Flammable refrigerants firefighter training: Hazard assessment and demonstrative testing

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May 2019

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The ongoing push toward sustainability of refrigeration systems will require the adoption of low global warming potential (GWP) refrigerants to meet the shift in environmental regulations. Fire safety is a lingering issue with the new age of flammable refrigerants being adopted and first responders may not be familiar with the change in material hazards or the appropriate response procedures required to safely handle these fire scenarios.

This project is part of the overall two-year project with a goal to enhance firefighter safety and reduce potential injury by providing training on the hazards from appliances with flammable refrigerants. It will document the information about flammable refrigerants technologies and the hazards to emergency responders and develop interactive training modules to transfer the knowledge to the fire service.

This report is focused to develop material documenting the hazards associated with flammable refrigerant technologies and the risks posed to the first responders. The material documentation included a literature review, Task 1, identifying baseline information on flammable refrigerants, their existing usage and implementation into products, potential integration into future technologies, and finally any existing guidance and best practices on response and tactics. A hazard assessment examined the current and potential use cases for refrigerants, the various technologies in which they are employed, the types of environments in which they might be encountered, and the range of hazards associated with them.

The Fire Protection Research Foundation expresses gratitude to the report authors Noah L. Ryder, P.E. and Stephen J. Jordan, who are with Fire & Risk Alliance located in Rockville, Maryland, USA, and Peter B. Sunderland, Ph.D., who is with the University of Maryland, College Park, Maryland, USA. The Research Foundation appreciates the guidance provided by the Project Technical Panelists, the funding provided by the project sponsor.

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Keywords: refrigerants, air conditioning, flammability, toxicity, hazard, firefighting, training, global warming potential (GWP), A3, A2, A2L, A1

Report number: FPRF-2019-04

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PROJECT SPONSORS

This research is conducted as part of two year project funded by
DHS/FEMA Assistance to Firefighters Grant (AFG) Program.
Award No.: EMW-2016-FP-00647
EXECUTIVE SUMMARY

Environmental policy is causing a shift from the current refrigerants used in appliances to adoption of low global warming potential (GWP) refrigerants. The new class of refrigerants pose various hazards including increased flammability risks. With the shift towards more environmentally friendly fluids, preparation is necessary in fire protection for safe usage of flammable refrigerants. As new refrigerants with higher flammability are phased in, there will be new hazards the fire service and emergency responders will need to be aware of to adjust in firefighting tactics.

This report is focused to develop material documenting the hazards associated with flammable refrigerant technologies and the risks posed to the first responders. The material documentation included a literature review, identifying baseline information on flammable refrigerants, their existing usage and implementation into products, potential integration into future technologies, and finally any existing guidance and best practices on response and tactics. A hazard assessment examined the current and potential use cases for refrigerants, the various technologies in which they are employed, the types of environments in which they might be encountered, and the range of hazards associated with them.

The study indicates that these refrigerants pose a variety of hazards that must be balanced against their performance for specific applications. The potential hazards of refrigerants include toxic thermal decomposition and combustion products, increased flammability and explosion risks, and pressure release scenarios. The literature review conducted on these issues has identified a number of knowledge gaps, specifically from the perspective of fire service response to the evolving hazard of A2L refrigerants. While the potential production of HF and other toxic thermal degradation byproducts exists for all halocarbon refrigerants, the differences in toxic quantities produced by existing and new refrigerants needs further investigation to determine the increased risk associated with the switch to A2L refrigerants. At the time of this report the nature of the changing hazard has not been completely defined as standards governing refrigerant charges are still under review. It is the intent of this gap analysis to help guide training material that will assist first responders in the recognition, evaluation, and mitigation of any flammable refrigerant related hazards.
Flammable Refrigerants: Hazard Assessment and Demonstrative Testing

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May 3, 2019
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LIST OF ACRONYMS

A/C Air Conditioning
AHRI Air-Conditioning, Heating, & Refrigeration Institute
ANSI American National Standards Institute
ASHRAE American Society of Heating, Refrigerating, and Air-Conditioning Engineers
CFC Chlorofluorocarbons
CO2 Carbon Dioxide
DOE Department of Energy
EPA Environmental Protection Agency
FPRF Fire Protection Research Foundation
GWP Global Warming Potential
HCFC Hydrochlorofluorocarbons
HFC Hydrofluorocarbons
HFO Hydrofluoroolefins
HVAC&R Heating, Ventilation, Air Conditioning, and Refrigeration
NFPA National Fire Protection Association
ODP Ozone Depletion Potential
SNAP Significant New Alternatives Program
UL Underwriters Laboratories
1.0 PROJECT OVERVIEW

Fire & Risk Alliance, LLC (FRA), in collaboration with the University of Maryland Department of Fire Protection Engineering (UMD), is pleased to offer this report, Fire Fighter Flammable Refrigerants Training: Hazard Assessment and Demonstrative Tests, to the Fire Protection Research Foundation.

Prior work has focused on identifying the hazards associated with low GWP refrigerants. The results of completed and ongoing studies, conducted by the research team and others, indicate that a significant fire hazard exists along with other non-thermal hazards associated with the refrigerants. As such the specific goal of this research was to develop material documenting the hazards associated with flammable refrigerant technologies and the risks posed to first responders. The material documentation included a literature review, Task 1, identifying baseline information on flammable refrigerants, their existing usage and implementation into products, potential integration into future technologies, and existing guidance and best practices on response and tactics. At the time of this report the newest editions of standards governing flammable refrigerants and the implementation of A2L refrigerants were still under development. As a result, the hazard assessment examined the current and potential use cases for refrigerants, the various technologies in which they are employed, the types of environments in which they might be encountered, and the range of hazards associated with them. Additional analysis quantifying the increased risks associated with various refrigerant charges and the thermal decomposition of A2L refrigerants are opportunities identified for future work to educate firefighting best practices.

A summary of the Task 1 work was presented at a Stakeholder Workshop hosted by the Fire Protection Research Foundation in Quincy, MA, on September 5, 2018. The project team engaged in discussions with professionals from fire protection and flammable refrigerant relevant industries and generated recommendation for the development of a firefighter training curriculum. Based on the results of first two project tasks, the team provided technical guidance, planning and implementation of demonstrative tests involving simulated A2L refrigerant leakage and fire scenarios. Documentation of the demonstrative testing was coordinated to provide video footage of appliance fires involving the release of flammable refrigerants for use in developed training materials.
2.0 TASK 1: LITERATURE REVIEW AND HAZARD ASSESSMENT

2.1 Introduction

The main criteria in the selection of the hydrofluorocarbon (HFCs) refrigerants in use today for many applications is that they be non-ozone depleting, while maintaining safe operating conditions during use. As pressure from environmental organizations grows to phase out the use of these HFCs due to their high Global Warming Potential (GWP), many of the next generation of low GWP refrigerants being considered are flammable having an ASHRAE Standard 34 classification of A2, A2L or A3 and present other potential health and safety hazards.

The ongoing push toward sustainability of refrigeration systems will require the adoption of low global warming potential (GWP) refrigerants to meet environmental regulations. Fire safety is a lingering issue with the new age of flammable refrigerants being adopted and first responders may not be familiar with the change in material hazards or the appropriate response procedures required to safely handle these fire scenarios. The refrigerants presently being adopted, A2L or A1/A2L blends, present new challenges and risks that should be evaluated and understood.

The following provides a summary of the available literature and information pertaining to the characteristics and hazards associated with the various classifications of refrigerants. The report does not intend to offer recommendations for the storage, usage, or interaction with flammable refrigerants and is only intended to be a baseline record of the publicly available information at the time of development. Gaps identified from this report and finding of future work will provide guidance for emergency response training curriculum development.

