

Methodology Development for the Measurement of Refrigerant Flammability Limits

Kevin Turner, Arthur Benson, Michael Lundin, Ed Atchison, Dave Watson, Steve Campbell, Brian Finney, Glen Khlebutin, Riyaz Papar, and Mark B. Shiflett*



Cite This: <https://doi.org/10.1021/acs.iecr.5c01453>



Read Online

ACCESS |



Metrics & More

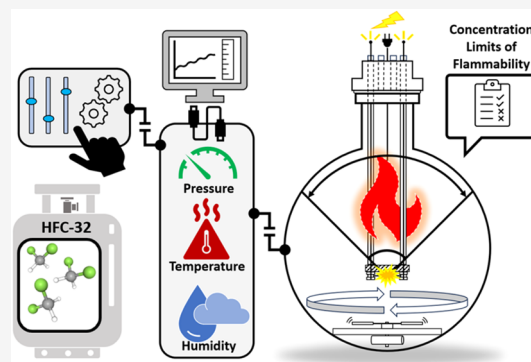


Article Recommendations



Supporting Information

ABSTRACT: Flammability has emerged as a challenge to the adoption of refrigerants with low global warming potential (GWP) and zero ozone depletion potential (ODP). Among the flammability criteria considered in safety standards, the concentration limits of flammability (i.e., flammability limits) require further empirical study. Existing methodologies can benefit from improved precision and reproducibility, particularly for refrigerants, and the reported data for current and next-generation refrigerants remains limited. In this study, an experimental apparatus following the ASTM E681–09 test method was developed that enabled precise control of temperature, pressure, humidity, and ignition strength. Reproducibility and comparison with literature measurements was investigated using mixtures of difluoromethane (HFC-32) and air. The lower and upper flammability limits (LFL and UFL) for HFC-32 were observed at 14.2 ± 0.2 and 26.8 ± 0.2 vol %, respectively, under average conditions of 23.0 ± 2.2 °C, 8.8 ± 0.5 g water/kg dry air, and 960.3 ± 1.0 mbar.



1. INTRODUCTION

Increasingly strict regulations on greenhouse gas emissions present challenges for refrigerant manufacturers balancing environmental goals and safety standards. Legacy refrigerants, including chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), played a key role in expanding heating, ventilation, air conditioning, and refrigeration (HVACR) technology by improving refrigerant performance, safety, and reliability compared with earlier options such as ammonia, sulfur dioxide, and hydrocarbons. However, soon after identifying the ozone depletion potential (ODP) of CFCs and HCFCs, the Vienna Convention and resulting Montreal Protocol (1987) set timelines for the phaseout of these substances.¹ Hydrofluorocarbon (HFC) alternatives were developed to eliminate ozone depletion concerns while preserving the historical improvements to refrigerant safety, such as low toxicity and nonflammability.²

Motivated by recent legislation, such as the Kigali Amendment (2016) and American Innovation and Manufacturing (AIM) Act (2020), a new transition is underway, targeting the global warming potential (GWP) of HFCs. The HVACR industry is pursuing the adoption of refrigerants with lower GWP by switching to hydrofluoroolefin (HFO) refrigerants and utilizing blends of low-GWP HFCs with HFOs. Despite the transition to low-GWP refrigerants, compromises have been necessary as no optimal single component or mixture of refrigerants has been developed to address all performance, safety, and sustainability requirements. A pressing concern

surrounding many HFO and HFC/HFO refrigerants with low-GWP is combustibility. This concern has driven extensive research aimed at equipping engineers and safety professionals with effective tools for assessing flammability hazards.

Whether used alone or as part of a binary or ternary mixture, many flammable refrigerants offer promising solutions to ozone depletion, global warming, and photochemical reactivity concerns.³ Among HFCs and HCFCs, substituting halogens with hydrogen within the refrigerant molecule can decrease atmospheric lifetimes but also increase the likelihood of refrigerant flammability.² Nonhalogenated refrigerants, such as ammonia and hydrocarbons (e.g., propane and isobutane) have gained renewed interest but present a much greater flammability hazard. Typically, existing hydrocarbon (HC) refrigerants are limited by charge size and used in much smaller equipment. HFO refrigerants are being commercialized but are classified as having low flammability, and hydrochlorofluoroolefin (HCFO) refrigerants are also under consideration but exhibit low ODP.² Trade-offs between environmental impact and safety across various refrigerant classes are shown in Table 1.

