

# REFRIGERANT FLAMMABILITY AN INTERNATIONAL PERSPECTIVE

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## Abstract

In response to global environmental threats industry has developed and introduced replacement refrigerants with zero ozone depletion potential and low global warming potential. In most cases hydrofluorocarbons (HFCs) have been found to be the ideal replacement. In some applications, hydrocarbons (HCs) or ammonia have been found to work well. Hydrocarbons, ammonia and some HFCs are flammable and special precautions must be taken to ensure the safety of the building occupants, the service technicians and the general public. This paper will focus on refrigerant flammability. With the introduction of equipment using flammable refrigerants it has become necessary to modify some standards to allow for the safe use of flammable refrigerants. Methods of determining the lower flammability limits of refrigerants are being updated and research programs are underway to evaluate the potential risk in the event of a leak.

## Introduction

The discovery that chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) could destroy stratospheric ozone resulted in the Montreal Protocol on Substances that Deplete the Ozone Layer. The CFCs have already been phased-out in developed countries and will be phased-out in developing countries (as defined by Article 5 of the Montreal Protocol) by January 1, 2010. The HCFCs will be phased-out in developed countries in 2030 and in developing countries in 2040. Many countries have already reduced their use of HCFCs and have accelerated the phase-out schedule. For example, in the European Union, HCFC consumption will be phased-out by January 1, 2010 and restrictions on their use are already in place.

In response to these global environmental threats industry has developed and introduced replacement refrigerants with zero ozone depletion potential and low global warming potential. In most cases hydrofluorocarbons (HFCs) have been found to be the ideal replacement. In some applications, hydrocarbons (HCs) or ammonia have been found to work well. Hydrocarbons, ammonia and some HFCs are flammable and special precautions must be taken to ensure the safety of the building occupants, the service technicians and the general public.

Determining whether or not a refrigerant is flammable and if so, how flammable can be a complicated task. For several years, this was not an issue since the fluorocarbons in use were nonflammable. With the phase-out of CFCs and HCFCs it became necessary to evaluate several alternatives, some of which were flammable. All of the alternative compounds have potential problems associated with their use. The HFCs being used today are very low in toxicity, have zero ozone depletion potential and low global warming potential relative to the chlorinated compounds which they replaced, but they are listed as controlled substances in the Kyoto Protocol. The hydrocarbons have

low toxicity, zero ozone depletion potential and very low global warming potential, however they are highly flammable. Their use requires special safety precautions. Ammonia is a very good refrigerant, but its use has been restricted to industrial applications because it is both toxic and flammable.

This paper will focus on refrigerant flammability. With the introduction of equipment using flammable refrigerants it has become necessary to modify some standards to allow for the safe use of flammable refrigerants. Methods of determining the lower flammability limits of refrigerants are being updated and research programs are underway to evaluate the potential risk in the event of a leak.

## Standards

There are several industry standards that deal with safety for the air conditioning and refrigeration industry. While compliance with the standards is voluntary they are frequently adopted by local authorities in codes and regulations, which makes compliance mandatory. The primary standards of interest relative to the use of flammable refrigerants are listed in Table 1.

Currently, the safety classification system used in ASHRAE Standard 34 is the basis for that used in the other standards around the world. This standard has 6 groupings based on toxicity and flammability data. (See Figure 1) The safety classification consists of two alphanumeric characters (e.g. A2 or B1). The upper case letter indicates the toxicity and the Arabic numeral indicates the flammability.

There are two safety groups based on toxicity, Class A - lower toxicity and Class B - higher toxicity. Refrigerants are assigned to Class A if they have an exposure limit of 400ppm or greater and to class B if the exposure limit is less than 400 ppm. The exposure limit is defined as the time weighted average concentration not having an adverse effect on nearly all workers who may be exposed to it day after day for a normal 40 hour workweek.

There are three groups for flammability, which are based on the lower flammability limit (LFL) and the heat of combustion (HOC). Class 1 (no flame propagation) indicates refrigerants that do not show flame propagation when tested as specified in air at 21°C and 101 kPa. Class 2 (lower flammability) indicates refrigerants having an LFL of more than 0.10 kg/m<sup>3</sup> at 21°C and 101 kPa and a heat of combustion of less than 19,000 kJ/kg. Class 3 (higher flammability) indicates refrigerants having an LFL less than or equal to 0.10 kg/m<sup>3</sup> at 21°C and 101 kPa or a heat of combustion greater than or equal to 19,000 kJ/kg. Table 2 provides a list of refrigerants classified as Class 2 and Class 3 in ASHRAE Standard 34.

