What Are A2L Refrigerants and Why Do We Need Them?

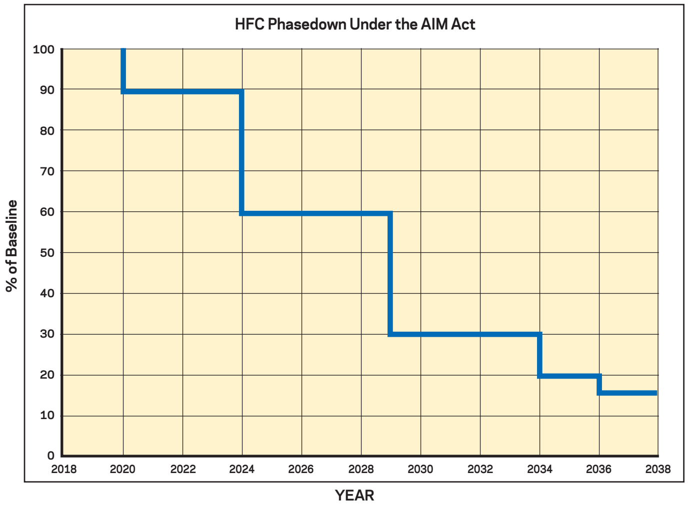
by Stephen Spletzer

Introduction

Regulations focused on combating climate change, at the global, regional, national, and even state level, are resulting in a transition of the Air-Conditioning & Refrigeration (ACR) industry towards lower Global Warming Potential (GWP) refrigerant solutions. At the international level, the Kigali Amendment to the Montreal Protocol has laid out the framework for a global phase-down of HFC refrigerants, which is defined on a GWP-weighted basis. Participating countries will have to reduce the GWP-weighted basis of their HFC/HCFC consumption levels down to 15 – 20 % of their established baselines. This amendment has been ratified so far by over one hundred and thirty countries and entered into force January 1, 2019.

While the US has not yet ratified the Kigali Amendment to the Montreal Protocol, the recent passage of the American Innovation and Manufacturing (AIM) Act gives the EPA the authority to phasedown HFC consumption over the next fifteen years (see Figure 1). Although implementation details of this phasedown are still under development, the EPA has started taking steps that would help enable the transition to lower GWP refrigerants. The recent SNAP 23 final rule makes acceptable, subject to use conditions, six new refrigerants for residential and light commercial air conditioning and heat pump applications. All six of these new refrigerants fall into the A2L safety group, as defined by ANSI/ASHRAE Standard 34.

Figure 1: HFC Phasedown Schedule Under the AIM Act



These and other innovative new refrigerants, such as hydrofluoroolefins (HFOs), have been developed with dramatically lower GWP values than HFCs. However, A2Ls and other alternatives (e.g. Hydrocarbons [HCs], Blends, etc.) have varying degrees of flammability. To this end, the ACR industry has spent the last several years preparing for a transition to flammable refrigerants. This report will give an overview of some of the lower GWP refrigerants developed, along with key factors that must be considered when working with flammable refrigerants. Safety classes and flammability parameters are also reviewed, as well as their effect on refrigerant selection. Finally, codes and standards impacts are also highlighted.

Table 1: Lower GWP Alternative Refrigerants*

Industry Standard Refrigerant (GWP)	Nonflammable Alternatives —Class 1 (GWP)	Lower Flammability Alternatives —Class 2L (GWP)
R-123 (77)	R-1233zd (5) Opteon™ XP30 - R-514A (7)	-------
R-134a (1430)	R-450A (604) Opteon™ XP10 - R-513A (631)	Opteon™ XL10 - R-1234yf (4) R-1234ze (7)
R-22 (1810) R-404A (3922)	R-448A (1387) Opteon™ XP40 - R-449A (1397) Opteon™ XP44 - R-452A (2140)	Opteon™ XL40 - R-454A (239) Opteon™ XL20 - R-454C (148)
R-410A (2088)	--------	Opteon™ XL41 - R-454B (466) R-32 (675)

