇ – correcting coefficient depending on the technical level and operational regime; it is also determined from tabular data;

P_s(38) – pressure of the saturated vapor of the liquid at temperature of 38°C, GPa.

By the filling of railway tank cars with petroleum products, the average amount of the total emissions in the atmosphere (kg/h) is calculated by the formula:

$$\Pi = 4,46 \cdot V_T \cdot P_s(38) \cdot M_v \cdot (K_{5C} + K_{5H}) \cdot K_8 \cdot (1 - \eta) \cdot 10^{-9} \quad (19),$$

where:

V_T – annual volume of the liquid filled in, m³/year;

K₈ – coefficient depending on the pressure of the saturated vapor and the climatic zone, determined from tabular data.

By the discharging the petroleum products from railway tank cars, the average amount of pollutants emitted in the atmosphere (kg/h) is calculated by the formula:

$$\Pi = 0,44 \cdot V_T \cdot P_s(38) \cdot M_v \cdot (K_{5C} - K_{5H}) \cdot 10^{-9} \quad (20),$$

where:

V_T – annual amount of the discharged liquid, m³/year;

Determination of the coefficient K_5 :

To determine the temperature of the gas-filled space in the vessel, it is necessary to have data on the average temperatures of the petroleum products present in the vessel for the six warmest and six coldest months of the year. For ground level metal and underground reinforced concrete tanks, these temperatures are calculated by the formulae:

$$t_{Ctank} = K_{1C} + K_{2C} \cdot t_{ac} + K_{3C} \cdot t_{Ctank} \quad (21)$$

$$t_{Htank} = K_{1H} + K_{2H} \cdot t_{ah} + K_{3H} \cdot t_{Htank} \quad (22),$$

where:

t_{ac} and t_{ah} are the arithmetical average values of the atmospheric air temperature for the six coldest and the six warmest months of the year, °C;

K_{1C}, K_{2C}, K_{3C} и K_{1H}, K_{2H}, K_{3H} – coefficients for six coldest and the six warmest months of the year, taken from tabular data;

t_{Ctank} and t_{Htank} – the average temperatures of the petroleum products in the tank for the six coldest and the six warmest months of the year, °C.

During the filling of railway tank cars with petroleum products, the temperature on the gas-filled space is determined as:

$$t_{CRT} = 0,5 \cdot (t_{ac} + t_{lc}) \quad (23)$$

$$t_{HRT} = 0,5 \cdot K_4 \cdot (t_{ah} + t_{lh}) \quad (24),$$

where:

K_4 – coefficient which is determined from tabular data for ground level tanks and unity for underground tanks;

t_{lc} and t_{lh} – arithmetic average values of the temperature of the liquid for the six coldest and the six warmest months of the year, °C. By the discharging of liquids from railway tank cars, the average temperature of the gas-filled space is assumed to be equal to that of the atmospheric air for this period:

$$t_{CRT} = t_{ac} \quad (25)$$

$$t_{HRT} = t_{ah} \quad (26)$$

Determination of the coefficient K_6 :

This coefficient is also taken from tabular data depending on the climatic zone where the factory is located, on the pressure of the saturated vapor P_s (38) and the tank turn over n :

$$n = \frac{V_t}{V} \quad (27)$$

where:

V_m – volume of liquid charged into the tank throughout the year, m³/year

V – tank volume, m³;

Determination of the pressure of the saturated vapor of the liquid $P_s(38)$:

For single component liquids, $P_s(38)$ is calculated by the formula:

$$\log(1,33 \cdot P_s(38)) = A - \frac{B}{311+c} \quad (28),$$

where :

A, B u C – constants depending on the nature of the substances.

