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## Fire Safety of 1, 2 and 2I Refrigerants: Myths and Reality

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# Fire Safety of 1, 2 and 2l Refrigerants: Myths and Reality

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**Abstract.** For many years fire safety measures for refrigerants were based on experimental data on their burning velocity and flammability limits in air. The analysis conducted in the paper and obtained experimental results show that knowledge of the flammability limits and the burning velocities is not enough to ensure the fire safety of the refrigerant. “Low flammable” substances may form explosive mixtures with air in wide range of conditions (initial concentration, pressure, temperature, ignition source (open hydrocarbon flame, hot surface)), even being a part of non-combustible mixture. One of the most underestimated things is an influence of open hydrocarbon flame as ignition source for halogenated substances not just from Class 2L (low flammable), but also from Class 1 (non-flammable). Mixtures of Class 1, 2L and 2 (lower flammable) refrigerants with lubricant oil should be also tested more carefully for their fire and explosion safety. In some cases the danger of “low flammable” substances may be underestimated due to the mismatch between test conditions and real conditions of use. It is also important that due to peculiarities of the process of mixing “low flammable” partially halogenated substances may form explosive mixtures with air at any mass of partially halogenated substance – the influence of mass factor must be also estimated more carefully.

## 1. Introduction

Flammable refrigerants present an immediate danger when released into the air. The refrigerant can combine with air at atmospheric pressure and ignite, causing a flame and possibly an explosion to occur. Because of the obvious hazards, the use of flammable refrigerants is restricted to controlled environments that have monitors, proper ventilation, explosion proof equipment and generally few people near the equipment (refineries, storage warehouses, breweries, etc.) [1]. For decades relevant safety measures have been taken in accordance with ANSI/ASHRAE Standard 15 [2], which demands were based on fire safety classification in ANSI/ASHRAE Standard 34 [3]. Till 2010 the Standard [3] established 3 classes of fire safety classification for refrigerants:

Class 1 (noncombustible): do not show flame propagation when tested in air at 60 °C and standard atmospheric pressure;

Class 2 (lower combustible): exhibit flame propagation when tested at 60 °C and atmospheric pressure, but have a LFL higher than 3.5 % by volume, and have a heat of combustion of less than 19,000 kJ/kg;



Class 3 (combustible): exhibit flame propagation when tested at 60 °C and atmospheric pressure, but have a LFL at or less than 3.5 % by volume, or have a heat of combustion that is equal to or greater than 19,000 kJ/kg.

The 2010 edition of ANSI/ASHRAE Standard 34 [3] added Subclass 2L to the existing Class 2 flammability classification of refrigerants:

Class 2L: as Class 2 but with a laminar speed of less than 0.1 m/s.

This change was intended to separate single component and blended refrigerants that are difficult to ignite and sustain a flame, from other Class 2 (and Class 3) flammable refrigerants [4].

“The expectation was that some of the Class 2L refrigerants would be commercialized and used as substitutes for Class A1 refrigerants that are in use today,” Dennis Dorman, chair of the Standard 15 committee, said. “Refrigerants in use today may come under regulatory pressure due to their relatively higher global warming potential (GWP). But to do this without major economic impact, Class 2L would have to be safely applied without the stringent application limitations imposed by Standard 15 on other flammable refrigerants. In other words, in order to be broadly applied, Class 2L refrigerants would need to be treated more like Class 1 than Class 2 or Class 3” [4] - these words established a myth on safety of 2L refrigerants, particularly, hydrofluorolefins (HFOs) and their blends. Here is some references reflecting current opinion of “refrigerant society” on flammability issues of 2L refrigerants:

- HFO-1234yf flammability characteristics are “milder than” those of hydrocarbon gases or HFC-152a [5];

- HFO-1234yf is a replacement for R-134a as a refrigerant in automotive air conditioners. HFO-1234yf is the first in a new class of refrigerants acquiring a global warming potential rating 335 times less than R-134a and an atmospheric lifetime of about 400 times shorter. This product is becoming more popular in many new vehicles in 2017 [6,7] – fire safety issues aren't mentioned!