*GWP values are based on 100 year AR4

Finding the Right Balance

Hydrofluorocarbons (HFCs) have served as the primary replacements to ozone depleting refrigerants (e.g. chlorofluorocarbons [CFCs] & hydrochlorofluorocarbons [HCFCs]) for almost three decades – products like R-134a, R-404A, and R-410A. However, many of these replacements have relatively high GWPs, and are thus the focus of current regulatory efforts to reduce the environmental impact of refrigerant emissions. Several nonflammable lower GWP refrigerants have been developed using HFO technology (see Table 1) and successfully introduced to the ACR market, including Opteon™ XP40 (R-449A), XP44 (R 452A), XP10 (R-513A), and XP30 (R-514A). While these products are having a significant effect on reducing the warming impact of ACR systems through both higher efficiencies and noticeably lower GWPs, several of them fall short of the very low GWP targets (< 150) imposed by some of the strictest regulatory requirements. Currently, there are no commercially available very low GWP non-flammable alternatives with pressures close to those of R-22, R-404A, and R-410A. For many existing applications, the industry must consider using flammable options (e.g. Opteon™ XL products) to meet future regulatory requirements (see Class 2L alternatives, Table 1).

Alternatives to existing higher GWP HFCs have been in use for decades. Industrial chemicals, such as hydrocarbons, ammonia (R-717), and CO_2, have low GWPs and are used in several applications; nevertheless, all these products have their limitations. Hydrocarbons are highly flammable (A3 safety rating - see ANSI/ASHRAE Standard 34), which typically limits their usage to smaller refrigerant charges in self-contained equipment. Ammonia has both higher toxicity and mild flammability (B2L safety rating), along with material compatibility concerns. Its usage still largely resides in industrial applications. CO_2 is non-flammable but has both very high pressures and a relatively low critical temperature (31°C), which affects its usage and efficiencies in certain geographies. Additionally, all these products require significant system redesigns from existing HFC system architectures.

Given the limitations of industrial chemicals, and the lack of very low GWP nonflammable alternatives for many applications, new and different solutions were required. The industry asked if new refrigerants could be developed that better balance the competing requirements for ACR system designs. Could fluids be found that would provide very low GWPs, while simultaneously reducing the risks associated with the use of highly flammable refrigerants and minimizing the level of system redesign required from using industrial chemicals? The answer to these questions is "Yes"!

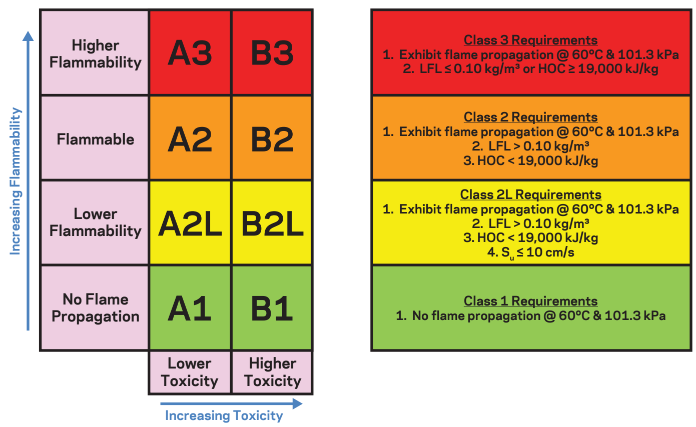
HFOs are recent entrants to the ACR marketplace. While chemically stable inside ACR systems, HFOs breakdown easily in the atmosphere, and therefore have very low GWPs and minimal impact on the environment. In fact, the GWPs of several HFOs are lower than those of industrial chemicals, such as CO_2. Some HFOs are non-flammable (A1 safety rating) but are low pressure (e.g. similar to R-123). Others are mildly flammable (A2L safety rating) with medium pressures (e.g. close to R-134a). While HFOs are promising low GWP alternatives to HFCs and HCFCs, they are noticeably lower in capacity than existing high-pressure products (e.g. R-22, R-404A, or R-410A) and cannot directly replace them in many applications. Therefore, they are often mixed with HFCs to produce lower GWP blends (e.g. Opteon™ XP and XL Products), many of which are also mildly flammable (A2L safety rating).

