

An extinguishing of a hydrogen jet flame by a supply of a gaseous suppressant into fuel and oxidizer

Yury Shebeko^{*}, Aleksey Shebeko^{*†}, Andrey Zuban^{*}, and Vladimir Navzenya^{*}

^{*}All Russian Scientific Research Institute for Fire Protection
VNIPO 12, Balashikha-3, Moscow Region, 143903, RUSSIA
TEL : +7-495-524-82-09

[†]Corresponding address : ay_shebeko@mail.ru

Received : November 24, 2010 Accepted : March 8, 2011

Abstract

An experimental determination of fire extinguishing concentrations of gaseous agents (CHF_3 , C_2HF_5 , C_4F_{10}) in relation to a hydrogen jet flame in air at their simultaneous supply into a fuel and an oxidizer have been carried out. It was revealed that limiting contents of the agents exceed substantially the values calculated according to Le Chatelier rule. This result is interpreted on the basis of the concept of an active chemical influence of fluorinated hydrocarbons on a flame, and this influence can be not only inhibitive, but sometimes also promotive. Analytical estimation were made, which confirm a possibility of a substantial heat release at an interaction of hydrogen with the fluorinated hydrocarbons. It was found that the standard method of a determination of minimum fire extinguishing concentrations using the criterion of a time required for extinguishing (10 ± 2) s gives a remarkable overestimation of the minimum fire extinguishing concentration in relation to the hydrogen jet flame.

Keywords : fire extinguishing concentration, hydrogen jet flame, Le Chatelier rule, fluorinated hydrocarbons.

Introduction

For a fire and explosion safety provision at an accidental release of flammable gases from a technological equipment it is interesting to study conditions of blow-out of jet flames. Many investigations were aimed on a decision of this problem (see for example¹⁾⁻¹²⁾). But these investigations were carried out as a rule either at a supply of a fire extinguishing gas into a fuel flow or an oxidizer flow. The works^{11),12)} are exceptions, in which limiting concentrations of extinguishing agents were determined experimentally and theoretically at their simultaneous supply into a fuel (methane) or an oxidizer (air). The substantial deviations from the classical Le Chatelier rule for the limiting concentrations of combustion were revealed (see also^{13),14)}). Another important question is a possibility of an improvement of the standard method for a determination of minimum fire extinguishing concentrations (MFEC) of gaseous agents. Now in Russian Federation the standard¹⁵⁾ determines such methods, among them the well known cup burner method is the most often applicable. In this method the MFEC value is determined using a limiting

extinguishing time equal to (10 ± 2)s. The analogous approach is stated in the standard¹⁶⁾. At the same time it is known that in the cup burner method the fire extinguishing time depends on the concentration of the gaseous agent. This time unlimitedly increases with an approach of the agent's concentration C_a to some limiting value $C_a^{0,17),19)}$. In the studies²⁰⁾⁻²²⁾ this limiting value C_a^0 was accepted as the minimum fire extinguishing concentration, because an application of the criterion of the extinguishing time (10 ± 2)s can lead to an overestimation of the MFEC value.

This study is aimed on an experimental determination of the fire extinguishing concentrations of gaseous agents in relation to a hydrogen jet flame in air at their simultaneous supply into the fuel and the oxidizer. Such data are absent in literature, but they can be useful from the viewpoint both a safe release of flammable gases from a technological equipment at accidental conditions and an improvement of methods for a determination of MFEC.