2. Calculation of the emissions from vessels containing multi-component liquids:

The amount of harmful substances (kg/h) emitted from vessels containing multi-component liquids can be calculated by the formula:

$$H_i = H \cdot C_i \cdot 10^{-2} \quad (29),$$

where:

C_i – mass concentration of the i^{th} component in petroleum products vapor, mass%;

H - total emissions from the corresponding vessel. It is calculated by formulae (18÷20). The pressure of the saturated vapor $P_s(38)$ for multi-component liquids (petroleum products) is taken from tabular data depending on the equivalent temperature of beginning of boiling of the liquid:

$$t_{eq} = t_{bb} + \frac{t_{eb}-t_{bb}}{8,8} \quad (30),$$

where:

t_{eb} u t_{bb} – temperatures of beginning and end of boiling of the multicomponent liquid, °C.

RESULTS AND DISCUSSION

To calculate the emissions of harmful substances leaked from the technological equipment by the production and processing of petroleum products, two methods were studied and employed:

- The method developed by V.M.Elterman;
- The method suggested by the Voeikov Main Geophysical Observatory.

The following diffuse sources of pollution were studied:

- reactor in the installation “Catalytic cracking”:

$D_r = 8,5$ m; $P = 0,19 \cdot 10^6$ Pa; $V = 598,39$ m³; $T_{av.} = 743^\circ\text{C}$ (with fresh catalyst); $T_{av.} = 763,57^\circ\text{C}$ (with exhausted catalyst); $\eta = 2$; $m = 0,04$ 1/h.

Vapor-gas mixture* - containing: cracking gas; vacuum distillate (350-500°C); light gas oil; heavy gas oil; circulating gas oil; water vapor.

The amount of harmful substances emitted by this object was calculated using both methods. The results obtained are presented in Tables 1 and 2.

Table 1. Data on the emissions of harmful substances from a reactor in the installation “Catalytic cracking” calculated by the method suggested by Voeikov Main Geophysical Observatory

№	Equipment type	Type and state of the fluid	Mole amount of the vapor of the mixture in the reactor	Outer diameter of the reactor	Reactor volume	Pressure in the reactor	Average temperature in the reactor	Amount of harmful substances emitted
			kg/kmol	m	m ³	Pa	K	kg/h
1.	Reactor in the installation “Catalytic cracking”	Vapor-gas mixture *	4480,35	8,5	598,39	1,9.10 ⁵	With fresh catalyst	
							743	4,051
							With exhausted catalyst	
							763,57	3,985

№	Equipment type	Type and state of the fluid	Mole amount of the vapor of the mixture in the reactor	Outer diameter of the reactor	Reactor volume	Pressure in the reactor	Coefficient of reserve	Coefficient Of non-hermeticity	Average temperature in the equipment	Amount of harmful substances emitted
			kg/kmol	m	m ³	Pa		1/h	K	kg/h
1.	Reactor in the installation on “Catalytic cracking”	Vapor-gas mixture *	4480,35	8,5	598,39	1,9.10 ⁵	2	0.04	With fresh catalyst	
									743	8,400
									With exhausted catalyst	
									763,57	8,360

Table 2. Data on the emissions of harmful substances from a reactor in the installation “Catalytic cracking” calculated by the method suggested by V. M. Elterman

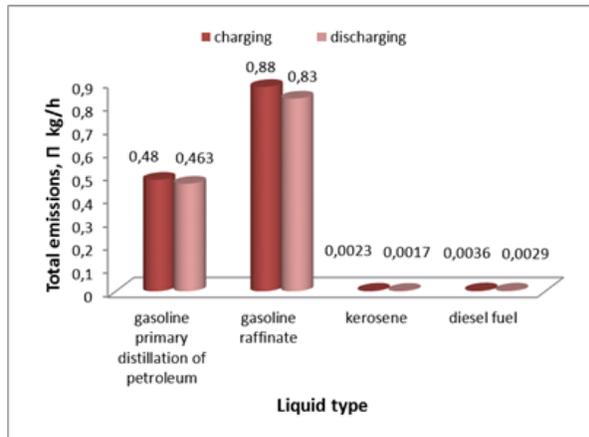
- tank and tankcar:

The calculations for the determination of the amount of harmful substances released by storage and transportation of petroleum products were carried out according to the method suggested by the Voeikov Main Geophysical Observatory.

