COMBUSTION SUPPRESSION OF METHANE BY CO_2/CF_3Br, CO_2/$C_2F_4Br_2$ AND N_2/CF_3I

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ABSTRACT

The conditions for inerting of methane-air blends by nitrogen and carbon dioxide with addition of halons (CF_3I, CF_3Br and $C_2F_4Br_2$) were studied. The minimal inerting concentration (MIC) drops significantly when those halons are added to nitrogen-CO_2 blends in amounts not exceeding 15 % by vol. Further increase in CF_3Br and $C_2F_4Br_2$ contents doesn't cause the drop of MIC, while the increase in CF_3I concentration above 15 % by vol. results in rapid growth of MIC up to values exceeding that of pure nitrogen.

It was established that CF_3I is a combustible gas, and its concentration limits of flame propagation in the air under normal conditions are 35-60 % by vol. Adding of CF_3I to a methane-air blend significantly extends the area of flame propagation.

1. Inerting of methane-air blends by carbon dioxide with addition of halons CF_3Br and $C_2F_4Br_2$.

The tests were carried out in spherical stainless steel autoclave of volume 9.8 l, at atmospheric pressure of the components and at room temperature.

The blends were prepared in the autoclave. The blend composition was set according to partial pressures of the components. To intensify convection of the test gases at mixing an electric hearting spiral was installed at the middle of the autoclave wall.

An igniter was set at the bottom of the autoclave, at 30-40 mm from its wall, close to its vertical axis. A piece of copper wire (0.1 mm in diameter, 6 mm in length) was used for the igniter. The igniter was fused under the action of voltage supplied by a condenser of capacity 10400 µF, preliminary charged to 270 volt. The charged condenser provided voltage with the help of a powerful pulse thyristor.

The major part of the condensed energy accumulated in the condenser was released in arc discharge. The igniter's energy was chosen on the basis of the results [1], where the influence of igniter's energy on experimentally determined MIC of several halons had been studied.

The test pressure was registered with the help of quick-response pressure sensor (the eigenfrequency of membrane oscillations greater then 10 kHz), electronic transducer and scope with concurrent digital recording. The flame propagation or its absence was set out from the form of the recorded pressure curve after actuating of the igniter.
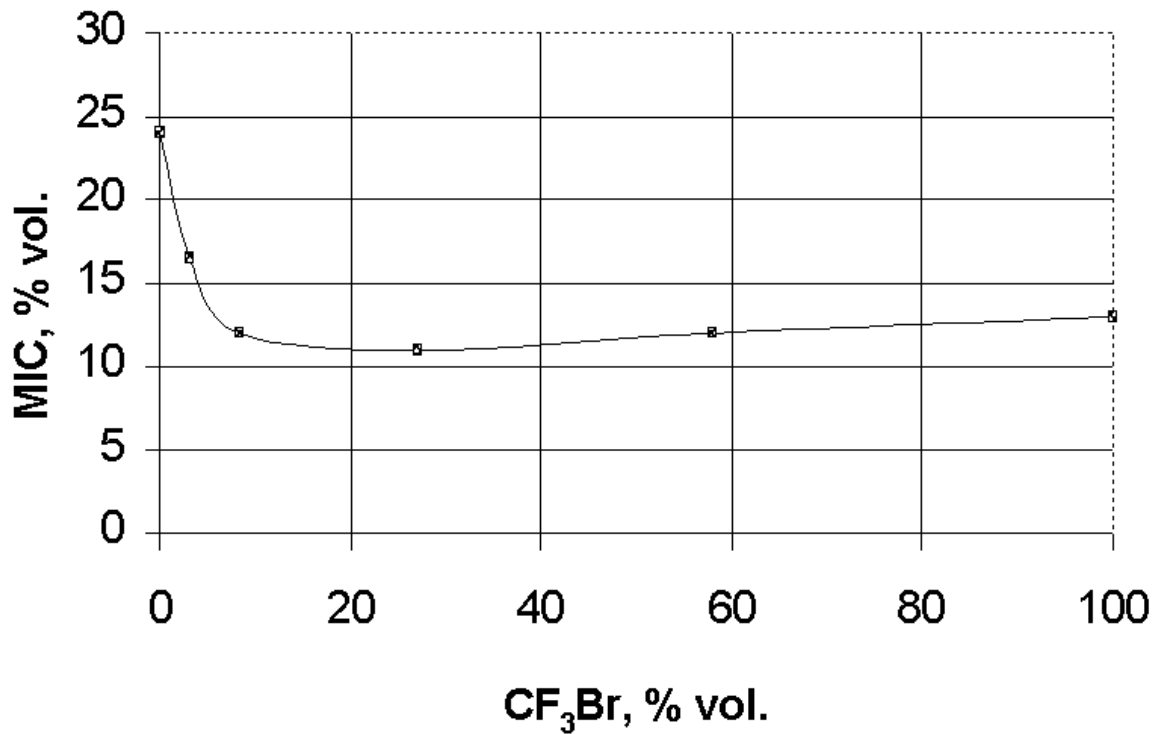