Received: April 16, 2025

Revised: October 2, 2025

Accepted: October 13, 2025



Table 1. Characteristics of Select Previous, Current, and Next-generation Refrigerants^a

refrigerant number	chemical name	safety classification	ODP	GWP ₁₀₀
CFC-12	dichlorodifluoromethane	A1 (no flame propagation)	0.75	12,500
HCFC-22	chlorodifluoromethane	A1 (no flame propagation)	0.038	1910
HFC-32	difluoromethane	A2L (lower flammability)	0	749
HFC-134a	1,1,1,2-tetrafluoroethane	A1 (no flame propagation)	0	1470
HFC-125	pentafluoroethane	A1 (no flame propagation)	0	3820
R-410A	50:50 wt % HFC-32/HFC-125	A1 (no flame propagation)	0	2285
HFO-1234yf	2,3,3,3-tetrafluoropropene	A2L (lower flammability)	0	<1
HCFO-1233zd(E)	trans-1-chloro-3,3,3-trifluoropropene	A1 (no flame propagation)	<0.0004	4
HC-290	propane	A3 (higher flammability)	0	<1
HC-600a	isobutane	A3 (higher flammability)	0	<1
R-717	ammonia	B2L (higher toxicity, lower flammability)	0	<1

^aODP and GWP values taken from World Meteorological Organization: Scientific Assessment of Ozone Depletion (WMO 2022).⁴ GWP for R-410A is calculated using a mass-weighted average.

Since flammability is a continuum described by many variables, the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) defines four classes for refrigerant flammability: 1 (no flame propagation), 2L (lower flammability), 2 (flammable), and 3 (higher flammability). Class 2 and 2L refrigerants differ in terms of burning velocity, while both differ from class 3 refrigerants in terms of lower flammability limit (LFL) and heat of combustion.⁵ Among the criteria used to classify refrigerant flammability, flammability limits have the largest impact on a refrigerant's specific application and the design of peripheral systems. These limits are of practical concern in safety considerations, informing decisions regarding the storage, handling, and operating conditions of potentially flammable refrigerants.

Generally, mixtures of fuel and oxidizer are flammable over a certain range of compositions bounded by a lower and upper flammability limit (LFL and UFL). These boundaries correspond to the minimum and maximum concentrations of fuel capable of sustaining combustion, respectively.⁶ Mixtures below the LFL lack sufficient fuel necessary to support a combustion reaction, while those above the UFL lack sufficient oxygen. Therefore, mixtures kept outside these limits pose a significantly lower flammability risk in the presence of an ignition source. In this context, a refrigerant with a lower LFL more readily forms a flammable mixture with air in a leakage scenario, so a greater ventilation requirement or smaller charge size is necessary to mitigate the hazard. The UFL has fewer practical implications but remains important, as a higher value may indicate a broader flammability range.

A more precise definition of flammability limits can be adapted from the Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases) given by the American Society for Testing and Materials (ASTM E681): flammability limits refer to the minimum and maximum concentration limits of a combustible substance that is capable of propagating a flame in a homogeneous and quiescent mixture of the combustible substance and a gaseous oxidizer under the specified conditions of test.⁷

Flammability, in this sense, is primarily concerned with the phenomenon of flame propagation, whereby an incipient flame must confer enough energy and free radicals on combustion of one layer in order to ignite the subsequent layer of unburned gas.⁸ When exposed to an external ignition source or subjected to elevated temperatures, combustible gas–air mixtures of varying composition can exhibit different degrees of flame propagation. Since this behavior can be influenced by several

factors, including gravity and flame geometry, it is necessary to distinguish experimentally determined limits from *fundamental flammability limits*—theoretical boundaries based on idealized conditions. Fundamental limits depend only on the initial temperature and pressure condition of the mixture⁹ and describe the compositions resulting in infinite, or self-sustaining flame propagation, beyond which any initiated flame will eventually extinguish.

Some researchers have argued that as long as experimentally determined limits are obtained under conditions similar to those found in practice, such limits may be used to assess potential flammability hazards and design installations that are safe.¹⁰ A similar argument can be made to justify wider, more conservative flammability limit measurements. Empirical methods include DIN 51649, EN 1839(T), EN 1839(B) ASTM E981, and ASTM E681, which rely on either pressure rise or visual observations as indications of flammability. Accurate measurements are challenging and highly sensitive to the specifics of the test method, leading to discrepancies among reported flammability limits. For example, some discrepancies can be explained by the required extent of flame propagation.¹¹ This may suggest that a better approximation of fundamental limits is needed, relying on application standards to impose safety margins, which may be material dependent.

