The Dangerous Fire Factors Formation the on an Oil and Gas Complex Objects When Using the Combustible Environment on the Tetrachlormethane Basis

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Abstract. Enterprises of the oil and gas complex related to the budgetary-forming ones and they provide about 50% of the annual budget in our country. At the same time, these enterprises regarded as the most fire-hazard objects. Currently the problems of fire safety provision for the objects of the oil and gas complex are the most especially actual. The development of the enterprises accompanied by a complication of the technological processes and production as well. These processes invariably entail an increase of amount of combustible gases, combustible and volatile flammable liquids at these objects of oil and gas industry. As a result, it became possible the appearance and uncontrolled development of the fires which are capable to lead to the large-scale anthropogenic disasters B along with significant human, material and ecologic losses. Therefore, an estimation of the fire safety for the substances utilized at the objects of oil and gas complex proves to be a key element for the provision of the fire safety at the protected objects.

1. Introduction

All of the objects involved in the oil and gas complex characterized by the presence and circulation of the great amounts of the explosive and fire-hazardous substances and materials. This fact enhances the probability of the fire occurrence in the emergencies. Moreover, a permanent presence of great amounts of fire-hazardous substances located at the limited territory is an inherent feature for such protected objects. The situation even more aggravated by the fact that rather often, the objects of oil and gas industry are located close to the human settlements; the number of the workers is often up to several hundred or even thousand persons; all these factors as a whole can result in the numerous victims if a possible accident or fire occurs. Thus, all these factors make new demands to a further development and improvements in the system of measures related with the prevention and elimination of the large-scale fires at the objects of production and storage of the oil products.

According to the statistical data on the accidents occurred at the objects of oil-refining and petrochemical industry the number of the fires as well as the number of the injured persons is every year decreased, these indicators for Russia are rather poor and they considerably surrender to the similar data for European countries and USA [2].
As an example, one should note that according to the statistical data fire accidents most often occur at the distribution oil depots in 48.3% of cases, in the oil tanks at the petroleum refineries in 27.7% cases, at the oil fields – in 14% and in the oil tanks of the oil pipelines – in 10% of the cases. The main crash scenarios that are dangerous for an oil enterprise and adjacent territory prove to be fire spillage, an explosion of air-fuel mixture and emergency gas pollution [2].

The problems of the estimation of the fire and explosion risk for the substances and materials are actual and they present a practical interest. Results obtained in such investigations can determine the mechanisms and establish mathematical models of formation for the fields of the dangerous fire factors arising in the cases of the different flammable media, which used at the objects of oil and gas complex. Basing on this knowledge it is possible to determine the measures intended at the decrease of the fire risk [3 – 7].

2. Relationship between determinants of the fire risks
Analysis of the world’s experience in describing the damages and losses in case of anthropogenic accidents including the fire ones indicates at the transition from non-reasonable concept of the absolute fire safety to that one of the acceptable and negligible damage. Currently a common tendency observed related with a rejection of the rigid regulations in the management of the fire risks. Unlike it a transition to the paradigm of the risks management based not on the determination of the methods for achieving of the fire safety but on the study of the characteristics for the system of the fire safety for the protected object and a freedom of choice concerning the ways of this goal achievement [8].

Russian Federation proceeded to the concept of flexible regulation in the field of fire safety provision at the legislative level. Practical application of this concept sets an actual task of the development and utilization of the algorithms for the estimation of the fire risk for various substances, a priori calculations that can done by researchers. Moreover, the development and improvements in the technique of the fire risk estimation for the substances used at the objects of oil and gas complex allow predicting consequences of the fires and explosions more accurately. As a result, it will be possible to provide the required measures on the fire protection; By-turn, these measures should be accounted in the determination of the calculated parameters of the fire risk [9].

Scientific substantiation of the principles and ways of provision for the industrial and fire safety at the protected objects due to the determination of the interrelations between the fire risk of the flammable media and composition of substances used at the objects of oil and gas complex, particularly when testing the oil products quality is an actual task as well.