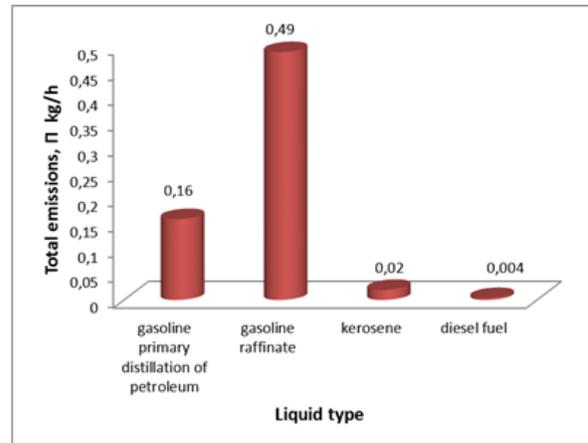
Table 3 and Figs.1-3 show the results obtained for the calculated emissions of harmful substances released by the storage and transportation of petroleum products. The diagrams presented in Figs.1-3 were made for better presentation. They illustrate the harmful substances emitted from vessels(tank/tank car) with multi-component liquids.

№	Equipment type	Liquid type	Liquid volume	Pressure of saturated vapor	Molecular weight of the liquid vapors	Efficiency coefficient of the gas catcher of the vessel	Temperature of the gas-filled space in the vessel for		Amount of harmful substances emitted in the atmosphere kg/h
			m ³ /year	GPa	g/mol		Six cold months of the year, °C	Six warm months of the year, °C	
1.	Tank /reinforced concrete/	Benzene	50 000	167,23	50	0,85	5,34	22,51	0,30 2
2.	Tank car /railway - charging/	Benzene	50 000	167,23	50	0,85	3,50	40,64	0,16 0
3.	Tank car /railway - discharging	Benzene	50 000	167,23	50	0,85	4,00	33,00	0,16 3

Table 3. Data on the emissions of harmful substances released from vesels containing single component liquids

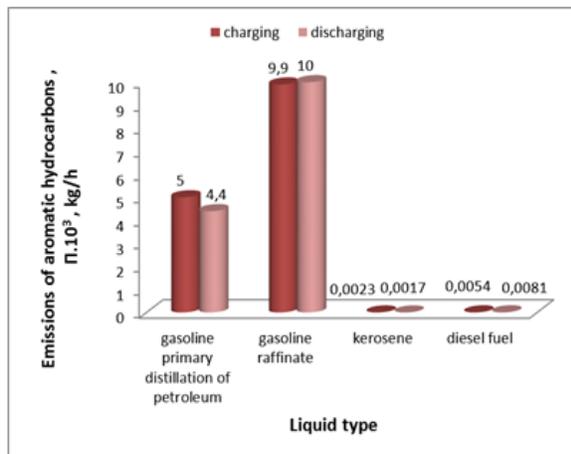


A

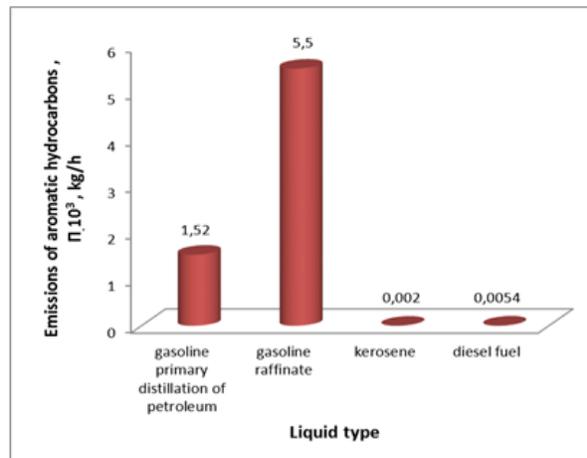


B

Fig.1. Total emissions (kg/h) from railway tank car A) and tank B) filled with multicomponent liquids (petroleum products)



