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Research of Fire Extinguishing Efficiency of Binary Mixtures of Pentafluoroethane (HFC-125) and Heptafluoropropane (HFC-227ea) with Nitrogen

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Abstract. The problem of using gaseous extinguishants to eliminate fire sources is to inhibit the active radicals of the flame, but at the same time it is necessary to take into account the change in the concentration of oxygen. Therefore, the object of research was the value of the extinguishing concentrations of both individual extinguishants and binary mixtures of halocarbons and inert gases during the elimination of heptanes burning. It has been proven that when nitrogen was supplied, gaseous combustion products were diluted and the relative radiation intensity of hydroxyl radicals decreased to 80 %; on the contrary, when pentafluoroethane (HFC-125) and heptafluoropropane (HFC-227ea) were supplied, the process of chemical inhibition of the combustion reaction took place which led to a significant reduction of the burning rate and, accordingly, the intensity of radiation of hydroxyl radicals by more than 4 times. The joint action of the inert gas and the combustion inhibitor in different ratios did not exceed the intensity of the radiation of hydroxyl radicals of the flame of the inhibitor itself. However, when an inert gas was introduced, the flame was being enriched with fuel and the number of hydroxyl radicals decreased, and the additional introduction of an inhibitor led to a more effective reduction of hydroxyl radicals in the flame. On the basis of the derived results of the experimental studies on the elimination of the fire source of a cup burner with binary mixtures of a halocarbon and an inert gas, it was established that a relatively small dilution of air with nitrogen led to a significant decrease in the extinguishing concentration of the combustion inhibitor. In particular, the extinguishing concentration of heptafluoropropane HFC-227ea for extinguishing n-heptane can be reduced by 2.0 times if, by adding nitrogen, the concentration of oxygen in the air is reduced from 20.5 to 19 % by volume, that is, by only 7 % (relative). The practical value lies in the fact that the derived results of determining the extinguishing concentration of halocarbons, nitrogen and their binary mixtures make it possible to establish the conditions for the elimination of fire sources.

1 Introduction

Currently, the use of automatic fire-fighting systems is one of the most important measures aimed at ensuring reliable fire protection of facilities with the presence of combustible materials. The most promising are systems used for fire prevention by creating the most reliable conditions for the operation of facilities, in particular, by inerting of the atmosphere in the technological equipment or in the room.

Thus, a significant number of fire-fighting systems equipped with halon 1301 or halon 2402, which are ozone-depleting substances and subject to the Montreal Protocol are operated at gas transportation enterprises. In addition, the reserves of halon 1301 and halon 2402 decrease every year, and there arises a need to gradually switch to the use of ozone friendly halocarbons and to include them in the design solutions of newly created gas fire-fighting systems.

Thus, the introduction of new technologies requires both taking into account up-to-date requirements for environmental protection and depends on more effective use of extinguishants. Ways of developing individual gaseous extinguishants, which can be produced using the domestic production and raw materials base, are almost exhausted, but the relevance of this issue remains. An alternative is to use a combination of fire extinguishing compounds, especially in increasing a certain extinguishing factor, for example, flame inhibition.
Therefore, establishing the parameters of the fire-extinguishing ability of binary mixtures of a combustion inhibitor and nitrogen meets the requirements of the concept of creating a unified national system of prevention and response to accidents, disasters and other emergency situations and, accordingly, determines the need for such research.

