Highly Effective Fire Extinguishing Mixtures of Iodinated and Fluorinated Hydrocarbons as a Way to Reduce Greenhouse Gas Emissions into the Atmosphere

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Abstract. One of possible ways to reduce the volume of the use of hydrofluorocarbons (HFCs) as gaseous fire suppressants is studied in the paper. Extinguishing mixtures of HFCs and some fluoroiodocarbons are investigated. It is theoretically predicted that fluoroiodohydrocarbons are effective inhibitors of conversion of fluorinated alkanes in a flame. Special experimental equipment allowing to measure fire extinguishing concentration of gaseous fire suppressant having high boiling point is described. Experiments show that fluoroiodohydrocarbons are effective means of reducing the use of gaseous fire extinguishing agents based on fluorinated alkanes, which are greenhouse gases: in the presence of insignificant addition of iodized substance the volume of fluorinated alkanes required for the extinguishing decreases several times. Creation of mixtures with the content of iodized components higher than 5 mass. is impractical because in this case the iodine-containing substance will exceed safe level of its use from the point of view of toxicity

1. Introduction
Fluorinated hydrocarbons (HFCs) are widely used in fire suppression, in particular, HFC 23 (CF3H), HFC 125 (C2F5H) and HFC 227ea (C3F7H). It is well known that these substances have zero ozone depleting potential (ODP), but they are powerful greenhouse gases having tens and hundreds of years of atmospheric lifetime and thermally influencing the atmosphere thousands of times higher than carbon dioxide due to their global warming potential, GWP (see table 1). Modern situation in fire safety does not allow to ban the usage of HFCs in gaseous fire suppression. In accordance with international agreement [2] consumption of HFCs in any sector of their application should be reduced in the developed countries by 85 % by 2036.
Table 1. Ecological characteristics of some gaseous fire suppressants [1].

|                | Ozone Depleting potential (ODP) | Global Warming Potential (GWP) | Atmospheric Lifetime, years |
|----------------|---------------------------------|-------------------------------|-----------------------------|
| HFC 23         | 0                               | 14,200                        | 222.0                       |
| HFC 125        | 0                               | 3,420                         | 28.2                        |
| HFC 227ea      | 0                               | 3,580                         | 38.9                        |

One of the possible ways to reduce the volume of the use of HFCs as gaseous fire suppressants is to create fire extinguishing gas mixture, one component of which is a substance having a large value of GWP (for example, CF₃H, C₂F₃H or C₃F₇H), and the other is a chemical compound having short atmospheric lifetime. The effect of creating a mixed agent will be maximum if its extinguishing concentration is lower than the extinguishing concentration of HFC included into the mixture. This paper is devoted to study of such mixtures of fluorinated and iodinated hydrocarbons.

To compare reaction rates of some bimolecular chemical reactions reaction rate constant \( k(T) \) is used in this paper in the Arrhenius form

\[
k(T) = A(T)\left(\frac{T}{298}\right)^n e^{-\frac{E}{RT}},
\]

where \( A \) – preexponential factor, molecule·cm⁻³·s⁻¹, \( T \) – temperature, K, \( R \) – universal gas constant, kJ·mole⁻¹·K⁻¹, \( E \) – activation energy, kJ·mole⁻¹.

2. Theoretical study of possibilities to improve extinguishing efficiency of HFCs

There are two opposite processes that determines fire extinguishing efficiency of fluorinated alkanes. It was revealed in [3] that HFCs are able to inhibit hydrocarbon flames due to reaction with hydrogen atoms. But it was also shown [3,4] that HFCs are able to influenced oxidation being added to lean combustible gaseous mixtures. This process reveals itself as an additional heat release in chemical reactions of fluorinated substances with oxygen atoms and hydroxyl radicals. It promotes combustion process and adversely affects fire extinguishing properties of fluorinated hydrocarbon.

As it follows from [5], the mechanism of destruction of HFCs in flames is substantially different for CF₃H and heavier HFCs. In particular, it was shown in [5] that initial stages of destruction of trifluoromethane are its reactions with O and OH while for heavier HFCs (C₂F₅H, C₃F₇H) reaction with hydrogen atom and subsequent monomolecular decay of C₂F₅ or C₃F₇ radicals towards to CF₃ and CF₂ formation also play substantial role.