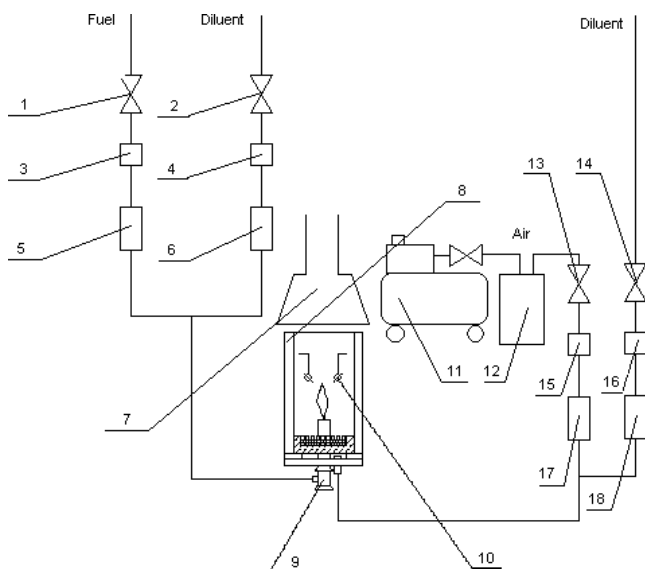


Fig. 1 Diagram of the experimental set-up.
1, 2, 13, 14-valves for a fine regulation of gaseous flows;
3, 4, 15, 16 - electrically driven valves; 5, 6, 17, 18 -
rotameters; 7 - exhaust ventilation; 8 - glass cylinder;
9 - burner; 10 - ignition electrodes; 11 - compressor;
12 - buffer vessel.

Experimental

Experiments were carried out on a set-up, which diagram is presented in Fig.1. The experimental methodology was the following.

A creation of a mixture of a fuel and an extinguishing gas was made in a flow mixer at a supply of hydrogen and an agent into a common pipeline through the electrically driven valves 3 and 4 and the rotameters 5 and 6. The valves 1 and 2 were used for a regulation of gaseous flows. A length of the common pipeline was not lower than 20 diameters of the pipeline, therefore a rather good quality of mixing was provided. The common pipeline was connected with a burner having an internal diameter 10 mm. The rotameters used in this study had working characteristics normalized by air. For an application of these rotameters for gases other than air the measured data were recalculated by the formula,

$$Q_2 = Q_1 \sqrt{\rho_1 / \rho_2},$$

where Q_2 is a flow rate of a fire extinguishing agent; Q_1 is the value measured by the rotameter; ρ_1 and ρ_2 are densities of air and the agent. The ratio ρ_1 / ρ_2 in this formula can be replaced by the ratio M_1 / M_2 , where M_1 and M_2 are the molar masses of air and the agent. The flow rate of the fire extinguishing agent supplied into air was measured by the analogous method.

An output of the gaseous pipeline for a supply of a mixture of air and diluents was located near a burner tube (a distance between this output and the burner tube was 4 cm). In order to prevent of an influence of ambient air the burner was located inside a glass cylinder (8) with a diameter 10cm. For a provision of a uniformity of the flow of the mixture of air and the diluents a layer of glass balls of a diameter 8mm with a thickness 4cm was located in the bottom of the cylinder. A flammable gas was ignited by an electrical spark at an electrical discharge between

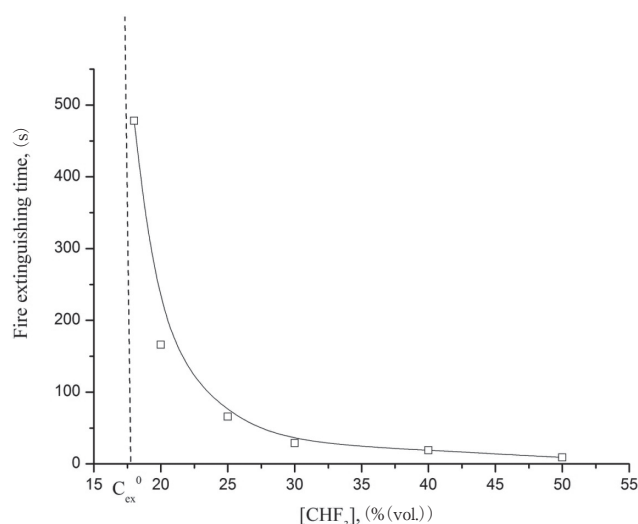


Fig. 2 Typical dependence of a fire extinguishing time on a fluorinated agent concentration at a supply of the agent into air (on the example of trifluoromethane CHF₃).

the electrodes (10). Combustion products were removed by an exhaust ventilation. Hydrogen was used as a fuel gas, and trifluoromethane CHF₃, pentafluoroethane C₂HF₅ and perfluorobutane C₄F₁₀ were diluents. Constant flow rates of the compositions fuel-diluent and air-diluent were maintained. The flow rates of the compositions fuel-diluent and air-diluent are equal to 0,47 и 3,3 l/min appropriately. A flame extinguishing was detected by a web-camera.