2.2 Refrigerant History

In the early 19th century mechanical refrigeration started with the use of water, air, ammonia, sulfur dioxide and carbon dioxide. In 1834 Jacob Perkins patented a vapor-compression refrigeration system using ethyl ether. Perkins refrigeration system was comprised of a compressor, condenser, expansion device and an evaporator. In 1863 Charles Tellier created the first high pressure system to use methyl ether which reduced the risk of drawing air into the system keeping it from forming an explosive mixture [1] [2]. In the early 20th century classic refrigerants were replaced with chlorofluorocarbons (CFCs), the second generation of refrigerants. Thomas Midgley’s research in 1928 aimed to find stable refrigerants that are neither toxic nor flammable. Midgley determined that dichlorodifluoromethane, R-12 was a stable compound for refrigeration purposes. In 1931, R-12 began to be commercially produced and was followed by R-11 in 1932 and R-13 in 1945 for low temperature applications. Chlorofluorocarbons, hydrochlorofluorocarbons, R-22, and an azeotropic (constant boiling point) mixture named R-502 dominated the second generation of refrigerants [2].

In 1987, an international treaty named The Montreal Protocol, signed by 197 parties to date, limited the production and consumption of CFCs. The London Amendment of 1990 called for a global phaseout of CFCs by 2000 in developed countries and 2010 in developing countries. In 1997, The Montreal Protocol expanded under the Montreal Amendment to address the continued threats of ozone depletion and governments world-wide started phasing out the use of hydrochlorofluorocarbons (HCFC), including R-22, a popular residential climate control refrigerant. In the United States most new manufactured air conditioning systems and heat pumps use R-410A as the refrigerant as a result of these changes [3]. Most recently, the Kigali
Amendment of 2016 schedules the phase down the production and consumption of HFCs. Imposed regulations on the global use of ozone depleting substances were already producing measurable results in 2008 when stratospheric chlorine abundances were measured to be 10% lower than peak values reached in the late 1990s and were continuing to decrease [4]. Recent studies have shown that the regulations originating from the Montreal Protocol have resulted in ozone healing and the Antarctic ozone hole is anticipated to disappear by the middle of the 21st century [5].

2.3 Common Refrigerants and Their Properties

Common refrigerants are typically classified according to one of four different categories based on the chemical components and structure of the compound: chlorofluorocarbons; hydrochlorofluorocarbons; hydrofluorocarbons; or hydrofluorolefins.

Chlorofluorocarbons (CFCs) are classified as halocarbons and are nontoxic, nonflammable chemicals containing atoms of carbon, chlorine, and fluorine. An example of a CFC is dichlorodifluoromethane (R-12) which is listed as A1 in the safety group category and has a GWP of 8500. In 1974, two University of California chemists, Professor F. Sherwood Rowland and Dr. Mario Molina, showed that the CFCs could be a major source of inorganic chlorine in the stratosphere following their photolytic decomposition by UV radiation. In addition, they determined that some of the released chlorine would become active in destroying ozone in the stratosphere. As it turns out, chlorine released from CFCs destroys ozone in catalytic reactions where 100,000 molecules of ozone can be destroyed per chlorine atom released. A loss of stratospheric ozone results in more harmful UV-B radiation reaching the Earth's surface [6].

Hydrochlorofluorocarbons (HCFCs) are classified as chemical compounds that contain hydrogen, fluorine, and carbon atoms. An example of an HCFC is chlorodifluoromethane (R-22) which is listed as A1 in the safety group category and has a GWP of 1700. HCFC compounds react differently from CFCs due to the presence of a hydrogen atom in HCFCs which causes these chemicals to decompose photochemically before they reach the stratosphere. HFCs do not contain chlorine and thus do not directly attack the ozone layer. HCFCs and HFCs survive in the atmosphere for 2 to 40 years, compared with about 150 years for CFCs [7] [8].

Hydrofluorocarbons (HFCs) are man-made greenhouse gases used in air conditioning, refrigeration, solvents, foam blowing agents, and aerosols. Many HFCs remain in the atmosphere for less than 15 years. The use of HFCs is growing due to wide spread adoption as replacements for the ozone depleting substances (ODS) of CFCs and HCFCs being phased out under the Montreal Protocol. An example of an HFC is R-410A, a 50:50 (by weight) blend of R-32 (difluoromethane) and R-125 (pentafluoro-ethane). Although R-410A has zero ozone depletion potential (ODP), it is a greenhouse gas with a global warming potential (GWP) of 2,100 and is classified as A1 in the safety group category [9].

Hydrofluorolefins (HFOs) are composed from hydrogen, fluorine and carbon. The only difference between HFC and HFO is that they are unsaturated, meaning that they have at least one double bond. Such molecules are named olefins or alkenes; hence it is correct to name such refrigerants as HFC, HFA or HFO. The presence of the carbon-carbon double bond is not unique for HFOs as there are other unsaturated compounds to be found, as for example unsaturated hydrocarbons (e.g. propene). HFOs are relatively stable compounds but are more reactive than HFC due to the reactivity of the carbon–carbon bond. This also reduces their global warming
potential and therefore became favorable property in light of increasing concerns on climate change.

2.4 Codes and Standards

There exists a number of codes and standards that define the flammable refrigerant ecosystem and include guidance for naming conventions, hazard classifications, material property testing procedures and equipment, and installation requirements and limitation. This section identifies some of these standards and provides limited background information as it pertains to this report. For more comprehensive information pertaining to the associated standards for flammable refrigerants, please refer directly to the standard documentation.

2.4.1 ASHRAE 34

The American Society of Heating, Refrigeration and Air-Conditioning Engineers (ASHRAE) focuses on advancing the arts and sciences of heating, ventilation, air conditions and refrigeration to serve humanity and promote a sustainable world. This organization has developed a naming convention for common refrigerants instead of using the chemical or trade name. This standard is intended to provide a uniform system of identifying safety classifications based on flammability and toxicity data and identifies typical concentration limits.

2.4.1.1 Refrigerant Naming Convention

Per ASHRAE 34, an identifying number shall be assigned to each refrigerant. It consists of a prefix consisting of letters and a suffix comprised of digits. The prefix is composed of the letter R (for refrigerant): R22, R134a, R600a, R717. At times the letter C is used in the prefix to denote carbon and can be preceded by B, C or F, or a combination of these letters in the same order, to indicate the presence of bromine, chlorine or fluorine. Compounds containing hydrogen must be preceded by the letter H. Examples of these naming styles include HCFC22 and HFC134a. These prefixes are intended for use in non-technical publications. At times the brand or manufacturer name is also used; however, these names should not be used in official documents such as identification labels.

The suffix component of the name is dependent on type of the compound and the purity of the refrigerant. The four classification categories described here include hydrocarbons and derivatives thereof, azeotropic and zeotropic mixtures, miscellaneous organic compounds, and inorganic compounds.

For hydrocarbons and derivatives thereof, the numerical suffix is determined from the chemical composition of the refrigerant and most typically represented by a three-digit number. The identifier is composed of: the number of carbon (C) atoms less one; the number of hydrogen (H) atoms plus one; and the number of fluorine (F) atoms. In cases where the number of carbon atoms is null, the first digit on the identifier is dropped. Although refrigerants containing bromine (Br) are no longer manufactured, they were traditionally indicated with the addition of the letter B after the identification number followed by the number of atoms present. Finally, the number of chlorine (Cl) atoms can be found by subtracting the number of fluorine, bromide, and hydrogen atoms from the total number of available carbon bonds: 4 for methane derivatives (CH4), 6 for ethane derivatives (C2H6), and continuing as such for larger hydrocarbons. For example, the compound R022, known and presented as R22, contains a single carbon atom, a single hydrogen atom, and two fluorine atoms. As a methane derivative, it is then calculated that the
compound must also contain a single chlorine atom resulting in a chemical composition of CHClF$_2$ and a chemical name of chlorodifluoromethane.

For cyclic derivatives, the letter C is used before the refrigerant’s identification number as in RC318, or octafluorocyclobutane, C$_4$F$_8$. In the case of isomers, each compound has the same number, with the most symmetrical one indicated by the number alone. As the isomers become more and more unsymmetrical, successive lowercase letters are appended. For example, R134 and R134a have the same chemical composition but differing chemical structures and as such, R134a is more ideal for use as a refrigerant [10].

Mixtures are designated by their respective refrigerant numbers and mass proportions. Refrigerants are further named in order of increasing normal boiling points of the components. Zeotropic mixtures, with components of differing boiling points, shall be assigned an identifying number in the 400 series. This number designates which components are in the mixture but not the amount of each. To differentiate among zeotropic mixtures having the same components with different mass percentages, an uppercase letter is added as a suffix in chronological order of the refrigerant’s approval by ASHRAE: R407A (R32/R125/R134a (20/40/40)) contains R32/R125/R134a at a mass ratio of 20/40/40. Azeotropic mixtures, constant boiling point mixtures, are assigned an identifying number in the 500 series: R507 (R125/R143a (50/50)) [10].

