Paper ID 1122
DOI:10.18462/iir.hfo.2018.1122

AN OVERVIEW OF HOW FLAMMABLE REFRIGERANTS ARE CHANGING THE RAC LANDSCAPE

Stephen Spletzer[(a)], Patrick Coughlan[(b)], Joachim Gerstel[(c)]

[(a)] The Chemours Company
974 Centre Road, Bldg 711, Wilmington, DE, 19805, USA, stephen.spletzer@chemours.com
[(b)] The Chemours Company
974 Centre Road, Bldg 711, Wilmington, DE, 19805, USA, patrick.coughlan@chemours.com
[(c)] Chemours Deutschland GmbH
Frankfurter Str. 229, 63263 Neu-Isenberg, Germany, joachim.gerstel@chemours.com

ABSTRACT

International and regional regulations, aimed at combating climate change, are resulting in a transition of the Refrigeration and Air-Conditioning (RAC) industry towards lower Global Warming Potential (GWP) refrigerant solutions. One of the consequences of these actions is that many of these alternatives (e.g. some hydrofluoroolefins [HFOs], hydrocarbons [HCs], etc.) are flammable. To this end, the RAC industry has spent the last several years preparing for this transition. This report will give an overview of some of the key factors that must be considered when working with flammable refrigerants. Regulatory drivers are discussed. Safety classes and flammability parameters are reviewed, as well as their effect on refrigerant selection. Finally, codes and standards impacts are also highlighted.

Keywords: A2L, A3, ASHRAE, ASTM, Burning Velocity, Butane Lighter, CFCs, D3065, E582, E681, Flame Projection, Flammable, Glow Wire, GWP, HCs, HCFCs, Heat of Combustion, HFCs, HFOs, HOC, IEC, Ignition, ISO, LFL, Lower Flammability Limit, MIE, Minimum Ignition Energy, RAC, Refrigerant, Regulations, Safety, S_u, UFL, Upper Flammability Limit

1. INTRODUCTION

Hydrofluorocarbons (HFCs) have served as the primary replacements to ozone depleting refrigerants (e.g. chlorofluorocarbons [CFCs] & hydrochlorofluorocarbons [HCFCs]) for almost three decades. 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. Many lower GWP alternatives being offered to meet these regulatory requirements are flammable, such as HCs, some HFOs, certain HFCs (e.g. R-32), and some HFO/HFC blends. However, there are significant differences in the relative flammability of these refrigerants, as well as the risks their usage poses.

2. REGULATORY DRIVERS

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. Different starting baselines and step-down schedules have been set up for different country groupings. The end result is that 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 by over twenty countries at this time, which means that it will enter into force January 1, 2019.

In response to the Kigali Amendment, regional and national regulations are taking form in many parts of the world. The F-Gas regulations in Europe, which preceded Kigali, have already established a series of step-downs in EU HFC consumption, coupled with application specific GWP limits that will come into effect over the next several years. Japan and Canada have also established application specific GWP limits. In the USA, the EPA has introduced several SNAP rules which approve lower GWP alternatives. Other countries and regions are developing different approaches. However, a common prevailing thread throughout all of these policies is that the GWPs of the refrigerants the

RAC industry uses will have to be dramatically reduced to meet these regulatory obligations.

3. REFRIGERANT ALTERNATIVES

A number of alternatives to existing higher GWP HFCs are currently in use. Industrial chemicals, such as hydrocarbons, ammonia, and CO_2, have low GWPs and are seeing increasing application. However, all of these products have their limitations. Hydrocarbons are highly flammable (A3 safety rating - ANSI/ASHRAE Standard 34-2016 – see also ISO 817-2014), 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 high pressures and a relatively low critical temperature (31°C), which affects its usage and efficiencies in certain geographies.

Certain HFCs, such as R-152a and R-32, have low to medium GWP, but are also flammable. HFOs have low GWP. 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, many of which are also mildly flammable (A2L safety rating).

Table 1 lists a sampling of some of the lower GWP fluorochemical-based alternative refrigerants that are similar in pressure to existing industry standard products. From here, we can see that non-flammable low GWP alternatives are available for large centrifugal chillers (e.g. R-514A). Similar pressure, non-flammable alternatives with reduced GWPs have also been developed for R-134a, R-22, R-404A, and R-410A. However, there are no currently available very low GWP non-flammable alternatives with pressures similar to R-22, R-404A, and R-410A. For many existing applications, the industry must consider using flammable options to meet future regulatory requirements.