In the case of blends, the classification method in ASHRAE Standard 34 requires a study of the fractionation of the blend. The LFL and HOC are determined on the worst-case fractionated formulation. Initially ASHRAE Standard 34 listed a dual classification for blends, one for the refrigerant as formulated and one for the worst case fractionation. However, other standards, which use the safety classification considered only the worst case classification, so ASHRAE Standard 34 has now dropped the dual classification system and lists only the worst case classification.

EN 378 *Refrigerating systems and heat pumps – Safety and environmental requirements*, defines 6 safety groups similar to ASHRAE Standard 34, however the

European Standards body has chosen to combine some of the groups resulting in 3 groups as indicated below:

L1 = A1

L2 = A2, B1, B2

L3 = A3, B3

The safety precautions are then defined for the use of refrigerants based on these 3 groups. The refrigerant is classified in that group requiring the more stringent precautions where there is doubt under which group a refrigerant is to be classified.

ISO Standard 817, Organic Refrigerants – Number Designation does not currently include a means of assigning a safety classification to refrigerants, but a working group is revising the standard to add refrigerant safety classifications. The working group reviewed the classifications used in other standards and agreed that the criteria set out in ASHRAE Standard 34 using 6 groupings would be proposed for use in ISO 817.<sup>1</sup>

IEC Standard 60335-2-24, was revised in 2000 and now allows up to 150g of a flammable refrigerant in household refrigerating appliances. A proposed change to IEC 60335-2-40, would allow for the use of flammable refrigerants in electrical hear pumps, air-conditioners and dehumidifiers. As in 335-2-40, up to 150 g can be used without any restrictions relative to the room size and ventilation. Charges sizes greater than 150 g require special precautions. The room size is restricted based on refrigerant charge and ventilation.

### **Measuring Flammability**

The method for determining the LFL of a refrigerant has been modified in recent years to accommodate the introduction of refrigerants that had marginal flammability. It was discovered that factors such as the ignition source, vessel size and relative humidity could have a significant impact on the determination of the LFL.

The flammability subcommittee of ASHRAE Standard 34 is developing an addendum to the standard with detailed instructions on how to measure the LFL of a refrigerant. In the proposed addendum, the flammability tests will be conducted in a 12L spherical glass flask. The ignition source will be a spark from a transformer secondary rated at 15 kV and 30 mA alternating current with a 0.4 second spark duration. (see figure 2 for a diagram of the test apparatus) The absolute humidity of the air used for mixing is controlled to 0.0088 grams of water per gram of dry air (which equates to 50% relative humidity at 23.0°C and 101.3kPa.) All flammability tests are recorded using a video recorder. A playback device capable of freeze frame and single frame advance is used to view the test and assist in determining if the material is flammable.<sup>2</sup>

A refrigerant-air concentration is considered flammable if flame propagation occurs in at least two of three flammability tests on that refrigerant-air concentration. A flame propagation is any combustion, that having moved upward and outward from the point of ignition to the walls of the flask, is continuous along an arc that is greater than that subtended by an angle equal to 90 degrees as measured from the point of ignition to the walls of the flask. The determination is made by observing the test on a video monitor with an overlay indicating the 90 degree angle.

For a refrigerant with more than one component you must consider not only the nominal formulation of the refrigerant, but also how the refrigerant composition will change in the event of a leak. The proposed addendum requires that the several

fractionation scenarios be considered and the LFL of the worst-case fractionated formulation be tested.

The ISO Working Group revising ISO Standard 817, Organic Refrigerants – Number Designation is in the process of adding a method of classifying refrigerants based on toxicity and flammability. The WG is considering the classification method in ASHRAE Standard 34, but is also considering proposals from others. Kataoka has suggested that the LFL and Heat of Combustion used in ASHRAE Standard does not provide a consistent ranking of refrigerants based on their flammability. Kataoka proposed using the ratio of the stoichiometric concentration to the LFL concentration.<sup>3</sup> This ratio is defined as:

$$R = C_{\text{stoichiometric}} / C_{\text{LFL}}$$

In addition, Kondo has developed a term he refers to as the RF-Number as a new index of the combustion hazard of a refrigerant. The RF-Number considers both the probability of ignition and the power of combustion. It is defined as

$$RF = [\sqrt{(UL)-L}] / L \times (Q/M)$$

Where U = Upper Flammable Limit  
L = Lower Flammable limit  
Q = Heat of Combustion  
M = Molar Mass

Clodic et.al. have proposed measuring burning velocity as a criterion for the flammability classification of refrigerants. Burning velocity permits the classification based on fundamental properties related to combustion and is also a measurable property. Burning velocity can be related to the level of damage for explosion in real conditions of explosion. Research on this is continuing at Ecole de Mines in Paris.

