

FLAMMABILITY OF HFC/HCFC –AIR MIXTURES AT ELEVATED PRESSURES

Ya. **A.** Lissotchkin, V. I. Poznyak, and **E.** G. Belevtcev
Russian Scientific Center, Applied Chemistry
197198 St. Petersburg **RUSSIA**

INTRODUCTION

At present some mixtures of halocarbon agents and air are considered nonexplosive substances at atmospheric pressure on the basis of the existing test standards (e.g., standard ASTM E **681 USA**, Occupational Safety Standard System, 12.1.044 Russia). At the same time experimental data [1] point to a possibility of deflagration of mixtures of HFC–134a, HCFC–22 and air at higher pressures.

Thermodynamic calculation of the adiabatic temperature of the reaction products of these halocarbon agents with air oxygen gives a value over 2000 K, which confirms a possibility of deflagration conditions of this reaction course. The reasons for the absence of deflagration for these agents at atmospheric pressure can be the following: (1) increase of a flame propagation critical diameter to the value of the diameter of the testing vessel at pressure reduction, and (2) increase of a minimal ignition energy to values exceeding the energy of the used igniter at pressure decrease. Both parameters are functions of a testing method rather than of the fundamental property of the substance [2].

The aim of this study was to determine the minimal ignition energy for mixtures of HFC–125, HFC–134a, HCFC–22, and air at various pressures.

Equipment

The schematic diagram of an installation for testing deflagration of mixtures of halocarbon agents and air is presented in Figure 1. Experiments were carried out in a spherical autoclave of 10-liter volume. The autoclave was supplied with a hatch for inspection and cleaning, sockets for installation of pressure transducers, thermocouples and an igniter and a jacket for thermostatting. The autoclave was joined by means of valves to a pressure relief system, vacuum line, and to feeding systems of compressed air, gases, and vapors used for preparation of the mixtures.

The mixtures of given composition were prepared directly in the autoclave according to the partial pressures of reagents. To reduce the mixing time by means of convection, an electrically heated Nichrome spiral was used. The time of complete mixing reagents was fixed by means of chemical analysis. The process of deflagration was registered by a pressure transducer. Two open-junction thermocouples were installed inside the autoclave (one thermocouple was at the top of the autoclave, another one was installed by the wall in the middle of the autoclave). A signal from the thermocouples was registered simultaneously with indications of the pressure transducer on a light-beam recording oscillograph.

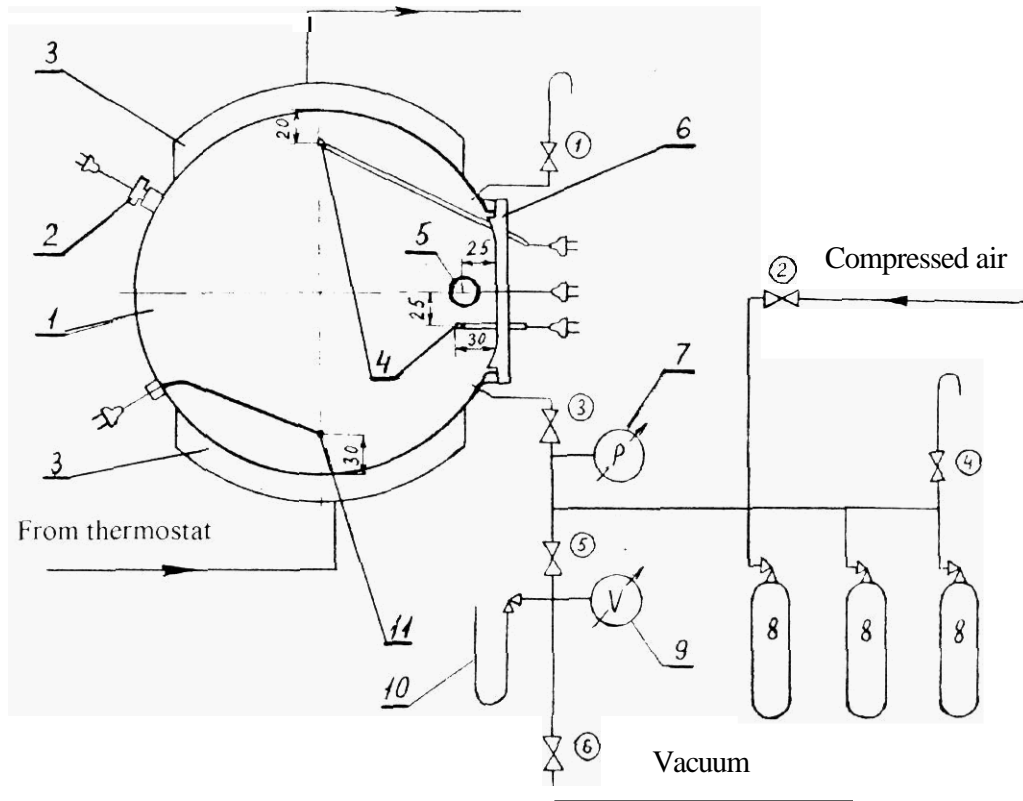


Figure 1. Schematic diagram of the test apparatus.
 1 – autoclave, 2 – pressure transducer, 3 – jacket for thermostating, 4 – thermocouples, 5 – heating coil, 6 – manhole, 7 – manometer, 8 – cylinders, 9 – vacuumeter, 10 – mercury vacuumeter, 11 – pyrotechnic igniter, 1, 2, 6, – valves