2 Analysis of Literature Data

In [1], a 20L spherical device and a schlieren system were used to study the suppression effect of CF_3I on the hydrogen explosion pressure and flame characteristics. The results show that CF_3I can promote and inhibit the pressure parameters of hydrogen under lean fuel, but only inhibit the pressure parameters of hydrogen under equivalence ratios and rich fuel. Such as, φ = 0.6, adding 10 % CF_3I, the maximum explosion pressure increased by 8.8 %, φ = 1, adding 5 % CF_3I, the maximum explosion pressure decreased by 25 %. Different from the explosion pressure, the laminar burning velocity of hydrogen with different equivalence ratio decreases gradually with the increase of CF_3I concentration. Numerical simulation was used to reveal the mechanism of CF_3I inhibiting hydrogen. The results show that the concentration of active free radicals(H, O, OH) decreases with the increase of trifluoroiodomethane concentration. Further analysis on the rate of production and sensitivity of H free radicals found that R822 and R839 are the main generation reactions of H free radicals in the fluorine- and iodine-containing elemental reactions, and R1397, R1396, R1391 and R859 are the main consumption of H free radicals reaction. The elementary reaction with the greatest inhibitory effect on H free radicals is R1391, and the elementary reaction with the greatest promoting effect is R850.
In study [2], due to the severe damage of Halon to the stratospheric ozone layer, the urgent need for substitutions for Halon has driven the search for potential alternatives. As a perfluoroolefin substance, R1216 (1,1,2,3,3,3-hexafluoro-1-propene) has a similar chemical structure to the widely used 2-bromo-3,3,3-trifluoro-1-ene (CF_3CBr_2=CH_2, 2-BTP) extinguishants. This study revealed the thermal decomposition and fire-extinguishing performance of R1216 using theoretical calculations and experimental measurements. It was found that R1216 has high thermal stability and does not decompose at 600°C, and not only achieves the purpose of chemical extinguishment by generating perfluoroalkanes, perfluoroolefins and $CF_3\cdot$ radicals that can capture H· and OH· radicals in the flame to interrupt the chain reactions of combustion, but also achieve the goal of cooling by absorbing heat through bond breaking. A combination of physical and chemical inhibition makes R1216 ideal for fire suppression (6.78 and 7.40 % vol for methane and propane flames, respectively). R1216 does not contain Br· and has a global warming potential of 0, which is more environmentally friendly. These findings suggested that R1216 may be a potential Halon substitute with promising applications and deserved further evaluation.
The safety issue of ethanol gasoline and the methods to control or weaken its explosion have attracted attention [3]. To clarify the effect of $C_6F_{12}O$ (perfluoro(2-methyl-3-pentanone)) on the explosion of ethanol gasoline-air mixtures and intrinsic mechanism, the explosion overpressure and flame propagation behavior under different equivalence ratios (φ = 0.6–0.8) and $C_6F_{12}O$ concentrations (χ_{inh} = 0–4.0 %) were experimentally obtained. The detailed inhibitor reaction process was also obtained by CHEMKIN based on a new assembly kinetic mechanism. The results show that the effects of $C_6F_{12}O$ on the explosion characteristics of ethanol gasoline varied with χ_{inh} and φ. For rich flames, $C_6F_{12}O$ is more effective than and heptafluoropropane (C_3HF_7) and nitrogen (N_2) in suppressing explosions; for lean and equivalence ratio flames, the addition of $C_6F_{12}O$ may result in more severe explosions. The decrease in chemical reactivity is mainly because the mole

fractions of OH and H radicals and the proportion of paths H radicals involved decrease after adding $C_6F_{12}O$, and R1500: $CF_3COF + H = CF_3CO + HF$, R965: $CF_2{:}O + H = CF{:}O + HF$, R863: $CF_3 + H = CF_2 + HF$ are main suppressing reactions.

Paper [4] this work presents a thoroughgoing theoretical study on the OH-initiated combustion chemical kinetics and atmospheric degradation mechanism of C_4F_9N by employing high-level quantum chemical methods and RRKM/master-equation theory. Stationary points on potential energy surface were cautiously investigated at B3LYP/6-311++G(d,p) level for geometry optimizations, and thereby their single-point energies were refined by applying CCSD(T)/6-311++G(d,p) method. Based on quantum calculations, kinetics and branching ratios for the major channels were predicted within 300–3000 K and 0.01–100 atm by solving the RRKM/master-equations. The OH addition to C_4F_9N generating M1 dominates the overall kinetics at low temperatures. Subsequently, its two β-scission channels of C–C bonds to $CF_3CF_2N{-}CF(OH) + CF_3$ and $CF_2{-}NCF(OH)CF_3 + CF_3$ become competitive and play a lead role in whole $C_4F_9N + OH$ system at the corresponding high temperatures and elevated pressures. The CF_3 radical generated prompts these two routes to potentially have the significant contribution to flame inhibition in actual applications. Additionally, the complex degradation pathways of C_4F_9N were also looked into by successively reacting with various oxides, including OH, O_2, NO, and HO_2, to finally generate the removal products $CF_3CF_2N(OOH)CF(OH)CF_3$, CF_3CFO, and CF_3CF_2NO. The atmospheric lifetime of C_4F_9N was evaluated as 49 years regarding to the kinetic for one step addition of OH radical.

In [5], the fluorinated materials developed to replace materials banned from manufacture under the Montreal Protocol are themselves contributors to environment damage. In particular, their contribution to global warming is under scrutiny from customers, regulators and pressure groups. This paper provides a comparison of the global warming and other impacts associated with two possible replacements for Halon 1301 (a banned fire extinguishant), namely an 'in-kind' compound CF_3CHFCF_3 (HFC-227ea) and a 'not-in-kind' blend of nitrogen, argon and carbon dioxide (IG-541). The impacts associated with the manufacture and deployment of the HFC-227ea are found to be substantially greater than those of the inert gas mixture designed for the same fire-extinguishing duty. The impacts during manufacture reveal an important issue for the widely used measure of global warming impact—the so-called Total Equivalent Warming Impact (TEWI). The present work clearly reveals that where impacts associated with manufacture are significant, the scope of the TEWI analysis needs to cover the manufacturing process if it is to be meaningful.