### **Research Programs**

There are two research programs underway that are relevant to the determination of refrigerant flammability. The first is being sponsored by ASHRAE and is measuring the LFL of several refrigerants listed in ASHRAE Standard 34. Since the method has been changed, it was necessary to reevaluate all the data that was available on the refrigerants and where necessary determine the LFL using the new method. The laboratory work has been completed and the report is being reviewed. It is expected that a final report will be published later this year. This will provide a source for LFLs for several refrigerants, which have all been conducted using the same method.

There is also a research program underway at Ecole de Mines in Paris to evaluate the potential of using the burning velocity as a means of classifying refrigerants. This data will be compared to room tests to determine the risk of use.

### **Use of Flammable Refrigerants**

In the United States, codes and regulations currently prohibit the use of flammable refrigerants in occupied spaces out of a concern for the immediate safety of the building occupants. In the event of a leak, no matter how remote a possibility that is,

it is possible that the refrigerant could ignite. There is a fear on the part of manufacturers that if there is a fire and they chose a flammable refrigerant when there were nonflammable options available, they will be liable for damages. Since lawsuits often result in large financial awards to the injured party, most companies will not use flammable refrigerants in the United States.

In Europe, the situation is different. There have already been millions of household refrigerators sold in Europe with very few accidents. Refrigerators in Europe tend to be smaller than those in the United States with less features which means that charge sizes are smaller and there are fewer ignition sources in the refrigerator itself. Europeans are also concerned with safety, but they are more likely to consider the threat of global climate change to be as serious a threat as the possibility of a fire from using a flammable refrigerant.

In Japan flammable refrigerants are regulated by the High Pressure Gas Law, in which refrigerants are categorized into three types in terms of flammability. The three categories are very similar to the three classes in ASHRAE 34.

Approach to flammable refrigerants in Japan seems somewhere between the US and Europe. Users are very much concerned about product safety and manufacturers are very carefully studying safety of refrigerants and equipment. Some of Japanese manufacturers recently launched refrigerators with iso-butane as a refrigerant. The manufacturers explained that they had carried out safety investigations for 10 years and concluded that the charge amount less than 50g was sufficiently safe.<sup>4</sup> This charge amount is one-third of the allowable maximum amount specified by IEC60335-2-24.

Risk assessments on flammable refrigerants have been conducted for other applications. According to the Japanese Refrigeration and Air Conditioning Industry Association risk assessment on residential air-conditioners<sup>5</sup>, risk during their use is relatively low, but servicing and disposal result in high risk, which seems unacceptable to both users and manufacturers, as shown in Table 3.

## Conclusions

Determining whether or not a refrigerant is flammable and if so, how flammable can be a complicated task. For several years, this was not an issue since the fluorocarbons in use were nonflammable. With the phase-out of CFCs and HCFCs it became necessary to evaluate several alternatives, some of which were flammable. All of the alternative compounds have potential problems associated with their use. The HFCs being used today are very low in toxicity, have zero ozone depletion potential and low global warming potential relative to the chlorinated compounds that they replaced, but they are listed as controlled substances in the Kyoto Protocol. The hydrocarbons have low toxicity, zero ozone depletion potential and very low global warming potential, however they are highly flammable. Their use requires special safety precautions. Ammonia is a very good refrigerant, but its use has been restricted to industrial applications because it is both toxic and flammable.

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The method of determining the LFL of a refrigerant has been modified in recent years to accommodate the introduction of refrigerants that had marginal flammability. There are also proposals under consideration to modify the safety classification method.

### **References**

<sup>1</sup>Walter, William F., Designation and safety classification of refrigerants – proposed changes to ISO Standard 817, IEA Heat Pump Newsletter, Volume 18, No. 3/2000

<sup>2</sup>Richard, Robert G., Refrigerant flammability testing in large volume vessels, Air Conditioning and Refrigeration Technology Institute, MCLR Project 665-52400, March 1998.