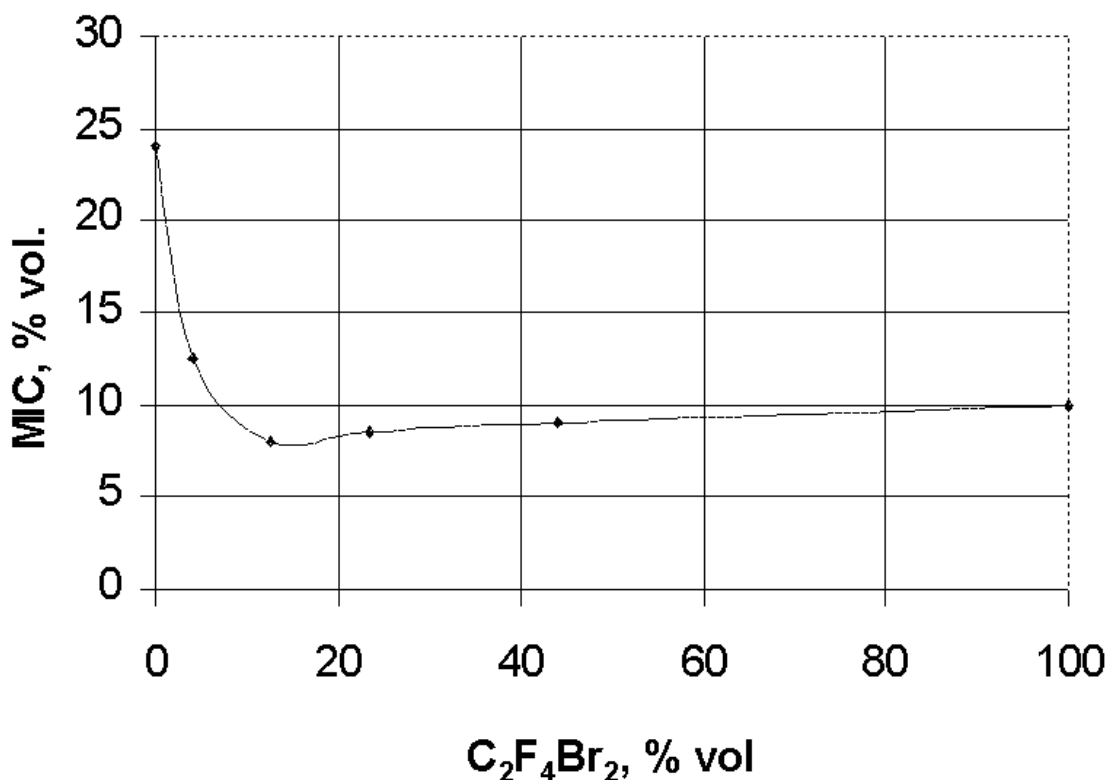**Fig. 1. MIC mixtures $CF_3Br + CO_2$ versus CF_3Br fraction in CO_2**

Fig. 2. MIC mixtures $C_2F_4Br_2$ + CO_2 versus $C_2F_4Br_2$ fraction in CO_2.

MIC of a halons-CO_2 blend was determined in a test series conducted with variable content of the halons in stochiometric methane-air mixtures. Those test results are shown in Fig. 1 and 2. One may see that MIC goes down considerably when halon is added to CO_2 in amounts up to 15 % by vol.. Further increase in those halons (CF_3Br and $C_2F_4Br_2$) content results not in drop but in slight growth of MIC.

2. Inerting of methane-air blends by nitrogen with addition of CF_3I.

The tests were carried out at atmospheric pressure and room temperature in vertical glass vessel, 80 mm in diameter, 240 mm in height. An organic glass plate was used for the vessel bottom. The plate bounced at explosion thus preventing the vessel from damage.

The process for those blends preparation was similar with that above-stated.