In study [6], a kinetic model is presented for high-temperature oxidation and combustion of the refrigerants: 2,3,3,3-tetrafluoropropene (R-1234yf), 1,3,3,3-tetrafluoropropene (R-1234ze(E)), and 3,3,3-trifluoropropene (R-1243zf) at atmospheric pressure. The kinetic model is based on: GRI-Mech-3.0 and previously developed models for the inhibition of hydrocarbon flames by 2-bromo-3,3,3-trifluoropropene (2-BTP) and C_1-C_2 hydrofluorocarbons. The model includes 1001 reactions and 105 species. Thermodynamic equilibrium calculations indicate a maximum combustion temperature of 2047 K, 2037 K, and 2312 K for R-1234yf, R-1234ze(E), and R-1243zf, respectively, in air for standard conditions. Calculations of the 1D, steady, adiabatic, laminar burning velocity for these refrigerants with air or oxygen-enriched air indicate reasonable agreement with experimental data from the literature when the burning velocity is above 10 cm/s. The simulations are used to understand the relevant reactions. Despite the relatively high F/H ratio in the reactants (2), the combustion is dominated by reactions with radical pool radicals typical of hydrocarbons (O, OH, and H). The combustion of R-1234yf or R-1234ze(E) is characterized by a two-zone flame, the second of which is a slow reaction zone accounting for CO and CF_2O consumption and additional temperature rise of a few hundred K. Simulations of the effects of water vapor on the burning velocity of R-1234yf and R-1234ze(E) capture qualitatively the trends in the experimental results. For certain values of the equivalence ratio and oxygen content of air, the premixed flame structure shows temperature peak in the main reaction zone higher than the equilibrium value.

In study [7], reactions of HBr with radicals are involved in atmospheric chemistry and in the mechanism of operation of bromine-containing flame retardants. The rate coefficients for two such reactions, HBr + OH and HBr + CH_3, are available from earlier experiments at near or below room temperature, relevant for atmospheric chemistry, and in this domain, the activation energy for both has been found to be negative. However, no experimental data are available at combustion temperatures. In this work, to provide reliable data needed for modeling the action of brominated flame suppressants, we used the quasiclassical trajectory (QCT) method in combination with high-level ab initio potential energy surfaces to evaluate the rate coefficients of the two title reactions at combustion temperatures. The QCT calculations have been validated by reproducing the experimental rate coefficients at room temperature. At temperatures between 600 and 3200 K, the QCT rate coefficients display positive activation energies. The conventional transition state theory has been tested against the rate data obtained by the QCT method and was found to overestimate not only the rate coefficients but also the activation energies.

In [8], a study was conducted hydrogen is considered a leading clean energy carrier and versatile industrial raw material, playing a crucial role in driving down greenhouse gas emissions. Ensuring the safe utilization of hydrogen holds paramount significance. The present study investigated the variation law of the lower flammability limit of hydrogen under the influence of inhibitors (carbon dioxide, nitrogen, and heptafluoropropane) through experimental testing. The critical inhibitory concentration required for complete suppression was determined. Additionally, the explosive characteristics under the influence of inhibitors were evaluated, and the inhibitory mechanism was analyzed in conjunction with chemical kinetics. With an increase in the quantity of inhibitors added, there was a corresponding increase in the lower flammability limit of hydrogen, as demonstrated by the results. When 10% volume fraction of heptafluoropropane was added, the lower flammability limit of hydrogen increased by 94.74 %. At lean Burn conditions, the inhibitory effect of carbon dioxide on the maximum explosion pressure, adiabatic flame temperature, and heat release rate of hydrogen was higher than that of nitrogen. When the heptafluoropropane inhibitor was added, the explosion pressure, adiabatic flame temperature, and heat release rate of Hydrogen-Air flame showed an increasing trend followed by a significant decrease. As the addition of heptafluoropropane inhibitor increased, the consumption of active free radicals such as hydrogen radicals and hydroxyl by fluorine-containing free radicals interrupted the chain reaction, thus inhibiting the combustion reaction process. Additionally, it was determined that the critical inhibitory concentrations of the three inhibitors for hydrogen with different volume fractions are ranked in order from low to high as heptafluoropropane < carbon dioxide < nitrogen. The research results can promote the safe utilization of hydrogen energy.

Paper [9] considers this study examines the suppression effectiveness of fluorinated species CHF_3 and C_2HF_5 on the premixed hydrogen-air explosions experimentally and numerically. The results demonstrate that as for stoichiometric and rich hydrogen-air mixtures, both CHF_3 and C_2HF_5 can effectively reduce thermal expansion ratio and increase flame thickness, and then reduce the influence of hydrodynamic instability on the flame acceleration. Laminar burning velocity, the maximum of explosion pressure, the maximum rate of pressure rise and the absolute value of pressure impulse all decrease with increasing suppressant concentration at various equivalent ratios. The maximum of explosion pressures for stoichiometric flames is decreased by 11.54 % with 2 % CHF_3 added, and decreased rapidly by 40.39 % with 2 % C_2HF_5 added. The hydrogen-rich mixtures cannot be ignited when C_2HF_5 content reaches 10 %. Numerical simulations have confirmed that both CHF_3 and C_2HF_5 can effectively reduce the concentration of active radicals with the decrease order of H > OH > O. C_2HF_5 is more effective in suppressing explosions than CHF_3 by converting more H atoms to HF formation through the elementary reactions CHF_2 + H <=> CHF + HF, CF_2:O + H <=> CF:O + HF, and CF_2 + H = CF + HF.