Table 1: Lower GWP Alternative Refrigerants*

Industry Standard Refrigerant (GWP)	**Non-Flammable Alternatives – Class 1** (GWP)	**Mildly Flammable Alternatives – Class 2L** (GWP)
R-123 (79)	**R-1233zd** (1) **R-514A** (2)	-------
R-134a (1300)	**R-450A** (547) **R-513A** (573)	**R-1234yf** (< 1) **R-1234ze** (< 1)
R-22 (1760) **R-404A** (3943)	**R-448A** (1273) **R-449A** (1282)	**R-454A** (238) **R-454C** (146)
R-410A (1924)	**R-463A** (1377)	**R-32** (677) **R-452B** (676) **R-454B** (467)

*GWP values are based on 100 Year AR5

There are two main groups of flammable refrigerants competing to fill the requirements of lower GWP alternatives for many RAC applications – A3s (i.e. hydrocarbons) and A2Ls, which consist primarily of the HFC R-32, HFOs, and HFO-based blends. While all of 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.

4. SAFETY CLASSIFICATIONS & FLAMMABILITY PARAMETERS

Safety groups of refrigerants are based on the ANSI/ASHRAE Standard 34 (2016) requirements for toxicity and flammability. Toxicity is divided into two classes – A for lower toxicity and B for higher toxicity. Flammability is divided into three distinct classes – Class 1, Class 2, and Class 3. Class 2 also has a Subclass 2L. 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 1, along with criteria for the different flammability classes.

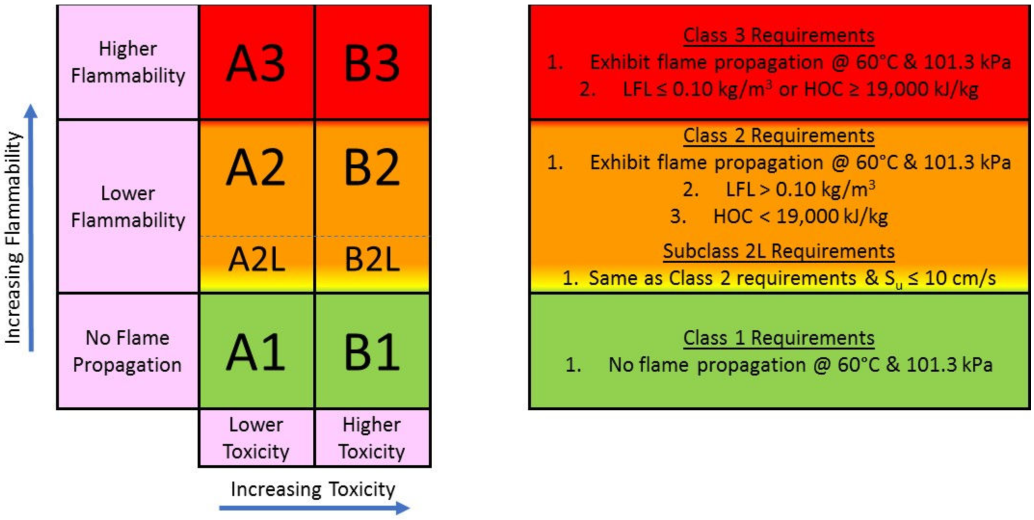

Figure 1: Safety Groups & Flammability Test Requirements

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)* (2002). 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 looking at 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. R-290, or 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

4.1 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* (2001). 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 2. This suggests that a flammable concentration was produced at the candle flame with R-290. 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.

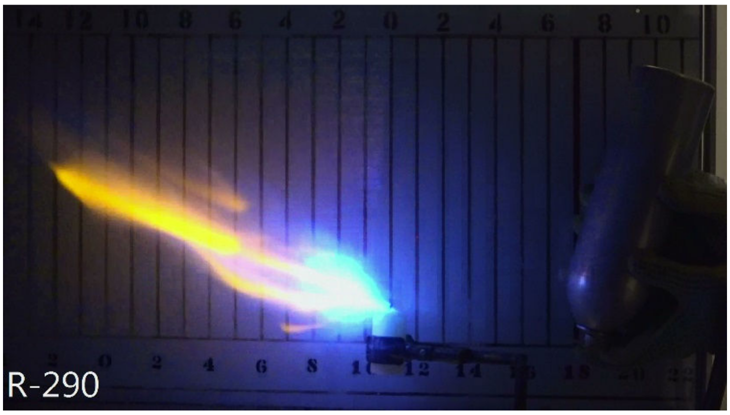

Figure 2: Image of an R-290 Flame Projection Test Run

4.2 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 (2013) at 1 mJ is shown below in Figure 3. 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 (see Section 5).

