ОПРЕДЕЛЯНЕ ЕМИСИИТЕ ОТ ВЪГЛЕВОДОРОДИ ПРИ СЪХРАНЕНИЕТО И ТРАНСПОРТА НА НЕФТОПРОДУКТИ

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DETERMINATION OF HYDROCARBON EMISSIONS BY STORAGE ANDTRANSPORTATION OF PETROLEUM PRODUCTS

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ABSTRACT

The biggest and most significant share in environmental pollution are industry and transport. In particular, petroleum industry is also one of the sources of air pollution. The amount of hazardous substances emitted varies in wide range depending on the grade of the crude oil processed, the efficiency of the treatment itself and the products obtained. In this respect, the aim of the present paper is to determine the emissions of hydrocarbons by the storage and transportation of petroleum products. The discussion is focused on the so called nonpoint sources arising from disturbed technological regime, non-hermeticity of equipment and piping, lack or inefficient ventilation systems, etc.

Key words: *emissions, hydrocarbons, liquid petroleum products, storage, transportation.*

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INTRODUCTION

Industry and transport have the highest share in environment pollution [1]. 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.

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 [2, 3].

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 [2÷5]:

Possible sources of emissions of light hydrocarbons and sulfur compounds are also the storage, transportation and processing of crude oil and it 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 cracking 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 relation to the mentioned above, the aim of the present work is to determine the emissions of hydrocarbons by the storage and transportation of petroleum products. The objects of the study are the so called nonpoint sources of pollution caused by disturbed technological regime, non-hermetic of equipment and piping, lack or inefficient ventilation systems, etc.

EXPERIMENTAL

1. Formulation of the tasks

As objects of the present work, nonpoint sources of pollution were assumed and particularly – storage tank and railway tank. Such a vessel can be a significant source of emission of hazardous substances contaminating mainly the ground layer of the atmosphere. The tasks to be solved were formulated as follows:

- **Calculation of the emissions of hydrocarbons by the storage of petroleum products:**
  - Emissions from vessels containing single component liquids;
  - Emissions from vessels containing multicomponent liquid.

2.Description of the method of calculation of hydrocarbon emissions by storage and transportation of petroleum products

For the calculation of the emissions of hydrocarbons by the storage and transportation of petroleum products, the method developed by the Main Geophysical Observatory A.I.Voeikov.

- **Calculation of the emissions from vessels containing single component liquids:**

The quantity of the pollutants emitted from tanks in the atmosphere (kg/h) due to evaporation was calculated by the formula:

$$\Pi = 4{,}46.V_{\mathrm{T}}.P_s(38).M_v.(\mathrm{K}_{5C} + \mathrm{K}_{5H}).\left(\mathrm{K}_6.\mathrm{K}_7(1-\eta)\right).10^{-9} \quad (1),$$

where:

V_T – volume of the liquid in the tank for 1 year, m^3/year.;

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

η – coefficient of efficiency of the tank's gas trap;

$\mathrm{K}_{5C}, \mathrm{K}_{5H}$ –correction factors depending on the saturated vapor pressure $P_s(38)$ and the temperature in the gas space *T* during hot and cold weather throughout the year;

K_6 –correction factor depending on the saturated vapor pressure, determined from reference tables;

K_7 – correction factor depending on the technical level and exploitation regime, also determined from reference tables;

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

When railway tanks are charged with petroleum products, the average amount of the entire emission in the atmosphere is calculated by the following equation:

$$П = 4{,}46.V_T.P_s(38).M_v.(К_{5C} + К_{5H}).К_8.(1 - \eta).10^{-9} \quad (2),$$

where:

V_T - annual amount of the liquid poured, m^3/year;

$К_8$ – coefficient depending on the saturated vapor pressure and the climatic zone, determined from reference tables.