In work [10], it was proposed to investigate to explore the inhibition and enhancement of hydrogen explosion by perfluorohexanone ($CF_3CF_2COCF(CF_3)_2$), the experiments are conducted by changing the equivalence ratio, inhibitor content, initial pressure and initial temperature, and the maximum explosion overpressure (MEO), maximum rate of pressure rise (MRPR) and critical content of

explosion inhibition are obtained. The adiabatic flame temperature, sensitivity coefficient and mole fraction of active radicals are calculated using CHEMKIN. The results show that on the lean side, the sub-inhibitory perfluorohexanone generates CO to be involved in the combustion, and the formation of HF releases lots of heat, which causes the combustion enhancement. On the stoichiometric and rich sides, H is captured by other fluorides, exhibiting the inhibitory effect. Increasing the initial pressure (initial temperature) causes an increase (decrease) in the MEO and the MRPR. As the equivalence ratio increases, initial pressure reduces and initial temperature increases, the critical content of explosion inhibition is effectively reduced.

In [11], a numerical investigation is performed to understand the inhibition characteristics of CF_3H in a periodically oscillating methane–air jet diffusion flame formed over a cup burner. A detailed chemical kinetic mechanism having 82 species and 1510 elementary-reaction steps is used. Calculations made without adding agent yielded an oscillating flame with a flicker frequency of 11 Hz, which compared well with that obtained in the experiment. The minimum concentration of agent required for extinguishing the cup-burner flame is determined by adding CF_3H to the air stream and by increasing its volume fraction gradually until the flame is completely extinguished. Addition of CF_3H at volume fractions up to 10.05 % did not affect the cup-burner flame temperature significantly. Extinction of a cup-burner flame took place as the base of the flame became destabilized, and the unstable flame base moved downstream in search of a new stabilization location. The predicted minimum concentrations of CF_3H for extinguishing the flame obtained by (1) replacing the air with CF_3H and (2) replacing the N_2 in the air with CF_3H are 10.1 and 19.2 %, respectively. These concentrations compare favorably with the corresponding measured values of 11.7 and 20.3 %, respectively. For validation, calculations are also made for the steady counterflow diffusion flames with different concentrations of CF_3H in the air stream and the predicted volume fractions of agent at extinction are in good agreement with the experimental values published in the literature. Examination of the reaction rates for the cup-burner flames indicates that the reactions with fluorinated species reduce the concentration of chain-carrying radicals in the flame. The effect is stronger at the flame base than further up in the trailing part of the flame, leading to destabilization at the flame base prior to extinction in the trailing region, and yielding the observed blowoff-type extinction.

In [12], computations of cup-burner flames in normal gravity have been performed using propane as the fuel to reveal the combustion inhibition and enhancement by the CF_3Br (halon 1301) and potential alternative fire-extinguishing agents (C_2HF_5, $C_2HF_3Cl_2$, and $C_3H_2F_3Br$). The time-dependent, two-dimensional numerical code used includes a detailed kinetic model (up to 241 species and 3918 reactions), diffusive transport, and a gray-gas radiation model. The peak reactivity spot (i.e., reaction kernel) at the flame base stabilizes a trailing flame, which is inclined inwardly by a buoyancy-induced entrainment flow. As the volume fraction of agent in the coflow increases gradually, the premixed-like reaction kernel weakens, thus inducing the flame base detachment from the burner rim and blowoff-type extinguishment eventually. The two-zone flame structure (with two heat-release-rate peaks) is formed in the trailing diffusion flame. The H_2O formed in the inner zone is converted further, primarily in the outer zone, to HF and CF_2O through exothermic reactions most significantly with the C_2HF_5 addition. The total heat release of the entire flame decreases (inhibiting) for CF_3Br but increases (enhancing) for the halon alternative agents, particularly C_2HF_5 and $C_2HF_3Cl_2$. Addition of C_2HF_5 results in unusual (non-chain branching) reactions.

Thus, it has been established from literary sources that the rate of flame burning of organic substances occurred according to a chain mechanism due to the formation of free radicals in the flame and is proportionally dependent on the concentration of hydroxyl radicals, the inhibition of which required the use of effective environmentally friendly combustion inhibitors. Therefore, establishing the parameters of the use of halocarbons and their mixture with inert gases and their influence on the process of extinguishing the flame determined the need for research in this sphere.

Purpose of the research. The purpose of this work is the revelation of specific features of interaction of active flame radicals with extinguishants and research of the processes of flame extinguishing which is the base for application both new and modernized extinguishants.

3 Materials and Research Methods

In order to identify the effect on the active radicals of the flame of some gaseous extinguishants such as pentafluoroethane (HFC-125), heptafluoropropane (HFC-227ea) and nitrogen, experimental studies were conducted. The work was carried out at a test rig for researching the inhibitory properties of solid, liquid and gaseous substances. Flame radiation was recorded using the SDL-1 spectrometer [13]. A decrease in the radiation intensity of the 3064 A band belonging to the OH radical, which is responsible for the propagation of the combustion chain reaction was taken as a measure of the inhibitory effect. n-heptane vapour obtained by the carburation method was used as a combustible substance.