IGNITER

A pyrotechnical composition based on a mixture of fine-dispersed powders of BaO_2 (88.5% by mass), Al (8.85% by mass) and acetylcellulose binder (2.65% by mass) was used as the igniter. The mixture was prepared as tablets of different mass. Combustion of the composition was initiated by means of the electrically heated Nichrome wire. The energy fed to the gas mixture was evaluated by a pressure rise in the autoclave when the pyrotechnical composition burned in air in the absence of halocarbon agents (Figure 2). Within the range of air pressure change of 1-5 bar and the range of mass change from 0.06 to 0.48 g, the energy fed to the gas was equal to $2300 \pm 200 \text{ J/g}$. The time of the composition combustion was ca. 0.1 sec.

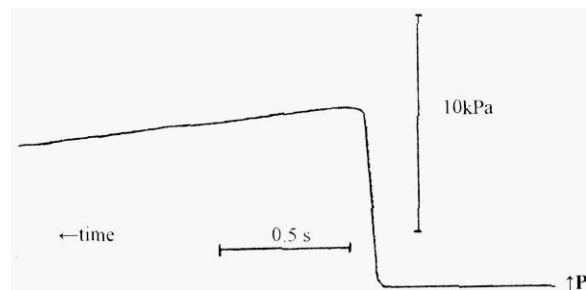


Figure 2. Oscillogram: Pressure change in the autoclave at combustion of the pyrotechnical composition.

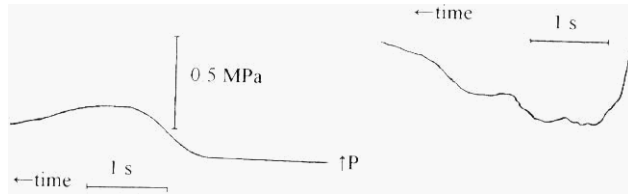
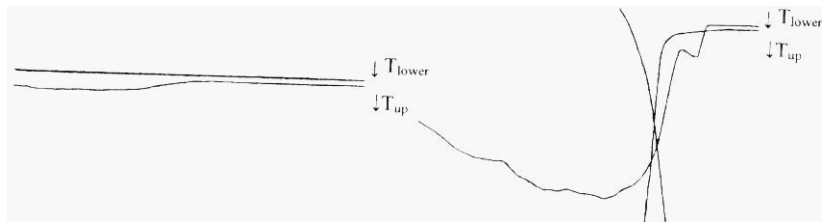
RESULTS

A number of experiments at different starting pressures (P_0) of stoichiometric mixture of halocarbon/air at the same mass of the pyrotechnical composition were carried out to determine the dependence of the minimal ignition energy of gas mixtures on the pressure. The following charge masses were used: 0.03, 0.06, 0.12, 0.24, 0.48, and 0.96 g. The mass scatter did not exceed 10% within one lot.

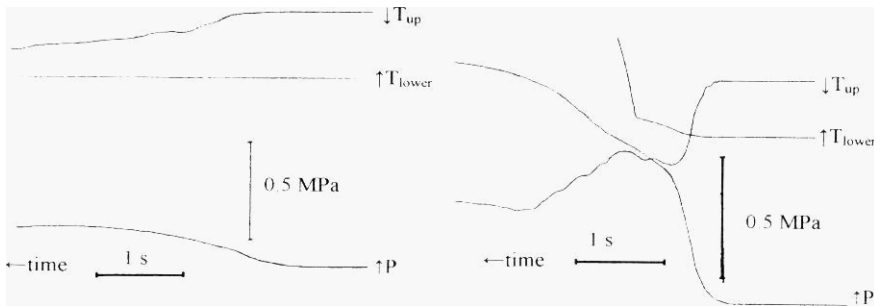
A pressure change in the autoclave after inflammation of the pyrotechnical composition was registered by the pressure transducer. Additional information was provided by indications of the thermocouples. Figure 3 gives typical oscillograms in the transition area from combustibility to flammability. As the starting pressure of the mixture is increased, the researchers observed a growth of the maximal pressure registered after the pyrotechnical composition was used up. There is a transition area of the pressure values where a slight pressure rise ($0.2P_0$ – $0.5P_0$) is observed when the time of pyrotechnical composition burning expires (ca. 0.1 sec). This points to an increase in the size of the hot spot during the process of convection rise. The subsequent combustion process takes place in the upper part of the autoclave under the cooling influence of the wall and the flame goes out. At a further increase of the starting pressure the combustion process occupies a bigger part of the autoclave, which is registered by the lower thermocouple. This transition is recognized as the beginning of deflagration.