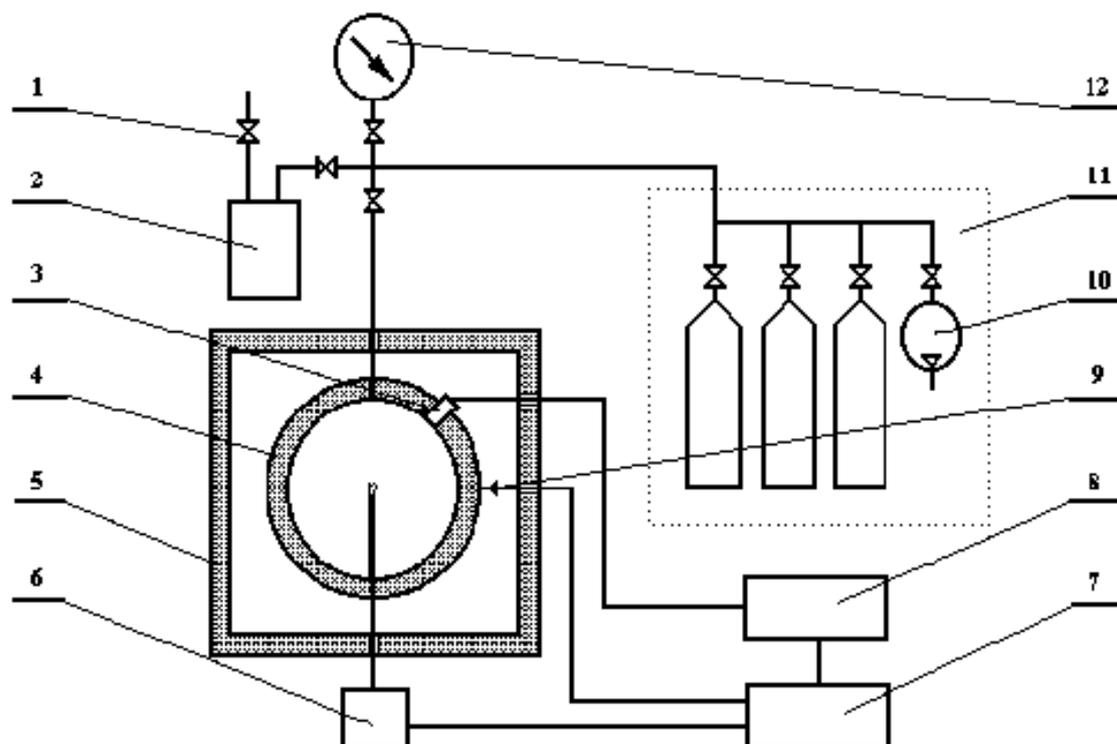
- As it follows from the risk assessment, the use of HFO-1234yf doesn't carry a significant additional risk of ignition in comparison with R134a for substitution of which it was developed. Numerous sectoral risk assessments have been carried out, including in the real world, which have modelled a variety of leakage options in the presence of different sources of ignition. In these tests it was extremely difficult to ignite the refrigerant in the presence of very high temperature sources, and none of the tests showed flame propagation [8];

- HFO-1234yf is classified as slightly flammable, however, tests have shown that this gas does not ignite under normal conditions, and, when used in automotive air conditioners, is as safe as R134a [9].

Besides of these “opinions” and “expectations” we didn't find any suitable technical information supporting the existing approach to fire safety of refrigerants besides of the data on flammability limits and flame velocity determined for individual substances in accordance with [10]. This paper is devoted to give more data to fill the gap.

## 2. Experimental

Experiments were executed on a set-up "Variant" presented at Fig.1. A reaction vessel (4) of this set-up has a spherical form with diameter 20 cm (volume 4.2 l) made from stainless steel. The set-up has a system for preparing of gaseous mixtures (11) by partial pressures after evacuation of the reaction vessel to residual pressure not higher than 0.5 kPa. Gaseous mixtures were ignited by fused nichrom wire, having diameter 0.2 and length 3 mm, at supplying electrical voltage 42 V on it (ignition energy near 10 J). Registration of a flame propagation was made by pressure detector "Saphire-22" (3) with time constant  $3 \cdot 10^{-3}$  s with recording of signal on storing oscilloscope (8). It was accepted that flame propagation takes place, if a pressure increase is higher than 30 kPa. Experiments were carried out at temperature 293 K and pressure 101 kPa. Each experiment was repeated not less than three times. A relative error of all measured values did not exceed 10 %.



**Figure 1.** Experimental set-up "Variant": 1 - valve; 2 – steam generator; 3 – pressure detector; 4 – reaction vessel; 5- thermostat; 6 – ignition source; 7 – control panel; 8 - oscilloscope; 9 - thermocouple; 10 – vacuum pump; 11 – system for preparing of gaseous mixtures; 12 – vacuum gauge.

### 3. Results and discussion

Our experimental results on determination of flammability limits and burning velocity for some substances mixed with air are presented in Table 1, where. LFL – lower flammability limit, UFL – upper flammability limit, MIE – minimum ignition energy, N/A – not applicable; HFC – hydrofluorocarbon, HFO – hydrofluorolefin, Blend 3.5 – mixture of 70 mass. %  $C_2H_5Br$  – 30 mass. %  $CO_2$ .