The igniter was set at 80 mm from the vessel bottom close to its axis of symmetry. Hot molybdenum-rhenium wire spiral was used for the igniter. The wire diameter was 0.2 mm, the spiral diameter was about 3 mm, the length of the wire was 142 mm, the height of the spiral was 8-10 mm. Heating the spiral was provided through connecting it to a condenser of 1400 µF capacity, charged to 200V. Voltage from the charged condenser was fed to the spiral with the help of a power pulse thyristor. The spiral design temperature was 2000^0C. The maximal

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temperature of the spiral was achieved in about 5 ms after actuating of the thyristor (established by the maximum of the spiral's luminescence registered by a photodiode).

The concentration of the main substance in CF_3I was at least 97%, and the main additive was C_3F_7I.

The fact of ignition and flame propagation was observed visually. In some tests vidio filming was used.

The type of igniter was selected basing on the results of [1,2], where it had been shown that application of a spark high-voltage igniter resulted in underestimation of MICs for halons, and even more for CF_3I. We preferred the hot spiral that blends eyes of its observer not so much as the igniter described in section 1. It makes visual control of the process more comfortable.

The results of MIC determination depending on the content of CF_3I in blends with N_2 are shown in Fig. 3. The results show drastic decrease of those blends inerting ability when the content of CF_3I in blend with N_2 exceeds 15 % by vol..
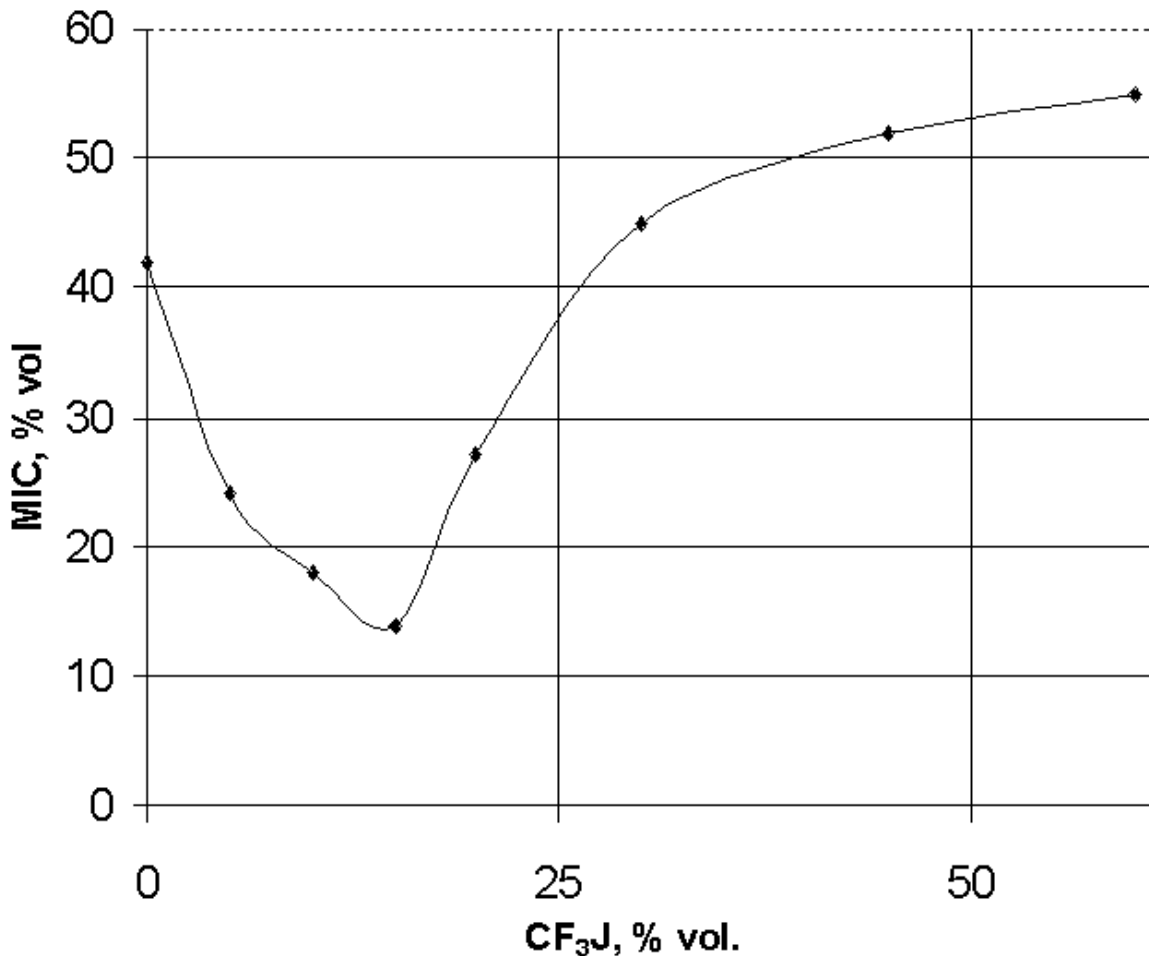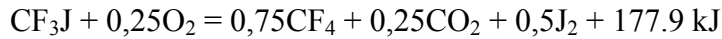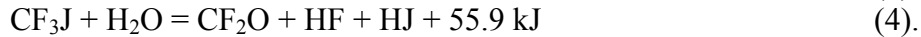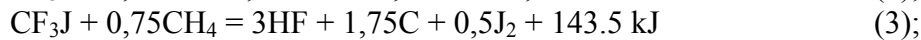