Inert gases were supplied to the burner together with n-heptane vapours while controlling the flow rate with a flow meter. With the help of the gas dosing unit, a certain amount of pentafluoroethane (HFC-125) and heptafluoropropane (HFC-227ea) vapours (gases) were supplied to the burner nozzle to determine the extinguishing concentration.

To study of the laws of using binary mixtures of fire extinguishants to eliminate burning, a device for determining the extinguishing concentrations of gaseous extinguishants was used, which has been modified [14]. The required concentration of halocarbon was produced in the gas-air mixture block and the mixture was supplied to the test chamber where the fire source was located [15].

The principle of determining the extinguishing concentration of gaseous extinguishants by the “cup burner” method (EC-CB) is based on the creation of a laminar flow of a gas-air mixture of a given composition by mixing in dynamic conditions the flows of its components, which come from dosing devices with given flow rates. The upward flow of the gas-air mixture sweeps the test fire. By gradually increasing the consumption of gaseous extinguishant, extinguishing the flame of the test fire is achieved. The volumetric concentration of the gaseous extinguishant at this moment, calculated from the consumption values of the components of the gas-air mixture, is considered the extinguishing concentration [16].

The value of the extinguishing concentration of nitrogen C_{ex} (% by volume) was determined by the following formula:

$$C_{ex} = V_g \times 100/(V_g + V_o) \quad (1)$$

where V_g – is the nitrogen flow rate (dm^3/min.) at which extinguishing of fire in test fire is achieved; V_o – is the oxidizer flow rate (dm^3/min.).

4 Discussion of Results

The results of determining the characteristics of the interaction with the flame of inert gases and halocarbons are shown in Fig. 1.

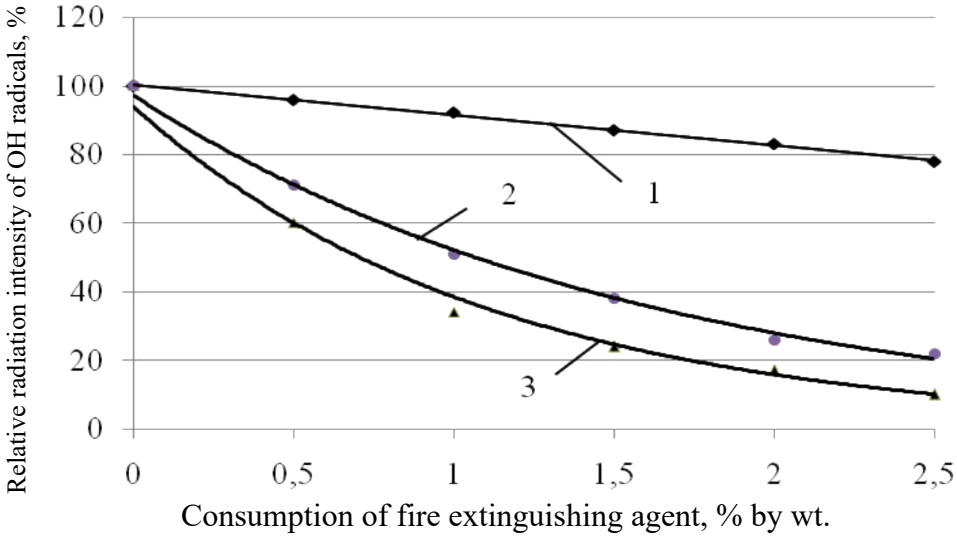

Fig.1. Dependency of relative radiation intensity of hydroxyl radicals on the flow rate of gaseous extinguishants supplied to n-heptane flame: 1 – nitrogen; 2 – pentafluoroethane (HFC-125); 3 – heptafluoropropane (HFC-227ea)

The resulting dependences demonstrate a decrease in radiation intensity. When nitrogen is supplied, gaseous combustion products are diluted and the relative radiation intensity of hydroxyl radicals decreases to 80 %; on the contrary, when pentafluoroethane (HFC-125) and heptafluoropropane (HFC-227ea) are supplied, the process of chemical inhibition of the combustion reaction takes place, which leads to a significant reduction in the burning rate and, accordingly, the radiation intensity of hydroxyl radicals more than 4 times.

Since it is impossible to predict the nature of the joint action of halocarbons and inert gases on the combustion reaction, experimental studies were conducted on the effect of mixtures of nitrogen with pentafluoroethane (HFC-125) and heptafluoropropane (HFC-227ea) on the flame. The results of the research are shown in Fig. 2.

