

# Research on new generation inhibitors

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**Abstract.** This article investigates the specific application of inhibitors in firefighting. The main emphasis is placed on the application of temperature-activated water jets (TAW). A generalized model of droplet motion in highly heated heat flows has been presented, taking into account not only the local heating of the droplet from heat flows, but also the integral, depending on the geometric and velocity characteristics of its motion.

## 1 Introduction

One of the most promising means of volumetric fire extinguishing is temperature-activated water (hereafter-TAW), the high efficiency of its application for volumetric fire extinguishing is experimentally confirmed in the works [1-5]. TAW jets are a two-phase system consisting of vapor and droplet phase, the main mechanism of extinguishing TAW is the cooling of the combustion zone, that is, the impact on the physical side of combustion [4, 15]. However, research in the works [6-10] suggest that formulations that affect the chemical nature of the flame, that is, inhibit the combustion zone, have the greatest effectiveness. Extinguishing flame can be extinguished by inhibiting compositions as early as 0.5-1 % of their volume concentration by blocking radical-chain reactions occurring in the combustion zone [6, 7]. Thus, research aimed at increasing the efficiency of volumetric fire extinguishing by TAW jets by giving them inhibiting properties is relevant.

## 2 Materials and methods

Combustion inhibition processes can be explained in terms of the theory of branched-chain combustion processes, for which self-heating and therefore the mechanism of extinguishing by cooling are not determinative [6, 7].

During combustion, atoms and radicals, carriers of chains (hereinafter referred to as CC) are formed first, then they react rapidly and an avalanche-like CBR of combustion is formed. In addition to the process of generation of CC, processes of their death occur, but their molar rate is many times lower, so to inhibit these processes, chemically active substances - inhibitors are introduced. The mechanism of their action is based on the capture of CC and reducing their concentration to a critical level, at which the rate of cutting of CC will be less than the rate of their capture.

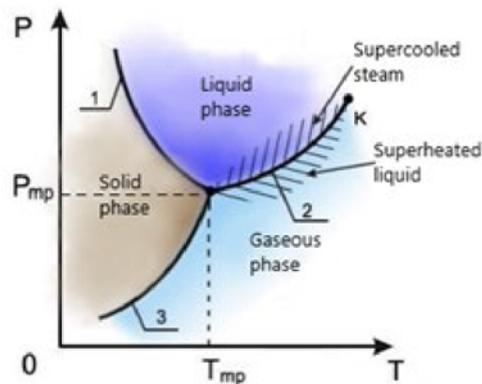
Thus, the conditional rate of inhibition is directly proportional to the velocity characteristics of CC and inhibitor particles. This shows that to achieve maximum

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effectiveness of inhibitors it is necessary to deliver active particles into the zone of flame burning, overcoming turbulent flows of formed combustion products. The TAW droplet phase can be used to deliver inhibitory components to the flame zone due to their ability to be injected with air into the combustion zone [3-5].

The essence of obtaining TAW, in the physical sense, is to feed water at high pressure (45-100 atm) into a heat exchanger. In the heat exchanger, the water is initially heated to a temperature of 180 to 300 degrees Celsius, then piped to atomiser barrels and becomes metastable water for only a few seconds [15]. Soon after explosive boiling produces TAW jets with particle sizes ranging from 0.01 to 10.0  $\mu\text{m}$ , which are similar in quality to warm fog or clouds. TAW jets can be seen graphically in the analysis of P-T and P-V phase state diagrams (Fig. 1 and Fig. 2) of water. Metastable states, i.e. when one phase is in the range of temperatures and pressures of the other phase, are characteristic of the various water modifications. These same metastable states can also be present for phase states [12]. Picture 1 shows a scheme of metastable state zones at phase transition from liquid to gas. Above line 2 there is a region that corresponds to a fairly cooled vapour, and below that a superheated liquid. At accumulation of steam (Fig. 2) the metastable state region in the pressure diagram P-V is between the curve connecting the points of equilibrium states (hereinafter referred to as binodal) at different temperatures T for liquid and steam (respectively points A and B), and spinodal - curve connecting points C and D [11].