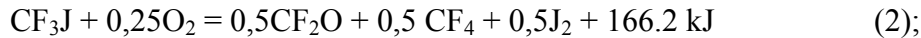**Fig. 3. MIC mixtures CF_3J-N_2 versus CF_3J fraction in nitrogen.**

When the content of CF$_3$I in blend with N$_2$ is more than 27 % by vol. then MIC of the blend exceeds that of pure N$_2$. As heat capacity per one mole of CF$_3$I exceeds considerably that of nitrogen we have to assume that CF$_3$I is involved in combustion process thus favoring the increase in heat-release. It may be due to the reactions as follows:

$$CF_3J = 0,5C_2F_6 + 0,5J_2 + 51.6 \text{ kJ} \tag{1};$$
$$CF_3J + 0,25O_2 = 0,75CF_4 + 0,25CO_2 + 0,5J_2 + 177.9 \text{ kJ}$$
$$\text{or}$$
$$CF_3J + 0,25O_2 = 0,5CF_2O + 0,5\ CF_4 + 0,5J_2 + 166.2 \text{ kJ} \tag{2};$$
$$CF_3J + 0,75CH_4 = 3HF + 1,75C + 0,5J_2 + 143.5 \text{ kJ} \tag{3};$$
$$CF_3J + H_2O = CF_2O + HF + HJ + 55.9 \text{ kJ} \tag{4}.$$

The heats of reactants and products formation are taken from [3].

Taking into account above-stated, extra tests of blends CF$_3$J − methane - air were carried out with the purpose to specify the limits of fire propagation in this ternary system. Their results are shown in Fig. 4..
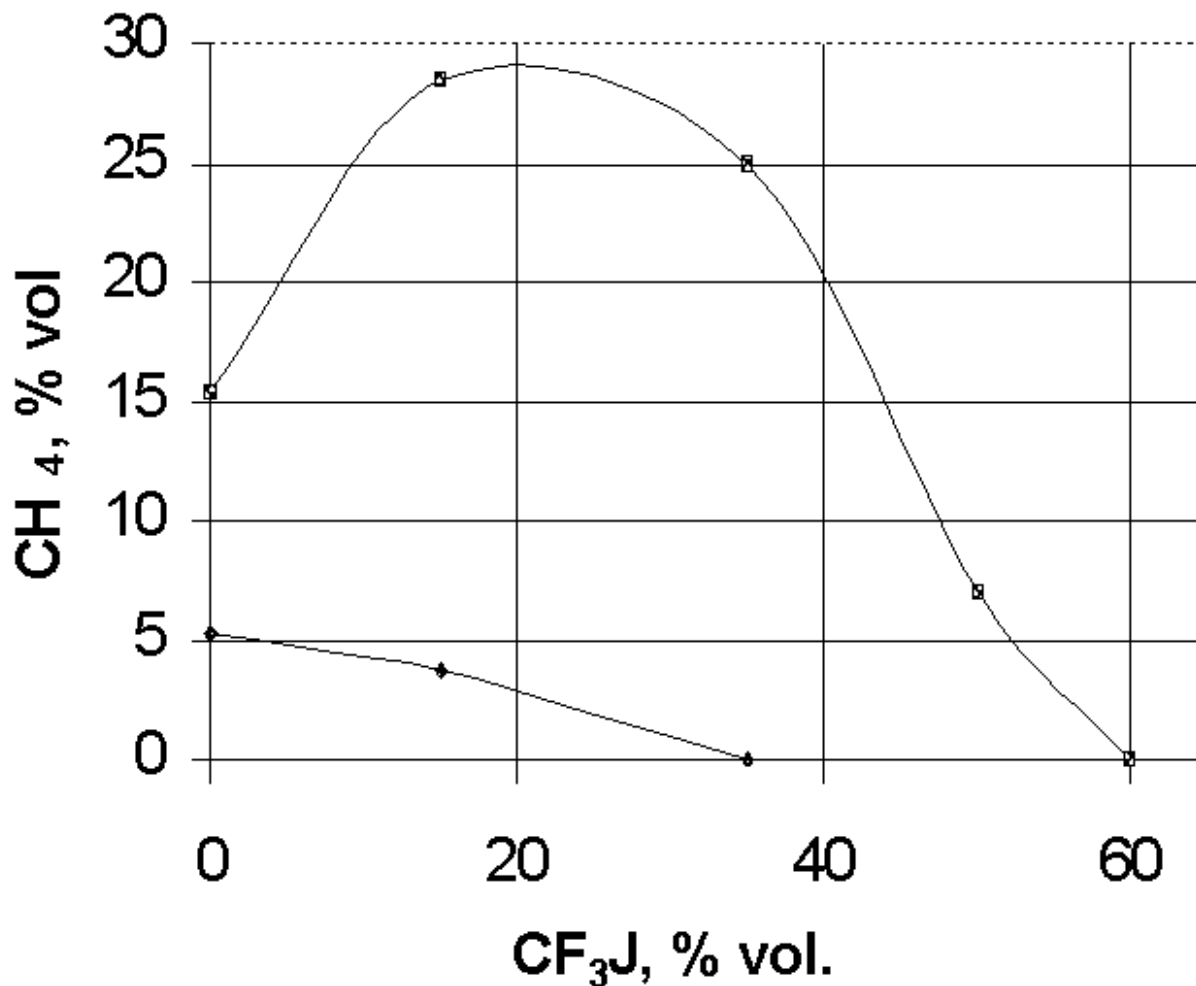