For refrigerants, the distinction between intrinsic combustion behavior and experimental observations is particularly important. These limits must be determined experimentally and cannot presently be calculated from first principles.¹² However, the accuracy and reproducibility of refrigerant flammability limit measurements across different methods and laboratories remains limited. Uncertainties are largely unquantified, which undermines the comparability of results and complicates efforts to develop computational frameworks and predictive models. Without detailed documentation of apparatus configurations and testing procedures, it becomes difficult to trace how observed limits depart from a refrigerant's fundamental combustion properties. While it is unlikely that further improvements to experimental methodologies will significantly alter existing ASHRAE classifications, such refinements are essential for enhancing measurement reproducibility and generating traceable data. This work aims to provide a technically transparent implementation of a flammability limit testing apparatus suitable for refrigerant testing. The complete design is presented, including flow configuration, equipment specification, and instrument selec-

tion. Emphasis is placed on identifying areas of uncertainty and ensuring precise control of test conditions.

2. MATERIALS AND METHODS

2.1. Materials. Difluoromethane (HFC-32, CH_2F_2 ; CAS No. 75-10-5) with a minimum purity of 99.9 wt % was supplied by Hudson Technologies Company (Champaign, IL). HFC-32 is a commercial refrigerant used both as a single component and in mixtures such as R-410A (50:50 wt % HFC-32/HFC-125). HFC-32 is commonly used to evaluate flammability limit test results due to its appreciable flammability limits and relatively low GWP.

2.2. Methods. **2.2.1. ASTM E681 Overview.** ASTM E681-09 (reapproved 2023) is internationally recognized, and although the specific construction of the experimental apparatus and procedure may vary, there are a few key features. A sealed test vessel is initially evacuated. Combustible gas is introduced, mixed with air, and ignited using a high-voltage spark. The concentration of combustible gas is varied until the mixture can propagate a flame introduced by an ignition source. Flame propagation is established through visual observation criteria. A recent modification to ASTM E681 (Annex A1) provides details for testing materials with large quenching distances that may be difficult to ignite.⁷ Most halogenated refrigerants meet this requirement and are considered borderline flammable materials, exhibiting less distinct flammability limits.

This work focuses on specifications given by ASHRAE Standard 34,⁵ which utilizes ASTM E681, in the design of a flammability testing apparatus. Potential modifications and recommendations are discussed, particularly in regard to addressing areas of uncertainty. Ultimately, an apparatus compliant with ASTM E681-09 guidelines was constructed to facilitate baseline data comparison and remain consistent with ASHRAE classification schemes. A detailed design and procedure is provided in the [Supporting Information](#).

2.2.2. Test Vessel. A test vessel of sufficient size is necessary to avoid physical and thermal interference with the flame front. Confined test vessels exhibit quenching effects whereby the walls of the test vessel act as a heat sink.¹³ This implies narrower flammability limits can be expected in smaller vessels due to heat transferred to the walls by radiation, convection, and conduction. However, wider limits have also been observed in relatively small tubes; this has been attributed to the formation of convective velocity fields that accelerate flame propagation, as well as heat radiated from the incipient flame itself and reflected by the vessel walls.^{13,14}

Regardless, above a critical dimension, experimentally measured limits are not significantly impacted by the vessel's size and geometry, converging on a certain value.¹⁴ However, due to the additional cost, complexity, and safety hazard associated with large-scale flammability experiments, a reasonable approximation must be made. The current strategy is to correlate visual observations made in confined vessels with those obtained in much larger test vessels. Specifically, ASTM E681 relies on benchmark tests conducted in a large 200-L tube.¹⁵ These tests, performed using refrigerant mixtures (HFC-134a/HFC-152a and HFC-125/HFC-152a), offer a close approximation of infinite flame propagation with negligible wall effects. According to the report, "In both cases at the same composition the transition in the large volume tube from non-flame propagation to flame propagation coincided with a 90° angle flame cap in the 12 liter ASTM

E681 test apparatus."¹⁵ Thus, for borderline flammable materials, ASTM E681 incorporates the following visual criteria for flame propagation in a 12-L flask:

"Flame propagation is defined as flames that having spread upward and outward to the walls of the flask, are continuous along an arc that is greater than that subtended by an angle equal to 90 deg, as measured from the point of ignition to the walls of the flask. The flame shall be continuous along the arc at the flask wall."⁷ (See [Figure 1](#)).