Miscellaneous organic compounds are be assigned a number in the 600 series in numerical order R600a, isobutane, is one example. The 700 series is reserved for inorganic compounds where identification numbers are formed by adding the relative molecular mass of components to 700, Ammonia, having a molar mass of 17, is assigned R717 [10].

**2.4.1.2 Toxicity Classification**

The toxic hazard posed by refrigerants is classified as part of ASHRAE 34. This classification includes a letter prefix (either “A” or “B”) to identify the toxic hazard group [11]:

- **Group A** – Permissible exposure limit (PEL) $\geq$ 400 ppm
- **Group B** – Permissible exposure limit (PEL) < 400 ppm

Group A refrigerants have a lower toxicity than Group B refrigerants. Since mid to late 20$^{th}$ century, Group A1 refrigerants were the only classes of refrigerant used for household, commercial refrigeration, and air-conditioning equipment for several decades, with the exception of ammonia (R-717, a Group B2 refrigerant) for specific applications [12]. Examples of Group A refrigerants include CFCs, HCFCs, some hydrocarbons, and most of the low-GWP HFC refrigerants such as R-32 and R-1234yf. Group B refrigerants have a higher toxicity and are thus much less common due to the increased health consequences of a leak. It is worth noting that the toxicity classifications are based on the material properties in its natural state, but may not be indicative of toxicity after thermal degradation.

**2.4.1.3 Flammability Classification**

ASHRAE 34 classifies the flammability of refrigerants. The classification includes a number, and possibly letter suffix, to identify the flammability hazard class based on the lower flammable
limit (LFL), burning velocity, and heat of combustion. The flammability classes specified in ASHRAE 34 are:

- **Class 1** – No flame propagation in air
- **Class 2L** – Same as Class 2, with burning velocity less than 10 cm/s
- **Class 2** – LFL greater than 0.1 kg/m$^3$; heat of combustion less than 19 kJ/g
- **Class 3** – LFL less than 3.5% or heat of combustion greater than 19 kJ/g

Class 1 refrigerants, such as R-134a, R-410A, and R-22, do not propagate a flame in air at standard conditions. Class 2 refrigerants do propagate a flame but are relative lower flammability in terms of their flammable limits and heat of combustion. Examples of Class 2 refrigerants include R-141b, and R-143a. Class 2L, a subclass of Class 2, is a recent addition to the ASHRAE 34 classification scheme and includes refrigerants such as R-32, R-452B, R-455A, R-457A, and R-1234yf. Due to their low burning velocity and high minimum ignition energy, Class 2L refrigerants are more difficult to ignite than other Class 2 refrigerants. Refrigerants with a higher flammability, such as hydrocarbons R-170 (ethane), R-290 (propane), and R-600a (isobutane), are classified as Class 3. Class 3 refrigerants have lower flammable limits and greater heat of combustion values that result in a greater fire hazard [11].

### 2.4.2 ASTM E681

ASTM E681: Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases) defines a test measurement apparatus and approach used for the determination of upper and lower flammability limits of flammable refrigerant gases. Using a 12L vessel, a mixture of refrigerant is mixed with air for a duration of 5 minutes after which an electrode is sparked and the result observed. If ignition is observed and a critical 90° arc is achieved, the concentration of gas is considered to be flammable. Concentrations defining the lower and upper flammability limits can be determined using this measurement approach [13].

#### 2.4.2.1 ASTM E681 Proposed Revisions

A study conducted at the University of Maryland proposed revisions to improve the test method for A2L refrigerants in ASTM E681, Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases). The findings of the report included a clarification or change to the flammability criteria, a new approach to measuring pressure, updated materials and parts specifications, and revisions to the heating system implementation amongst other recommendations. The work done under these projects in an ongoing effort to improve the measurements of flammability properties used to categorize refrigerants [14].

### 2.4.3 Other Codes and Standards

There exists a large number of standards and regulations pertaining to the handling, use, installation, and maintenance of refrigerants and appliance that utilize them. A few of those codes and standards not mentioned in this report include:

- BS EN378: “Safety and Environmental Requirements for Refrigeration Systems and Heat Pumps”
ISO 817: “Refrigerants - Designation and safety classification”
ISO 5149: “Refrigerating systems and heat pumps: Safety and environmental requirements”
UL 2182: “Standard for Refrigerants”

2.5 Refrigerant Applications
Different refrigerants are used for different applications, and the introduction new low GWP alternative refrigerants impacts these applications differently. The United States Environmental Protection Agency (EPA) Significant New Alternatives Policy (SNAP) program maintains lists of acceptable substitutes that are updated annually for a wide range of refrigerant applications [15], which can be broadly categorized as:

- Air Conditioning,
- Food Storage, and
- Industrial Processes.

The nomenclature used in this report for the refrigerant applications follows that used by the EPA. It is outside the scope of this literature review to discuss all the possible refrigerant applications in detail. For further details on specific applications, and the acceptable refrigerants for those applications, consult the EPA SNAP website [15].

Air conditioning applications of refrigerants are typically segregated into motor vehicle air conditioning (MVAC) systems and stationary air conditioning systems. MVAC systems are treated separately, in part, due to likelihood of accidents and location of portions of the systems within the passenger compartment. R-12 and, more recently, R-134a are being replaced in MVAC applications by refrigerants with lower GWP such as R-1234yf, R-744 (CO₂), or R-152a [16].

Residential and commercial air conditions systems such as window air conditioners, packaged terminal air conditioners (PTAC), split heat pumps, and commercial rooftop units are examples of stationary air conditioning systems. R-410A is the primary refrigerant used in residential AC systems, however it has a GWP of 2,100. Research has been conducted on the risk associated with using Class 2L refrigerants with lower GWP such as R-32 and R-1234yf in residential split heat pump systems [17] and commercial rooftop units [18]. Class 2L and Class 3 refrigerants such as R-32 and R-290 have been approved for specific air conditioning applications by EPA.

Food storage encompasses household refrigerators and freezers, retail food refrigeration, refrigerated transport, cold storage warehouses and other related appliances such as wine coolers and mini fridges. Class 3 refrigerants such as R-290 (Propane) and R-600a (Isobutane) are approved by EPA for household refrigerators and freezers under certain conditions, and guidance in UL 60335-2-24 provides charge limits for Class 2 and 3 flammable refrigerants.
Retail food refrigeration includes standalone equipment such as refrigerators, freezers, and reach-in units, refrigerated food processing and dispensing equipment for products such as chilled and frozen beverages, ice cream, yogurt, and smoothies, and remote condensing units such as those installed in convenience stores, butcher shops, supermarkets, and restaurants. R-404A and R-134a are commonly used in retail food refrigeration applications, however Class 2L and Class 3 refrigerants with lower GWP are being considered as replacements. Risk assessments and recommendations on how both Class 2L refrigerants (R-32, R-1234yf, and R-1234ze(E)) [19], as well as Class 3 refrigerants (R-290 (propane)) [20] could be used for retail food storage applications have recently been developed. Cold storage warehouses typically use ammonia as the refrigerant.

Industrial processes that use refrigerants include chillers to cool water for building comfort cooling, and industrial process air conditioning or refrigeration. R717 (ammonia), a Class 2B refrigerant, is commonly used for industrial applications due its efficiency and minimal environmental impact. However, risk assessments have evaluated the use of Class A2, A2L, and A3 refrigerants are also acceptable for industrial applications by the EPA.

### 2.6 Refrigerant Hazards

Refrigerants pose a variety of hazards that must be balanced against their performance for specific applications. In general, potential hazards of refrigerants include toxicity, flammability, and pressure release. This section discusses these hazards in the context of the current and next generation of refrigerants with low GWP.