**Fig. 1.** Diagram of metastable states during the liquid-gas phase transition: 1-melting curve; 2-evaporation curve; 3-sublimation curve; K-critical point ( $T_k=647,35\text{ }^\circ\text{K}$ ,  $P_k=218,5\text{ atm.}$ ),

Source: <https://thepresentation.ru/fizika/kondensirovannoe-sostoyanie-veshchestva-4>

## 2.1 Mathematical modelling of AW droplet evaporation in a high-temperature environment

Consider a flowchart for writing a programme to determine the selection of droplet distribution in the polydisperse droplet phase of a TAW jet for extinguishing a turbine and marine oil spill fire in the engine room of a gas compressor station (Figure 1).

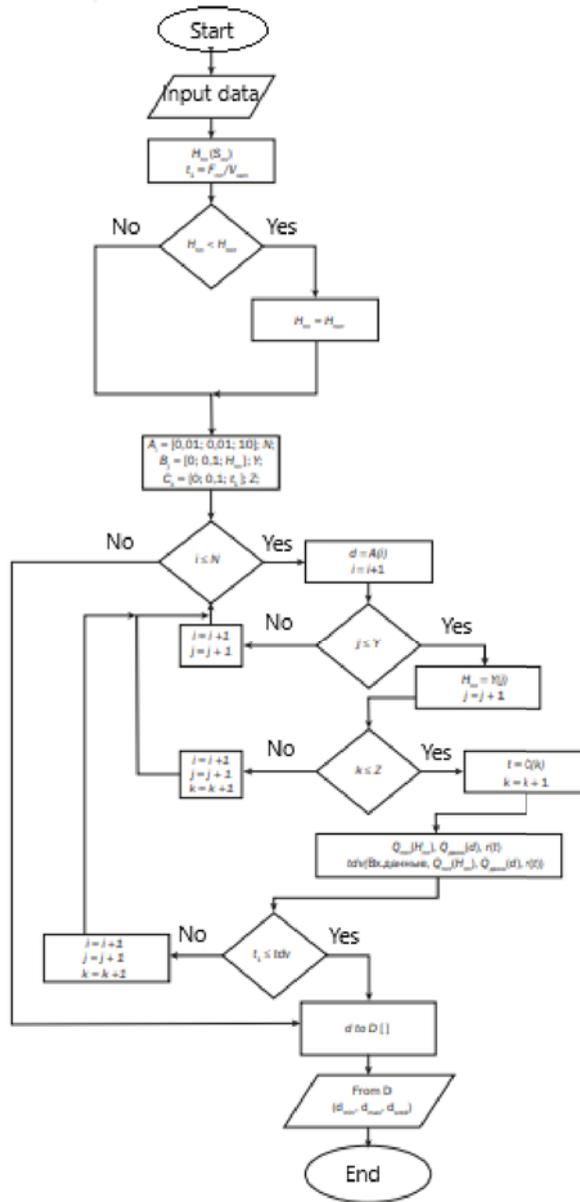


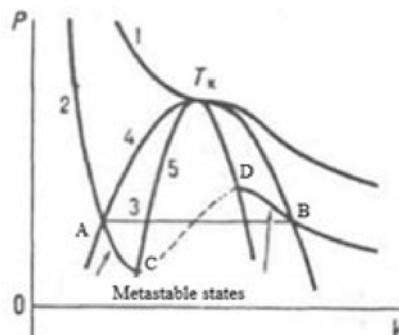
Fig. 2. Block diagram for finding effective droplet distribution in a TAW jet