Results and discussion

In Fig. 2 the typical results of a determination of a time required to a flame extinguishing τ_{ex} on a concentration of the diluent (CHF₃) supplied into an air flow are presented.

It can be seen that according to the data¹⁷⁻²²⁾ the time τ_{ex} increases substantially with a decrease of the diluents concentration C_{ex}^a in air. This dependence can be described by a formula

$$\tau_{ex} = A / (C_{ex}^a - C_{ex0}^a) \quad (1)$$

where A and C_{ex0}^a are constants. According to^{19,20)} the value C_{ex0}^a is the minimum fire extinguishing concentration, because at the lower values of the diluents concentration a flame extinguishing is impossible at any duration of a supply of the composition air-diluents into the cylinder. For the data presented in Fig. 2 the value C_{ex0}^a is near 17% (vol). It should be noted that at an application the time interval $10 \pm 2s$ ^{15,16)} as the criterion of a flame extinguishing the MFEC value will be near 45 % (vol). From this point of view this time criterion hardly can be effectively used for a determination of MFEC. In our study we used the value C_{ex0}^a as MFEC, which was calculated with an application of the analytical approximation (1) and the least square method for a processing of the experimental data characterizing a dependence of τ_{ex} on C_{ex0}^a at a given diluents's concentration in the hydrogen-fluorinated agent composition.

In Figs. 3-5 the results of the experimental determination of the minimum fire extinguishing

concentrations of the fluorinated agents at their supply into air on their content in the composition fuel-diluent are presented. It can be seen that these dependences are characterized by a substantial nonlinearity that is a deviation from the classical Le Chatelier rule takes place¹³⁾. It should be noted that rather high concentrations of the fluorinated agents are required for an extinguishing of a jet flame at their supply into hydrogen (up to 60% (vol.) in the case of CHF₃). These values are remarkably higher than calculated by the formula obtained earlier^{11),12),14)}:

$$C^f = 4,84\beta \left[\frac{C_{ex0}^a}{1 - (C_{ex0}^a/100)} - \frac{C^a}{1 - (C^a/100)} \right] / \left(1 + 4.84\beta \left[\frac{C_{ex0}^a}{100 - C_{ex0}^a} - \frac{C^a}{100 - C^a} \right] \right) \quad (2)$$

where C^f and C^a are concentrations of diluents supplied simultaneously in the fuel and air, % (vol.); β is a stoichiometric coefficient of oxygen in a reaction of combustion (for hydrogen $\beta = 0.5$).

From Figs. 3-5 it can be seen that the experimental values C^f exceed as a rule the values calculated by the formula (2). This result differs qualitatively from the obtained earlier^{11),12)} for the case, when methane was used as a fuel, and rather good agreement between the experiment and the theory was found. A probable reason of this difference is the following. For combustion of hydrogen the fluorinated agents act as additional oxidizers^{23),25)}, therefore the fire extinguishing concentrations of the fluorinated agents supplied into the fuel are very large and can reach 60 % (vol.) (Fig. 3).

In the studies^{23),25)} a dual role of the fluorinated hydrocarbons as inhibitors and promoters of combustion was revealed. The inhibitive action of the fluorinated agents has the following peculiarities²⁶⁾⁻²⁸⁾:

- an initial inhibitors are consumed mainly in reactions with the radicals H, O and OH. A balance between these reactions depends on a mixture composition. The inhibitor is not regenerated;

- products of the reactions of the initial inhibitors interact also with the radicals H, O and OH, and this determines an effectiveness of inhibition;

- chemical conversion of the fluorinated hydrocarbons in flames cause a formation of large quantities of HF.