A special place among the substances that most often used at the objects of oil and gas complex belongs to carbon tetrachloride [10].

It known that the estimation of the fire risk can performed based on analysis of the physical phenomena proceeding during fire-hazardous situations, fires explosions [11]. It should kept in mind that the development of fire-hazardous situation is considered step-by-step with the account of the point of its appearance at the protected object, the level of potential risk at each stage as well as the possibility of its localization and elimination. A possibility of systematic development of the situation with fire described with the use of objective function of the fire risk (OFFR) [12].

One of the main determining factors of the fire risk at the object at oil and gas complex is boiling of the flammable substance along with an intensive emission of the vapors and, consequently, increase of the concentration of the flammable medium components in the area of respiration of the persons who are present at the object during the fire. In addition, boiling of the mixtures at the temperatures that are below the combustion temperature also increases the risk of appearance of open flame at the protected object.

3. Regularities of space-time distribution of the fire damaging factors
To find the regularities of the space-time distribution for the damaging factors and their characteristics in a dependence on the chemical composition of the fire substance, conditions of combustion and
parameters of the environment it found mechanism of the formation of the hazardous fire factors when using mixed combustible fuels at the objects of oil and gas complex.

The fields of the fire risk factors (FFRF) arising under the use of combustible fuels based on solvent application can be divided into the following two types of classes.

First, these are FFRF described within the frames of power-entropy concept, determined by the physical processes (evaporation, boiling and some others) and by the chemical process of burning.

According to the results of the laboratory experiments, we obtained the expressions and approximation for the fire risk (with an accuracy uniformly better than 1.5%) with the use of function of the following form:

\[ F(n) = \frac{1 - \exp(-\alpha n)}{1 - \exp(-\alpha)} + \sigma(n - n_e) \]

Where \( n_e \) is correction to Raul’s law; \( \sigma(n_e) \) is a step function; \( \alpha \) is a constant which is determined from the condition of the best coincidence of the approximation with the experimental results.

Algorithm for the regression description of the processes concerned with formation of the fields of fire risk factors divided into the following two factors.

At the first stage, an additive part over concentrations of the components separated.

At the second stage, non-additive contribution into the process described.

Such approach made it possible to determine parameters of a fire with an accuracy sufficient for the practical applications and to formulate a set of the technical and organizational arrangements reducing the risk of fire development at the objects where solvent mixtures are applied.

Let us consider fire-hazardous properties of carbon tetrachloride and its mixtures in details. This reagent itself is non-flammable and it even used previously for fires extinguishing. However, under high temperatures it is capable to form phosgene and molecular chlorine [3, 4].

Analysis of the stages in the mechanism of development of the fire-hazardous situation connected with decomposition of carbon tetrachloride should account for the places of the occurrence at the object of risk estimation, the level of potential danger of each stage as well as the possibility of its localization and elimination.

First, these phenomena can occur in the area of open flame with the following transfer of toxic agents to the area where people found or in the ways of evacuation with the airflow or due to the diffusion.

Second, even in the absence of the open flame it is possible to observe a local increase of temperature due to the heat transfer (first of all, in metals) up to the values resulting in decomposition of carbon tetrachloride.

Since a mechanism triggering succession of the negative impacts is an increase of carbon tetrachloride concentration in the gaseous phase that is especially intensive under boiling an objective function of the risk should first describe just this effect. When using (or because of formation in the process of firefighting) of the complex liquid systems at the object it is also required the calculation of the dependence for the boiling temperature on the relative concentrations of their components.

According to the results of the performed calculations related to physical and chemical properties of the binary combustible fluids with a composition of “carbon tetrachloride – organic solvent” a decrease of the boiling temperature was observed due to the deviation from Raul’s law and this fact enhances the fire risk.

A typical dependence of the fire risk (R) mixtures containing carbon tetrachloride on the temperature and relative concentration of the components presented in Fig. 1.
Figure 1. Typical dependence of the fire risk for the mixture of «carbon tetrachloride – methanol» on the indoor temperature.

