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INFLUENCE OF PETROL AND PETROLEUM COMPONENTS' VAPOURS ON HUMAN ORGANISM

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Abstract. The work deals with the analysis of sources and ingression of petroleum vapours into environment, as well as with petrol losses and the dependence of the vapours concentration on the tank volume and the ambient temperature. The concentration of petroleum vapours at the petrol station and the individual risk of hazard level have been calculated. The chemical composition of petrol is shown, toxicity of its components and their influence on the human organism as a whole are analyzed.

Key words: sources of pollution, vapours, petrol, hydrocarbons, risk, toxicity, diseases..

1. Introduction

Nowadays, the tendency to increase the number of motor vehicles is steadily increasing, which leads to the increase in the number of petrol stations and, accordingly, to the growth of petroleum products sales volume. At petrol stations the fuel components are emitted to the atmosphere, and the increasing number of them causes significant pollution of the environment. Since the petrol stations are located not only around the city, but also in places of mass accumulation of people, recently there has been a deterioration of the ecological situation in cities, which has a negative impact on people's health. Harmful substances in the air, even in small amount, make the human body less protected against adverse external factors, weaken immune properties, cause the emergence and exacerbation of various diseases.

The sources of air pollution and, therefore the environment, are the evaporation of petroleum products that occur during the supply and storage of fuel, as well as refueling of motor vehicles. About 20 % of pollutants emitted to the atmosphere by stationary sources are mutagenic, i.e., they enhazard a health not only to the current, but also the coming generations [1].

Above the surface of any tanks filled with petrol (gasoline) and diesel fuel, air-petrol mixtures are formed that contain a certain amount of petroleum vapours. The concentration of these vapours in the gas space increases during tanks filling, but the bulk of hydrocarbon vapours accumulate in the air during petroleum products storage in containers, the discharge of petrol into the tanks of petrol stations, and refueling of cars [2]. Statistics show that the amount of hydrocarbons lost as a result of evaporation accounts 16 % for oil refineries, 32 % for oil storages and 52 % for petrol stations. The share of individual components in the total emissions depends on equipment, its operation parameters, skill and discipline of stations staff. Estimated values of individual sources in the total emissions are: emissions at the refueling of cars 30 %, emissions from oil and petroleum products from tankers 25 %, the same emissions during maintenance and repair of technological equipment 20 %, emissions due to equipment malfunction 15 %, other sources 10 % [3]. The evaporation of petroleum products under statistical conditions is influenced by various factors: ambient temperature, atmospheric pressure, volume and pressure of gas space, contact area of petroleum product with gas space [4].

2. Results of the research

2.1. Dependence of petrol vapours concentration in the air on the tank volume and the ambient temperature. Determination of the individual risk of hazard level

Evaporation from the tanks mainly occurs as a result of "small" and "big" breathings. Vapours from "small breathing" are caused by changes in ambient temperatures [4]. As the temperature of the air increases during daytime, the surface of the tanks is heated, the pressure and temperature of the gas-vapour mixture increases.

These results in the actuation of breathing valve installed in the tank and the release of the vapor mixture to the environment. "Big breathing" arises during the displacement of the air-petrol mixture to the environment in the process of tank filling. The volume of "big breathing" is approximately equivalent to the amount of petroleum product filling the tank. Vapours volume in the case of "big breathings" increases with the increase in the number of tank "filling-discharge" cycles and depend on the climatic zone [4]. It was established that the saturation rate by vapours is proportional to the evaporation surface area. Franchuk et al. [5] showed that the displacement of the petrol-air mixture during "small breathings" is 0.1–0.15 m^3/h per 1 m^3 of the tank, and during "big breathings" – 15–60 m^3 per year, depending on the tank capacity [5]. It was estimated that more than 4 kg of petroleum products per month evaporate from 1 m^2 of the overland tank surface, and the average petrol station emits 2–6 tons of fuel per year due to evaporation processes [6].

Antropchenko et al. [7] studied the dependence of petrol vapours concentration in the air on the tank volume and the ambient temperature and calculated the individual risk of hazard level on the basis of air pollution values received at the petrol station. It was established that the increase in temperature and tank volume increases the concentration of petroleum products in the air and, accordingly, the level of individual risk. In winter, spring and autumn seasons there is a decrease in the concentration of petrol evaporations with the increase in the tank volume, since a larger volume of tank means a larger radius of gas pollution and, accordingly, a larger volume of air in which gas vapor is dispersed. Hence, the level of individual risk is reduced.