There are two main groups of flammable refrigerants competing to fill the requirements of lower GWP alternatives for many ACR applications – A3s (i.e. hydrocarbons) and A2Ls, which consist primarily of the HFC R-32, HFOs, and HFO-based blends. While all these products are flammable, there are considerable differences in their safety classifications and flammability parameters. These differences affect how these products can be safely applied, and impact the relative risks associated with their usage.

Safety Classifications & Flammability Parameters

Safety groups of refrigerants are based on ANSI/ASHRAE Standard 34 (2019) requirements for toxicity and flammability. Toxicity is divided into two classes – A for lower toxicity and B for higher toxicity. Higher toxicity refrigerants (e.g. R-123 and R-717) are typically limited to indirect systems, such as chillers in machine rooms. Flammability is divided into four distinct classes – Class 1, Class 2L, Class 2, and Class 3. Hydrocarbons, like propane or isobutane, have A3 safety ratings. Many HFOs or HFO based blends, and some HFCs have A2L safety ratings. A matrix of refrigerant safety groups is displayed in Figure 2, along with criteria for the different flammability classes.

Figure 2: Safety Groups & Flammability Test Requirements



One requirement of all flammable refrigerant safety classes (i.e. 2L, 2, & 3) is that flame propagation must occur when tested using ASTM E681, Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases). It is important to note though that some refrigerants that are typically described as non-flammable, with a safety class of 1 that exhibit no flame propagation, may decompose when exposed to a flame. When evaluating the testing requirements for each class, it can be difficult for the casual observer to assess the overall impact different classes have on equipment design or safety. However, several flammability parameters are also listed in the testing requirements, including Lower Flammability Limit (LFL), Heat of Combustion (HOC), and Burning Velocity (S_u).

Flammability parameters must be considered when making objective comparisons of the relative impact different refrigerants have on system design and safety. A list of the major flammability parameters is shown in Table 2, along with property data for R-1234yf, R-32, and R-290. R-1234yf is an HFO while R-32 is an HFC. Both have an A2L safety rating and are used as alternatives to higher GWP refrigerants, or as components in refrigerant blends, such as Opteon™ XL20 (R-454C), Opteon™ XL40 (R-454A), and Opteon™ XL41 (R-454B). R-290, or refrigerant-grade propane (A3 safety rating), is a hydrocarbon which is seeing increased usage in self-contained commercial refrigeration equipment.

Table 2: Refrigerant Flammability Parameters

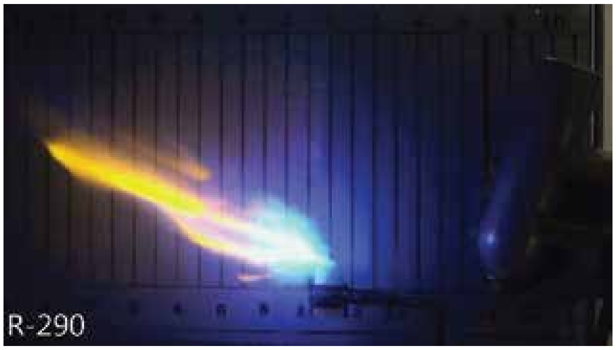
Refrigerant ASHRAE Designation #	R-1234yf	R-32	R-290
ASHRAE Safety Group	A2L	A2L	A3
Lower Flammability Limit (LFL) (Vol. % in air / kg/m³)	6.2 / 0.289	14.4 / 0.307	2.2 / 0.038
Upper Flammability Limit (UFL) (Vol. % in air)	12.3	29.3	10.0
UFL – LFL (Vol. % in air)	6.1	14.9	7.8
Minimum Ignition Energy (MIE) (mJ)	> 5,000	30 – 100	0.25
Burning Velocity (S_u) (cm/s)	1.5	6.7	46
Heat of Combustion (HOC) (kJ/g)	10.7	9.4	46.3

