Seven burning questions about mildly-flammable refrigerants

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Concerns about global warming are strong motivation to adopt new, lower global warming potential (GWP) halogen refrigerants that break down quickly in the atmosphere. This reactivity can present new hazards if these mildly-flammable refrigerants leak into residences where ignition sources are present. Seven questions about these refrigerants are addressed to offer insight into flammability test methods, ignition source viability, leak detectors, and hydrogen fluoride (HF) hazards.

Introduction

Since the phase-out of chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants, beginning in 1987, most new heat pumps have used non-flammable hydrofluorocarbons (HFCs) as the working fluid. Unfortunately, these have high GWPs. The environmental impact is tremendous: on average, residential air conditioning systems leak 8.5 % of their charge annually into the atmosphere [1].

There are four safety classes of refrigerant flammability: 1, 2L, 2, and 3, in order of increasing flammability per standards ANSI/ASHRAE 34 [2] and ISO 817 [3]. Refrigerant charge limits generally decrease with increasing flammability class. During the next decade it is expected that most new residential heat pumps will transition to Subclass 2L halogen refrigerants, which are mildly flammable. These include R-32, R-143a, R-1234yf, R-1234ze, and many blends. Their fire hazards are the primary impediment to their adoption.

Subclass 2L refrigerants must meet three flammability requirements: a lower heating value (LHV) below 19 kJ/g; a lower flammability limit (LFL) above 100 g/m^3 or 3.5 %; and a laminar burning velocity below 10 cm/s [2-4]. All three requirements are determined by small-scale combustion tests. Tests at large scale indicate that 2L refrigerants are difficult to ignite and unlikely to produce strong blasts upon burning.

Seven Burning Questions

1. How are lower flammability limits (LFLs) measured?

The standard method for measuring refrigerant LFLs is ASTM E681. Results from ASTM E681 are tied not only to refrigerant classifications, but also to charge limits that are based on the LFL and the room size. Furthermore, it is the only test that can qualify a refrigerant as Class 1 (non-flammable).

ASTM E681 makes visual observations of premixed flames propagating in a 12 L glass vessel. The LFL is defined as producing flames that burn upward and outward along a 90° cone. Unfortunately, ASTM E681 suffers from relatively poor accuracy and disparate LFL determinations [5]. For example, the LFL for R-32 has been reported between 13.5 – 14.8 %.

Our research [5] has recommended five relatively simple changes to ASTM E681 that, if adopted, are expected to significantly improve the test's accuracy. For example, the vessel material should be transparent polycarbonate to avoid etching, venting should not be allowed during the measurement period, and the electrodes should be horizontal. The vessel assembly shown in Fig. 1 incorporates these changes.

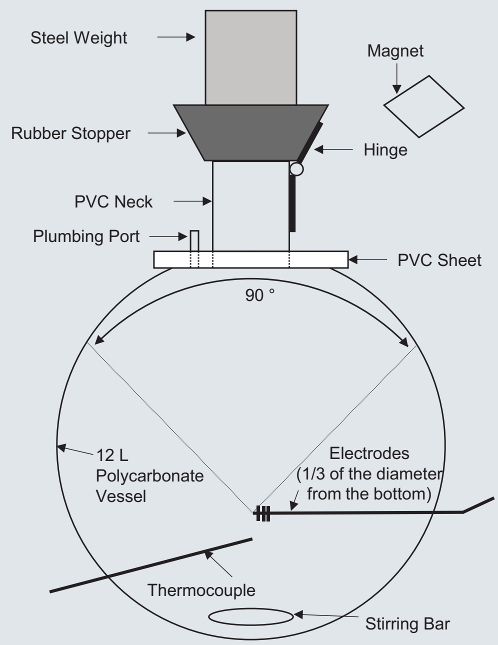

Fig. 1: Schematic of the proposed polycarbonate vessel assembly, reproduced from Ref. [5]. The 90° cone shown represents the location of a flame at the LFL.

Representative images of halogen refrigerant flames near their LFLs are shown in Fig. 2. Vertical electrodes (required by the existing standard) are seen to create a large hole in the top of the flame. Horizontal electrodes, facilitated by the design of Fig. 1, eliminate such holes and thus improve accuracy.

2.Can non-flammable refrigerants burn?

At room temperature they cannot, but there are two key scenarios where sufficient external heat is applied that Class 1 halogen refrigerants will burn exothermically and emit a large amount of hydrogen fluoride (HF). Many refrigerant leaks are accompanied by aerosolized lubricating oil. In the presence of a viable ignition source, this oil can ignite the surrounding Class 1 halogen refrigerant in a fireball.

If an external fire impinges on a refrigeration system with a Class 1 halogen refrigerant, this can weaken the containment and/or increase the internal pressure, resulting in a loss of containment. The resulting refrigerant jet will ignite if it encounters the flames.

3. Is it hard to ignite a Subclass 2L refrigerant?

Subclass 2L refrigerants are much harder to ignite than Class 3 refrigerants (such as propane and butane). This is principally because they have large quenching distances – on the order of 8 – 25 mm [5]. The minimum ignition energy for a typical 2L halogen is 10 J, compared to 3×10^{-4} J for methane. Between these energies, a typical static electric discharge releases 0.1 J. Thus, although 2L refrigerants can be ignited by open flames or unenclosed yellow-hot heating wires, they cannot be ignited by typical motors, electrical switches, or resistive heating devices such as toasters, hair dryers, and space heaters [6].