When petroleum products are discharged from railway tanks, the calculation of the average amount of the entire emission in the air (kg/h) is calculated by the expression:

$$П = 0{,}44.V_T.P_s(38).M_v.(К_{5C} - К_{5H}).10^{-9} \quad (3),$$

where:

V_T - annual amount of the discharged liquid, m^3/year;

Determination of the coefficient $К_5$:

To determine the temperature in the gas space of the tank, it necessary to have data on the average temperature of the petroleum products in the vessel for the six coldest and warmest months in the year. For above ground метал and underground tanks built from reinforced concrete, this temperature is determined by the formulae:

$$t_{Гtank} = К_{1C} + К_{2C}.t_{ac} + K_{3C}.t_{TCtank} \quad (4)$$

$$t_{ГHtank} = К_{1H} + К_{2H}.t_{ah} + K_{3H}.t_{THtank} \quad (5),$$

where:

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

$К_{1C}, К_{2C}, K_{3C}$ и $К_{1H}, К_{2H}, K_{3H}$ – correcting factors for the six warmest and six coldest months of the year, taken from reference tables;

t_{TCtank} and t_{THtank} – average temperature of the petroleum products in the tank during the six coldest and six warmest months of the year, °C.

By the charging of railway tanks with liquids, the temperature in the gas space is determined as follows:

$$t_{Г_{CRT}} = 0{,}5.(t_{ac} + t_{тc}) \quad (6)$$

$$t_{Г_{HRT}} = 0{,}5.К_4.(t_{ah} + t_{тh}) \quad (7),$$

where:

$К_4$ – correction factor which is assumed to be unity for underground tanks and taken from reference tables for above ground tanks;

$t_{тc}$ and $t_{тh}$ – arithmetic average values of the temperature of the liquid for the six coldest and six warmest months of the year, °C.

By discharge of liquids from railway tanks, the average temperature of the gas space is assumed to be equal to the average temperature of the atmospheric air for the same period.:

$$t_{Г_{CRT}} = t_{ac} \quad (8)$$

$$t_{Г_{HRT}} = t_{ah} \quad (9)$$

Determination of the coefficient $К_6$:

This coefficient is taken from reference tables depending on the location of the facility/installation in certain climatic zone, on the saturated vapor pressure $P_s(38)$ tank turnover ratio n:

$$n = \frac{V_т}{V} \quad (10),$$

where:

$V_т$ – volume of the liquid charged in the tank throughout the year, m^3/year;

V – tank volume, m^3;

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

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

$$\log(1{,}33.P_s(38) = A - \frac{B}{311+C} \qquad (11),$$

where:

A, B и C – constant depending on the nature of the substances.

- **Calculation of the emissions from tanks containing multicomponent liquids:**

The quantity of hazardous substances (kg/h) emitted from vessels containing multicomponent liquids can be calculated by the formula:

$$\Pi_i = \Pi\,.C_i.10^{-2} \qquad (12),$$

where:

C_i – mass concentration of the ith component in the vapors of the petroleum products, mass %;

Π - total emissions from the vessel. It is calculated by formulae (1÷3).

The pressure of the saturated vapors $P_s(38)$ for multicomponent liquids (petroleum products) is taken from reference tables depending on the equivalent temperature of the beginning of boiling of the liquid:

$$t_{eq} = t_{bb} + \frac{t_{eb} - t_{bb}}{8{,}8} \qquad (13),$$

where:

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

EXPERIMENTAL

The calculations for the determination of the quantities of the pollutants emitted by the storage and transportation of petroleum products were made according to a method suggested by the Main geophysical observatory A.I.Voeikov. It was thoroughly studied and the emissions of liquid petroleum products from nonpoint sources of pollution (storage tank and railway tanks) were determined.

Table 1 and Figs.1-3 show the results obtained for the calculated emissions of hazardous substances released by the storage and transportation of petroleum products. The diagrams in Figs.1-3 were drawn for better assessment of the results. They show the data on the hazardous substances emitted from vessels (tank/railway tank) charged with multicomponent liquids.

Table 1. Data on the emissions of hazardous substances from vessels containing single component liquids

№	Vessel type	Liquid type	Liquid volume	Pressure of the unsaturated vapor	Molecular weight of the vapors of the liquid	Efficiency coefficient of the vessel's gas trap	Temperature of the gas space in the vessel for:		Quantity of hazardous substances ereleased in the atmosphere
			m^3/year	GPa	g/mol		Six cold months, °C	Six warm months,°C	kg/h
1.	Tank /reinforced concrete/	benzene	50 000	167,23	50	0,85	5,34	22,51	0,302
2.	Railway tank /charging/	Benzene	50 000	167,23	50	0,85	3,50	40,64	0,160
3.	Railway tank /discharging/	benzene	50 000	167,23	50	0,85	4,00	33,00	0,163