Figure 3: Progressive Images of an R-290 Minimum Ignition Energy Test Run @ 1 mJ

4.3 Burning Velocity & Butane Lighter Tests

Burning Velocity (S_u) is defined as "the maximum velocity (in./s [cm/s]) at which a laminar flame propagates in a normal direction relative to the unburned gas ahead of it" (ANSI/ASHRAE Standard 34-2016). This property is used to help classify A2L refrigerants, which must have a burning velocity $\leq$ 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.

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 4 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

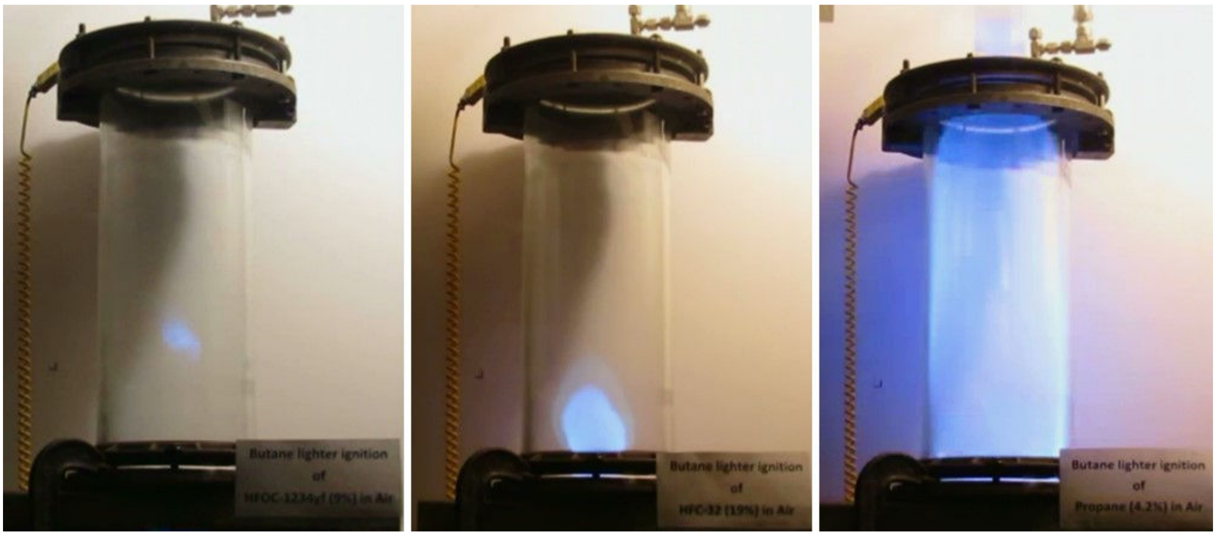

Figure 4: Butane Lighter Tests @ 0.083 s Post-Ignition (R-1234yf [L], R-32 [C], R-290 [R])

4.4 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 RAC 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 RAC 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 5 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

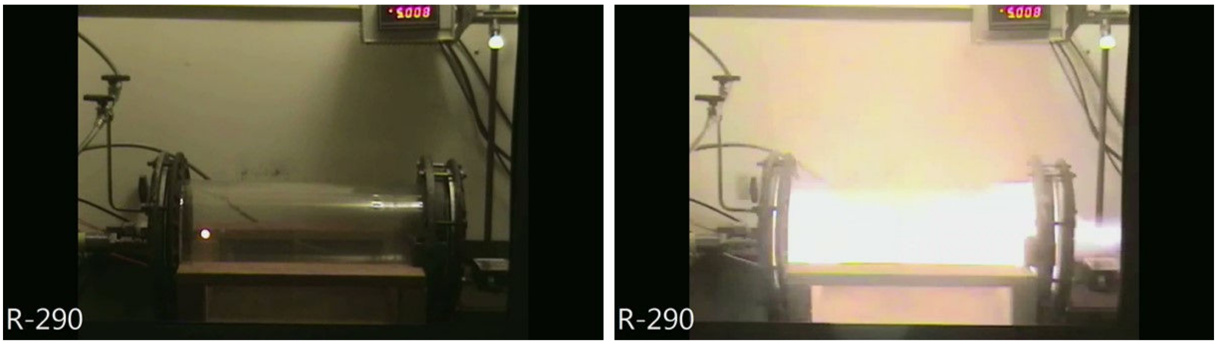

Figure 5: Glow Wire Test with R-290 (Test Activation [L], 0.066 s from Initial Flame Front [R])

5. 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 RAC 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 recently 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. IEC 60335-2-40 Edition 6 (2018), 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 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 RAC applications.