Because the inhibitor regeneration does not take place, the rather high inertization effectiveness of the fluorinated hydrocarbons is caused both by the reactions of their molecules and intermediate products of their interactions with the radicals H, O and OH. The larger is a molecule of the agent the larger is a number of the intermediate products, which can cause a chain termination at the reactions of these products with the radicals H, O and OH, and the higher is an inhibitive effectiveness of the agent. This conclusion is confirmed by the experimental data obtained in this study (Figs. 3-5). For example, the MFEC values of CHF₃, C₂HF₅ and C₄F₁₀ at the supply of the agents into air are 16.0, 12.5 and 6.0 % (vol.) respectively, that is the larger is the inhibitor molecule the lower is the MFEC value. The minimum fire extinguishing

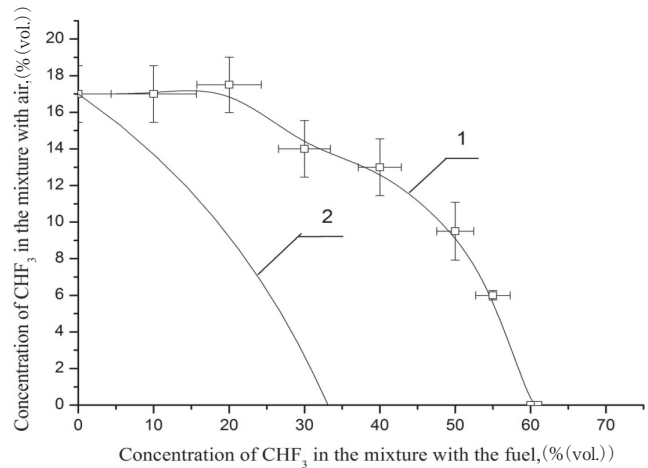


Fig. 3 Dependence of the minimum fire extinguishing concentration of CHF₃ at a supply into air on its content in the mixture with hydrogen. 1 - experiment; 2 - calculations by the formula (2).

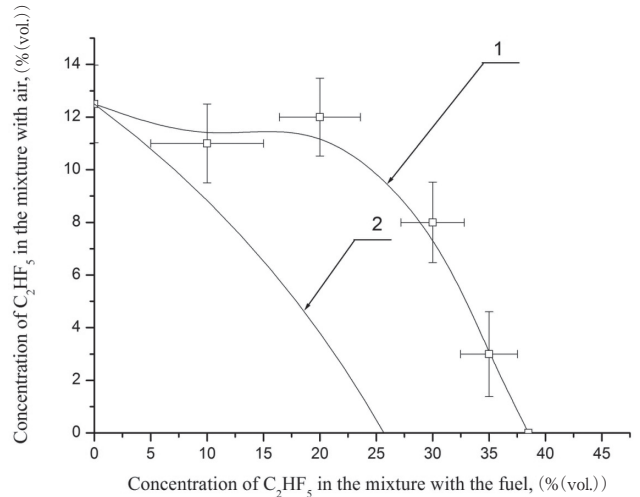


Fig. 4 Dependence of the minimum fire extinguishing concentration of C₂HF₅ at a supply into air on its content in the mixture with hydrogen. 1 - experiment; 2 - calculations by the formula (2).

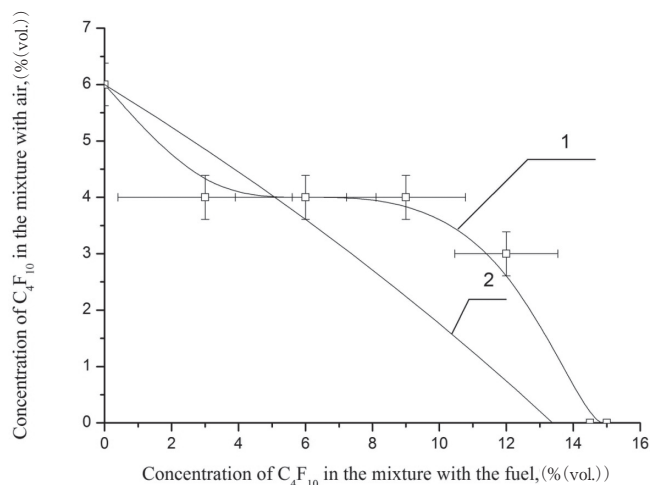
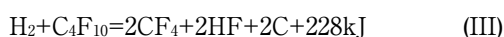
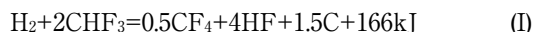


Fig. 5 Dependence of the minimum fire extinguishing concentration of C₄F₁₀ at a supply into air on its content in the mixture with hydrogen. 1 - experiment; 2 - calculations by the formula (2).

concentrations of the agents at their supply into the fuel have qualitatively the same dependence (the MFEC values in this case are equal to 60, 38 and 15 % (vol.)).