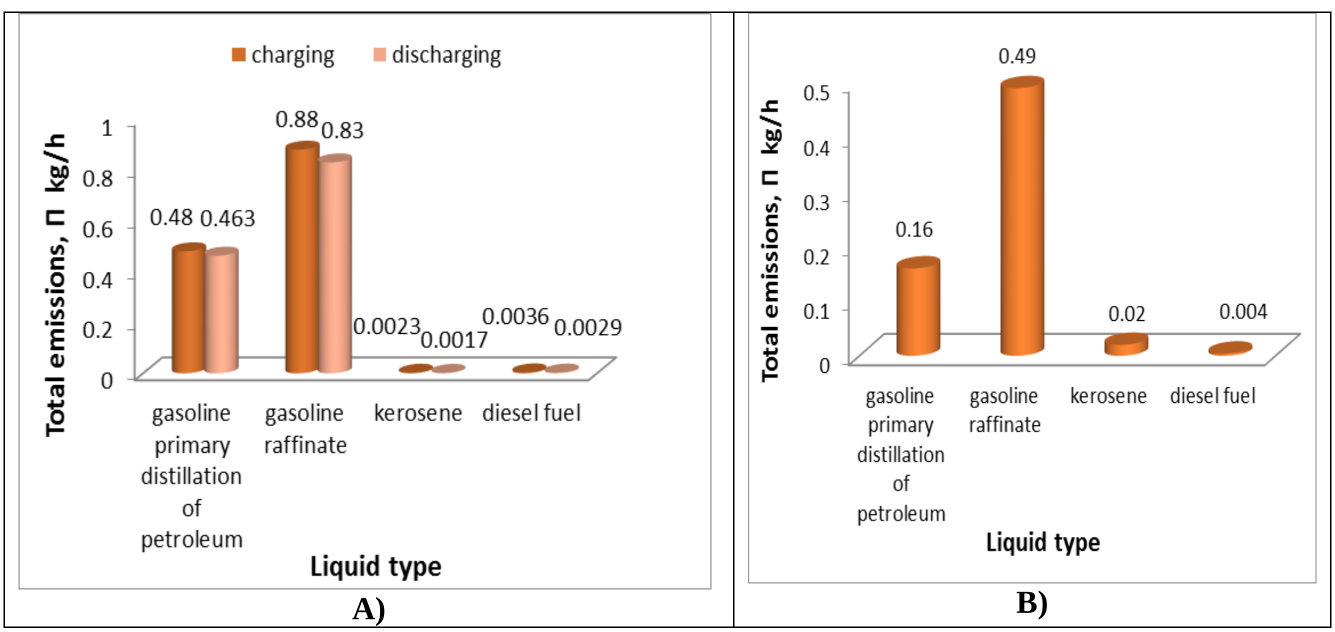
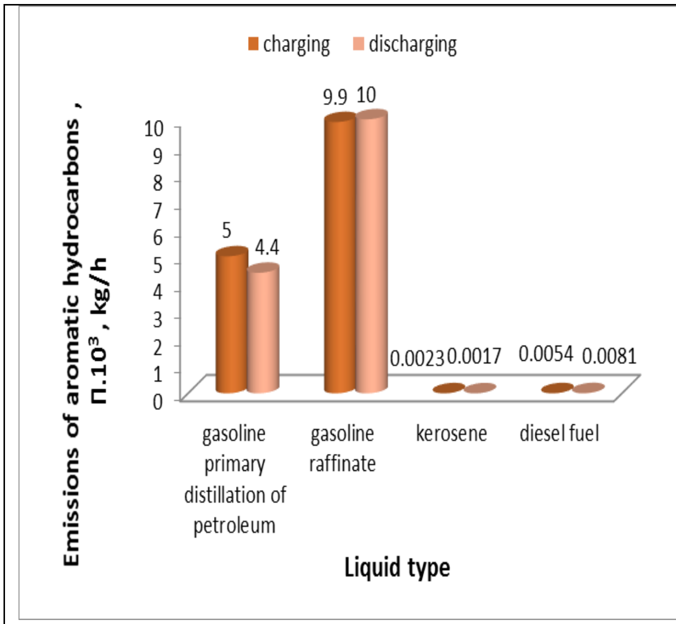
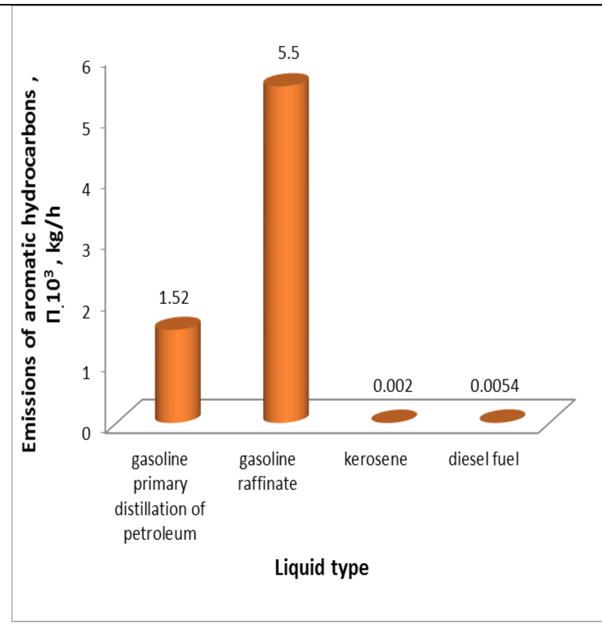