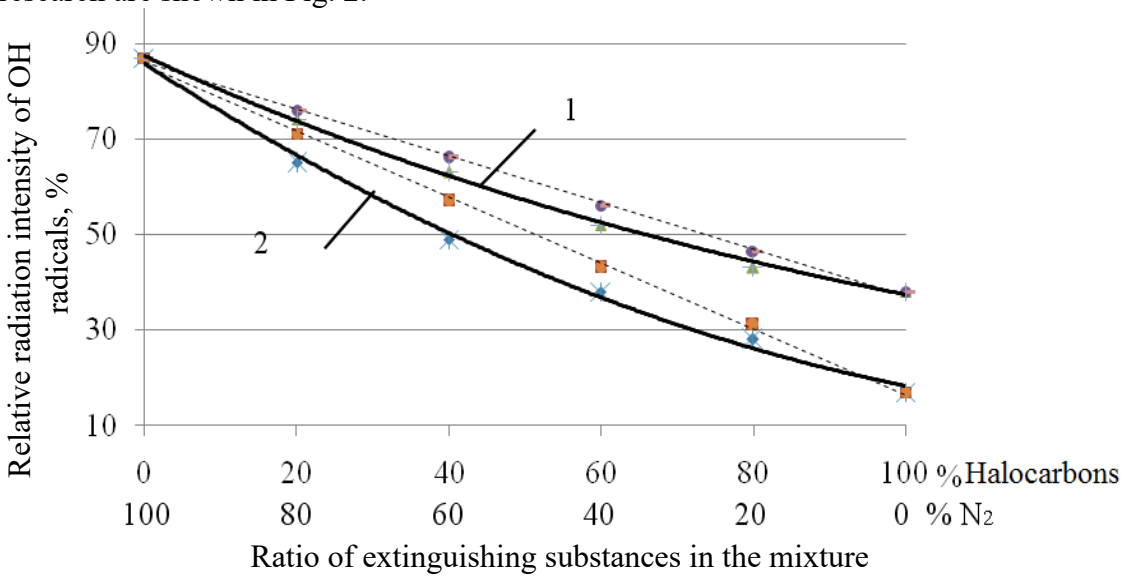

Fig. 2. Dependency of relative radiation intensity of hydroxyl radicals on the ratio in the mixture of gaseous extinguishants supplied to n-heptane flame: 1 – pentafluoroethane (HFC-125) and nitrogen; 2 – heptafluoropropane (HFC-227ea) and nitrogen. The dashed line shows additive effect of joint action

It can be seen from Fig. 2 that the effect of the mixture of inert gas and combustion inhibitor in different ratios does not exceed the intensity of the radiation of hydroxyl radicals of the flame of the inhibitor itself, but the effect of deviation from additivity towards synergistic action is noted. When an inert gas is introduced, the flame is enriched with fuel and the number of hydroxyl radicals

decreases, while the additional introduction of an inhibitor leads to a more effective reduction of hydroxyl radicals in the flame.

It is known that lower concentrations of halocarbons are required to stop flame burning in oxygen-depleted gas environments, since this effect is achieved by using so-called combined compositions. The basis for the use of "halocarbon + inert gas" compositions was the fact that extinguishing concentration of halocarbon depends on the oxygen content and its nature is quite complex.

To confirm this dependence, a cycle of studies of the regularities and mechanism of this effect was carried out by extinguishing heptane flame with two-component gas fire extinguishants. Mixtures of pentafluoroethane HFC-125 and heptafluoropropane HFC-227ea with nitrogen were studied to determine the extinguishing concentration when extinguishing heptane. Experimental data on extinguishing concentrations during extinguishing of n-heptane using their combinations are shown in Fig. 3 and 4.

The results derived by us of the extinguishing concentration by the "cup burner" method (Fig. 3) show a significant difference in the action of the combustion inhibitor and the inert gas when extinguishing the flame.

As can be seen from Fig. 4, the results deviate significantly from the linear dependence, that is, there is a significant deviation from additivity caused by the synergistic effect of the combustion inhibitor and the inert gas. Thus, a relatively small dilution of air with nitrogen leads to a significant decrease in the extinguishing concentration of the combustion inhibitor, where extinguishing the flame of a gas-air environment with a variable oxygen content was conducted using the inhibitors of pentafluoroethane (HFC-125) and heptafluoropropane (HFC-227ea).

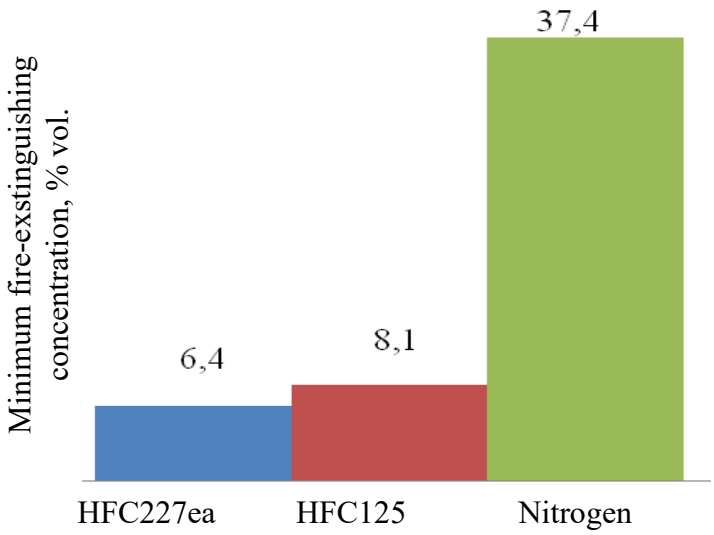

Fig. 3. Results of the determination of extinguishing concentrations when extinguishing n-heptane flame with gaseous extinguishants

In particular, the extinguishing concentration of heptafluoropropane HFC-227ea for extinguishing n-heptane can be reduced by 2.0 times if, by adding nitrogen, the concentration of oxygen in the air is reduced from 20.5 to 19 % by volume, i.e. by only by 7 % (relative) (Fig. 4 , curve 2).