It was determined that the fire risk is proportional to the concentration of carbon tetrachloride in the mixture.

Typical objective function of the fire risk in case of utilizing carbon tetrachloride presented in Figs. 2, 3.

Figure 2. Objective function describing fire risk of carbon tetrachloride in the reduced humidity indoor.

In figures 2, 3 one can see the regions where the mechanisms of carbon tetrachloride boiling are realized (76 °C), the area where phosgene is formed (250 °C) formation of the free chlorine (500 °C) as well. Maximum value of the elasticity coefficient for the formation of phosgene (in the plot this is the greatest rate in the change of the risk estimation near the temperature of 250 °C) while the largest value of \( C \) coefficient represents the maximum value of the fire risk in this process.
Thus, technical arrangements comprising in an increase of humidity in case of using carbon tetrachloride make it possible considerably reduce the risk of phosgene formation since under excess of water a great part of carbon tetrachloride decomposed with formation of CO₂. In this case, the fire danger is less than under water deficiency and so; the greatest danger is the mechanism of free chlorine formation at 500°C.

Optimization of the technical solutions directed at the decrease of the fire risk requires an account of the space distribution for the fields of risk factors.

4. Dependence of the integral fire risk
Let us consider local combustion if a gas phase. From the physical viewpoint, this model describes drop-by-drop spraying of combustible liquid. In the frames of the model, temperature field is isotropic relative to the center of combustion and quite rapidly decays with the distance from the center. Mechanism of the uniform combustion in a gas phase realized under the bulk boiling of liquids. This mechanism realized in the area of the open flame.

It is possible to observe a local increase of temperature due to the heat transfer along the building structures (first of all, metal ones) up to the values resulting in decomposition of carbon tetrachloride up to phosgene formation (the latter one is formed even during smoking of a cigarette in the air with carbon tetrachloride. Toxic substances due to decomposition of carbon tetrachloride are transported to the area where there are people or to the routes of their evacuation because of convective or diffusion transfer. Efficiency of the mechanism responsible for an increase of the fire risk connected with boiling considerably enhanced when using of multicomponent solutions as compared with the pure liquids. This effect determined by the deviation of the boiling temperature for the complex system from the additive value for the ideal infinitely diluted solution. The value of this deviation determined by the relative concentration of the components \( n \), thus resulting in a concentration dependence of the fire risk.

Behaviour of the integral fire risk \( \tilde{R} \) in a dependence of the mean distance between the burning drops presented in Fig. 4.
Figure 4. Dependence of the integral fire risk on the mean distance between the points of local temperature increase.

One can see the regions of the rapid danger enhancement under increase of the density of burning drops and overlapping of the areas with toxic contamination (in the lim $r_{\text{max}} \rightarrow 0$) according to Fig. 4. As well as the region of small densities where a great part of premise is characterized by a fixed temperature $T_0$. So here, the value of the fire risk for a mixture is also close to constant value.

5. Conclusion
This, it was found that the characteristics of physical and chemical processes occurring under carbon tetrachloride boiling and a combustible mixture on its basis determine the following variants of a decrease of the fire risk:

1) Location of all the premises where people permanently stay as well as the ways of their evacuation should be higher than the reservoirs for storing and utilization of carbon tetrachloride;

2) Ways for evacuation of the personnel as well as the premises should have ventilation holed in bottom;

3) In order to prevent formation the areas of a local temperature increase up to the values providing decomposition of carbon tetrachloride with the formation of high-toxic components heat-insulating materials should utilized.

When applying binary mixtures of «carbon tetrachloride – combustible organic solvent» and «water – combustible organic solvent» it is necessary to provide certain arrangements concerned with a decrease of the temperature up to the minimal boiling temperature determined by the deviations from Raul’s law. This measure especially important for combustible fluids comprised of organic components where corrections to Raul’s law are large enough since in this case a considerable decrease of $t_{\text{boil}}$ for the mixtures realized in a wide range of the concentrations.

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