Accordingly, it can be expected that when a substance is added to trifluoromethane that can not only effectively inhibit combustion processes, but also suppress the transformation of trifluoromethane in a flame effectively competing with reactions

\[
\text{CF}_3\text{H} + \text{O} \rightarrow \text{CF}_3 + \text{OH}, \quad (2)
\]

\[
\text{CF}_3\text{H} + \text{OH} \rightarrow \text{CF}_3 + \text{H}_2\text{O}, \quad (3)
\]

fire extinguishing efficiency of such a mixture may became significantly higher than the effectiveness of trifluoromethane as an individual gaseous fire suppressant.

Consider trifluoroidomethane as such an additive. This substance, on the one hand, is capable of substantially suppressing the processes of gas-phase combustion, effectively competing with the limiting reaction of the branching of reaction chains

\[
\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}, \quad (4)
\]

through the reaction

\[
\text{H} + \text{CF}_3\text{I} \rightarrow \text{CF}_3 + \text{HI}, \quad (5)
\]

Based on the kinetic parameters of the reactions (4) \( A_4 = 3.3 \cdot 10^{-10}, n_4 = 0, E_4 = 70.34 \) [6] and (5) \( A_5 = 8.3 \cdot 10^{11}, n_5 = 0, E_5 = 4.18 \) [7]), we obtain that at a concentration of trifluoroidomethane in air [CF₃I] = 1% vol. at a temperature of \( T = 1000 \) K the ratio of the rates of reactions (5) and (4) is \( w_5/w_4 \).
= 32.5, that is, reaction (5) is 32.5 times faster than reaction (4). This will undoubtedly lead to inhibition of the combustion process, the limiting stage of which is reaction (4).

In addition, HI formed in reaction (5) is itself an effective combustion inhibitor, even more effective than CF3I, since its reaction with atomic hydrogen

\[ H + HI \rightarrow H_2 + I \]  \hspace{1cm} (6)

due to its kinetic parameters \( (A_6 = 7.87 \cdot 10^{11}, n_6 = 0, E_6 = 2.74 \) [8]) proceeds faster than reaction (5). Hydrogen iodide is also able to regenerate in a flame, which further enhances the inhibitory effect:

\[ I + M \rightarrow I_2 + M, \]  \hspace{1cm} (7)

where M is any third particle,

\[ H + I_2 \rightarrow HI + I. \]  \hspace{1cm} (8)

On the other hand, elementary processes

\[ CF_3I + O \rightarrow CF_3 + IO \]  \hspace{1cm} (9)
\[ CF_3I + OH \rightarrow CF_3 + HOI \]  \hspace{1cm} (10)

are able to effectively compete with the trifluoromethane oxidation reactions (2) and (3), accompanied by significant heat release. The kinetic parameters of reactions (9) and (10) are as follows: for reaction (9) \( A_9 = 1.3 \cdot 10^{11}, n_9 = 0, E_9 = 2.21 \) [9]; for reaction (10) \( A_{10} = 5.8 \cdot 10^{12}, n_{10} = 0, E_{10} = 11.3 \) [10]. Then, at a CF3I concentration even 5 times lower than the CF3H concentration and temperature of \( T = 1000 \text{ K} \), the ratios of the rates of competing reactions (9) and (2), (10) and (3) are \( w_9 / w_2 = 51.2 \) and \( w_{10} / w_3 = 2.0 \) respectively, that is, processes (9) and (10) proceed several times faster. Similarly, it can be easily shown that reactions (9) and (10) are capable not only of inhibiting the trifluoromethane oxidation reactions (2) and (3) but also the oxidation of fluorinated radicals CF3 and CF2, thereby sharply decreasing the additional heat release accompanying destruction of CF3H in flame.