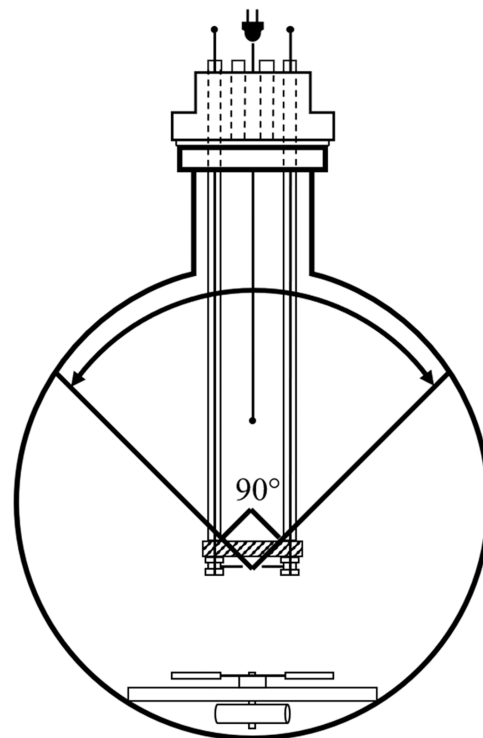


Figure 1. 90° visual criterion for flame propagation.

The choice of construction material is also an important consideration. Naturally, the flask must withstand the temperature and pressure variations required during testing while transparency is required to make visual observations. Borosilicate glass is commonly chosen, as specified by ASTM E681 and ASHRAE 34. When HFCs, or similar fluorinated compounds, are present in the test mixture, gaseous hydrogen fluoride (HF) forms as a combustion product. Over time, the accumulation of HF etches the test vessel walls, reducing transparency.³ Recent investigations using polycarbonate spheres indicate that etching can be effectively mitigated,¹⁶ yet the effect of different material properties (e.g., thermal conductivity) remains unclear. Nevertheless, the test vessel and all components should be clean and dry to ensure residual materials do not influence the observed flammability limits, especially during final trials.⁷ After repeated cleaning, roughly 50 tests were conducted using HFC-32 in a Pyrex No. 4260-12L flask before etching started to hinder visual observations.

2.2.3. Test Vessel Cover. A cover assembly rests on top of the test vessel to support the necessary pipe connections, electrodes, and temperature monitoring device.⁷ To avoid contaminating the test mixture, the assembly must satisfy a strict vacuum requirement and minimize leaks. However, the recommended No. 14 rubber stopper is difficult to machine and prone to leakage, creating challenges in accommodating