Classification for ethyl bromide and Blend 3.5 is given formally with regards to their properties ( $C_2H_5Br$  and Blend 3.5 were used in 1960s-70s as fire suppressants and have never used as refrigerants).

As it follows from Table 1, our test method and ASTM E681-09 (2015) [10] show the same results. Let's see if there is enough information on the flammability limits and the burning velocities to ensure the fire safety of the refrigerant.

It is known that some liquids (in particular, halogenated organics such as  $C_2H_5Br$ ,  $CH_2Cl_2$ ,  $C_3H_4Cl_4$ ,  $C_6H_4F_{10}O$ ,  $C_3H_4F_3Cl$ ,  $C_2H_3F_3O$ ,  $C_2HCl_3$ ) are not able to burn steadily, but their vapors are able to form explosive mixtures with air (have flammability limits) [11]. All these substances can be classified as Class 2L substances. As it was already mentioned, smaller fire safety measures should be taken for class 2 refrigerants. But as it follows from the examples below, 2L substances, even being a component of a non-combustible mixture, may form explosive environments in wide range of conditions.

**Case 1:** 1970, USSR, Baku – explosion of Blend 3.5 during fire suppression in fuel tank filled with aviation fuel. Volume of the tank was 3000 m<sup>3</sup>.

**Case 2:** 1975, USSR – explosion of Blend 3.5 during application of hand-held fire extinguisher for fire extinguishing of small pull fire of transformer oil in transformer substation. 1 person was injured.

As a result, the Ministry of Energy banned using of Blend 3.5 fire extinguishers at the objects under its control [12,13].

**Table 1.** Flammability limits and burning velocities.

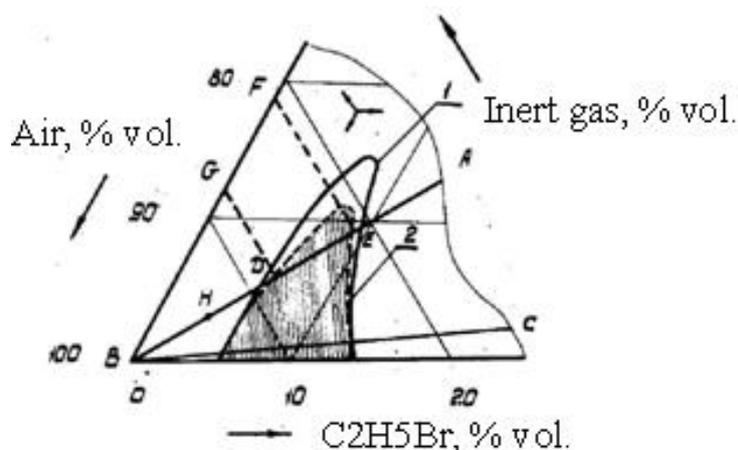
Substance	LFL, vol. % in Air	UFL, vol. % in Air	MIE, mJ	Burning velocity, cm/s	Classification as to [3]
Propane C <sub>3</sub> H <sub>8</sub>	2.2 <sup>1,2</sup>	10.0 <sup>1,2</sup>	0.25 <sup>1</sup>	46.0 <sup>1,2</sup>	3
HFC-152a CF <sub>2</sub> HCH <sub>3</sub>	3.9 <sup>1,2</sup>	16.9 <sup>1,2</sup>	0.38 <sup>1</sup>	23.0 <sup>1,2</sup>	2
HFC-32 CF <sub>2</sub> H <sub>2</sub>	14.4 <sup>1,2</sup>	29.3 <sup>1,2</sup>	30-100 <sup>1</sup>	6.7 <sup>1,2</sup>	2L
Ammonia NH <sub>3</sub>	15.0 <sup>1,2</sup>	28.0 <sup>1,2</sup>	100-300 <sup>1</sup>	7.2 <sup>1,2</sup>	2L
HFO-1234yf CH <sub>2</sub> =CFCF <sub>3</sub>	6.2 <sup>1,2</sup>	12.3 <sup>1,2</sup>	>5000 <sup>1</sup>	1.5 <sup>1,2</sup>	2L
HFC-134a CF <sub>3</sub> CFH <sub>2</sub>	None <sup>1,2</sup>	None <sup>1,2</sup>	None <sup>1</sup>	None <sup>1,2</sup>	1
HFC-125 CF <sub>3</sub> CF <sub>2</sub> H	None <sup>2</sup>	None <sup>2</sup>	N/A <sup>2</sup>	None <sup>2</sup>	1
HFO- 1233zd(E) CF <sub>3</sub> CH=CHCl	None <sup>2</sup>	None <sup>2</sup>	N/A <sup>2</sup>	None <sup>2</sup>	1
Ethyl bromide CH <sub>3</sub> CH <sub>2</sub> Br	6.8 <sup>2</sup>	11.2 <sup>2</sup>	N/A <sup>2</sup>	3.5 <sup>2</sup>	2L
Blend 3.5	None <sup>2</sup>	None <sup>2</sup>	N/A <sup>2</sup>	None <sup>2</sup>	1