#### 2.6.1 Toxicity

The potential health effects from exposure to refrigerants vary for each type of refrigerant. Information for a specific refrigerant is included in the Safety Data Sheet for the substance. Calm [21] summarized toxicity data for 25 common refrigerants from over 200 toxicology studies. Later work by Calm [22] expanded on the refrigerant toxicity summary and developed acute toxicity exposure limits (ATEL) and recommended refrigerant concentration limits (RCL) for 99 different refrigerants and blends available at that time (circa 2000). These studies focused on the following toxicological effects from acute inhalation exposures from unintended releases of refrigerants: lethality, cardiac sensitization, anesthetic and central nervous system (CNS) effects, and other effects which may impair escape. Cardiac sensitization refers to an effect where the heart is more sensitive to certain compounds, such as adrenaline or epinephrine, which may result in an irregular heart beat (cardiac arrhythmia), a potentially fatal condition. Anesthetic effects reduce the sensation of pain and other sensory stimulation. CNS effects include depression, distraction, stimulation, or other behavioral modifications. Escape-impairing effects include things such as blinding, reduce vision due to irritation, or severe sensory irritation. In general, the alternative refrigerants developed are neither highly toxic or even toxic according to federal Occupational Safety and Health Administration (OSHA) regulations, and many of the safety concerns with new refrigerants result from lack of information rather than increased hazard levels [22].

More recently, concerns have been expressed about the decomposition of some low-GWP refrigerants into carbonyl halides such as carbonyl fluoride, as well as hydrogen fluoride (HF), during fires. These concerns have been primarily in the automotive industry, with the replacement of R-134a with R-1234yf by automakers in Europe to comply with European
Commission Directive 2006/40/EC [23]. Carbonyl fluoride (COF₂) is a highly-corrosive gas that causes severe irritation to the eyes, skin, and airways. HF is also highly corrosive, with a strong irritating odor, that can cause rapid irritation to the eyes, nose and throat, and may result in severe and sometimes delayed health effects. A European Commission Joint Research Centre (JRC) report [24] on the subject found that there was no release of hydrogen fluoride (HF) during tests of R-1234yf reflecting “normal or foreseeable conditions of use.” However, elevated levels of HF were possible under extreme test conditions that are highly unlikely to occur at the same time. Industry response to the concern of HF generation by refrigerants in fires notes that potential for HF generation exists for all halocarbon refrigerants, including R-134a. R-134a has been safely used for the previous decade without any reports of HF exposure to occupants or first responders [25].

### 2.6.2 Flammability

A number of risk assessments have examined the risk of ignition of Class A2L refrigerants in a range of applications, including residential heat pumps [17], industrial chiller systems [26], commercial kitchen roof top units (RTUs) [18] [19], and commercial reach-in / walk-in coolers [19]. A similar assessment has also been completed for Class 3 refrigerants (R-290, propane) in commercial reach-in / walk-in coolers [20]. In general, these studies have shown the risk of ignition is relatively low and made recommendations on how to limit the risk for the specific applications and refrigerants examined.

Work has also been done to evaluate potential ignition sources for A2L refrigerants in residential and industrial applications [27]. Flammable mixture of four Class A2L refrigerants (R-32, R-452B, R-1234yf, and R-1234ze) were exposed to 15 potential ignition sources. Only four of these ignition sources (hot wire, safety match, barbeque lighter flame, and candle flame) resulted in deflagrations or localized flames. The 11 ignition sources that did not ignite any of the A2L refrigerant mixtures were a lit cigarette, sparks from a barbeque lighter, an electrical plug and receptacle under load, turning a light switch on and off, a hand mixer, a cordless drill, friction sparks, a hair dryer, a toaster, a hot plate, and an electric space heater.

In a project organized by the Air-Conditioning, Heating, and Refrigeration Technology Institute (AHRTI), UL conducted an extensive series of large scale refrigerant leak and ignition tests with Class A2L refrigerants [28]. Although testing was used to investigate the potential for ignition and fire hazard in representative residential and commercial installations, it is important to note that the ignition source placement and leakages were arranged to help facilitate the ignition of refrigerant and understand the severity of ignition events. The testing was divided into several test series. One series of tests looked at parametric variations of temperature and humidity, the presence of obstructions, the refrigerant release quantity, and the presence of lubricating oil on the ignition of A2L refrigerants. Another series of tests investigated residential and commercial refrigerant ignition scenarios, including a Packaged Terminal Air Conditioner (PTAC) unit in a motel room, a rooftop unit in commercial kitchen, a walk-in cooler; a reach-in refrigerator in a convenience store, a residential split HVAC unit in a utility closet, a residential split HVAC unit servicing error; and a residential split HVAC unit hermetic electrical pass-through terminal failure. Some of the significant findings of this work are:

- In many cases, refrigerant leaks resulted in 2-phase releases, refrigerant fog, or pools of liquid refrigerants. Previous testing, modeling, and risk studies typically only consider a
vapor release. Evaporation of the pools of liquid refrigerants that collected in low areas resulted in high refrigerant concentrations at floor level.

- Although A2L refrigerants have low burning velocities, this did not prevent flame spread in many of the scenarios considered, and ignitions occur when the air velocity was greater than the laminar burning velocity of the refrigerants.

- Obstructions, such as furniture, located near the refrigerant leak location influence the mixing of the refrigerant, and may develop a flammable mixture above the LFL in a local area that would otherwise disperse without the obstructions present.

- Results from the reach-in cooler tests showed A2L refrigerant releases greater than 300g resulted in ignition.

- No ignition was observed in the five commercial kitchen tests due to a significant amount of the refrigerant remaining within the roof top unit or associated ductwork.

- The location of the refrigerant discharge influenced ignition results for the walk-in cooler tests. Discharges near the condensate drain resulted in flammable refrigerant mixtures at floor level. The walk-in cooler door positioned had little impact on ignition results. All ignitions occurred remote from the cooler (i.e. on the opposite side of the room).

- For the residential air conditioner scenario, most of the flaming occurred near the return grill. Starting the blower fan in the HVAC unit reduced the time for flaming in the hallway but caused flames to be drawn into the HVAC unit.

Concerns have been expressed about the flammability of low-GWP refrigerants used in motor vehicle air conditioning systems with the replacement of R-134 with R-1234yf by automakers in Europe to comply with European Commission Directive 2006/40/EC [23]. These concerns were based on testing conducted by one automaker using R-1234yf refrigerant in one of their vehicles. However, subsequent testing and review by the European Commission’s Joint Research Centre (JRC) [24] found that testing showed no ignition of refrigerant R-1234yf during conditions reflecting “normal or foreseeable conditions of use.” Testing conducted under extreme conditions showed ignition of the refrigerant R-1234yf, in contrast to no ignition with R-134. However, the report notes that the extreme test conditions are highly unlikely to occur at the same time, and that just because it is possible to obtain higher levels of safety does not indicate that a product, in this case R-1234yf, is dangerous.

### 2.6.3 Pressure Release

Refrigerants are typically stored as a liquified gas at elevated pressures of approximately 250 to 300 psig. A sudden release of pressurized refrigerant can pose a number of physical hazards, including frostbite from skin contact with released refrigerant, asphyxiation from the displacement of oxygen, and injuries from an overpressure or tank rupture [21]. However, these hazards are inherent to any compressed gas, and are not specific to flammable refrigerants. One additional hazard posed by a pressurized release of Class 2, Class 2L, or Class 3 refrigerants is the increased chance of a flame jet, as the pressurized release of refrigerant is ignited, compared to a Class 1 refrigerant.

The University of Maryland (UMD) conducted tests at the Maryland Fire Research Institute on the UMD campus to evaluate appliances containing A2L refrigerants exposed to an external fire source. Tests were conducted with packaged terminal air conditioners (PTAC) using either R-32
or R-410A as the refrigerant. R-410A is a Class A1 refrigerant that is commonly used in residential and commercial air conditioning units. R-32 is a Class A2L refrigerant with a lower GWP than R-410A. In both tests, the sudden failure of refrigerant containment during a fire exposure caused a rapid depressurization and large jet flames. These fires were simulated in Task 3: Demonstrative Testing using commonly encountered appliances as shown in Figure 6. This sudden jetting can pose a significant direct risk to fire fighters and also can lead to a rapidly growing fire when in the presence of other combustibles.