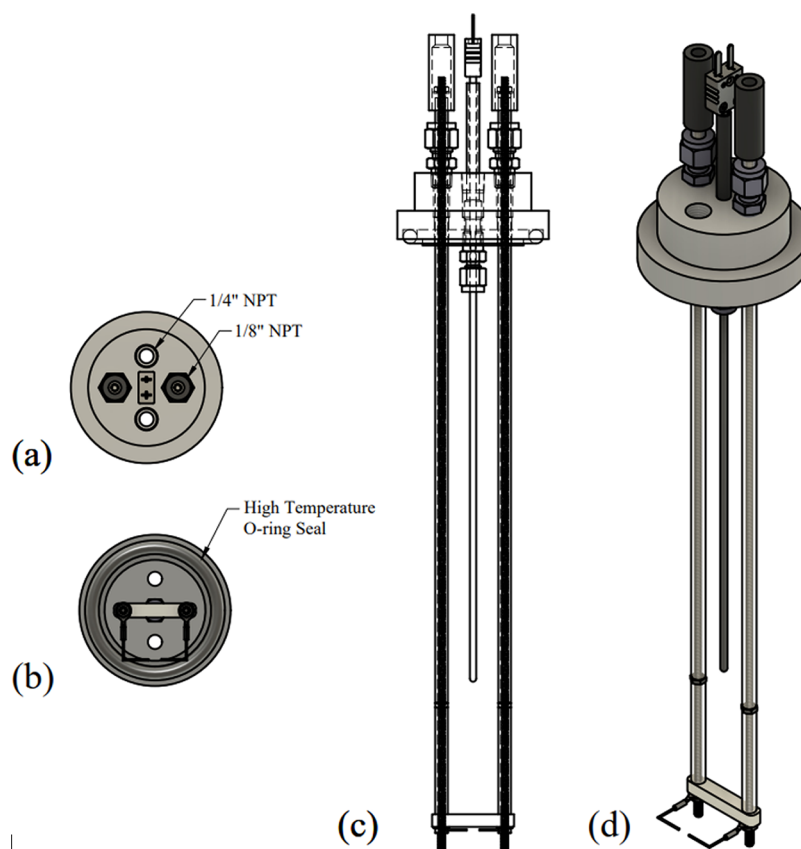


Figure 2. Stopper assembly. (a) Top view, (b) Bottom view, (c) Side view with hidden edges, and (d) Isometric view.

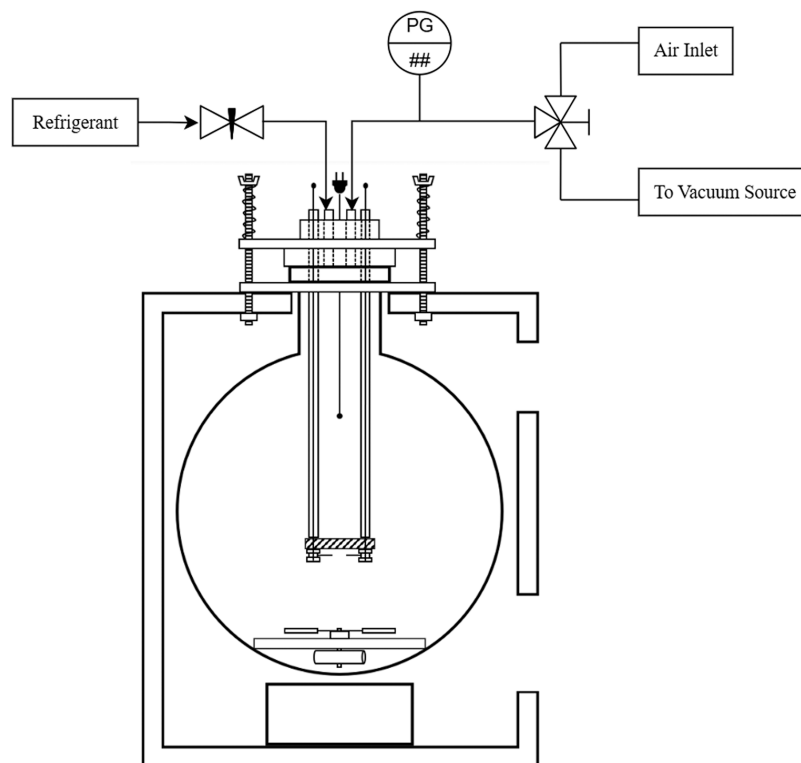


Figure 3. Test vessel cover assembly showing pipe connections, electrodes, connected volumes, temperature monitoring device, stirring device, and cover clamp. Not shown to scale.

multiple connections (i.e., stopper penetrations).¹⁷ A polytetrafluoroethylene (PTFE) stopper was designed and

constructed, as shown in Figure 2, offering greater machinability and chemical resistance. During final trials, the vacuum