Apart from the emissions of petrol vapours at the petrol station there are emissions of diesel fuel vapours from the tanks, as well as petrol and kerosene from the fuel-filling columns. Therefore, we determined the vapours concentration of the mentioned petroleum products in the air from these sources at one of the petrol stations. The researches were carried out in the warm period of the year from the following sources of emissions: a column for petrol filling – 1 unit, a column for diesel fuel filling – 1 unit, a standpipe for petroleum loading – 1 unit, a standpipe for diesel fuel loading – 1 unit, storage tanks for diesel fuel – 4 units by volume of 73 m^3 and 2 units by volume of 26 and 400 m^3, storage tanks for petrol – 6 units by volume of 73 m^3 and 1 unit by volume of 26 m^3. Total emissions of pollutants were calculated relative to the raw material consumption [6]. Calculations have shown that emissions of petrol and kerosene vapours increase according to the tanks volume, both from the filling columns and from each tank separately. They were 201–204 mg/m^3 from every diesel fuel tanks and 287–293 mg/m^3 from every petrol tanks. Total amount was 1482 mg/m^3, which significantly exceeds their maximum permissible concentrations: 100 mg/m^3 for petrol and 300 mg/m^3 for kerosene [8].

From the ratio of received (RD) and permissible (PD) doses we calculated individual risk of hazard level RI according to the formula [9]:

$$RI = \frac{RD}{PD} \cdot k_b ,$$

where k_b is the coefficient of 2.4; 1.3; 1 and 0.86 for the compounds of 1; 2; 3 and 4 hazard classes, respectively; at the actual concentration less than the maximum permissible, regardless of the hazard class, k_b = 1. The obtained levels of individual risk were evaluated using the scale given in Table 1 [9].

Table 1

Scale of hazard levels

Hazard level	Individual risk
Minimal	< 0,1
Permissible	0.1–1.0
Moderate	1–5
High	5–10
Very high	> 10

According to GOST 12.1.007 [10], the hazard class of petrol in the case of inhalation effect – 3 (substances are moderate hazardous). So, the calculated risk RI = 4.94 is almost at the boundary of the medium and high hazard level.

2.2. Chemical composition of petrol, its influence on the human body

Since the temperature limits of boiling petrol are in the range of 35–205 °C, and diesel fuel 180–350 °C, air pollution is mainly due to the petrol evaporation. The motor petrol is a mixture of petrol fractions obtained from various technological processes of oil refining – direct distillation, thermal cracking, catalytic cracking, catalytic reforming, hydrocracking, as well as of products of isomerization, alkylation and aromatization with the adding of individual high-octane hydrocarbon components and additives that improve operational properties [9].

Petrol extracted from different oils by different methods differs not only in the total content of hydrocarbons, but also in the composition of individual hydrocarbons. For example, straight-run petrol generally consists of paraffinic and naphthenic hydrocarbons (cyclopentane and cyclohexane derivatives); thermal cracking petrol contains aromatic, branched paraffinic and unsaturated hydrocarbons (olefins and cycloolefins). Catalytic cracking petrol has many (up to 63 %) branched chain hydrocarbons. Petrol after cracking processes has toluene and high-boiling alkylbenzenes. Some petrols contain paraffinic hydrocarbons from pentane to isononane – 40 %, naphthenic hydrocarbons – from cyclopentane to cyclic hydrocarbons C_9H_{18} – 52 %, aromatics – benzene, toluene, xylenes (ortho, para, meta) – 15 % [9].

One can see that the chemical composition of petrol can vary depending on the oil nature, the method of its distillation, the purification method, as well as the type and properties of additives.

The results of studies indicate that the impact of petroleum products on the human body depends on the concentration of these vapours in the air, the residence time in a gas-polluted environment, the physiological resistance to the action of harmful substances. The toxicity of petrol vapours is determined primarily by the combination of hydrocarbons which belong to its composition, therefore the toxicity of the mixture is higher than the toxicity of individual components.