![Simulated A2L release from small commercial icemaker](image)

Figure 1: Simulated A2L release from small commercial icemaker

### 2.7 Evolution of Firefighting, Overhaul and Safety Procedures

This section outlines the currently available information as it pertains to the operations of fire service personal for incidents involving flammable refrigerants. Although the discussion on the toxicity of the flammable refrigerants is ongoing, specifically focused on the risk associated with byproducts of combustion and thermal degradation, there is a lack of publicly available information pertaining to adjusted fire fighter tactics.

#### 2.7.1 Mobile Air Conditioning Systems

Mobile air conditioning system refrigerants, specifically the class A2L refrigerant R1234yf, have been the topic of a number of research studies. While the new refrigerant alternatives being used are primarily non-toxic in their typical operating state, there are conditions under which these substances can produce toxic environments. Specifically, the generation of hydrofluoric acid (HF) from the combustion or thermal decomposition of R1234yf is a concern for first responders and general consumer safety. Although studies and publications by manufacturers have identified the potential that, under ideal fire scenarios, levels of HF can be produced in the engine compartment of a vehicle that exceed the Acute Exposure Guideline level 2 (AGEL-2), the manufacturer recommends that professional fire responders “observe and practice their training when responding to car fires” [29]. The reviewed literature also indicated that currently used
fluorocarbon refrigerants, like R134a, also emit the toxic products of HF and CO$_2$ during thermal decomposition [30] making the relative releases of toxic byproducts, and the propensity of the various refrigerant types to do so, an important area of future research.

Due to the perceived risks associated with fighting fires in vehicles containing the A2L refrigerant R1234yf, the national firefighting association of Germany, in collaboration with Environmental Action Germany (DUH), has requested the identification of R1234yf refrigerants in vehicles by means of a windshield sticker. The organization believes that “the lower ignition temperature compared to the previous refrigerant R134a and the risk of releasing hydrofluoric acid make it potentially dangerous to rescuers in the event of a collision” [31]. Additional information as to how this identification would potentially change operating procedures or PPE requirements is not provided.

Recently, the EPA approved R452a for transport refrigeration applications and it is now offered as an option on new trailer refrigeration systems [32]. While much attention has been paid to the consumer vehicle, information pertaining to potential changes in refrigerant type and charge for commercial refrigerated vehicles is limited and should be evaluated further.

### 2.7.2 Residential and Commercial Refrigeration

It has been expressed in the literature that the fire service personnel have concerns with the maximum charge limits for common refrigeration units using the A2L classification of refrigerant and the lack of fire service involvement in discussions [33]. A shortage of information pertaining to quantification of the evolving residential and commercial fire hazard associated with the A2L refrigerants was noted. Changes to the charge limits of refrigerants, in addition to changes in the refrigerant classification used, may initiate evolution of fire department operating procedures under specific fire conditions. For example, the interaction of flammable refrigerants with common multi-gas sensors is unquantified and would be beneficial to characterize in order to determine if additional gas sensors focused on refrigerant may be necessary for the detection of these leakage scenarios.

### 2.7.3 Industrial Refrigeration

The Australian institute of Refrigeration, Air Conditioning and Heating’s (AIRAH) Flammable Refrigerants safety guide recommends that systems of changes greater than or equal to 5kg be communicated to the local fire service. If the refrigerant is changed or the system decommissioned, then this change should also be communicated to the fire service. The guide also recommends that a fixed gas detection be installed for systems with charge quantities of 5kg or greater. Emergency response preplanning is also conducted in accordance with the industry guide which recommends including procedures for fixed detections system alarm response including details on “the systems shut down procedure and occupant evacuation procedure” [34].

In the United States, the guidance of NFPA 1 applies to installations with refrigerant charges exceeding 30 pounds. This limit applies both to unit or system installations. Large refrigerant installation guidance references ASHREA 15 [12].

### 2.8 Conclusions

The ongoing push toward sustainability of refrigeration systems will require the adoption of low global warming potential (GWP) refrigerants. These refrigerants pose a variety of hazards that must be balanced against their performance for specific applications. The potential hazards of
refrigerants include toxic thermal decomposition and combustion products, increased flammability and explosion risks, and pressure release scenarios. The literature review conducted on these issues has identified a number of knowledge gaps, specifically from the perspective of fire service response to the evolving hazard of A2L refrigerants. At the time of this report the nature of the changing hazard has not been completely defined as standards governing refrigerant charges are still under review and several gaps in the available literature are present.

According to publications by refrigerant manufacturers, the hazards associated with HF exposure in vehicle fires containing new A2L refrigerants are similar to that of the current refrigerants used in mobile air conditioner applications. While the potential production of HF and other toxic thermal degradation byproducts exists for all halocarbon refrigerants, the differences in toxic quantities produced by existing and new refrigerants needs further investigation to determine the increased risk associated with the switch to A2L refrigerants. Similarly, for residential and commercial refrigeration applications, the toxicity of a release of A2L refrigerant exposed to thermal decomposition is uncharacterized and could affect future recommendations for proper PPE. In scenarios where the leakage of flammable refrigerants could result in accumulations approaching the lower explosive limit, there exists no information on the interaction of these refrigerants with typical multi-gas sensors typically available to first responders. While some limited guidance is provided in open literature for building owners pertaining to refrigerant detection, no such guidance or recommendations exist for the fire service at this time.

It is the intent of this gap analysis to help guide future research and the development of training material that will assist first responders in the recognition, evaluation, and mitigation of any flammable refrigerant related hazards.
3.0 TASK 2: STAKEHOLDER WORKSHOP

A stakeholder workshop was hosted by the Fire Protection Research Foundation in Quincy, MA on September 5, 2018. The 45 participants at the workshop represented a key cross section of stakeholders in disciplines surrounding the application of flammable refrigerants. The workshop focused on the general concepts of refrigerants and anticipated changes to the associated fire and health risks associated with the transition to A2L refrigerants. Training and educational requirements and concerns for both first responders, technicians, and servicing personnel were also discussed. Specifically, the workshop focused on key areas of: relevant codes and standards; hazard identification; emergency response tactics; post incident considerations; knowledge gaps; and outreach needs.

FRA presented the finding of Task 1: Literature Review and Hazard Assessment at the stakeholder workshop amongst presentations pertaining to: Significant New Alternatives Policy (SNAP), EPA; an overview of flammable refrigerant information in codes and standards, UL; guidelines for servicing, safe handling, transport, and storage of flammable refrigerants, Association of Home Appliance Manufacturers (AHAM); end user sector, Target Properties; and NFPA Emerging Technologies Program, NFPA. Slides presented by FRA are provided for reference in Appendix A of this document will complete meeting minutes available from the Fire Protection Research Foundation [35]. Discussions from the workshop will be valuable to the development of a firefighter training program focused on the new hazards and tactics associated with flammable refrigerants.
4.0 TASK 3: DEMONSTRATIVE TESTING

Task 3 involves the provision of technical guidance, planning and implementation of the demonstrative tests. Based on the outcome of the prior tasks the research team provided guidance and developed an experimental plan for the full-scale demonstrative tests observing the limitations posed by budget, facility, and number of tests. The objective of the demonstrative testing was to conduct a series of tests that can provide useful information about consequences from common appliance failure modes as well as insight into more severe consequences that may be encountered for larger scale appliances. The testing included scenarios in which the fire spreads to the appliance resulting in the release of flammable refrigerant thus further contributing to the fire growth and associated environmental hazards.

4.1 Overview

The ongoing push toward sustainability of refrigeration systems will require the adoption of low global warming potential (GWP) refrigerants within the span of a few years. The fire safety of these relatively new refrigerants is a lingering issue as first responders may lack familiarity with the change in material hazards necessary to develop appropriate response tactics when such materials may be present.

The objective of the test plan/demonstrative tests was to yield a series of tests that can provide useful information about consequences from common appliance failure modes as well as insight into more severe consequences that may be encountered, specifically with the new classes of refrigerants being used in business or industrial applications. The testing encompassed scenarios in which the fire spreads to the appliance resulting in the release of flammable refrigerant thus further contributing to the fire growth and associated environmental hazards. Testing was conducted in a repeatable and controlled manner to assist in the development of training materials and video documentation of the resulting appliance failures and was based on the outcome of prior project tasks.