The notations in the flowchart are as follows: Input data - block of data to be entered before performing the calculation ( $V, F, C_v, T_0$  - is the initial temperature of the water droplets,  $qC, T_1$  is the final temperature of the water droplets,  $qC, N, p$  - water density,  $kg/m^3, S$ );  $H(S)$  - the operation of finding the flame height depending on the area of the combustion mirror,  $m$ ;  $H$  - room ceiling height,  $m$ ;  $A, B, C$  - arrays of drop diameters, flame height and time, respectively;  $N, Y, Z$  - number of elements in arrays  $A, B$  and  $C$  respectively;  $i, j, k$  - changing numbers of elements in arrays when performing cycles;  $Q(H)$  - operation of finding the intensity of heat flow depending on measurement height,  $kW/(m/s^2)$ ;  $Q(d)$  -

operation of finding the amount of heat received by a droplet during its movement as a function of its diameter,  $m$ ;  $r(t)$  - operation of finding the specific heat of vaporization as a function of its movement,  $J/kg$ ;  $tdv$  (input data,  $Q(H)$ ,  $Q(d)$ ,  $r(t)$ ) - finding evaporation time of a drop of a certain diameter from the data calculated in cycles,  $s$ ;  $d$  to  $D$  - the operation of filling the array  $D$  with values of drop diameters, the evaporation time of which exceeds the time of movement of the drop through the flame; From  $D$  ( $d_{min}$ ,  $d_{max}$ ,  $d_{mean}$ ) - identification of the minimum, maximum, mean diameter drops and their number to determine the effective parameters of the jet TAW.

The simulation showed that in order to extinguish a typical machine-room of a gas-compressor station it is necessary to deliver TAW droplets having a minimum diameter of  $1.25 \mu m$ , an average diameter of  $3.2 \mu m$  and a maximum diameter of  $6.6 \mu m$ . In this case, their heating time to boiling point will be at least 2.5 seconds.

Investigation of the process of heating a droplet to boiling point leads to a conclusion that when the polydisperse droplet phase of TAW jet is delivered to the fire place, not a surface heating of a droplet takes place, but layer-by-layer heating. Therefore, when the droplets move in a polydisperse group, uneven evaporation will occur. To assure uniform evaporation it is necessary that droplets of medium diameter -  $3.2 \mu m$  should have the highest density of distribution in the TAW jet, in the lower part of the jet correspondingly there should be heavier droplets with diameter to  $6.6 \mu m$ , in the upper part of the jet - those with diameter not more than  $1.25 \mu m$ . In this way a sufficiently uniform heating density is ensured and a uniform evaporation is realised.



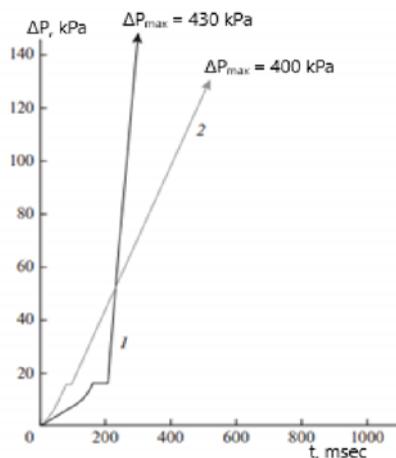
**Fig. 3.** Dependences  $P$ - $V$  at  $T_k$  (1) and less than  $T_k$  (2): CD – labil states (a state of instability not only to strong, but also to weak perturbations); straight line 3 connects the equilibrium states of liquid and vapor; B 4 – binodal; 5 – spinodal;  $T_k$  – critical point. Source: <https://xumuk.ru/encyklopedia/1562.html>

In the following, we consider in more detail the effect of trifluoromethane addition on the transition of propane-air mixture combustion into a chain-heat explosion (hereinafter referred to as CFE) mode. A number of fluorocarbons, including  $CF_3H$ , are known and widely used gas suppressants of gas-phase combustion. However, these products have a double effect on the combustion process: besides their inhibitory effect on gas combustion, which is most prominent when acting on rich mixtures and consists in the interaction of fluorocarbons and their conversion products with atomic hydrogen, fluorocarbons can transform into flames themselves, providing additional heat release during combustion [13]. In particular it was found [6] that  $CF_3H$ ,  $C_2F_5H$ ,  $C_3F_7H$  when added to poor hydrogen-air and methane-air mixtures are able to induced oxidation with heat release which intensifies combustion of basic (hydrogen-air or methane-air) mixture and significantly reduces inhibiting effect of fluorocarbons on burning process. In general, it can be concluded that the effect of fluorocarbons on the combustion of gas mixtures is determined by the competition of two components of the same process: the inhibiting effect of fluorocarbons on gas-phase

combustion and the heat release accompanying the process of their chemical transformation in the flame.