Fig. 4. Lower and upper limits of flammability mixtures CF$_3$J/CH$_4$/air.

As can be seen CF_3J burns in the air and in the absence of methane (apparently according to reaction 2). The concentration limits for fire propagation in CF_3J – air blend are 35 –60 % by vol. Adding of CF_3J appreciably extends the area of fire propagation in any methane – air blends. Therefore, on lean limit it acts as a fuel, but on high-grade limit (at the absence of oxygen) it apparently acts as an oxidant (for instant, reaction 3).

The camera-shot pictures of the fire propagation over CF_3J/air blend are shown in Fig. 5.
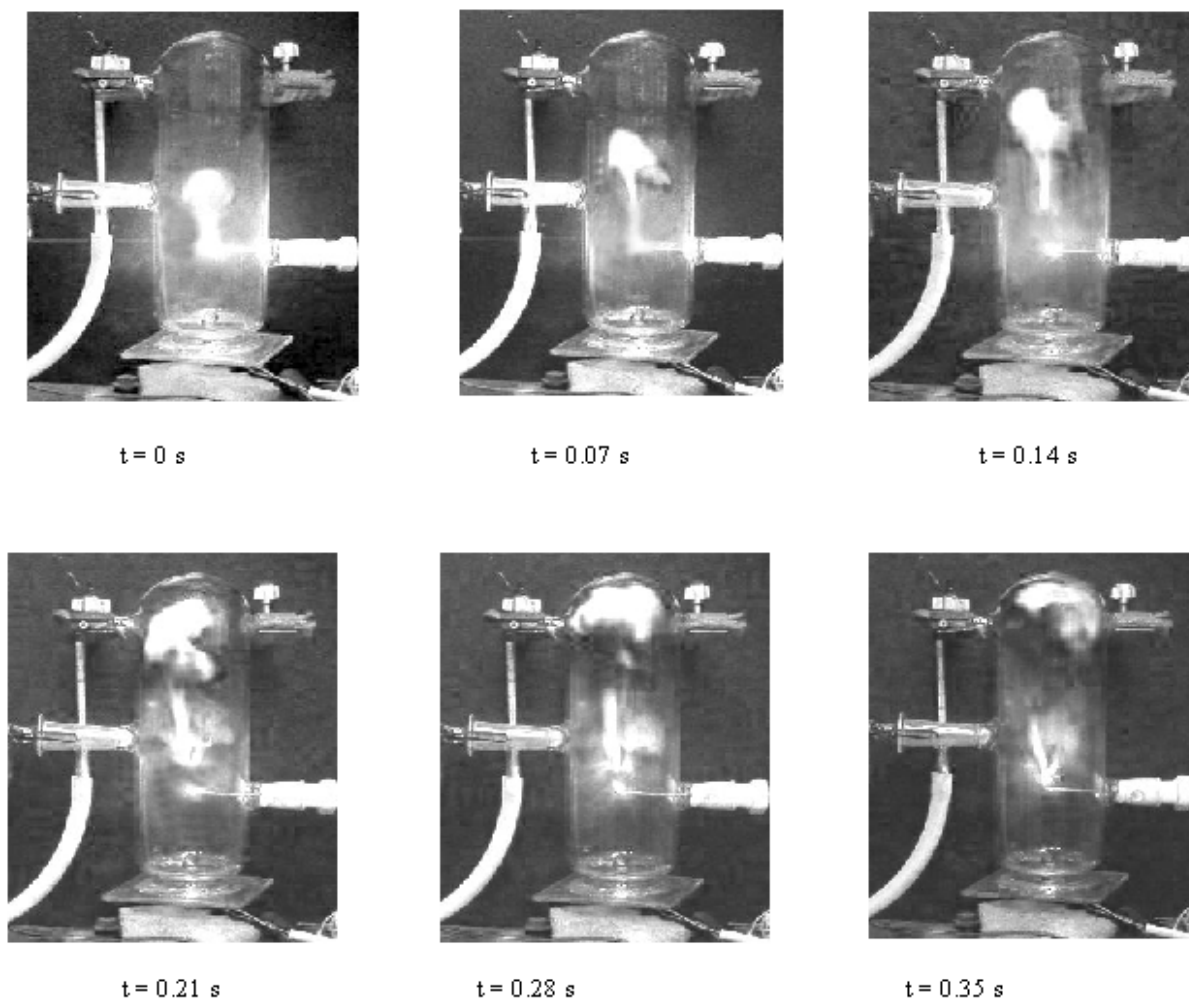