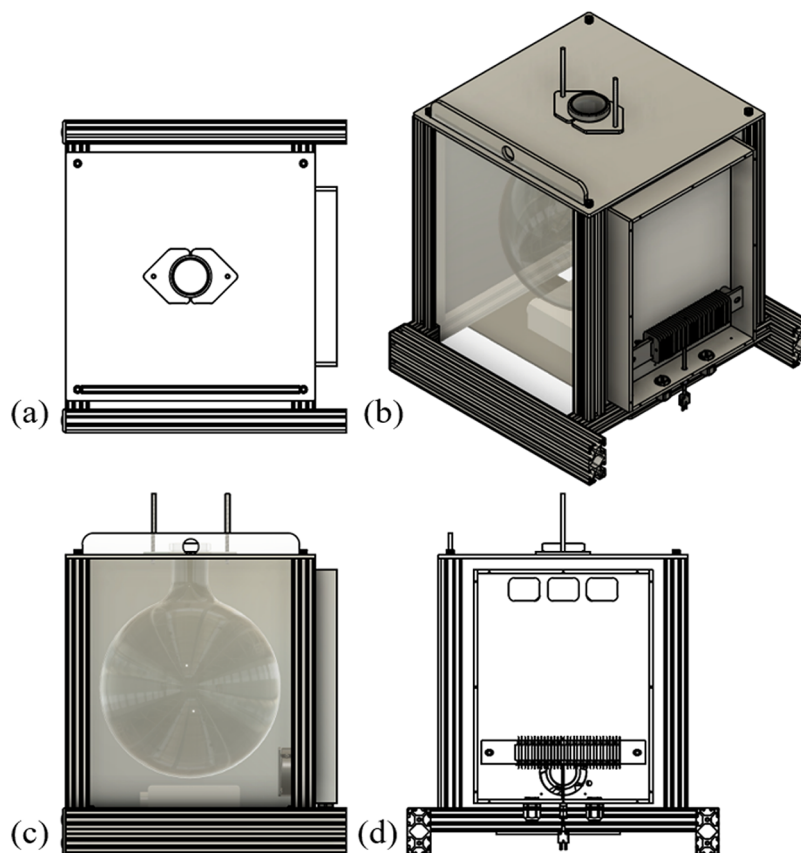


Figure 4. Thermostated test chamber. Insulation panels, stopper assembly, and rear panel are not shown. (a) Top view. (b) Side view. (c) Front view. (d) Back view: illustrates the heater box assembly used to circulate temperature regulated air.

condition of the system was evaluated to ensure the system did not leak more than 1 mbar/min isolated under a vacuum of 0.7 mbar or lower.

The stopper is lightly held by a spring-loaded cover clamp, as shown in Figure 3, to maintain a pressure seal during evacuation and sample introduction. Following ignition, ASTM E681 recommends releasing the clamp to vent excessive deflagration pressures, which avoids rupturing the flask. Consequently, the ASTM E681 method is limited to an initial test pressure of the local ambient or less.⁷

Depending on the specific construction of the test vessel cover, the onset of venting occurs at different magnitudes of overpressure due to variations in total weight and center of mass.¹⁷ The contributions of diverse venting behavior to uncertainty in the visual observations of flame propagation is discussed in Section 2.2.7. If the appropriate springs are selected and tensioned accordingly, it is possible to control venting behavior at a set overpressure and accommodate initial test pressures above local ambient conditions. Similar strategies have been developed using weighted stoppers or burst disks to establish reproducible venting conditions.^{16,18}

Careful consideration must be given to the active, connected volumes beyond the test vessel itself. Following sample introduction, gas fills the vessel and internal volume of the pressure gauge and piping. Primarily, this affects the homogeneity of the test mixture since regions of dilute or concentrated combustible gas may be present, and the mixture composition within the test vessel may deviate from that determined by partial pressure measurements. According to ASTM E681, an error analysis must be performed to account

for this difference. Although, no further details are provided, and it is rarely discussed in literature. It was estimated that the internal volume of the pressure gauge, fittings, and piping totaled 50 mL which represents 0.4% of the total volume.

2.2.4. Insulated Testing Chamber. ASTM E681 is flexible regarding the specific design of a thermostated test chamber, so long as it provides adequate temperature control, test manipulation, observation, and protection.⁷ Depicted in Figure 4, aluminum sheets (6.35 mm thickness) were selected as the construction material, ensuring the operator is protected in the event of explosion or implosion of the testing vessel. Removing a portion of the metal bottom along with a lightly held insulation panel facilitates explosion relief vertically downward, away from the operator. A transparent, polycarbonate (Lexan, SABIC) viewing shield is incorporated to allow for visual observations of flame propagation.

ASTM E681 recommends a cylindrical, perforated spacer to support and orient the test vessel.⁷ In this study, the test vessel was supported by its neck to ensure the orientation of the flask was repeatable throughout testing. Any tilt present during combustion can result in an irregular, asymmetrical flame front. In addition, this modification ensures the temperature-controlled air can circulate freely around the flask while facilitating insertion and removal from the test chamber. Generally, higher initial test temperatures result in wider flammability limits, so temperature must be carefully controlled. The specific components used to accommodate an elevated temperature flammability limit (ETFL) test at 60 °C, as required by ASHRAE Standard 34, are presented in Table 2. Based on the standard limits of error for Type K

thermocouples, the measurement uncertainty was taken as ± 2.2 °C.