4.2 Test Plan

Demonstrative testing was conducted at the FDNY training facility located on Randall’s Island, NY during the week of October 21st, 2018. Testing was conducted within one of the facility’s structures utilizing a number of training props to demonstrate gas releases from residential and commercial style appliances involving flammable refrigerants.

4.2.1 A2L Flammable Refrigerant Analogous

A2L Refrigerants offer a range of health, safety, and environmental concerns when released into the environment or ignited. To facilitate the safe and responsible operation of the proposed tests, an ethane/nitrogen gas analogy was used in place of the R-1234yf or R-1234ze refrigerant.

A number of low-GWP refrigerants are known to produce carbonyl halides such as carbonyl fluoride (COF2) and hydrogen fluoride (HF) as byproducts of combustion. COF2 and HF are both highly-corrosive gases which cause severe irritation to the eyes, skin, and airways and may result in severe and sometimes delayed health effects. Using R-1234yf or R-1234ze for the demonstrative testing would add an additional hazard to the fire testing environment which was determined to be unnecessary to achieve the goals of the demonstrative testing.
A nitrogen diluted ethane gas was selected to replicate the appearance of the A2L refrigerants of interest for purposes of the demonstrative testing and training video without posing a serious safety concern for video crew and others in attendance. The gas mixture was delivered to the leak location of interest at a volumetric ratio such that the visual and inertial properties of the fire are similar to that of a burning A2L refrigerant leak. Balance nitrogen was selected as the diluent as it is a readily available inert gas. Ethane was identified as the fuel source since it is easily ignitable, does not produce high toxic or corrosive byproducts during combustion, and has the same molecular weight as nitrogen which will keep the two components of the mixture from stratifying during delivery.

### 4.2.2 Refrigerant Fire Scenarios

After reviewing the available literature, the identified fire scenarios were selected based on typical refrigerant applications, anticipated leak scenarios, the location of potential fire sources and available testing props. Focus was given to the scenarios where A2L refrigerants may be encountered unexpectedly in residential type applications.

Typical refrigerant applications include industrial processes, food storage, and air conditioning applications. Although Class A2, A2L, and A3 refrigerants have been evaluated for use in large industrial process equipment, the size of such operations are beyond the scope of this demonstrative testing which seeks to highlight the consequences of common appliance failures. The demonstrative testing conducted made use of both residential and retail food storage units. A standard residential refrigerator was utilized in addition to an icemaker similar to what may be found behind a bar or in a restaurant. Residential window mounted air conditioning units were also used in the testing in addition to a ductless mini split residential air conditioning system.

#### 4.2.2.1 Fire Scenario Details

The fire scenario used for the demonstrative testing was selected such that each appliance could be used several times before becoming fully involved in the fire. A gravel filled line burner measuring 3’ in length and burning a premixed propane and air mixture was used to simulate an external fire load on the appliances of interest. A long duration, low flow leakage event was then simulated using a controlled release of the ethane/nitrogen mixture directed from the refrigerant coil of the device through the fire exposure. Testing conducted in this manner allowed extended releases for purposes of video collection and allowed for independent control of the gas leakage and exposure fire.

The scenarios identified in Table 1 are test scenarios that were used for the demonstrative testing. Repeat tests of the scenarios were conducted for purposes of video documentation. All the test scenarios evaluated utilized a single appliance per scenario.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Configuration</th>
<th>Tests Conducted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Window A/C</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Ductless Split A/C</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>Ice Maker</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Refrigerator</td>
<td>2</td>
</tr>
</tbody>
</table>
4.2.3 Data Acquisition

For each demonstrative test, experimental data related to temperature and heat flux were measured in the test environment. A Rescue Randy type manikin clothed in turnout gear was instrumented and placed within the enclosure in close proximity to the gas release scenario. Recorded measurements were used to quantitively identify any change in the fire environment resulting from the release of the refrigerant into the fire environment.

Type-K thermocouples were placed at several locations on the exterior of the turnout gear from the facepiece to the legs of the manikin. To measure the radiant heat exposure to a firefighter in close proximity to the equipment being tested, the Rescue Randy was instrumented with a water-cooled, Schmidt-Boelter style heat flux gauge. The gauge was oriented such that the sensing surface of the device was parallel to the shoulders of the manikin, protruding from the turnout gear near, and positioned near the center of mass of the Rescue Randy. Including the gauge in the measurements was intended to provide quantitative measurements of the change in heat flux experienced by a firefighter local to a flaming release of refrigerant. In total 9 thermocouples and a single heat flux gauge were used for the demonstrative tests with measurements recorded at a frequency of 2 Hz.

4.3 Test Procedure

Demonstrative testing procedures were developed to ensure that all tests are conducted in a safe, efficient, and repeatable manner. The equipment being tested was first positioned within the test enclosure. The gas supply piping was then installed within the equipment local to the location of the existing refrigerant lines with the leakage location positioned facing the exterior of the appliance. The external fire source and firefighter manikin were then positioned adjacent to the appliance. Instrumentation, cameras, and fuel supplies were checked prior to the start of the test. Emergency procedures were reviewed, the standby fire suppression team was positioned, and the external fire source was ignited. At the beginning of the test the gas burner flame was increased to produce a significant fire exposure to the appliance. The refrigerant leak was then initiated and held for a duration of time sufficient to document the consequence of the release. At the conclusion of each test, all gas flows were stopped and any remaining flames on the appliance were manually extinguished using a rechargeable Class A water extinguisher. A charged fire hose was also available but was not utilized in any suppression activities.

4.4 Demonstrative Testing Results

Demonstrative testing of the fire scenarios described was conducted and documented. For a number of the tests conducted, the manikin was positioned a few feet from the tested appliance, as shown in Figure 2. In the presented test, the gas burner flame was removed after ignition of the refrigerant gas flow. For all tests conducted, the measured temperatures on the exterior of the turnout gear peaked at nominally 70°C with ambient heat fluxes peaking to approximately 4 kW/m² for a 2 second duration. The measured heat fluxes throughout the remainder of testing remained below that 4 kW/m² observed maximum value. For testing of the third scenario involving the icemaker, Figure 3, the release was allowed to continue until the flames from the external fire source ignited the plastic on the cover of the appliance and then suppression was initiated. Additional demonstrative testing images are provided in Appendix B.
Figure 2: Demonstrative testing placement of manikin relative to split A/C unit.

Figure 3: Simulated release from icemaker.
5.0 FIRE SERVICE TRAINING CONTENT DEVELOPMENT

From the stakeholder workshop on flammable refrigerants, the need for fire service training material was identified as a key takeaway. Based on the demonstrative tests and workshop outcomes the team will develop a training program suitable for multiple delivery formats including online, live, and video/streaming dissemination. This work will be coordinated with the NFPA videographer to ensure that proper video and story-boarding are obtained to ensure training modules are sufficiently developed and clear. Training will focus on firefighter safety when dealing with appliances that may have flammable refrigerants during both fire suppression and overhaul phases of operation.