Thus, it can be expected that trifluoroiiodomethane, when used even in small concentrations as a component of a fire extinguishing mixture with trifluoromethane, on the one hand, being a strong inhibitor, is able to significantly reduce the heat release of the combustion process, which is affected by the mixed fire suppressant, and on the other hand, significantly reduce the heat release caused by destruction of CF3H in flame. Then the fire extinguishing concentration of trifluoromethane in the presence of the iodine-containing agent should significantly decrease.

Even more significant results in reducing fire-extinguishing concentration of greenhouse gas can be expected if heptafluoroiiodopropane is added to heptafluoropropane. For CF3I the kinetic parameters of its reaction with atomic hydrogen

\[ H + CF_3I \rightarrow CF_3 + HI \]  \hspace{1cm} (11)

are: \( A_{11} = 6.71 \cdot 10^{11}, n_{11} = 0, E_{11} = 3.8 \) [11]. Then the ratio of the rates of reactions (11) and (4) is \( w_{11} / w_4 = 572.9 \) [C3F3I] / [O2] at a temperature of 1000 K, whence we obtain that, for example, at [C3F3I] = 1% vol. \( w_{11} / w_4 = 27.6 \). That is, reaction (11) is more than 27 times faster than reaction (4), which will certainly lead to inhibition of the combustion process, the limiting stage of which is reaction (4). Thus, heptafluoroiodopropene has a strong flame inhibiting effect due to process (11) and the reactions of HI described above. If the addition of CF3I is able to effectively suppress the initial stage of the conversion of CF3H in flame, thereby it will be possible to significantly reduce the high heat release of subsequent decomposition reactions of CF3H, C2F5, C2F3, C2F4, slowing down the appearance of these intermediate substances. Accordingly, it can be expected that the fire extinguishing concentration of CF3H in the presence of CF3I will be significantly lower than when using heptafluoropropane as an individual gaseous fire suppressant.

Let us compare the rate of reactions of CF3I with atomic hydrogen (11) with the rate of a similar reaction CF3H

\[ H + CF_3H \rightarrow CF_3 + H_2, \]  \hspace{1cm} (12)

the kinetic parameters of which are: \( A_{12} = 3.63 \cdot 10^{10}, n_{12} = 0, E_{12} = 57 \) [12]. At a temperature \( T = 1000 \text{ K} \) and CF3I concentration that is 10 times less than CF3H concentration the ratio of the rates of reactions (11) and (12) is \( w_{11} / w_{12} = 10.6 \), that is, reaction (11) proceeds more than 10 times faster.

It can be easily shown that the reactions of CF3I with atomic oxygen and hydroxyl radical also effectively compete with analogous reactions of heptafluoropropane.
Thus, it can be expected that heptafluoroiodopropane, when used even in small concentrations as a component of a fire extinguishing mixture with heptafluoropropane, on the one hand, being a strong inhibitor, can significantly reduce the heat release of the combustion process, which is affected by the mixed suppressant, and on the other hand, significantly reduce the heat release during the conversion of C₃F₇H in flame. Since the additional heat release due to the conversion of C₃F₇H in flame is much stronger than during the conversion of CF₃H in flame [3], the fire extinguishing concentration of heptafluoropropane in the presence of an iodine-containing agent should decrease more strongly than for trifluoromethane with addition of iodinated hydrofluorocarbon.

3. Experimental

Because boiling point of heptafluoroiodopropane is high (about 40°C [13]), special experimental equipment was used in this work to measure its minimum extinguishing concentration for n-heptane.

The experiments were carried out at a set-up CYLINDER presented in figure 1. The main element of the set-up is a cylindrical vessel (3) having a volume of 53 dm³. The model fire source (1) also has a cylindrical shape with a diameter of 30 mm and a volume of 20 cm³. In each experiment the model fire source was filled with 19 cm³ of n-heptane.

The experiments were conducted at room temperature and atmospheric pressure in the following order. After evacuation of the vessel (5) using a vacuum pump (6) it was filled with a mixture of extinguishing agent and air of the required composition. The mixture was created directly in the vessel by partial pressures. Its composition was determined by a vacuum gauge (3), the mixture was set with an accuracy of 0.1% vol.