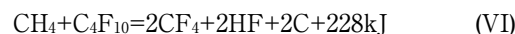
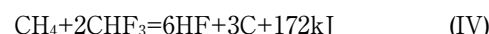
It is interesting to consider more detail the experimental result of the substantial exceeding by MFEC the values calculated by the formula (2) at the agents supply into the fuel, which was obtained in proposition that the agents are chemically inert. But the fluorinated hydrocarbons can act as additional oxidizers of hydrogen in a flame front due to the reaction²³⁾:



These reactions give a substantial heat release, and this effect can be qualitatively explained the mentioned above behavior of the minimum fire extinguishing concentrations. It should be noted also that the values of adiabatic temperatures at a constant pressure at a realization of the proposed reactions (I) - (III) for the appropriate stoichiometric mixtures are equal to 1050, 1000 and 1020 K respectively²³⁾.

Another possible reason of the mentioned above effect of the exceeding by the experimentally measured fluorinated hydrocarbons concentrations the calculated by the formula (2) is a different character of an action of the agents at their supply into air and the fuel. At an agents supply into air the reactions are inhibited, which take place at a diffusion of active centers (mainly H atoms) into the oxidizer (for example the chain branching reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ playing the main role at combustion of hydrogen). But at the agent's supply into hydrogen the fluorinated hydrocarbons does not inhibit combustion reactions, because of oxygen does not present in the fuel flow. Moreover an availability of the fluorinated hydrocarbons in the fuel flow causes the reactions (I) - (III), which give the additional heat release due to a partial hydrogen oxidation. The reactions (I) - (III) are much more less important at the agent's supply into air because of a presence of oxygen in this part of a flame front. Air is a more effective oxidizer in comparison with the fluorinated hydrocarbons. This is confirmed by the fact that air can form flammable mixtures with hydrogen and support a jet flame of this fuel as distinguished from the fluorinated agents.

It is interesting to compare the data in Figs. 3-5 with the results^{11),12)} obtained on the same experimental set-up for the case of a methane jet flame in air. As in this study it was found that the minimum fire extinguishing concentrations of the fluorinated hydrocarbons at their supply into the fuel exceed the values calculated according to the formula (2), but the difference between the experimental and the calculated data is much more lower in comparison with the case of hydrogen as a fuel. This is caused probably by the fact that an oxidation of methane by the fluorinated hydrocarbons in the reactions^{23),24)}



is more difficult in comparison with the case of hydrogen. This question is considered on the basis of an example of an analysis of combustion hydrogen and methane in air using on the basis of a concept of self-inhibition^{29),31)}. In the case of an oxidation by the fluorinated hydrocarbons a preliminary conversion of methane with a formation of radicals H, CH₃, CH₂ etc. is required for an active pass of this process. Without this conversion the reactions (IV)–(VI) hardly will be realized with a remarkable rate at temperatures 900-1000K (these temperatures can take place at an implementation of the reactions (IV)–(VI)^{23),24)}). Analogous reactions with a participation of hydrogen can proceed without a preliminary conversion of the fuel.

From this point of view it is easy to understand the results^{11),12)} on an extinguishing of a methane jet flame at a simultaneous supply of a chemically inert agent (nitrogen) into the fuel and air. It was found that the minimum fire extinguishing concentrations of nitrogen at its supply into the fuel are remarkably lower than calculated according to the formula (2). The probable reason of this effect is the following. Reactions in a part of a flame front close to a stoichiometric contour proceed with a participation of not methane molecules, but mainly via products of its conversion in a preflame zone. It can be expected that the higher is the temperature in the preflame zone the higher is the extent of a conversion of methane molecules and the higher is a rate of the chemical reactions. Additives of nitrogen into the fuel flow decrease the temperature in the flame front (and also in the preflame zone) with the following reduction of the extent of the conversion of methane and the rate of the chemical reaction near the stoichiometric contour.