Fig.1. Total emissions (kg/h) from a railway tank A)/storage tank B) charged with multicomponent liquids (petroleum products)



A)



B)

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

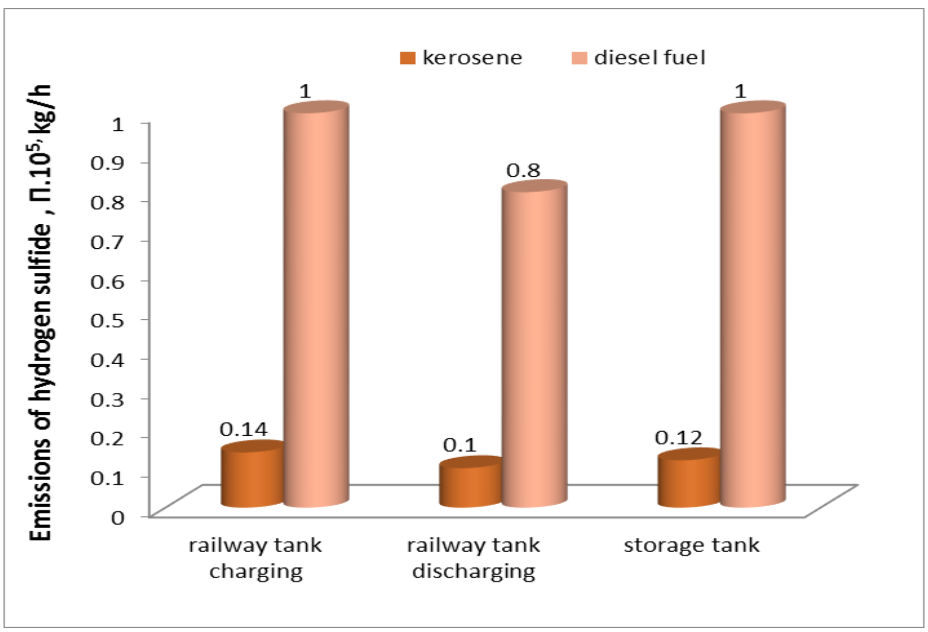


Fig.3. Emissions of hydrogen sulfide (kg/h) released in the atmosphere from railway tank /storage tank charged with multicomponent liquids (petroleum products)

CONCLUSION

The detailed analysis of the calculation formulae showed that the increase of saturated vapor pressure $Ps(38)$, the molecular weight of the vapor from the petroleum products and the coefficients depending on them with the increase of vessel volume results in an increase of the emissions of hazardous substances.

During storage and transportation operations, the loss of petroleum products are due mainly to failures of the different elements (leakage from taps and gaskets, spills and transportation in open vessels, etc.). Therefore, the quantitative and qualitative losses of petroleum fuels by transportation, storage and delivery can be substantially reduced if the equipment is maintained on a regular basis.

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