<sup>1</sup> – data from [3], <sup>2</sup> –our data

Main cause of these explosions is in the following [14]. At triple diagram for C<sub>2</sub>H<sub>5</sub>Br – CO<sub>2</sub> – air (Fig.2) a zone of flammability of ethyl bromide in environment of air and carbon dioxide is indicated by hatching. Directions of changing of concentrations are shown by arrows.

The sum of all three concentrations is equal to 100 % vol. at any point of the diagram. A straight line drawn from the vertex of the triangle, characterizes the mixtures with a constant ratio of the two components at variable concentrations of the third. For example, at any point of line AB the ratio between ethyl bromide and carbon dioxide is 1:1 while concentration of air varies from 0 at point A to 100 % vol. at point B. It is easy to see that line AB corresponds to Blend 3.5.

When Blend 3.5 discharges into protected volume, its initial composition (before dilution of equimolar mixture of ethyl bromide and carbon dioxide by air) corresponds to point A. During the filling of the protected volume by Blend 3.5 the mixing of the vapors of ethyl bromide and carbon dioxide with air takes place, and the volumetric ratio of all three components at any point of the filling space will be characterized by the line AB. The process of mixing goes in the direction from A to B. Line AB crosses zone of flammability in points E and D. Design extinguishing concentration of Blend 3.5 is equal to 6.7 % vol. This concentration of the blend corresponds to point H at the diagram (3.25 % vol. C<sub>2</sub>H<sub>5</sub>Br + 3.45 % vol. CO<sub>2</sub> + 93.3 % vol. air). This point is located outside the area of flammability. But in real conditions during fire extinguishing by Blend 3.5 in confined volume the formation of any mixtures along the line AB (including mixtures within the boundaries of the flammability region between points D and E), is possible.



**Figure 2.** Area of flammability of the system C<sub>2</sub>H<sub>5</sub>Br – air – inert gas:  
1 – for nitrogen; 2 – for carbon dioxide. AB – line of dilution of 3.5 blend by air.

**Case 3:** 1975, USSR, Odessa – explosion of 3.5 blend in engine compartment of commercial vessel during accidental discharge of total flooding fire suppression system. The explosion occurred after direct contact of extinguishing blend with heated surface of the engine. The main reason of the case is the stratification of the mixture during storage and the preferential discharge of ethylbromide with the subsequent formation of the combustible mixture of C<sub>2</sub>H<sub>5</sub>Br with air.

**Case 4:** 1974, USSR, Moscow Region, chemical plant – detonation in technological pipeline of a mixture containing CH<sub>2</sub>Cl<sub>2</sub> and some other partially halogenated substances at elevated pressure and temperature. The mixture detonated in spite of that preliminary tests showed that the mixture is nonflammable. 17 people killed.

As it follows from the examples, so called “low flammable” substances may form explosive mixtures with air in wide range of conditions (initial concentration, pressure, temperature, ignition source (open hydrocarbon flame, hot surface)), even being a part noncombustible mixture (for example, with CO<sub>2</sub> or N<sub>2</sub>). On our opinion, one of the most underestimated things is open hydrocarbon flame as ignition source for halogenated substances not just from Class 2L, but also from Class 1. The results of cupburner test [15] shows that HFO-1233zd(E) which is Class 1 refrigerant, may maintain sustainable combustion in presence of piloting hydrocarbon flame (HFO-1233zd(E) forms high-temperature blue flame, see Fig. 3).