Our experiments on a determination of the minimum fire extinguishing concentrations of nitrogen supplied with air and hydrogen show the following. The MFEC values of N₂ at the supply into air could not be determined. At the supply of pure nitrogen the fire extinguishing time was 290 s, and at the supply of the composition 96 % N₂+4% air into the reaction vessel the fire extinguishing was not obtained up to the time of 20 min. It is caused probably due to very high values of $C_{\text{ex}0}^a$ for nitrogen. The $C_{\text{ex}0}^a$ value can be evaluated by the formula^{11),12)}

$$C_{\text{ex}0}^a = C_{\text{ex}0}^f / (4.84\beta (1 - C_{\text{ex}0}^f/100) + C_{\text{ex}0}^f/100) \quad (3)$$

where $C_{\text{ex}0}^f$ the minimum fire extinguishing concentration of the chemically inert agent at its supply into a fuel. The value $C_{\text{ex}0}^f$ is equal to 75% (vol.) for combustion of the mixture of hydrogen and nitrogen in air¹⁾. In this case $C_{\text{ex}0}^a = 88\%$ (vol.), and the limiting oxygen concentrations in the oxidizing composition air-nitrogen is near 5% (vol.). At this low limiting oxygen concentration the space non-uniformities in the nitrogen distribution in

the volume of the reaction cylinder are noticeable, and the jet flame occurs to be possible due to an availability of local spaces with the oxygen concentration higher than 5% (vol.) around the internal volume of the cylinder.

Conclusions

In this study an experimental determination of the minimum fire extinguishing concentrations of the fluorinated agents (CHF_3 , C_2HF_5 , C_4F_{10}) in relation to a hydrogen jet flame at their simultaneous supply into a fuel and an oxidizer was carried out. A substantial exceeding by the experimentally measured limiting concentrations of the fluorinated hydrocarbons the values calculated according Le Chatelier rule was obtained, despite of this rule describes the experimental data for a methane jet flame with additives of the same agents rather good. This result is interpreted on the basis of a concept of an active participation of the fluorinated hydrocarbons in combustion processes both as inhibitors and promoters. An analytical evaluation of a heat release at an interaction of hydrogen with the fluorinated agents were carried out, which confirm a possibility of a promotive action of these agents. It was found that the standard method of a determination of the minimum fire extinguishing concentrations based on the value of the extinguishing time (10 ± 2)s can lead to a substantial overestimation of MFEC for hydrogen jet flame in air. On the basis of the obtained results two main practical recommendations can be made: firstly, the possible promotive effects should be taken into account at a practical application of the fluorinated hydrocarbons as fire extinguishing tools, and secondly, the standard method of a MFEC determination needs to be improved.