All hydrocarbons affect the cardiovascular system and blood indices, in particular. In this case, there takes place a decrease in the number of red blood cells and hemoglobin, as well as violation of the activity of the endocrine glands and liver damage. Paraffin hydrocarbons are chemically most inert, but still exhibit toxic effects. With the increase in the number of carbon atoms, the strength of their narcotic effect increases, but their own effect is weakened by insignificant solubility in water and blood [10]. The instability of the central nervous system reactions due to the influence of petrol vapours appears not only at high but also at low concentrations of vapours. In particular, octane causes deep anesthesia, the hydrocarbons C5–C7 cause a narcotic effect and paralyze the activity of the central nervous and respiratory system. Hexan is a very poisonous substance of neuroparalytic action; it causes headache, impaired vision and coordination of movements, intoxication, paralysis of nervous, motor and respiratory systems [5].

The effects of poisoning can be even more serious at the high content of benzene in petrol. Benzene has hemopathogenic effect, causes narcotic intoxication, seizures, strikes the eyes and leads to lethal consequences at significantly lower concentrations than petrol ones [4]. In serum benzene dissolves 10 times better than in water. In cases of acute poisoning there are general phenomena: headache, dizziness, tinnitus, intoxication, languor; in worst cases – mental disorders, delirium, seizures. In case of chronic intoxications, which are observed in the working environment more often than acute ones, the main symptoms of poisoning are changes in vascular walls, serious damage of haemopoiesis organs and marrow. At the same time, a short-term increase in the number of leukocytes is observed, and then a steady reduction (leukopenia) occurs (in serious cases the reduction is to 500 leukocytes per 1 mm^3 of blood when the standard is 600–8000). There is also a reduction in the number of other morphological elements of blood – platelets, neutrophils, and red blood cells. As a result of leukopenia, the body's resistance to infections, colds, flu, furunculosis and other diseases is reduced. Then hemorrhagic phenomena appear – gingival bleeding from the gums, internal hemorrhages from skin small capillaries, menstrual irregularities, etc. Local effects on the skin are appeared in the form of dermatitis and eczema. Maximum permissible concentration (MPC) of benzene vapor in the air is 20 mg/m^3 [8].

Toluene and xylene act on the body similarly to benzene, but their effect is less, first of all regarding the changes in blood. Their maximum permissible concentration in the air is 50 mg/m^3 [8]. The mass fraction of benzene in petrol of all brands should be less than 5 % [8], and the total content of aromatic hydrocarbons in petrol of A-80 grade should be no more than 42 %, A-92 and A-95 – 45 %, A-98 – 48 % [9].

The toxicity of petroleum products significantly increases in the processing of sulfuric oil. Depending on the petrol grade, the content of bound sulfur in it should be less than 0.05–0.15 %. The lower sulfur content, the higher quality of petrol [9].

The most harmful to the human body is the combination of hydrocarbons and hydrogen sulfide. In this case the toxicity occurs faster than with their separate effect, especially at elevated temperatures [10]. H_2S affects the central nervous system, oxidation processes and blood. In small amounts hydrogen sulfide suppresses the central nervous system, in moderate – excites it, in large ones – causes paralysis of the respiratory and vascular systems. Hydrogen sulfide also has a negative effect on the mechanisms of oxidative processes, reduces the blood ability to be saturated with oxygen. In case of chronic poisoning by H_2S, the ability of hemoglobin to absorb oxygen decreases to 80–85 %, at acute poisoning – up to 15 %; it also decreases the oxidative capacity of tissues. Adaptation to hydrogen sulfide does not occur, but sensuality increases. After previous light poisoning the repeated poisoning becomes possible at lower concentrations. When the effect of hydrogen sulfide is combined with other hydrocarbons, its toxic impact can change. The combined action significantly exceeds the sum of these components individual effects [11]. The average daily MPC of hydrogen sulfide is 0.008 mg/m^3 [8].

Sulfur dioxide (sulfurous anhydride) is the petrol component, the evaporation of which also pollutes the atmosphere. It is a particularly irritating gas that can be recognized by smell and taste, even if it is strongly diluted. It irritates the upper respiratory tract, causes inflammation of the nasal mucosa and nasopharynx, eyes, bronchi. High concentrations of sulfur dioxide in the air cause asphyxiation, loss of consciousness. Its toxic effect appears already at concentrations of 20–30 mg/m^3, which reduces the body's resistance to respiratory diseases. At concentrations of 30–60 mg/m^3 in the air SO_2 affects the mucous of airways and eyes, at 120 mg/m^3 causes asphyxiation [11]. The oxygen atoms of this gas have high reactivity easily enter the chemical reactions with molecules that form the skin cells structure, resulting in serious damage of the skin biochemical equilibrium. The action of sulfur dioxide on the respiratory system increases in the presence of water vapor (fog) with the formation of secondary pollutant – sulfuric acid, the drops of which move over a considerable distance and, getting into the lungs, destroy them [12]. The average daily MPC of sulfur dioxide is 0.05 mg/m^3 [8].