![Figure 1. Experimental set-up CYLINDER.](image)

1 – model fire source; 2 – hermetically sealed opening; 3 – vacuum gauge; 4 – window; 5 – vessel; 6 – vacuum pump.

The required time to achieve uniformity of the gaseous medium in the vessel (5) was 10 minutes. After its expiration, a pre-filled 19 cm³ of n-heptane was ignited in the model fire source (1). After boiling the fuel in the model fire source it was introduced into the vessel (5) through the opening (2). The moment of extinguishment of the flame was determined through the window (4). The time of 12-
14 seconds was used as the criterion for the absence of extinguishing, since during this time the model fire source is extinguished due to the consumption of oxygen in the vessel (5).

4. Obtained results
Theoretical prediction that the fire extinguishing concentration of trifluoromethane in presence of an iodine-containing agent should significantly decrease is convincingly proved by experimental results shown in figure 2. The influence of CF$_3$I additive on the value of the minimum fire extinguishing concentration of CF$_3$H when extinguishing n-heptane was investigated.

![Figure 2. Influence of CF$_3$I addition on trifluoromethane’s minimum extinguishing concentration for n-heptane combustion.](image)

It is easy to see that when only 10 % mass. of CF$_3$I is added to trifluoromethane its minimum fire extinguishing concentration decreases from 12.2 % vol. to 5.5 % vol., that is, more than 2 times.

Experimental studies were also carried out on the effect of C$_3$F$_7$I additive on the value of the minimum fire extinguishing concentration of C$_3$F$_7$H for n-heptane, the results of which are shown in figure 3.

As it was predicted in section 2 of this article, even more significant results can be obtained in reducing the fire extinguishing concentration of greenhouse gases if heptafluorooiodopropane is added to heptafluoropropane. It follows the obtained data that addition of only 5 % mass. of heptafluorooiodopropane to heptafluoropropane causes decrease of minimum fire extinguishing concentration of C$_3$F$_7$H for n-heptane from 6.4 % vol. to 2.5 % vol., that is, more than 2.5 times. Thus, it has been shown that fluoroiodohydrocarbons are an effective means of reducing the use of gaseous fire extinguishing agents based on fluorinated alkanes, which are greenhouse gases.

When creating a fire extinguishing mixture of trifluoromethane and trifluorooiodomethane containing 10 % mass. of CF$_3$I, suppression of combustion of n-heptane will require 2.46 times less trifluoromethane than in the case of its use as individual fire extinguishing agent. An even greater effect is achieved when creating a fire extinguishing mixture of heptafluoropropane and heptafluorooiodopropane, for which, with a content of only 5 % mass. of C$_3$F$_7$I in the mixture the extinguishing of combustion of n-heptane requires 2.86 times less heptafluoropropane than in the case of its use as individual extinguishing substance.
Figure 3. Influence of C₃F-I addition on heptafluoropropane’s minimum extinguishing concentration for n-heptane combustion.

It is also important to note that trifluoroiodomethane and heptafluoroiodopropane have extremely short atmospheric lifetime (1.15 days [14]). Accordingly, their global warming potential (GWP) is less than 1. It means that CF₃I and C₃F₇I rapidly decompose in the atmosphere and their addition to fluorinated alkanes will reduce the use of greenhouse gases in fire suppression in any case.

Creation of mixtures with a higher content of iodized components is impractical, since in this case the iodine-containing substance will exceed safe level of its use from the point of view of toxicity (no observed adverse effect level (NOAEL) is 0.4 % vol. for both of iodides investigated in this paper [14]).

5. Conclusions
It was theoretically predicted that fluoroiodohydrocarbons are effective inhibitors of the conversion of fluorinated alkanes in flame.

It was shown experimentally that fluoroiodohydrocarbons are effective means of reducing the use of gaseous fire extinguishing agents based on fluorinated alkanes, which are greenhouse gases. In the presence of insignificant addition of iodized substance the volume of fluorinated alkanes required for extinguishing decreases several times.

Creation of mixtures with the content of iodized components higher than 5 mass. is impractical, since in this case the iodine-containing substance will exceed safe level of its use from the point of view of toxicity.

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