Chromatographic analysis of the combustion products has shown a dramatic reduction in the oxygen concentration, formation of tetrafluoromethane, carbon dioxide, and admittedly phosgene. The method of analysis did not allow determination of the percentage of hydrogen fluoride in the combustion products.

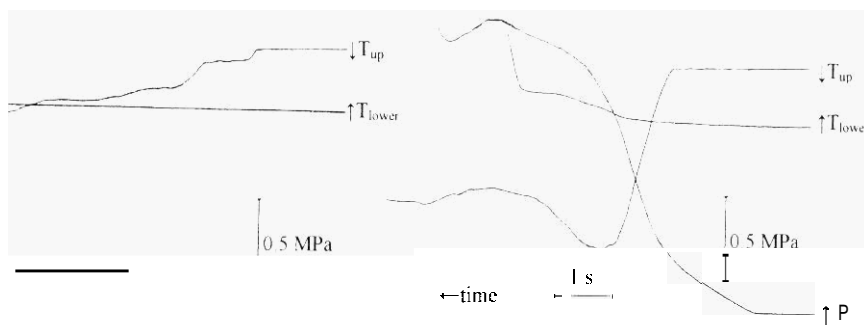
It was impossible to carry out experiments at atmospheric pressure for these substances because the ignition energy necessary for their inflammation was found to be too great for the autoclave of 10-liter volume. The extrapolation of the results obtained to the atmospheric pressure (at the assumption $E_{\text{ign, min}} = 1/P^n$) allows evaluation of the minimal ignition energy of such mixtures at the pressure of 1 atm. The exponent of power n was determined by the results of experiments at elevated pressures (Table 1).



$P_0 = 0.44 \text{ MPa}$ $P_0 = 0.46 \text{ MPa}$
HFC-134a + air, 13/87 vol.%; $E_{\text{ign.}} = 0.14 \text{ kJ}$



$P_0 = 0.58 \text{ MPa}$ $P_0 = 0.60 \text{ MPa}$
HCFC-22 + air, 30/70 vol.%; $E_{\text{ign.}} = 0.07 \text{ kJ}$



$P_0 = 1.2 \text{ MPa}$ $P_0 = 1.4 \text{ MPa}$
HFC-125 + air, 17/83 vol.%; $E_{\text{ign.}} = 1.1 \text{ kJ}$

Figure 3. Oscillograms of changes of pressure and temperature in the autoclave at inflammation of the mixtures of halocarbon+air.

TABLE 1. MINIMAL IGNITION ENERGY FOR MIXTURES OF HALOCARBON-AIR AT DIFFERENT PRESSURES.

Mixture	P, MPA	Eign, KJ
HFC-I34A + air 13/87, vol. %	0.56	0.07
	0.46	0.14
	0.34	0.28
	0.1	6.8 (extrapolated values)
HCFC-22 + air 30/70, vol. %	0.59	0.07
	0.43	0.14
	0.27	0.28
	0.1	1.6 (extrapolated values)
HFC-125 + air 17/83, vol. %	1.3	1.1
	0.8	2.2
	0.1	60 (extrapolated values)

CONCLUSIONS

The study conducted has shown that the minimal ignition energies of the mixtures of halocarbon agents-air investigated significantly exceed the ignition sources recommended by the existing standards (spark, hot wire, match). To ignite such mixtures, it is necessary to feed energy of over 0.1 kJ even at elevated pressures. It is possible to evaluate the required size of the hot spot to initiate deflagration by calculation of the mass of the reaction mixture that will be heated to the self-ignition temperature when such energy is fed. Taking into account changes in substance density at heating and combustion of the primary flame source, the authors have concluded that the volume of the autoclave at testing at atmospheric pressure should be 1 m³ minimum for testing HFC-I34a and HCFC-22 and not less 10m³ for HFC-125. We believe that the experimental results on inflammation of the mixtures of HFC-125, HFC-134a, and HCFC-22 obtained at elevated pressures cast doubt on the conclusion that they are nonexplosive at atmospheric pressure.

REFERENCES

1. Dekleva, Th. W., Lindlay, A. A., and Powell, Ph., "Flammability and Reactivity of Select HFCs and Mixtures," *ASHRAE Journal*, p. 40-47, Dec. 1993.
2. D. Lewis, G. von Elbe, *Combustion, Flames and Explosions of Gases*, second edition, 1961.