Highly hazardous components of petroleum products are mercaptans and nitrogen oxides. Mercaptans (RSH) are organic derivatives of hydrogen sulfide containing aliphatic, aromatic or heterocyclic compounds. They are formed under thermal effect on the oil containing sulfur, and show a special toxicity. Mercaptans are found in vapours of petroleum products at lower concentrations in comparison with hydrogen sulfide; they have a specific odor, which can be detected in the air even at concentrations of 2·10–9 mg/m^3. Their content in petrol of all grades should be less than 0.001 % [10].

Nitrogen dioxide (NO_2) is a reddish-brown asphyxianting gas, which affects directly the respiratory tissue and prevents the lungs function. Nitrogen dioxide refers to substances of acute action, which requires control over their content in the air. It has an irritating effect on the respiratory tract, leads to pulmonary edema, suppresses aerobic and stimulates anaerobic oxidation in the pulmonary tissue. When getting into the human body, NO_2 in contact with moisture forms nitrous and nitric acid, which erode air-cells. Various chronic diseases are developing if somebody contact with nitrogen dioxide for a long time: rhinopharyngolaringitis, erosion, perforation of the nasal septum, tracheitis, bronchitis, pneumosclerosis [13]. The daily average MPC of nitrogen dioxide is 0.04 mg/m^3 [8].

When standardizing the maximum permissible concentrations of pollutants in the air, the summation of the harmful effects of individual substances is taken into account. It should be noted that the compounds of petrol hydrocarbons (NxOy, NxHy, etc.), which are formed in the atmosphere as a result of photochemical reactions under the influence of sunlight, have two orders of magnitude higher toxicity than the individual hydrocarbons [1].

3. Discussion of results

Results of the analysis regarding the petrol effect on the human body show that its toxicity increases when the combination of hydrocarbons which are components of petrol takes place. Petrol vapours get into organism through the respiratory tract or as a result of absorption by blood from the gastrointestinal tract, which causes partial dissolution of lipids in the body. Due to the low solubility coefficient of petrol vapours in water, and therefore in blood and other body fluids, the inhalation of them results in very rapid saturation of the body with hydrocarbons and other components of the fuel. All types of petrol have a clearly defined effect on the cardiovascular system. One-time and repeated effects of even small concentrations of petrol vapours cause an unstable state of the nervous system of humans and animals. The irritation of the receptors causes excitation in the cerebral cortex, followed by a violation of vision and auditory ability. In the case of acute poisoning, the state resembles alcoholic intoxication at the concentration of petrol vapours in the air of 0.005–0.01 g/m^3 [5].

When petrol is inhaled with the concentration of 1.35–3.15 g/m^3 for 10 minutes, there is no negative effects; the concentration of 4.5–9 g/m^3 for 30 minutes causes pain in the eyes and irritation of the mucous membranes; the concentration of 12.6–31.5 g/m^3 – dizziness, loss of consciousness, difficult breathing; more than 45 g/m^3 is considered lethal concentration for a human. A permanent work with the petrol concentration in the air of 250–300 mg/m^3 causes a violation of reproductive functions – hypofunction of the ovaries, bleeding, deterioration of lactation for women; it also affects the digestive system, especially the liver and pancreas. The smell threshold of petrol is 40 mg/m^3 [5].

Petrol can also penetrate through the skin. The skin does not prevent the penetration of aliphatic hydrocarbons with the amount of carbon in the chain up to 20, and aromatic compounds penetrating through the skin very rapidly, cause inflammation and eczema [5].