References

- 1) V. Karpov, *Fire and Explosion Safety*, 3, 36 (1998) (in Russian).
- 2) V. Karpov, *Fire and Explosion Safety*, 4, 40 (1998) (in Russian).
- 3) G. Golinevich, V. Karpov, and A. Fedotov, *Physics of Combustion and Explosion*, 27, 5 (1991) (in Russian).
- 4) G. Kalghatgi, *Combustion Science and Technology*, 26, 233 (1981).
- 5) G. Kalghatgi, *Combustion Science and Technology*, 26, 241 (1981).
- 6) V. Vranos, E. Taback, and C. Shipman, *Combustion and Flame*, 12, 253 (1968).
- 7) F. Takahashi, G. Linteris, and V. Katta, *Combustion and Flame*, 155, 37 (2008).
- 8) S. Liu, C. Soteriou, M. Colket, and J. Senecal, *Fire Safety Journal*, 43, 589 (2008).
- 9) N. Saito, Y. Saso, Y. Ogawa, Y. Otsu, and H. Kukui, *Fire Safety Science. Proceedings of the Fifth International Symposium on Fire Safety Science*, pp. 901-910, IAFSS, Melbourne (1997).
- 10) G. Chamberlain, D. Bradley, P. Gaskell, X. Gu., and D. Emerson, *Fifth International Seminar on Fire and Explosion Hazards*, pp. 394-403, University of Edinburgh, Edinburgh (2008).
- 11) V. Azatyan, Yu. Shebeko, A. Shebeko, and V. Navzenya *Fire Safety*, 1, 54 (2008) (in Russian).
- 12) V. Azatyan, Yu. Shebeko, A. Shebeko, and V. Navzenya, *Seventh International Symposium on Hazards, Prevention, and Mitigation of Industrial Explosions*, pp. 231-241, Torus Press, St. Petersburg (2008).
- 13) R. Chen and R. Axelbaum, *Combustion and Flame*, 142, 62 (2005).
- 14) V. Azatyan, Yu. Shebeko, and A. Shebeko *Fire Safety*, 3, 12 (2007) (in Russian).
- 15) Standard GOST R 53280.3-2009. Automatic fire extinguishing systems. Fire extinguishing agents. Part3. Gaseous fire extinguishing agents. General technical requirements. Testing methods (in Russian).
- 16) NFPA 2001: Standard on Clean Agent Fire Extinguishing Systems. 2008. Edition.
- 17) V. Nikolaev and V. Kryukov, "Combustion and Fire Extinguishing of Polymers in Oxygen-Enriched Atmospheres", p. 74, VNIPO, Moscow (1979) (in Russian).
- 18) V. Eremin, V. Nikolaev, and V. Mikhailov, "Combustion and Fire Extinguishing of Polymers in Oxygen-Enriched Atmospheres", p. 42, VNIPO, Moscow (1981) (in Russian).
- 19) V. Nikolaev and G. Golinevich, "Combustion and Fire Extinguishing of Polymers in Oxygen-enriched Atmospheres", p. 48, VNIPO, Moscow (1981) (in Russian).
- 20) E. Zamishevsky, Yu. Shebeko, A. Trunev, V. Navzenya, and A. Zaitzev, *Physics of Combustion and Explosion*, 34, 2 (in Russian).
- 21) Yu. Shebeko, A. Korolchenko, E. Zamishevski, A. Trunev, V. Navzenya, and A. Zaitzev, *Second International Seminar on Fire and Explosion Hazard of Substances and Venting of Deflagrations*, pp. 769-778, VNIPO, Moscow (1998).
- 22) Yu. Shebeko, A. Korolchenko, E. Zamishevsky, A. Trunev, V. Navzenya, and A. Zaitzev, *Fire and Explosion Safety*, 8, 2 (1999) (in Russian).
- 23) V. Azatyan, Yu. Shebeko, A. Shebeko, and V. Navzenya, *Fire Safety*, 3, 40 (2008) (in Russian).
- 24) V. Azatyan, Yu. Shebeko, A. Shebeko, and V. Navzenya, "Nonequilibrium Phenomena. Plasma, Combustion, Atmosphere". Edited by G. D. Roy, S. M. Frolov, A. M. Starik, p. 221, Torus Press, Moscow (2009).
- 25) V. Azatyan, Yu. Shebeko, I. Bolodian, A. Shebeko, V. Navzenya, and A. Tomilin, *Fifth International Seminar on Fire and Explosion Hazards*, pp. 273-281, University of Edinburgh, Edinburgh (2008).
- 26) S. Kopylov and S. Koltzov, *Fire Safety*, 2, 56 (2005) (in Russian).
- 27) V. Babushok, T. Noto, and D. Burgess, *Combustion and Flame*, 107, 351 (1996).
- 28) G. Linteris, *Combustion and Flame*, 107, 475 (1996).
- 29) V. Azatyan, I. Bolodian, V. Navzenya, and Yu. Shebeko *Journal of Physical Chemistry*, 76, 775 (2002) (in Russian).
- 30) Yu. Shebeko, A. Shebeko, V. Navzenya, and V. Azatyan *Fire Safety*, 4, 65 (2005) (in Russian).
- 31) V. Azatyan, Yu. Shebeko, A. Shebeko, and V. Navzenya, *Journal of Loss Prevention in the Process Industries*, 20, 494 (2007).