t = 0 s   t = 0.07 s   t = 0.14 s

t = 0.21 s   t = 0.28 s   t = 0.35 s

Fig. 5. Video of propagation of flame in mixtures CF3J (47.5% vol.)/air.

3. Explosion pressure and rate of pressure increase during the explosion of CF_3J/methane/air blends.

The tests were carried out in a steel cylindrical vertical autoclave of 0.325 l volume (48 mm in diameter).

The process for the blends preparation, pressure measurement and registration during the tests were similar to those described in section 1. The pressure sensor was set at the top of the autoclave.

The igniter described in item 2, was located at 30 – 35 mm from the autoclave bottom close to its axis of symmetry.

In Fig. 6 one of the pressure oscillograms of CF_3J – air blend burning is shown. The maximal increase in pressure was 2.2 bar, the maximal rate of the pressure increase was 13 bar/s.

The dependence of the maximal increase in pressure on the CF_3J content in the blend with air during our tests is shown in Fig. 7.

Therefore, the results shown in Fig. 6 and 7 confirm that CF_3J is a combustible gas. The concentration limits of the flame propagation coincided with those determined during the tests, described in section 2.
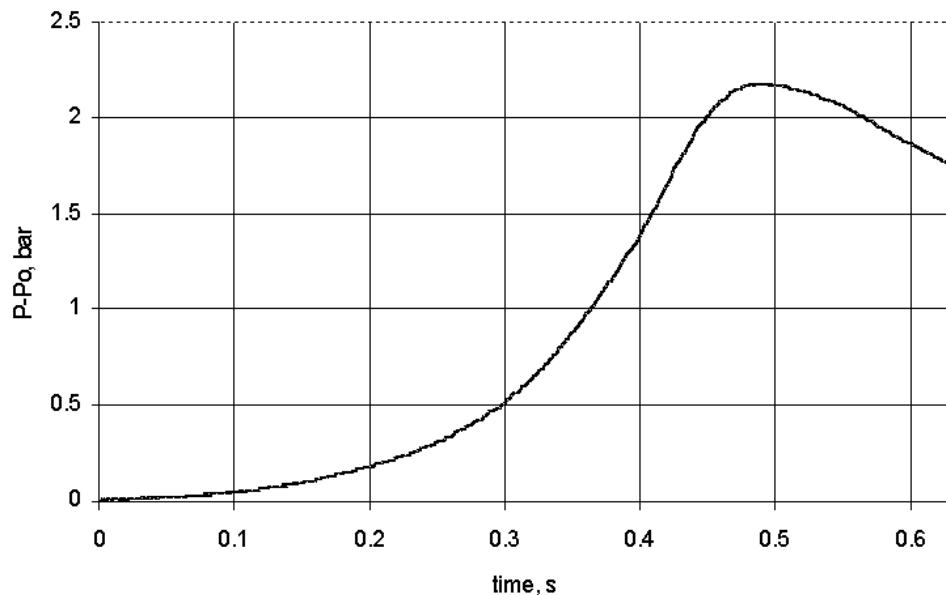
TEST N12