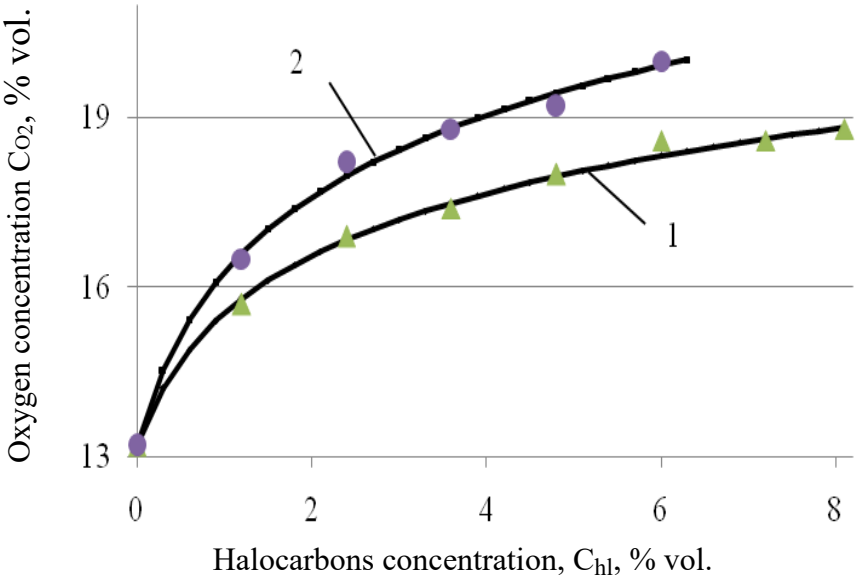

Fig. 4. Conditions of n-heptane burning cessation in mixtures of air with two-component gaseous extinguishant for the following mixtures: 1 – pentafluoroethane (HFC-125) and nitrogen; 2 – heptafluoropropane (GFC-227ea) and nitrogen

Thus, as the addition of the heptafluoropropane inhibitor increases, the consumption of active free radicals such as hydrogen and hydroxyl radicals by fluorine-containing free radicals interrupts the chain reaction, thus inhibiting the combustion reaction process, and a relatively small dilution of air with nitrogen results in a substantial reduction of free radicals of flame and reducing the amount of combustion inhibitor. In addition, it was determined that the critical inhibitory concentrations of two inhibitors for combustible media with different volume fractions were located in the order from low to high as heptafluoropropane < pentafluoroethane < nitrogen, since heptafluoropropane contained a larger number of fluorine atoms which react with active flame radicals.

Therefore, the elimination of fire sources is closely related to the reduction of oxygen concentration in the gas-air environment which is confirmed by [16, 17]. However, heptafluoropropane is more effective in flame suppression than pentafluoroethane because it converts more H atoms to form HF.

Consequently, the elimination of fire sites is closely related to a decrease in the concentration of oxygen in the gas-air environment, which is confirmed in [19, 20]. The results of the experimental studies conducted can be used as input data for the technical and economic justification of the choice of the quantitative ratio of the inert gas and the combustion inhibitor in case of their joint application for the purpose of preventing and extinguishing fires.

Summary

The experimental studies have established that when nitrogen was supplied, gaseous combustion products were diluted and the relative radiation intensity of hydroxyl radicals decreased to 80 %, on the contrary, when pentafluoroethane (HFC-125) and heptafluoropropane (HFC-227ea) were supplied, a process of chemical inhibition of the combustion reaction took place, which led to a significant decrease in the burning rate and, accordingly, the intensity of radiation of hydroxyl radicals by more than 4 times.

The joint effect of the inert gas and the combustion inhibitor in different ratios does not exceed the intensity of the radiation of hydroxyl radicals of the flame of the inhibitor itself. However, when an inert gas is introduced, the flame is enriched with fuel and the number of hydroxyl radicals decreases, and the additional introduction of an inhibitor leads to a more effective reduction of hydroxyl radicals in the flame.

On the basis of the derived results of experimental studies on the elimination of the fire source of a cup burner with binary mixtures of a halocarbon and an inert gas, it was established that a relatively small dilution of air with nitrogen led to a significant decrease in the extinguishing concentration of the combustion inhibitor. In particular, the extinguishing concentration of heptafluoropropane for extinguishing n-heptane can be reduced by 2.0 times if, by adding nitrogen, the concentration of oxygen in the air is reduced from 20.5 to 19 % by volume, that is, by only 7 % relative.
Further research will be aimed at studying the processes of inerting of combustible media, establishing the relationship between the components and properties of binary mixtures of gaseous extinguishants and their optimization.

References

[1] Z.-M. Luo, F. Nan, F.-M. Cheng, R.-K. Li, B. Su, Study on the inhibition of hydrogen explosion pressure and flame propagation by trifluoroiodomethane. International Journal of Hydrogen Energy. 49 (2023) 670–680.