The workshop emphasized the need to educate fire service personnel on the shift in refrigerant materials and adjust tactics accordingly when responding to refrigeration applications. Development of the fire service content should include the following outcomes of the stakeholder workshop to educate and facilitate changing tactics:

- Codes and standards – Provide an overview of relevant codes and standards as they pertain to fire service operations.
- Hazard identification – Fire service awareness of the different scenarios which may involve flammable refrigerants.
  - Residential fires: The expected quantities of flammable refrigerants charges are small but present in window a/c units, refrigerators, dehumidifiers etc.
  - Commercial structures: Larger charge quantities are likely and proper preplanning is crucial in identifying these hazards.
  - Transportation: Ventilation may be an issue with incidents involving vehicles in parking structures or maintenance facility. Incidents involving refrigerated transportation vehicles should be treated with caution.
  - Warehouse: The main concerns identified include bulk storage and storage arrangements on a large scale.
- Emergency Response – Underlying concern was expressed in the products of combustion, recommended clarification of possible symptoms for exposed emergency responders during and post event, adequacy of PPE, and de-contamination for post event.
- Post incident considerations – Emphasize that proper PPE should be used for post incident operations, overhaul and investigations. The release of Hydrogen Fluoride (HF) and exposure were noted of concern at the workshop. Supple application of water will dilute the HF quickly, however it does not completely eliminate the hazard.
- Knowledge Gaps – An overarching task group including members from ASHRAE, UL, NFPA and others to disseminate the materials to the applicable parties was recommended. The need for continued partnerships between industry, fire protection engineers, and the fire service was identified.
6.0 REFERENCES


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A. TECHNICAL WORKSHOP PRESENTATION

Flammable Refrigerants
Literature Review and Hazard Assessment

Prepared for:

Prepared by:

Team Introduction

- Dr. Peter Sunderland, University of Maryland (UMD)
  - Professor of Fire Protection Engineering at the University of Maryland
  - NCIMR Staff Scientist at NASA Glenn Research Center
  - Expertise in combustion and fire protection, including refrigerant flammability, soot formation and oxidation, microgravity combustion, hydrogen flames, laminar diffusion flames, sodium fires, battery fires, vehicle fires, and diagnostics development.
  - Co-author of over 40 journal articles and over 150 conference papers.
- Noah Ryder, P.E. - Fire & Risk Alliance (FRA)
  - B.S. and M.S. in Fire Protection Engineering from University of Maryland
  - 20 years of experience in engineering consulting and applied research
  - Managing Partner at FRA
  - Visiting Research Associate and Lecturer at the University of Maryland, Department of Fire Protection Engineering and Associate Professor at University of Waterloo.
Project Introduction

- Current refrigerants in use today
  - Hydrofluorocarbon (HFC) refrigerants
  - Selection based on: non-ozone depleting, safety of use
  - High Global Warming Potential (GWP)
- Next generation of refrigerants
  - A2L refrigerants and blends of HFOs with HFCs refrigerants.
  - Flammable: ASHRAE Standard 34 classification of A2, A2L or A3.
- Fire safety and material hazards are an ongoing issue with A2L’s
  - Change in material hazards with new refrigerants
  - First responder tactics
  - Toxic byproduct production: Hydrogen fluoride (HF) and Carbonyl fluoride (COF₂)

Overview

- Background
  - History, Common Refrigerants and Properties, Applications
- Refrigerant Hazards
  - Toxicity, Flammability, Pressure Release
- Firefighting and Overhaul
  - Hazard Identification, Vehicle Fire Response, Safety Measures
- Future Work
  - CFD Simulations, Demonstrative Testing
- Conclusions
REFRIGERANT BACKGROUND

Refrigerant History

- Start of mechanical refrigeration
  - Early 19th century
  - Water, air, ammonia, sulfur dioxide and carbon dioxide
- The second generation of refrigerants
  - Early 20th century
  - Classic refrigerants were replaced with chlorofluorocarbons (CFCs)
- The Montreal Protocol
  - 1987: Limited the production and consumption of CFCs
  - 1996: Governments world-wide started phasing out the use of chlorodifluoromethane (R-22)
  - 2010: End of global CFC production
- By 2008, stratospheric chlorine abundances were 10% lower than peak values of the late 1990s and were continuing to decrease.
Common Refrigerants

Chlorofluorocarbons (CFCs)
- Halocarbons
- Nontoxic, nonflammable
- Contain atoms of carbon, fluorine, and chlorine
  - $\text{C}_{x}\text{F}_{y}\text{Cl}_{z}$ and $\text{C}_{x}\text{F}_{y}$
- Reacts with UV light and releases Chlorine atoms
  - $\text{CCl}_2\text{F} \rightarrow \text{CCl}_3\text{F} + \text{Cl}$
  - Destroys ozone in catalytic reactions where 100,000 molecules of ozone can be destroyed per chlorine atom.

Hydrochlorofluorocarbon (HCFC)
- Contains atoms of hydrogen, carbon, fluorine, and chlorine
  - $\text{CCl}_x\text{F}_y\text{H}_z$, and $\text{C}_x\text{F}_y\text{H}_z$
- Decompose photochemically before they reach the stratosphere.
  - Do not release chlorine atoms and thus do not attack the ozone layer

Common Refrigerants

Hydrofluorocarbons (HFCs)
- Contains carbon, fluorine, and hydrogen
  - $\text{C}_{x}\text{F}_{y}\text{H}_z$, $\text{C}_x\text{F}_y\text{H}_z$, $\text{C}_x\text{F}_y\text{H}_z$, and $\text{C}_x\text{F}_y\text{H}_z$
- Used in air conditioning, refrigeration, solvents, foam blowing agents, and aerosols.
- Zero Ozone Depletion Potential (ODP)
- Greenhouse gas
  - Global Warming Potential (GWP)
- R-410A: 50:50 (by weight) blend of R-32 (difluoromethane) and R-125 (pentfluoro-ethane)
  - GWP of 2,100

Hydrofluoroolefins (HFOs)
- 4th generation of refrigerants
- Contains carbon, fluorine, and hydrogen
  - Unsaturated hydrocarbon containing at least one carbon–carbon double bond
- Zero ODP
- Low GWP
  - 0.1% GWP of HFCs
- 2,3,3,3-tetrafluoropropene (HFO-1234yf)
ASHRAE 34 Naming Convention

- Prefix
  - R for refrigerant
  - C is used in the prefix to denote carbon
    - Preceded by B, C or F (or a combination of these letters in the same order) to indicate the presence of bromine, chlorine or fluorine
  - Compounds containing hydrogen must be preceded by the letter H
  - Examples: HCFC22, HFC134a.

- Suffix
  - Example: R22 (chlorodifluoromethane – CHF2)
    - 0: Number of carbon atoms – 1
    - 2: Number of hydrogen atoms + 1
    - 2: Number of fluorine atoms
    - Number of chlorine atoms: 1 (4 minus 1 hydrogen atom and minus 2 fluorine atoms)

ASHRAE 34 Naming Convention

- For cyclic derivatives, the letter C is used before the refrigerant’s identification number
  - Example: RC318 (octafluorocyclobutane – C₆F₈)

- Isomers in the ethane series
  - Each has the same number
  - Most symmetrical one indicated by the number alone
  - As isomers become more and more unsymmetrical, successive lowercase letters (i.e. a, b or c) are appended
  - Example: R134 and R134a
ASHRAE 34 Naming Convention

- Zeotropic mixtures
  - 400 series
  - An uppercase letter suffix differentiates mass percentages.
  - Example: R407A (R32/R125/R134a (20/40/40)), R407B (R32/R125/R134a (10/70/20))
- Zeotropic mixtures of 50/50 composition
  - 500 series
  - Example: R507 (R125/R143a [50/50])
- Miscellaneous organic compounds
  - 600 series
  - Example: R600a (isobutane)
- Inorganic compounds
  - 700 series
  - Identification numbers are formed by adding the relative molecular mass of components to 700
  - Example: R717 (ammonia)

Refrigerant Testing Methods

- Bomb Calorimeter
  - ASTM D240 / D4809
- Flammability Limits
  - ASTM E681
- Minimum Ignition Energy and Quenching Distance
  - ASTM E582
- Autoignition Temperature
  - ASTM E659
Refrigerant Applications

- Industrial Processes
- Food Storage
  - Household refrigerators and freezers
  - Retail food refrigeration
    - Standalone equipment
    - Refrigerated food processing and dispensing equipment
  - Refrigerated transport
  - Cold storage warehouses
- Air Conditioning
  - Motor vehicle air conditioning (MVAC) systems
  - Stationary air conditioning systems
    - Packaged terminal air conditioners (PTAC)
    - Split heat pumps
    - Commercial rooftop units
Flammability

- ASHRAE 34 classifies the flammability of refrigerants based on:
  - Lower flammable limit (LFL)
  - Burning velocity
  - Heat of combustion

- The classification includes a number, and possibly letter suffix, to identify the flammability hazard class:
  - Class 1: No flame propagation in air
  - Class 2L: Same as Class 2, with burning velocity less than 10 cm/s
  - Class 2I: LFL greater than 0.1 kg/m³ (ASHRAE), 3.5% (ISO); heat of combustion less than 19 kJ/g
  - Class 3: heat of combustion greater than 19 kJ/g