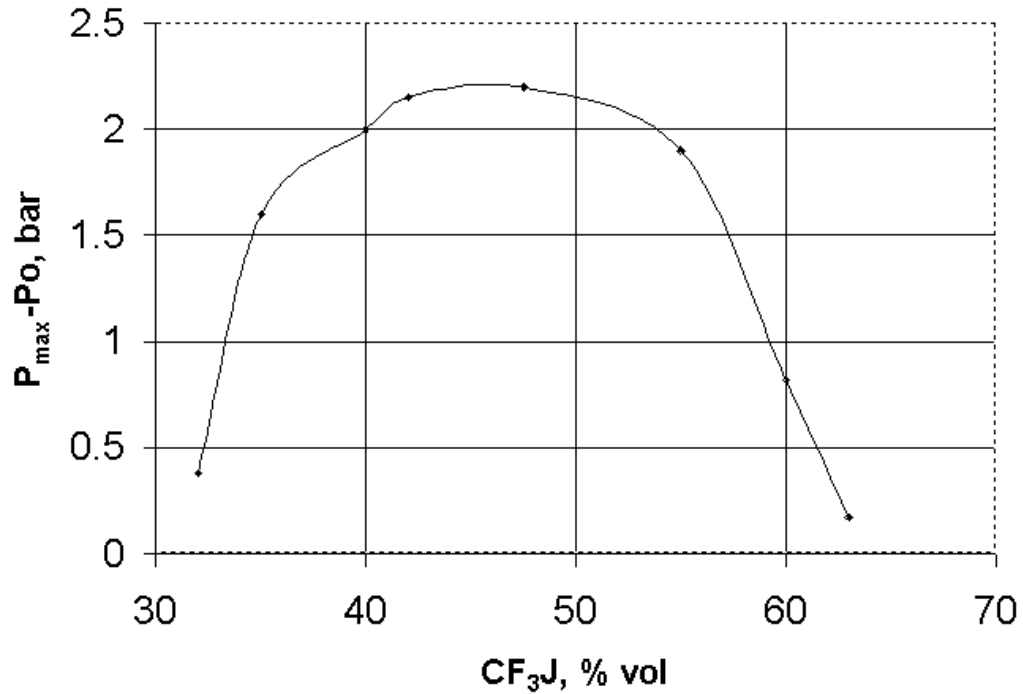**Fig. 6. Pressure oscillogram in explosion of the mixture (47.5 % vol. CF_3J + 52.5 % vol. air).**

**Fig. 7 Dependence of maximum explosion pressure
of CF$_3$J/air mixtures on CF$_3$J concentration.**

During the second test run the concentration of methane (6 % by vol.) was unvaried, but those of CF$_3$J and air were variable. The results of those tests are shown in Fig. 8.
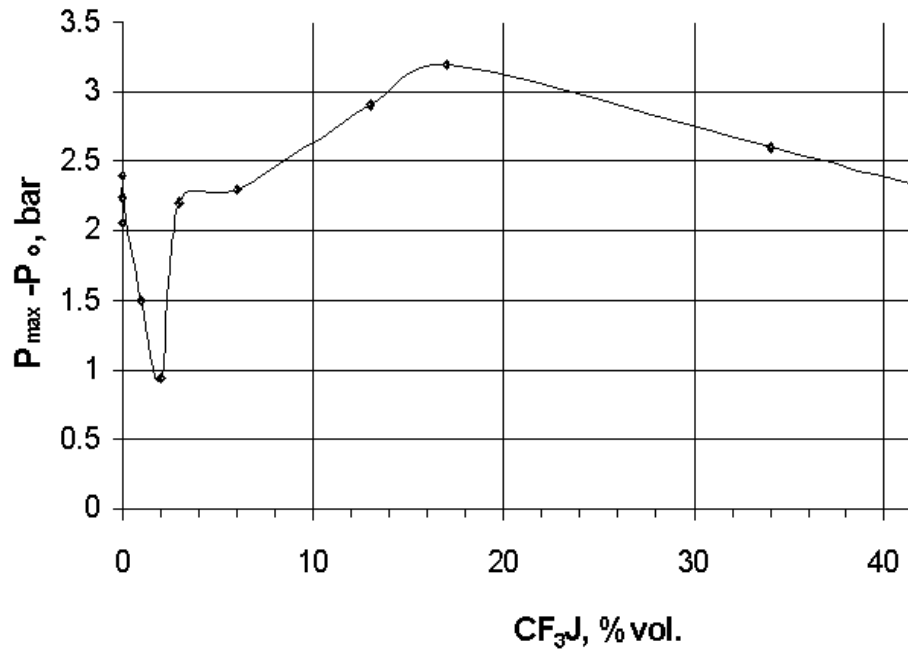