A



B

Fig. 2. Emissions of aromatic hydrocarbons (kg/h) from railway tank car A) and tank B) filled with multicomponent liquids (petroleum products)

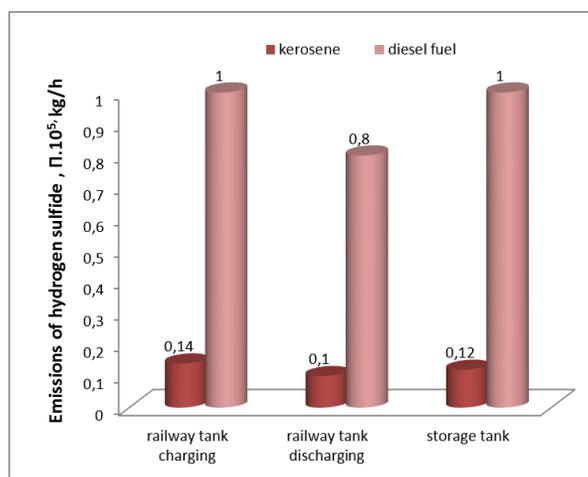


Fig. 3. Emissions of hydrogen sulfide (kg/h), from railway tank car A) and tank B) filled with multicomponent liquids (petroleum products)

CONCLUSION

The following conclusions can be made as a result of the studies carried out and the results obtained:

Methods for calculating the emissions of harmful substances released from the technological equipment by oil processing were studied and applied. As a result, the emissions of harmful substances were determined with precision high enough for practical purposes so the contamination of the ground layer atmosphere.

During the transportation and storage operations, the losses of petroleum products are due mainly to faulty devices (leaks from taps and gaskets, spills, transportation in open vessels, etc.). Thus, the quantitative and qualitative losses of petroleum products by transportation, storage, and preparation

could be substantially diminished by periodic maintenance operations on the equipment.

Results were obtained on the amounts of harmful substances emitted from the technological equipment by the production, processing, storage and transportation of petroleum products. As diffuse sources of pollution, three objects were studied: reactor in the installation “Catalytic cracking”, tank and tank car.

The comprehensive analysis of the calculation formulae showed that emissions are substantially higher for vessels of higher volume, increased pressure of the saturated vapor $P_s(38)$, higher molecular weight of the petroleum products vapors and the coefficients depending on it..

REFERENCES

- [1]. Hauptmanns, Ulr., Process and Plant Safety, “Springer” (2013).
- [2]. Nikolaeva Z., Analysis of the Ground Level Concentrations of Ozone in Atmospheric Air, *Journal Oxidation Communications*, 2017;40 (1-II):469-476.
- [3]. Nikolaeva, Z., A model for calculation of the air quality index for ozone, *International Journal of Scientific Engineering and Applied Science*, 2017, 3 (4):33-38.
- [4]. Tasheva, Y., Y. Koleva, The Potential Risk of Petroleum Propyl Mercaptan in the Environment, *Proceedings of the Fifth International Scientific Conference – FMNS2013, 12 – 16 June 2013, Faculty of Mathematics and Natural Science, South-West University “Neofit Rilski”*, 2013, 4: 72 – 75,.
- [5]. Koleva, Y., Y. Tasheva, The persistence, bioaccumulation and toxic estimation of some sulfur compounds in the environment, *Petroleum & Coal*, 2012, 54 (3): 220 - 224.
- [6]. Elterman, V.M., Ventilation of chemical production lines, “Khimiya”, Moscow, 1980.(in Russian)
- [7]. Elterman, V.M., Protection of the atmospheric air at chemical and petrochemical plants, Khimiya, Moscow, 1985. .(in Russian)