Flammability Limits, ASTM E681, & ASTM D3065

Flammability limits are determined using the previously mentioned ASTM E681 test standard. All flammable refrigerants, whether having lower (e.g. A2L) or higher (e.g. A3) flammability, can propagate a flame and therefore will have flammability limits. These limits (LFL & UFL) define the minimum and maximum concentrations of a substance in air that can propagate a flame. Below the LFL, there is not enough fuel to sustain a fire. Above the UFL, the concentration is too high, and there is insufficient oxygen in the air. The lower the LFL, the higher the risk, as a flammable concentration can be more easily reached from a leak. The larger the difference between the UFL and LFL, the larger the concentration window is where an ignition event could potentially occur. As seen in Table 2, R-290 has a much lower LFL than both R-32 and R-1234yf. Therefore, it is potentially easier to reach a flammable concentration from a leak with R-290. This is typical of A3s versus A2Ls, as hydrocarbons (A3s) tend to have lower flammability limits than A2Ls. Additionally, the molecular weights of these molecules also tend to be lower than those of A2Ls, meaning less mass is required to reach a flammable concentration. This is critical when designing equipment, as it plays largely into system charge size.

The potential impact of the difference in LFLs during "leak scenarios" can be more easily visually demonstrated using the ASTM D3065, Standard Test Methods for Flammability of Aerosol Products. In this standard, a Flame Projection Test is used to look at potential flammability hazards of aerosol products. An aerosol can is sprayed across a lit candle. If a flame propagates, the extension of the flame is measured and recorded. R-1234yf, R-32, and R-290 were all tested using this procedure. When the can was held in the upright position and sprayed across the candle, the candle was extinguished by all three refrigerants. While concentrations were not measured here, this suggests that the refrigerant-air mixtures sprayed across the candle flame did not reach the LFL before extinguishing the candle for all three refrigerants. Since these are medium to high pressure refrigerants, the refrigerant-air mixtures moved at considerable velocity, which likely helped to extinguish the candle. The can was then inverted so that liquid refrigerant fed into the nozzle instead of vapor. This resulted in higher concentrations of refrigerant being fed across the candle. In all test runs with both A2L products (R-1234yf and R-32), the candle was still extinguished, which again suggests that the LFL concentration was not reached at the candle while the flame was still lit. However, with propane, a large flame was produced, as shown in Figure 3. This suggests that a flammable concentration was produced at the candle flame with R-290. This is not surprising, as propane is often used as a soldering gas. It is important to note though that while A2L refrigerants are harder to ignite than A3s, an open flame can ignite any flammable refrigerant when a flammable concentration is reached.