<sup>3</sup>Kataoka, Osami, Flammability index for refrigerant standards, IEA Heat Pump Newsletter, Volume 18, No. 3/2000

<sup>4</sup>“HYDROCARBON FRIDGES HIT ENVIRONMENT-SAVVY JAPAN”, Japan Times, Mar. 19, 2002

<sup>5</sup>Yao, Kenji, “Risk Assessments for Room Air Conditioner with Propane”, The International Symposium on HCFC Alternative refrigerants and Environmental Technology 2000, Dec 7-8, 2000

## Tables

Table 1: Standards

Organization	Standard #	Title
ASHRAE	34	Designation and Safety Classification of Refrigerants
ASHRAE	15	Safety Standard for Mechanical Refrigeration
EN	378	Refrigerating systems and heat pumps – Safety and environmental requirements
ISO	817	Organic Refrigerants – Number Designation
ISO	5149	Mechanical refrigerating systems used for cooling and heating – safety requirements
IEC	60335-2-24	Particular requirements for refrigerating appliances, ice-cream appliances and ice-makers
IEC	60335-2-40	Particular requirements for electrical heat pumps, air-conditioners and dehumidifiers.

Table 2. Flammable Refrigerants listed in ASHRAE Standard 34-2001

Refrigerant Number	Identification	Formula or (Composition)	Safety Group
30	dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	B2
32	difluoromethane	CH <sub>2</sub> F <sub>2</sub>	A2
40	chloromethane	CH <sub>3</sub> Cl	B2
611	methyl formate	HCOOCH <sub>3</sub>	B2
7170	ammonia	NH <sub>3</sub>	B2
142b	1-chloro-1,1-difluoroethane	CH <sub>3</sub> CClF <sub>2</sub>	A2
143a	1,1,1-trifluoroethane	CH <sub>3</sub> CF <sub>3</sub>	A2
152a	1,1-difluoroethane	CH <sub>3</sub> CHF <sub>2</sub>	A2
406A	R-22/600a/142b	(55/4/41)	A2
411A	R-1270/22/152a	(1.5/87.5/11.0)	A2
411B	R-1270/22/152a	(3/94/3)	A2
412A	R-22/218/142b	(70/5/25)	A2
413A	R-218/134a/600a	(9/88/3)	A2
50	methane	CH <sub>4</sub>	A3
170	ethane	CH <sub>3</sub> CH <sub>3</sub>	A3
290	propane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	A3
600	butane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	A3
702	hydrogen	H <sub>2</sub>	A3
1150	ethane	CH <sub>2</sub> =CH <sub>2</sub>	A3
1270	propene	CH <sub>3</sub> CH=CH <sub>2</sub>	A3
600a	isobutane	CH(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>	A3

Table 3 Risk Assessment for Residential Air-conditioners

	Estimated Number of Fire [cases/year]	
	No Measures Against Flammability	With Measures
Installation	105 – 1190	< 1 – 2
In Use Indoors	< 1 – 7700	< 1
Service	650 – 1190	20 – 57
Disposal	1260 – 9100	29 – 36

**Figures**

I N C R E A S I N G	↑ F L A M M A B I L I T Y	SAFETY GROUP		
		Higher Flammability	A3	B3
		Lower Flammability	A2	B2
		No Flame Propagation	A1	B1
		Lower Toxicity	Higher Toxicity	
		→ INCREASING TOXICITY		

Figure 1 Refrigerant safety group classification

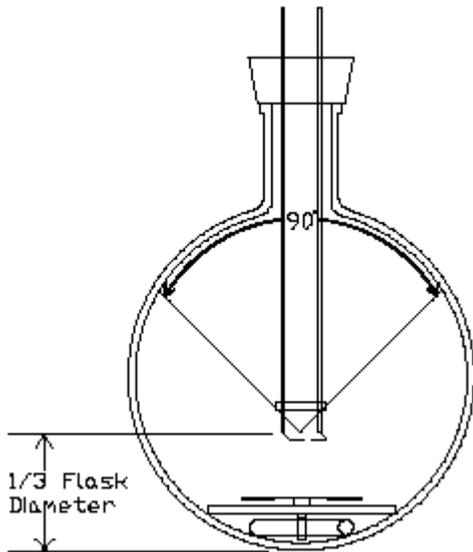


Figure 2 Flammability Test Apparatus