**Fig. 8. Dependence of maximum explosion pressure of
CF$_3$J/CH$_4$/air mixtures on CF$_3$J concentration
(CH$_4$ - 6% vol.).**

One may see that the inhibitory effect of CF_3J was observed when its content was up to 2% by vol. The further increase of CF_3J concentration caused growth both of the maximal explosion pressure and the maximal rate of pressure increase; apparently, it may be due to burning of CF_3J in oxygen, the content of oxygen being in excess with respect to methane. The decrease in the explosion parameters when CF_3J concentration achieved 17 % by vol. was obviously due to reaching stoichiometric ratio methane - CF_3J – oxygen.

During the third test run both methane (9 % by vol.) and oxygen (18 % vol.) concentrations were invariable, while those of CF_3J and nitrogen were variable. The tests results are shown in Fig.9. It can be seen that the inhibitory action of CF_3J on the rate of combustion stopped when the concentration reached 2 % vol.

It should be noted that the minimum of the function shown in Fig. 3, is also observed when the content of CF_3J in the blend is about 2 % vol.
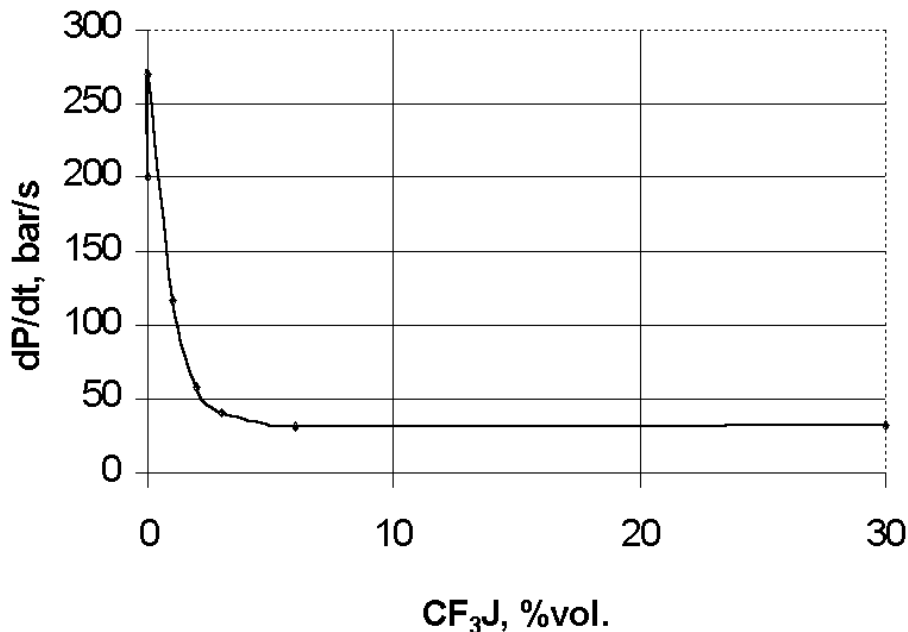

Fig. 9. Dependence of maximum explosion pressure rise rate of $CF_3J/CH_4/O_2/N_2$ mixtures on CF_3J concentration
(CH_4–9 % vol., O_2–21 % vol.)

CONCLUSIONS

1. Adding the halons under consideration to CO_2 and nitrogen in amounts up to 15 % vol. increases considerably the inerting ability of those gases. MIC of the blend CO_2 with 15 % of CF_3Br or $C_2F_4Br_2$ for methane-air blends is less than MIC of each of the pure halons.

2. CF_3J is a combustible gas and this fact should be apparently taken into account when designing fire-fighting systems using it.

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2. . Ya. A. Lisochkin,.V. I. Poznyak, E. G. Belevtcev. **DETERMINATION OF CF$_3$J INERTING CONCENTRATION METHANE-AIR AND HEPTANE-AIR MIXTURES, HOTWC**, Albuquerque, NM, 2002.

3. V. P. Glushko (ed.) **REFERENCE BOOK ON THE PROPERTIES OF INDIVIDUAL SUBSTANCES (in russian),** Nauka, Moscow (1978).