[2] S. Li, X. Zhang, X. Li, X. Wang, J. Li, Theoretical and experimental studies on the thermal decomposition and fire-extinguishing performance of 1,1,2,3,3,3-hexafluoro-1-propene (R1216). International Journal of Quantum Chemistry. 123(22) (2023) e27217.

[3] X. Mu, H. Cong, Z. Shao, Bi M. Mingshu, X. Wang, Experimental and theoretical research on the inhibition performance of ethanol gasoline/air explosion by $C_6F_{12}O$. Journal of Loss Prevention in the Process Industries. 83 (2023) 105088.

[4] J. Zhao, Y. Wang, B. Zhou, H. Bian, Chemical mechanism and atmospheric degradation of C_4F_9N initiated by OH radical: Ab initio kinetic exploration. International Journal of Quantum Chemistry. 123(5) (2023) e27049.

[5] R.E. Banks, E.K. Clarke, E.P. Johnson, P.N. Sharratt, Environmental Aspects of Fluorinated Materials: Part 31: Comparative Life-cycle Assessment of the Impacts Associated with Fire Extinguishants HFC-227ea and IG-541. Process Safety and Environmental Protection. 3 (76) (1998) 229-238.

[6] V.I. Babushok, D.R. Burgess, M.J. Hegetschweiler, G.T. Linteris, Flame propagation in the mixtures of O_2/N_2 oxidizer with fluorinated propene refrigerants (CH_2CFCF_3, $CHFCHCF_3$, CH_2CHCF_3). Combustion Science and Technology. 11(193) (2021) 1949–1972.

[7] S. Góger, P. Szabó, G. Czakó, G. Lendvay, Flame Inhibition Chemistry: Rate Coefficients of the Reactions of HBr with CH_3 and OH Radicals at High Temperatures Determined by Quasiclassical Trajectory Calculations. Energy and Fuels. 32(10) (2018) 10100–10105.

[8] H. Liang, T. Wang, Z. Luo, J. Deng, J. Shi, Investigation on the lower flammability limit and critical inhibition concentration of hydrogen under the influence of inhibitors. Fuel. 356 (2024) 129595.

[9] M. Gao, M. Bi, L. Ye, C. Yan, W. Gao, Suppression of hydrogen-air explosions by hydrofluorocarbons. Process Safety and Environmental Protection. 145 (2021) 378–387.

[10] J. Zhang, W. Gao, L. Chen, Y. Li, Inhibition and enhancement of hydrogen explosion by perfluorohexanone. International Journal of Hydrogen Energy. 53 (2024) 522–534.

[11] R.K. Viswanath, F. Takahashi, T. G. Linteris, Fire-suppression characteristics of CF_3H in a cup burner. Combustion and Flame. 144 (2006) 645–661.

[12] F. Takahashi, V.R. Katta, G.T. Linteris, V.I. Babushok, A computational study of extinguishment and enhancement of propane cup-burner flames by halon and alternative agents. Fire Safety Journal. 91 (2017) 688–694.

[13] B.G. Tagiev, G.M. Niftiev, F.Sh. Aidaev, Photoluminescence and electroluminescence of GaS: Tm single crystals. Solid State Communications. 4(55) (1985) 385–386.

[14] Y. Tsapko, K. Sokolenko, R. Vasylyshyn, O. Melnyk, A. Tsapko, O. Bondarenko, A. Karpuk, Establishing patterns of nitrogen application for fire safety of sunflower grain storage facilities. Eastern-European Journal of Enterprise Technologies. 10 (119) (5) (2022) 57–65.

[15] R. Likhnyovskyi, Y. Tsapko, V. Kovalenko, A. Onyshchuk, The Possibility of Using 1301 and 2402 Mixtures of Halons for Fire Extinguishing Purposes. Key Engineering Materials. 954 (2023) 135–144.

[16] ISO 14520-1. Gaseous fire-extinguishing systems. Physical properties and system design. Part 1: General requirements. 2023. 106. https://www.iso.org/standard/79444.html

[17] R. Likhnyovskyi, A. Tsapko, V. Kovalenko, O. Slutska, P. Illiuchenko, R. Kravchenko, M. Sukhanevych, Determining the thermal-physical characteristics of a coke foam layer in the fire protection of cable articles with foaming coating. Eastern-European Journal of Enterprise Technologies. 10 (122) (2023) 22–30.

[18] Y. Tsapko, R. Likhnyovskyi, A. Tsapko, V. Kovalenko, O. Slutska, P. Illiuchenko, K. Sokolenko, Y. Gulyk, Determining the patterns of extinguishing polar flammable liquids with a film-forming foaming agent. Eastern-European Journal of Enterprise Technologies. 3/10 (123) (2023) 48–56.

[19] H. Ji, Y. Li, H. Su, W. Cheng, X. Wu, Experimental investigation on the cooling and inerting effects of liquid nitrogen injected into a confined space. Symmetry. 11(4) (2019) 579.

[20] H. Liu, F. Wang, Research on N_2 - inhibitor-water mist fire prevention and extinguishing technology and equipment in coal mine goaf. PLoS ONE. 14(9) (2019) e0222003.