Figure 3: Image of an R-290 Flame Projection Test Run



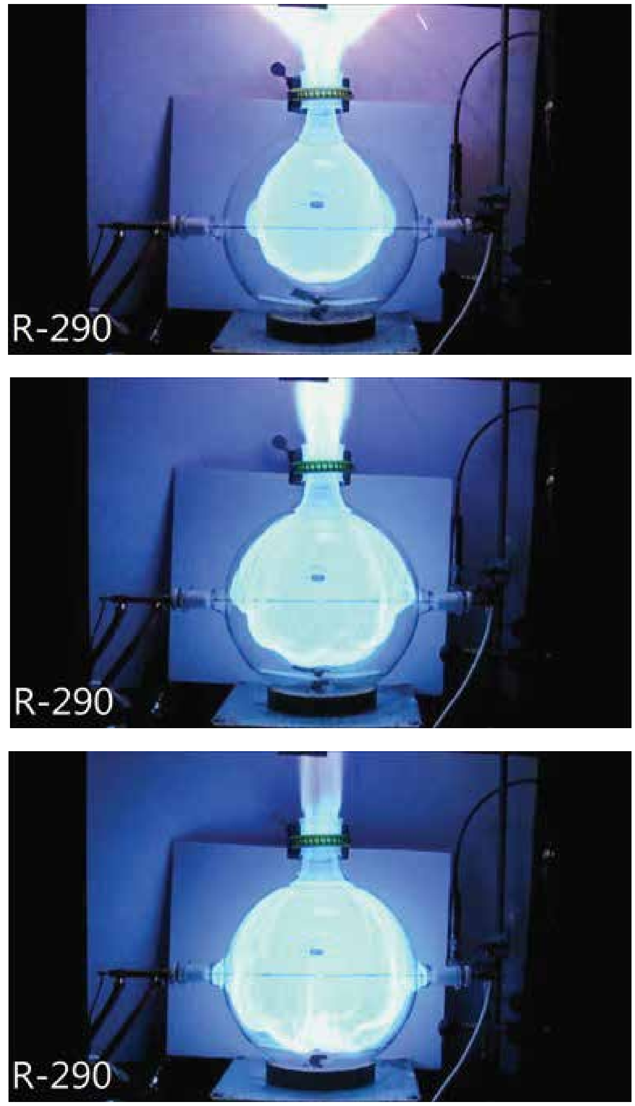
Minimum Ignition Energy & ASTM E582

Minimum Ignition Energy, or MIE, is also a critical flammability parameter to consider when designing equipment. This refers to the minimum amount of energy required to ignite a flammable gas/air mixture. Ignition sources below this level will not produce an ignition. Hydrocarbon vapors can be easily ignited by many energy sources, even sometimes by the lower levels produced by static electricity. An example of a propane ignition using ASTM E582 at 1 mJ is shown in Figure 4. The MIE of R-290, as seen in Table 2, is orders of magnitude lower than the levels required to ignite the A2L refrigerants. Implications of this difference are significant for both safety and equipment design, as components that are an ignition source with A3s may often not be an ignition source for A2Ls. This is discussed later, under Industry Activities & Implications for Codes & Standards.

Burning Velocity & Butane Lighter Tests

Burning Velocity (S_u) is defined as "the maximum velocity (cm/s) at which a laminar flame propagates in a normal direction relative to the unburned gas ahead of it" (ANSI/ASHRAE Standard 34). This property is used to help classify A2L refrigerants, which must have a burning velocity ≤ 10 cm/s. From Table 2, we see that R-290 (like other hydrocarbons) has a significantly higher S_u than the A2L products. This has implications for safety, as higher burning velocities can produce higher potential risks. Ignition events from A3 refrigerants with higher burning velocities can result in more rapid flame propagation and spread. Additionally, the more rapid flame propagation can also produce much more rapid rates of pressure rise, which can also increase the severity of ignition events.