Flammability Limits in Air

<table>
<thead>
<tr>
<th>Species</th>
<th>LFL (%)</th>
<th>UFL (%)</th>
<th>Dry Stoic. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-32</td>
<td>14.4a</td>
<td>29.3b</td>
<td>17.4</td>
</tr>
<tr>
<td>R-1234yf</td>
<td>6.2a</td>
<td>12.3b</td>
<td>7.8</td>
</tr>
<tr>
<td>R-1234ze</td>
<td>6.5a</td>
<td>9.5b</td>
<td>7.8</td>
</tr>
<tr>
<td>R-452B</td>
<td>11.5c</td>
<td>23.0f</td>
<td>14.7</td>
</tr>
<tr>
<td>Methane</td>
<td>4.6d</td>
<td>14.7d</td>
<td>9.5</td>
</tr>
</tbody>
</table>

(a) ANSI/ASHRAE Standard 15 vol 34, 2013. (b) ASHRI 0009, 2015.
(c) Cherwani et al, 2012.
### Quenching Distance

<table>
<thead>
<tr>
<th>Species</th>
<th>( L_0 ), mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-32</td>
<td>7.55(^a)</td>
</tr>
<tr>
<td>R-1234yf</td>
<td>24.8(^b)</td>
</tr>
<tr>
<td>Methane</td>
<td>2.0(^b)</td>
</tr>
</tbody>
</table>

\( ^a \) FRAE, 2014; \( ^b \) Tames, 2012.

### Minimum Ignition Energy

<table>
<thead>
<tr>
<th>Species</th>
<th>MIE, J</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-32</td>
<td>0.03 – 0.1(^a)</td>
</tr>
<tr>
<td>R-1234yf</td>
<td>5 – 10(^b)</td>
</tr>
<tr>
<td>R-1234ze</td>
<td>61 – 64(\times)^b</td>
</tr>
<tr>
<td>Methane</td>
<td>2.9e-4(^c)</td>
</tr>
</tbody>
</table>

\( ^a \) AHRI 800, 2015; \( ^b \) at 54 °C; \( ^c \) Tames, 2012.
Toxicity

- Permissible exposure limit (PEL)
  - Group A: PEL > 400 ppm
  - Group B: PEL < 400 ppm
- Information available on Safety Data Sheet for the substance.
- Toxic thermal decomposition
  - Hydrogen Fluoride (HF)
    - Strong, irritating odor
    - Causes rapid irritation to the eyes, nose and throat, and may result in severe and sometimes delayed health effects
    - NIOSH time-weighted average exposure for 10 hour workday: 3 ppm
  - Carbonyl Fluoride (COF₂)
    - Highly-corrosive gas
    - Causes severe irritation to the eyes, skin, and airways
    - NIOSH time-weighted average exposure for 10 hour workday: 2 ppm

HF

- In a fire, most of the F in refrigerants becomes HF.
- CH₃F₂ + (O₂ + 3.76 N₂) → CO₂ + 2 HF + 3.76 N₂
- HF is the greatest toxicity hazard of refrigerant fires.
- HF mole fractions are up to 50% following 1234yf-air combustion.
- 3 ppm NIOSH recommended time-weighted average for 10 hour workday.
- AEGL-2 limit for HF is 95 ppm, 10 mins.
- Irritancy perception is 3-5 ppm.
- HF is unique among acids for penetrating tissues – even small dermal exposures can cause severe systemic toxicity.
- BP is 20 °C.
COF₂

- Carbonyl fluoride.
- \( \text{C}_3\text{H}_2\text{F}_4 + 2.5 (\text{O}_2 + 3.76 \text{N}_2) \rightarrow 2 \text{CO}_2 + 4 \text{HF} + \text{COF}_2 + 9.4 \text{N}_2 \)
- 2 ppm NIOSH recommended time-weighted average for 10 hour workday.

Pressure Release

- Refrigerants are typically stored as a liquified gas
  - Elevated pressures of approximately 250 to 300 psig.
- A sudden release of pressurized refrigerant can pose a number of physical hazards:
  - Frostbite
  - Asphyxiation
  - Injuries from tank rupture
- Pressurized release of Class A2L or Class 3 refrigerants
  - Potential of flame jet from ignition of pressurized refrigerant release
Vehicle Warning Labels

- The German environmental group (DUH) and Germany's national firefighting association have called for warning stickers for the windscreens of cars containing R1234yf.

- Potential danger to rescuers in the event of a collision
  - Lower ignition temperature compared to the previous refrigerant (R134a)
  - Risk of releasing hydrofluoric acid make it potentially dangerous to rescuers in the event of a collision.
Vehicle Fire Response

- Different tactics should be applied for passenger vehicles compared to commercial vehicles.
  - Fuel load, refrigerant quantity, ignition sources
- Identify and mitigate potential ignition sources
  - Vehicle electronic system (series and parallel battery configurations)
  - Hot surface ignition
  - Open flame sources
- SCBA SOPs

Vehicle Fire Response

- When rescue crews arrive on scene the first question that must be answered is what was in the compartment.
- The type and amount of fuel must be determined before crews can safely approach the fire.
- The first step is to ventilate and suppress the fire.
- Ventilation can be done by opening a hole in the top of the compartment.
Hydrocarbon (HC) Refrigerant Safety

- Workers handling HC refrigerants are fully aware of the fire and explosion hazard
  - Identify the type of refrigerant in the refrigeration system
  - Associated hazards via safety data sheets
- Implement measures to prevent fire/explosions
  - Remove or prevent the accumulation of HC refrigerants
- Removed all potential ignition sources
  - Install flame-proof equipment
- No welding, brazing, soldering or cutting operation should be conducted on any system that contains or has contained HC refrigerants until all reasonably practicable steps have been taken to safely remove the HC refrigerant and the system has been certified by a competent person to be free of HC refrigerant.

Firefighting Best Practices

- Environmental awareness
- Understand hazards associated with refrigerants
  - Jetting fires
  - Pressurized refrigerant explosions
  - Thermal decomposition
- Identify warning signs
  - Fire proximity to equipment with refrigerant
  - Smells, eye irritation, etc.
- Act accordingly
  - SOPs for SCBA use
  - Positioning on the fireground (upwind vs downwind)
FUTURE WORK

CFD Modeling

• Evaluate dispersion and ignition of the flammable refrigerant releases
  — FDS, FLACS
• Broader exploration of the parameter space outside of what may be possible with the limited demonstrative tests.
  — Release size, location, environment
• The results of the CFD simulations will provide information in graphic format (video and stills) that can be used to supplement training materials and inform the demonstrative tests.

Example CFD output of gas concentration prior to ignition.
Demonstrative Testing

• Objective: A series of tests that can provide useful information about consequences from common appliance failure modes.
• Evaluate conditions under which more severe consequences may be encountered.
• The testing should encompass scenarios in which:
  — The fire originates from within the appliance
  — The appliance is exposed to an external fire source
  — Consumer and commercial systems

Conclusions

• The ongoing push toward sustainability of refrigeration systems will require the adoption of low global warming potential (GWP) refrigerants.
• Refrigerant hazards include concerns of toxicity, flammability, and pressure release.
• The risk of injury can be reduced by training emergency responders on the hazards associated with low GWP refrigerants.
• Governing organizations can institute new regulations that force manufactures to provide warning labels on products containing refrigerants to further warn of the risks and hazards.
• A safety training program should be instituted with the goal of informing and protecting individuals who may be working in close proximity to refrigerants under hazardous conditions.
Conclusions

New hazards are being introduced, in the absence of knowledge to the contrary you must assume you are dealing with a new LGWP refrigerant and take the necessary precautions.

References

B. DEMONSTRATIVE TEST DOCUMENTATION

B.1. Residential A/C Unit

Figure 4: Residential A/C unit release simulated.

B.2. Ductless Split A/C Unit

Figure 5: Ductless split A/C unit simulated release with reduced external fire exposure.
B.3. **Icemaker**

![Icemaker demonstration testing](image)

*Figure 6: Icemaker demonstrative testing; gas release with external fire reduced (left); fire size at time of suppression (right).*

B.4. **Refrigerator**

![Refrigerator release from internal fire](image)

*Figure 7: Release from internal fire of residential refrigerator.*