The described phenomena undoubtedly appear when trifluoromethane affects the combustion of propane-air mixture containing 8 vol.%  $C_3H_8$ , but the experimentally observed picture is much more complicated than that described in [6, 9]. In contrast to the data given in these works showing that the effect of induced oxidation of fluorocarbons appears only in poor hydrogen-air and methane-air mixtures, the effect of  $CF_3H$  on the burning of a rich propane-air mixture was found to increase  $\Delta P_{max}$  by 7.5-11% compared to the burning of propane-air mixture without  $CF_3H$  addition. It is important to note that such an increase in the maximum pressure developed during combustion (by an amount on the order of 10%) due to heat release during the conversion of trifluoromethane in the flame does not explain the second region with a pressure peak.

As can be seen from Fig. 3, the addition of 2 vol.%  $CF_3H$  has an inhibitory effect on chain combustion of the propane-air mixture before its transition into the HFC: the maximum rate of pressure build-up in the mixture containing trifluoromethane is half as high as  $(dP/dt)_{max}$  when the propane-air mixture without fluorocarbon addition is burnt. However, the situation changes essentially in the area of the developed DTV: the additional heat release caused by transformation of the fluorocarbon added to the propane-air mixture provides 5.3 times higher maximum rate of pressure rise in the mixture as compared to the propane-air mixture without addition, and also 30 kPa higher maximum pressure developed during combustion. It should also be noted that with increasing concentration of trifluoromethane in the mixture the  $\Delta P_{max}$  and  $(dP/dt)_{max}$  values decrease significantly, and in a situation where only simultaneous conditions are possible and transition to DTV is not possible, only the inhibitory effect of trifluoromethane is observed.



**Fig. 4.** Features of the effect of trifluoromethane on the combustion of a mixture of 8 vol.% propane - air: 1- 2 vol.%  $CF_3H$ , 2-0 vol.%  $CF_3H$ , Source: <https://sciencejournals.ru/view-article/?j=khimfiz&y=2020&v=39&n=7&a=KhimFiz2007007Kopylov>

The pattern observed experimentally in this work is not unique to the combustion of propane-air mixture. In work [10], in which photochemically induced combustion of a mixture of 1,1-difluoroethane with chlorine at initial atmospheric pressure in the presence of an oxygen inhibitor was studied, the presence of two different regions on the temperature-

time dependence at different oxygen concentrations was found, as well as in the present work. When the experimental results are accurately recorded, a similar characteristic dependence of pressure or temperature on time is observed in the combustion of fast-burning mixtures (e.g., hydrogen-air mixtures) at high (about atmospheric) initial pressures.

Further, among the most frequently used water-soluble inhibiting salts, potassium hexacyanoferrate (II) is the most effective.

### 3 Results

The high water solubility will be retained if the temperature is significantly increased. It was experimentally established [8, 9, 14] that the minimum extinguishing concentration (hereinafter - MEC) of potassium hexacyanoferrate (II) when using water at 20 °C was 3.5 %, at that the average diameter of droplets sprayed into the combustion zone was not less than 100 µm. Thus, at dosing this salt into the underheated water (water supplied from the TAW production unit by hoses up to the moment of explosive boiling is accepted to be called underheated) the reduction of IGC should be expected, as the diameter of drops obtained in the TAW jets varies from 0.01 to 10 µm.

Experimental studies to determine the effectiveness of inhibiting salts in TAB jets were carried out for solid combustible materials (SCM) and flammable liquids (FL).