Figure 4: Progressive Images of an R-290 Minimum Ignition Energy Test Run @ 1 mJ



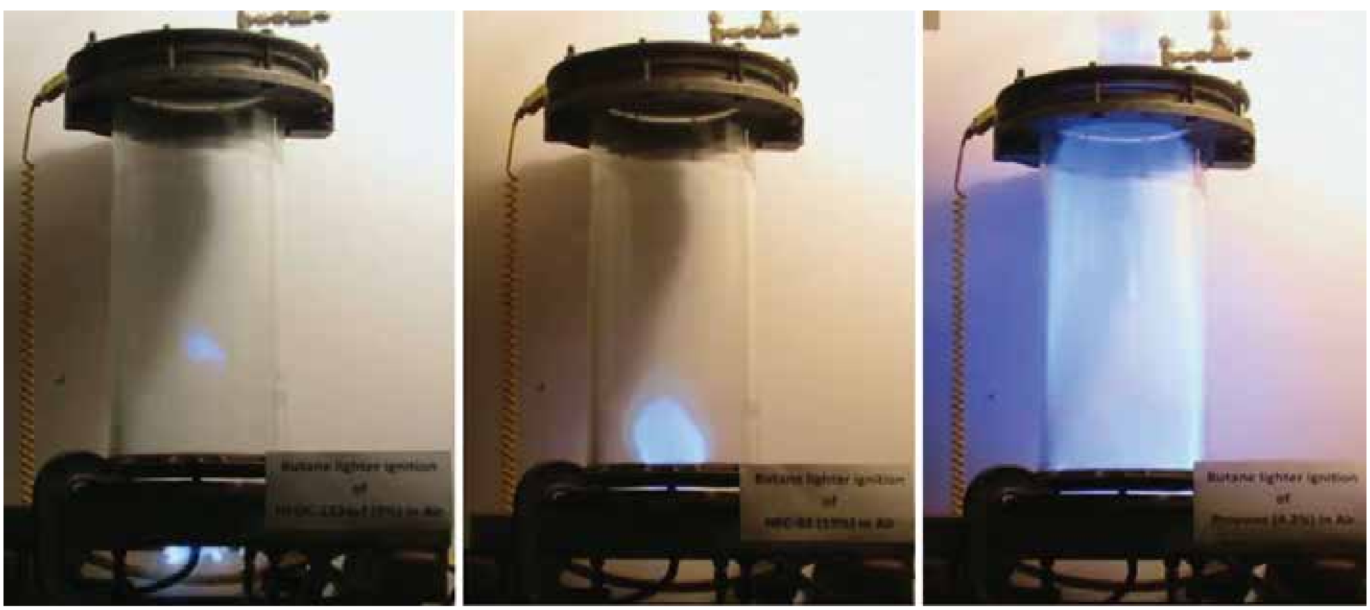
While not done specifically to characterize burning velocity or pressure rise, side-by-side images taken from videos of Butane Lighter Tests can give a sense of the differences in burning velocities and rates of pressure rise of different refrigerants. In this test set-up, a lit butane lighter is inserted into the bottom of a vertical vessel charged with flammable refrigerant. The flame travels up the vessel and pops a rubber stopper resting lightly on the top of the test assembly to relieve the rising pressure. "Worst-case concentrations" of R-1234yf, R-32, and R-290, which were slightly above stoichiometric for each refrigerant, were charged into the vessel and ignited. Table 3 shows the concentrations used during testing. Charge sizes for the A2L products were over five times larger than the charge size of R-290.

Figure 5 shows the test set-up for each refrigerant at 0.083 s after ignition has occurred. At this point in time the R-1234yf (which has the lowest S_u) produced the smallest flame. R-32, which has a higher burning velocity of 6.7 cm/s, shows a larger more developed flame spread. For R-290, which has a much higher burning velocity, the flame has already enveloped the vessel and exited out the top, extending out of view of the camera. Meanwhile the associated pressure rise from the R-290 ignition has launched the rubber stopper off the vessel at a high velocity, causing it to ricochet off the top of the fume hood. It should be noted that for each refrigerant ignition, the flame enveloped the entire vessel and the pressure rise ejected the rubber stopper. However, for R-1234yf and R-32, the flames traveled much slower and the stopper popped only slightly upwards, landing on the top of the vessel as opposed to being launched out of the fume hood.

Table 3: Butane Lighter Test Refrigerant Concentrations

Refrigerant ASHRAE Designation #	**R-1234yf**	**R-32**	**R-290**
ASHRAE Safety Group	A2L	A2L	A3
Stoichiometric Concentration (Vol. %)	7.73	17.32	4.02
Test Concentration (Vol. %)	9.0	19.0	4.2
Refrigerant Test Charge (g)	5.12	4.93	0.92

Figure 5: Butane Lighter Tests @ 0.083 s Post-Ignition (R-1234yf [L], R-32 [C], R-290 [R])