Petrol affects the central nervous system, causes acute and chronic poisoning, sometimes with a lethal outcome. The risk of acute poisoning exists at all stages of petrol production, transportation and usage as a solvent. At very high concentrations the acute poisoning occurs immediately. A short stay in the air with high content of petrol vapours causes headache, unpleasant sensations in the throat, cough, irritation of the mucous membrane of the eye, nose, and reddening of the face. Prolonged stay causes dizziness, instable gait, excitement (euphoria, irritability, dysarthria), slow pulse, moderate hypotonia. The high concentrations of petrol (if the victim is not immediately taken out of the contaminated atmosphere) cause strong motor excitation, fibrillary twitching of muscles followed by seizures and loss of consciousness. There are also dilation of the pupils, yellowness of sclera, lability of the pulse, muted heart sounds, weakening of the breath, enlargement of the liver, protein and urobilin in the urine. The breatout air has a smell of petrol. In serious cases an immediate death is possible. Occasionally there is a temporary post-toxic asthenia (headaches, dizziness, general weakness, disturbed dreams). Vegetative disorders and violations of the body's thermoregulation may persist for a long time. Sometimes there may be organic diseases of the central nervous system (a consequence of anoxaemia). Patients with functional disorders of the central and autonomic nervous system, cardiovascular diseases, tuberculosis, as well as pregnant women have a higher sensitivity to petrol. When poisoning with petrol takes place through the mouth there are following symptoms: a suffocating cough, nausea, vomiting, abdominal pain; a few hours later pneumonia progresses [12].

In case of chronic poisoning there are complaints of headaches, dizziness, sleep disorders, irritability, fatigue, weight loss, numbness of the fingers, cramps in the calf muscles, pain in the heart area. Functional disorders of the central nervous system are revealed, often with a tendency to hysterical reactions, vegetative disorders, chronic catarrh of the upper respiratory tract, conjunctivitis, moderate dyspeptic disorders. Often there are vascular disorders, susceptibility to vascular crises, hyperesthesia in the distal limb parts, and other neurological symptoms. For women the disease is more often manifested in the form of climacteric shifts, there is a violation of the menstrual cycle. The adaptation to the small concentrations of petrol is possible. However, the increased sensitivity to petrol may occur – mainly for people with functional diseases of the nervous system [12].

The intensity of petroleum products effect on petrol station staff was estimated on a scale of 1 to 7 points in the direction of increasing the disease severity [4]. The most severe are cardiovascular diseases, which received the highest number of points – 7; among the total number of diseases they account for 2.5 %. Such effects as fetotoxicity (negative effect on intrauterine), kidney necrosis, emphysema, pulmonary edema, necrosis of the liver, convulsions, neuropathy, reproductive function impairment have 6 points and account for 20 %. Pneumonia, changes in the lungs structure, hepatitis, violation of movements coordination – 5 points and 12.5 %; lymphatic cells hypergeneous, kidney atrophy, bronchitis, pulmonary haemorrhage, pancreatic dysfunction, liver dysfunction, testicular hypothyroidism – 4 points and 30 %; allergic reactions, kidney dysfunction, irritation of the lungs, decrease in the average volume of lungs, irritability, nausea, loss of appetite, visual impairment – 3 points and 20 %; irritation of the nasal mucosa, decreased sensitivity of the eye cornea, eye irritation, skin irritation – 2 points and 10 %.

The correlation of the scoring of the intensity of petroleum products effects on humans and their quantities are shown in Fig. 1.

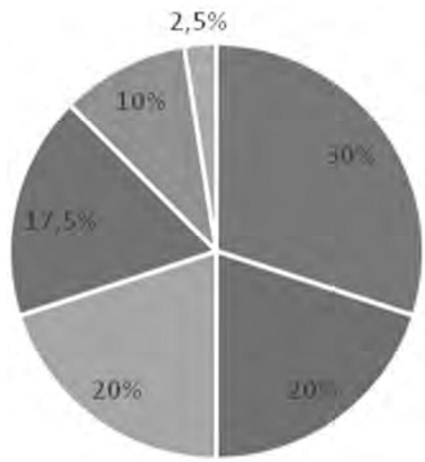

Fig. 1. The correlation of the scoring of the intensity of petroleum products effects on humans and their quantities

Conclusions

Thus, estimating the impact of petrol vapours on the health of petrol station stuff, we see that the increase in diversity of diseases with different degrees of their severity gains a considerable tendency; but the most widespread are pulmonary diseases. This problem is especially urgent, taking into account the increased pollution of air by toxic substances from other sources, in particular, spill of petroleum products and emissions of exhaust gases from motor vehicles. Therefore, in order to improve the ecological situation and to reduce the level of diseases, further work should be directed towards the improvement, implementation and use of methods for avoiding and reducing the emissions, in particular, by introducing some systems for light hydrocarbon fractions recovery during "filling-discharge" operations, their evaporation from the tanks and from other sources.

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