6. CONCLUSIONS

Regulations designed to reduce the impact of refrigerant emissions on the environment are leading the RAC industry towards the use of flammable refrigerants. From a properties standpoint, A2L refrigerants, often referred to as mildly flammable, have more favorable flammability parameters than A3s, allowing for larger charge sizes and easier integration of electrical components into system designs. Extensive research has been done to demonstrate differences between the relative safety of refrigerants, and how they can be successfully applied. More is needed. 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.

ACKNOWLEDGEMENTS

The authors would like to thank Mary Koban and Barbara Minor for their support during this effort.

NOMENCLATURE

A1	ASHRAE Safety Rating - Lower Toxicity, No Flame Propagation
A2	ASHRAE Safety Rating - Lower Toxicity, Lower Flammability
A2L	ASHRAE Safety Rating - Lower Toxicity, Lower Flammability with $S_u \leq 10$ cm/s
A3	ASHRAE Safety Rating - Lower Toxicity, Higher Flammability
ANSI	American National Standards Institute
AHRI	Air-Conditioning, Heating, & Refrigeration Institute
AR5	IPCC Fifth Assessment Report
ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning Engineers
ASTM	American Society for Testing and Materials
B1	ASHRAE Safety Rating - Higher Toxicity, No Flame Propagation
B2	ASHRAE Safety Rating - Higher Toxicity, Lower Flammability
B2L	ASHRAE Safety Rating - Higher Toxicity, Lower Flammability with $S_u \leq 10$ cm/s
B3	ASHRAE Safety Rating - Higher Toxicity, Higher Flammability
CFC	chlorofluorocarbon
EPA	Environmental Protection Agency
GWP	global warming potential
HC	hydrocarbon
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HFO	hydrofluoroolefin
HOC	heat of combustion
HSIT	hot surface ignition temperature
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
LFL	lower flammability limit
MIE	minimum ignition energy
RAC	Refrigeration and Air-Conditioning
SNAP	Significant New Alternatives Policy
S_u	burning velocity
UFL	upper flammability limit

REFERENCES

ANSI/ASHRAE Standard 34-2016. (2016). Designation and Safety Classification of Refrigerants. *American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE).* Atlanta, GA.

ASTM D3065 – 01. (2001). Standard Test Methods for Flammability of Aerosol Products. *American Society for Testing and Materials (ASTM)*. West Conshohocken, PA.

ASTM E582 – 07. (2013). Standard Test Methods for Minimum Ignition Energy and Quenching Distance in Gaseous Mixtures. *American Society for Testing and Materials (ASTM)*. West Conshohocken, PA.

ASTM E681 – 01. (2002). Standard Test Methods for Concentration Limits of Flammability of Chemicals (Vapors and Gases). *American Society for Testing and Materials (ASTM)*. West Conshohocken, PA.

IEC 60335-2-40, Sixth Edition. (2018). Household and Similar Electrical Appliances – Safety – Part 2-40: Particular requirements for electrical heat pumps, air-conditioners, and dehumidifiers. *International Electrotechnical Commission (IEC)*. Geneva, Switzerland.

ISO 5149-1. (2014). Refrigerating systems and heat pumps – Safety and environmental requirements. *International Organization for Standardization (ISO)*. Geneva, Switzerland.

ISO 817. (2014). Refrigerants – Designation and safety classification. *International Organization for Standardization (ISO)*. Geneva, Switzerland.

Kim, D., Sunderland, P., (2017). AHRI Report No. 8017. Investigation of Energy Produced by Potential Ignition Sources in Residential Application. *Air-Conditioning, Heating and Refrigeration Institute*. Arlington, VA.

Disclaimer: The information set forth herein is furnished free of charge and based on technical data that Chemours believes to be reliable. It is intended for use by persons having technical skill, at their own risk. Since conditions of use are outside our control, we make no warranties, expressed or implied and assume no liability in connection with any use of this information. Nothing herein is to be taken as a license to operate under, or a recommendation to infringe any patents or patent applications.