Heat of Combustion, Hot Surface Ignition Temperature, & Glow Wire

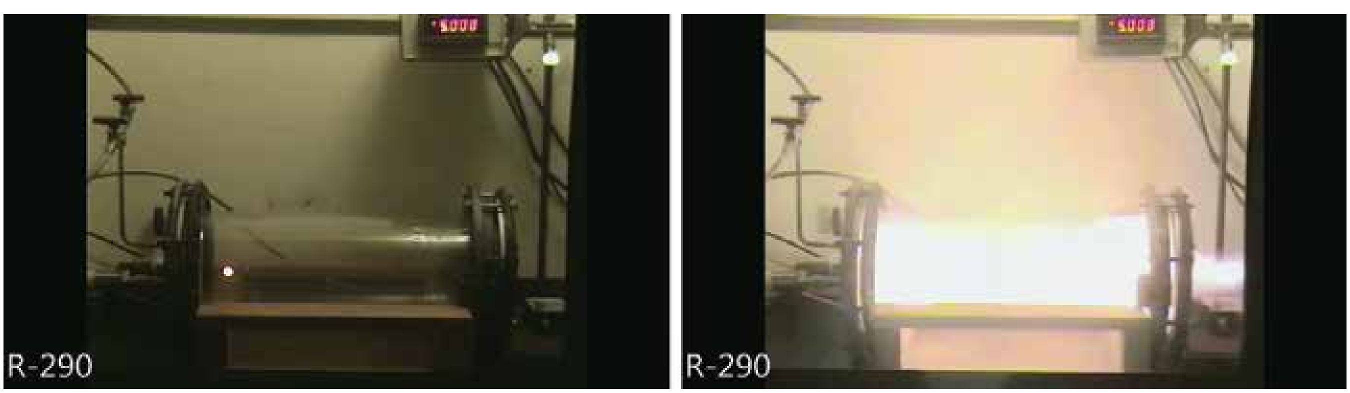
Heat of Combustion (HOC) is the heat per unit mass released during combustion of a substance. The higher the HOC, the greater the risk, as this can lead to higher temperatures during an ignition event, potentially increasing its severity. The HOC for R-290 is ≈ 4.5 – 5 times higher than that of the A2Ls.

While not previously mentioned, another refrigerant flammability parameter currently being investigated by the ACR industry is Hot Surface Ignition Temperature (HSIT). Hot surfaces can cause ignitions with flammable refrigerants. This is cause for concern, such as when selecting electric resistance heaters for use in a ACR system. Although not an HSIT test, Glow Wire tests can be used to simulate the effect an electric heater might have on a flammable refrigerant-air concentration. Test runs were conducted for R-1234yf, R-32, and R-290. A horizontal vessel was loaded with "worst case" concentrations of each refrigerant (see Table 4), with charge sizes of the A2Ls roughly 4.5 – 5 times larger than the charge of propane. A glow wire was heated for two minutes, or until ignition occurred. A rubber stopper on the right side of the vessel relieves pressure in the event of an ignition. The glow wire reaches estimated temperatures of 500 - 700°C. For both R-1234yf and R-32, the wire was heated for a full two minutes, with no ignitions occurring. However, with R-290, an ignition was initiated 3.53 s after the glow wire was activated. The images shown in Figure 6 display the start of the test (left), as well as an image captured 0.066 s after the first flame visual (right).

Table 4: Glow Wire Test Refrigerant Concentrations

Refrigerant ASHRAE Designation #	**R-1234yf**	**R-32**	**R-290**
ASHRAE Safety Group	A2L	A2L	A3
Stoichiometric Concentration (Vol. %)	7.73	17.32	4.02
Test Concentration (Vol. %)	8.13	20.0	4.5
Refrigerant Test Charge (g)	3.28	3.68	0.70

Figure 6: Glow Wire Test with R-290 (Test Activation [L], 0.066 s from Initial Flame Front [R])



Industry Activities & Implications for Codes & Standards

A great deal of research has been conducted over the last several years to improve our understanding of how to safely use flammable refrigerants, and the relative differences in the flammability of the different safety groups (e.g. A2L vs. A3). The learnings from this research are being used to shape codes and standards throughout the ACR industry. These learnings directly affect refrigerant charge sizes and other mitigation techniques used to limit or eliminate risks associated with refrigerant leaks.