**Figure 3.** Combustion of “non-combustible” HFO-1233zd(E) in presence of hydrocarbon flame.

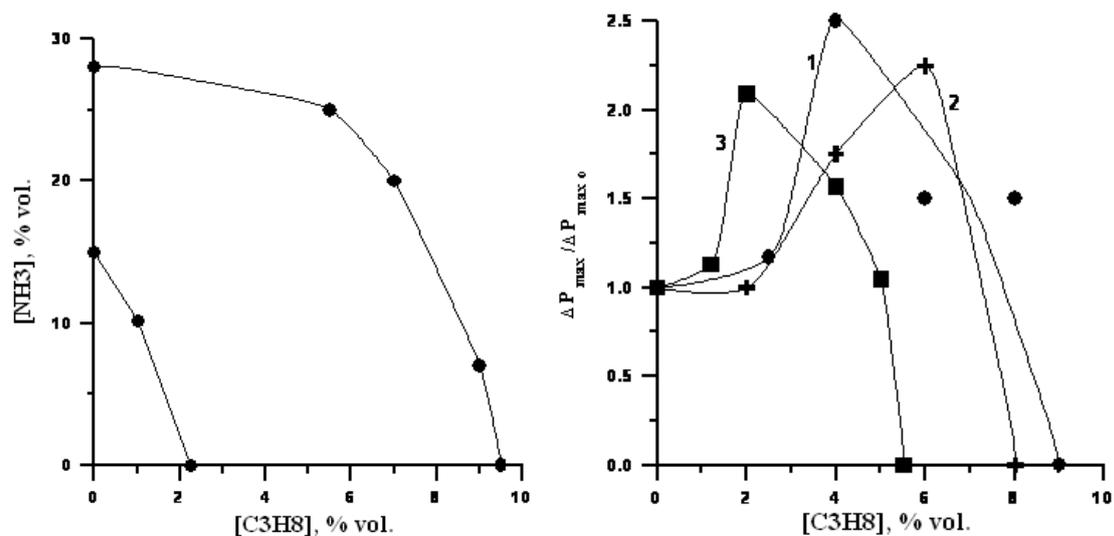
Figure 4 presents the results of live fire test, involving HFO-123434yf mixed with lubricant oil [16]. It is easy to see that if energy of ignition source is substantially higher than MIE, mixture of Class 2L refrigerant and lubricant oil may form a fire ball during accidental leakage from a condenser of automotive air conditioner. This result is not a surprise; such type of behavior of partially

halogenated substances was predicted in [17]. It was shown that even Class 1 refrigerants, particularly HFC-134a and HFC-125, will burn in mixtures with air at atmospheric pressure if the energy of the ignition source exceed 6.8 kJ and 60 kJ respectively.



**Figure 4.** Appearance of fire ball during accidental leakage of HFO-1234yf mixed with lubricant oil in presence of high energy ignition source.

On September 25, 2012, Daimler (Mercedes-Benz) published a press release on the results of additional tests of HFO-1234yf refrigerant in the real situation scenario that goes beyond the existing normative requirements [18]. In the scenario of the real situation, the refrigerant was dynamically sprayed under high pressure near the hot elements of the exhaust system of the test car. This scenario corresponds to a severe frontal collision in which a refrigerant tube is damaged; the test results show that Class 2L refrigerant can easily ignite in the hot atmosphere of the engine compartment [18]. According to Daimler, similar tests using R134a did not result in the ignition of the refrigerant. Even well-known Class 2 refrigerants, such as ammonia, may reveal unusual properties when mixed with hydrocarbons. Our experiments show that addition of propane to ammonia – air mixture expands its flammability limits (Fig. 5a) and causes elevation of maximum explosion pressure up to 2.5 times in comparison (Fig. 5b).



**Figure 5.** Flammability limits (a) and maximum explosion pressure (b) for ammonia – propylene-air mixtures. [NH<sub>3</sub>]: 1 - 17 vol. %; 2 - 20 vol. %; 3 - 25 vol. %.

If non-combustible HFCs are added to hydrocarbon – air mixture, they also cause elevation of maximum explosion pressure [19]. This effect is known as influenced oxidation of HFC during combustion of hydrocarbon – air mixture.

#### 4. Conclusions

The results of the paper show that knowledge of the flammability limits and the burning velocities is not enough to ensure the fire safety of the refrigerant. “Low flammable” substances may form explosive mixtures with air in wide range of conditions (initial concentration, pressure, temperature, ignition source (open hydrocarbon flame, hot surface)), even being a part noncombustible mixture. On our opinion, one of the most underestimated things is open hydrocarbon flame as ignition source for halogenated substances not just from Class 2L, but also from Class 1. ). Mixtures of Class 1, 2L and 2 (lower flammable) refrigerants with lubricant oil should be also tested more carefully for their fire and explosion safety.

In some cases the danger of “low flammable” substances may be underestimated due to the mismatch between test conditions and real conditions of use. It is also important that due to peculiarities of the process of mixing “low flammable” partially halogenated substances may form explosive mixtures with air at any mass of partially halogenated substance – the influence of mass factor must be also estimated more carefully.

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