4. Can Subclass 2L refrigerants suppress some flames?

Yes. Testing in our lab has identified several scenarios where 2L halogen refrigerants suppress flames [6]. For example, when a smoldering cigarette is introduced into a stoichiometric 2L/air mixture, the cigarette quickly extinguishes. When a 2L halogen fills a chamber with good mixing, this extinguishes a candle flame before the LFL is reached (see Fig. 3). These observations are consistent with the findings of Ref. [7], which showed halogens can act as either fuels or suppressants depending on the conditions.

5. What can we learn from past experience with ammonia fires?

As discussed by Ref. [7], ammonia is a 2L refrigerant with flammability characteristics similar to 2L halogen refrigerants. Ammonia is too toxic for most heat pump applications. However, its flammability is well understood, and its historical safety record offers a wealth of information for future risk analyses of 2L halogen refrigerant systems. For example, large ammonia leaks have ignited and resulted in blasts powerful enough to cause structural damage. Ammonia may be a good surrogate for 2L halogen refrigerants in research tests because its products of combustion are far less toxic.

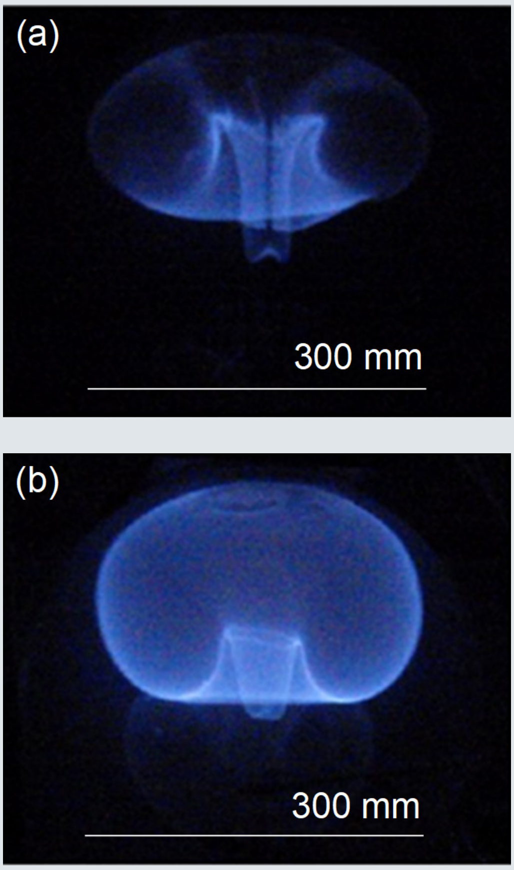

Fig. 2: Effect of electrode orientation on R-32/air flames near their flammability limit. Images (a) and (b) are for vertical and horizontal electrodes, respectively. Reproduced from Ref. [5].

Fig. 3: A candle flame undergoing extinguishment when R-32 is introduced with good mixing.

6. Do reliable area monitoring leak detectors exist?

Many technologies exist for detecting 2L halogen leaks [8]. These are normally optimized for either leak pinpointing or area monitoring. Pinpointing detectors are commonly used in servicing, where they are powered up for only a few minutes at a time. Reliable and affordable pinpointing detectors exist for 2L halogens.

Area monitoring detectors will be required for many future heat pump systems that use 2L refrigerants. These detectors will operate continuously, preferably without service for many years. Standards are being drafted that will require these detectors to have a 15 s (or shorter) response time to any concentration of 20 % (or higher) of the LFL [8]. Inexpensive detectors that meet these requirements do not yet exist. This gap may delay the release of these standards.

7. Is HF a major hazard?

Yes! For residential heat pump systems it could be a greater hazard than the other three flame hazards combined: secondary ignition of furnishings, blasts, and thermal injuries. HF volume fractions can be up to 50 % following a 2L halogen refrigerant fire. HF can be produced upon heating even with no flame present.

Two employees of a major research laboratory recently suffered HF injuries following test burns of 2L halogens. In one case an employee entered the burn room briefly during a test and without the required personal protective equipment. He later collapsed, presumably owing to cardiac arrest, and required hospitalization.

In another incident, an employee touched a wall interior to the burn room and immediately felt a burning sensation in his hand. There had been dozens of air changes, but a high concentration of HF persisted. This is surprising because no liquid water was present and HF has a boiling point of just 19.5 °C.

Subclass 2L fire hazards were discussed recently at a meeting of fire chiefs and fire marshals attended by the author. These experts expressed far more concern about the HF hazards than the other fire hazards associated with 2L halogen refrigerants. First responders, fire investigators, and remediation personnel will require specialized training and medical supplies when responding to fires involving 2L refrigerant leaks.

HF can also be produced when Class 1 halogen refrigerants encounter flames or heat. The key difference is that 2L refrigerants can ignite and burn on their own when there is a viable ignition source. An untrained resident or first responder may fully extinguish the fire with an extinguisher, only to perish later from contacting and/or inhaling the HF fumes.

Conclusions

Mildly-flammable halogen refrigerants are already being adopted owing to environmental concerns. These refrigerants present several new hazards, and further research is needed to address these. For example, the flammability limit test standard should be improved and new detectors should be developed. Perhaps their greatest hazard is the generation of toxic HF when these refrigerants burn.

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