ISO 5149-1 (2014), for example, has considered the differences in safety groups when assigning limits to refrigerant charge sizes. Varying limits of m_1, m_2, and m_3 are established based upon different mitigation requirements, and have caps based upon the LFLs of the individual refrigerants. For flammability class 2L refrigerants, these caps are increased by a factor of 1.5, as opposed to those for flammability classes 2 and 3, "in recognition of the lower burning velocity of these refrigerants, which lead to a reduced risk of ignition and impact". Table 5 shows examples of charge sizes for the three refrigerants tested in this report, based upon the limits established in ISO 5149. The charge limits of the A2Ls are roughly 11 – 12 times larger than for propane. A number of other safety standards are also establishing refrigerant charge limits, based upon the LFLs of refrigerants. This will allow for more applications to be designed using A2Ls, as opposed to A3s.

Table 5: **Examples of Refrigerant Charge Limit Caps Based on ISO 5149 (2014)**

ASHRAE #	R-1234yf	R-32	R-290
Safety Group	A2L	A2L	A3
m_1 (kg)	1.734	1.842	0.152
m_2 (kg)	11.271	11.973	0.988
m_3 (kg)	56.355	59.865	4.940

An AHRI study (AHRI Report No. 8017 - 2017) was conducted and reported on testing of potential ignition sources found in residences. This study found that many common ignition sources would not ignite A2L refrigerants. Four ignition sources did – hot wire, safety match, lighter flame insertion, and leak impinging on candle. Safety standards are being developed that differentiate sources of ignition for A2L refrigerants, versus A2s and A3s. UL 60335-2-40 3rd Edition (2019), for example, contains language that determines whether or not a component is a source of ignition for an A2L based on the use of flame arrest enclosures, quenching effect and opening size, or electrical switch load levels. Since many components that may be sources of ignition for A3s are not sources of ignition for A2Ls, a wider range of existing electrical components can be more easily implemented into the design of systems with mildly flammable A2L refrigerants. Other research is ongoing to further improve the application of flammables to ACR applications.

Conclusions

Regulations designed to reduce the impact of refrigerant emissions on the environment are leading the ACR industry towards the use of flammable refrigerants. From a properties standpoint, A2L refrigerants, often referred to as mildly flammable, have significantly more favorable flammability parameters than A3s, allowing for larger charge sizes and easier integration of electrical components into system designs. The development of A2L refrigerants (e.g. Opteon™ XL products) has increased the ability of the industry to safely meet strict GWP targets in a wider range of applications, such as R-454B to replace R-410A, and R-454A and R-454C to replace R-404A and R-22. Extensive research has been done to demonstrate differences between the relative safety of refrigerants, and how they can be successfully applied. Ultimately, successful implementation of flammable refrigerants will depend on properly integrating learnings from this research into codes and product/safety standards. Additionally, extensive education of the industry is required, particularly in the service sector.

About Opteon™ Refrigerants

The Opteon™ refrigerants portfolio offers the optimal balance of environmental sustainability, performance, safety, and cost to help meet both regulations and business goals.

Businesses trust Opteon™ refrigerants because they offer:

Low GWP
Up to a 99% reduction compared to previous refrigerant generations.

Zero ODP
The HFO-based refrigerant family is non-ozone depleting.

Ease-of-Conversion
Minimizing conversion costs and downtime.

Excellent Capacity
A near match to many HCFC- and HFC-based technologies.

Energy Efficiency
Reduced energy use creates long-term savings over the system's life.

Long-Term Regulatory Compliance
HFO-based refrigerants can meet or exceed global and local regulatory standards.

Knowledgeable Experts
With more than 85 years of industry experience, Chemours refrigerant experts can help customers achieve both compliance and peak performance.

Visit Opteon.com/regulations for more information on HFC replacements or to contact our experts.

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