Two assumptions were made based on this experiment:

1) as a result of explosive boiling, part of the inhibiting agent passes to the vapour phase with its subsequent dispersion in the environment, so that only part of the initially dissolved composition is delivered to the place of flame suppression;

2) explosive boiling in the barrel leads to chemical processes that change the qualitative and quantitative composition of the solution, due to the possible destruction of the complex anion of potassium hexacyanoferrate (II). This affects the reduction of the inhibiting ability of the solution.

To check the first assumption it is necessary to conduct an experimental study in a closed volume to eliminate the possibility of dispersion of the inhibiting agent outside the combustion zone. To test the second assumption, selected samples of salt solution in TAW were examined using chemical analysis methods. It was found that using the found relationship, it was possible to determine the necessary concentration of potassium hexacyanoferrate (II) in the solution for a given temperature regime in order to achieve the required IGC at the outlet of the barrel.

In-situ experiments on extinguishing of model A and B foci by potassium hexacyanoferrate (II) solutions in TAW allowed to establish that the effective concentration of inhibitory salt is above the experimentally established value of 3.5 % [8, 9]. It was found by laboratory studies that the increase in the value of the effective concentration of the inhibitory salt in TAW was due to the destruction of the complex anion of potassium hexacyanoferrate (II). Using gravimetric method the following dependence of potassium hexacyanoferrate (II) concentration in TAW4 solution after explosive boiling on the TAW feeding temperature regime was found:  $y = 80.884x - 0.557$  for temperature range 120-190 °C. The established dependence makes it possible to calculate the required IGC of potassium hexacyanoferrate (II) in TAW for effective suppression of combustion when extinguishing fires [10].

### 4 Discussion

Our article touched on a topic related to fire safety. The possibility of extinguishing a fire by inhibition method was considered. It is actively used in areas with special regimes where the

possibility of extinguishing by other methods is ruled out. Temperature-activated water is a promising tool for large premises. Due to its vapour state, it is able to reach any part of the burning surface, irrespective of the complexity of the terrain. However, a major disadvantage of these components is the high turbulence in rooms and the need to bring them as close to the point of ignition as possible. Modern building designs begin to take this into account. In industrial companies, for example, the volume of an entire building is taken into account in advance in order to be able to supply the required quantity of liquid propellants. There is also another approach. It is the point source of water for potentially hazardous processes. TAWs are not used in their pure form. Typically, an additional component has a tendency to corrode, so consideration must be given to each substance specifically. And in the absence of water, inhibitors will cause severe corrosion.

Inhibitors are much more widely available, but when used outdoors, they quickly volatilise into the environment. This is a primary blow to our planet's ozone layer. The halogen atoms that interact with ozone, destroying it, led to the adoption of the Montreal Protocol to the Vienna Convention for the Protection of the Ozone Layer in 1985. The result was the phasing out of many chemicals.

It is also dangerous to human health. Above all, it is toxic. Some of the halogenated hydrocarbons are highly toxic and therefore prohibited for use in firefighting.

## 5 Conclusions

The effectiveness of TAWs is determined by their ability to participate in chemical reactions, depending on the inhibiting agent. In its pure form, temperature-activated water is sometimes insufficient to affect the combustion zone. The solution is to add a chemically active inhibitor in a small concentration to the TAW, which will be more than sufficient. Hydrocarbon inhibitors containing olefin have been proven to be the most suitable, highly effective inhibitors. Acetylene with a small amount of oxygen is added to enhance decomposition. When selecting an inhibitor, the nature and specificity of the combustion process must be considered. TAB has been shown experimentally to suppress combustion of gases in all modes, such as ignition, combustion and explosion.

In the development of new inhibitors the following requirements must be applied: moderate toxicity, use of natural or synthetic raw materials. In addition to this, inhibitors must be as effective as possible in extinguishing fires when chemically hazardous substances are added in low concentrations.

Thus, in general, the demand for research into the use of new generation inhibitors is increasing every year. And the need to improve and upgrade existing technologies is only increasing every year. Thus, in general, the demand for research into the use of new generation inhibitors is increasing every year. And the need to improve and upgrade existing technologies is only increasing every year.

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