Table 2. Heating System Parts List

part description	supplier	product number	critical specifications
Blower	McMaster-Carr	7700N11	temperature range: -40 to 88 °C 115 V AC, 0.13 A 0.96 m ³ /min
Thermocouple Probes	Omega Engineering	KQXL18E12	diameter: 3.175 mm length: 30.48 cm type K
Temperature Controller	J-Kem Scientific	Model 270-K	temperature range: -50 to 1200 °C 120 V, 15 A, 1800 W max. sensitivity: 0.1 °C
Finned Strip Heater	McMaster-Carr	3575K424	maximum heat output: 650 °C 120 V AC, 6 A 725 W max.
Insulation Panels	McMaster-Carr	9328K41	rigid mineral wool thickness: 2.54 cm R value: 4.3

Finally, the test chamber incorporates a magnetic stirrer capable of functioning inside the test vessel (see [Supporting Information](#) for details). Thorough mixing ensures the mixture is homogeneous prior to ignition, required for consistency in the evaluation of flammability.³ Once mixed, mechanical stirring was stopped to allow the mixture to settle since remaining turbulence can affect the development of the flame front. ASHRAE recommends a maximum settling time of 2 min, presumably to minimize gravitational settling, or diffusional demixing, which occurs if the allotted settling time is too long.³ For HFC-32, however, some have argued this effect may be considered negligible.¹⁷

2.2.5. Ignition System. The strength and morphology of the ignition source is a critical parameter with regard to reproducibility. Ideally, the test mixture is brought to its minimum ignition energy (MIE) to clearly distinguish flame propagation from the dissipation of residual ignition energy. Rather than calculate the precise MIE, which may vary for each test mixture, practical ignition sources have been considered (e.g., matches, sparks, hot surfaces) with consistency among laboratories being the main priority.³ A high-power density is necessary to ensure that a small region of energy can ignite the mixture without creating appreciable turbulence.³ As a result, spark ignitors are considered the only acceptable ignition source according to ASTM E681, allowing for repeatable, fast-acting, and energy-dense ignitions.⁷ To avoid overstimulating combustion, the spark's duration should be controlled between 0.2 and 0.4 s.^{5,7}

For high voltage sparks, the electrodes are electrically insulated using epoxy-sealed glass rods that extend into the test vessel. Presumably, the location of the spark, positioned one-third of the diameter of the flask from the bottom of the flask,⁷ accommodates upward flame propagation and allows a distance for the ignition effects to dissipate. However, in this vertical configuration, the electrodes and flask neck can affect the behavior of the flame front.¹⁶

Careful attention must be paid to the spark's duration and specific construction of the high voltage system. There is no guarantee that the output power requirement is consistent across laboratories, and luminous tube transformers, like the one recommended by ASTM E681, are generally not precision devices.³ Notably, the transformer used to correlate benchmark 200-L tests¹⁵ had a lower rating (30 mA at 12 kV) than the one specified by ASTM E681 and ASHRAE 34 (30 mA at 15 kV).^{5,7}

In this study, the gap between the electrodes was set to 6.35 mm and checked periodically. Spark duration was controlled using a Raspberry Pi Pico microcontroller in conjunction with a solid-state relay to trigger the transformer, as specified in [Table 3](#). A 0.3 s spark duration was chosen because it provided

Table 3. Ignition System Parts List

equipment	supplier	product number	critical specifications
Allanson Neon Transformer Power Supply, Mfr. Model 1530BPX120	Ballast Shop	7700N11	secondary: 30 mA at 15 kV input current: 3.75 A input voltage: 120 V
Schneider Solid State Relay, Mfr. Model SSM1A16BD	Grainger	34UJ08	output voltage: 24 to 280 V AC maximum output current: 6 A response time: 0.5 ms

a representative value within the range stated by ASTM E681 (0.2 to 0.4 s).⁷ More specifically, if flame propagation is observed while the spark is still active, ASHRAE 34 recommends using a spark duration of less than 0.4 s but at least 0.2 s.⁵ Any error introduced by processing time and the relay's response time was considered negligible compared to the tolerance of ± 0.05 s established by ASHRAE 34.⁵

2.2.6. Humidification System. Air is the strongest oxidant considered in ASTM E681, typically taken at local ambient conditions. The moisture content of the air can suppress or enhance the combustion reaction, so the humidity condition should be controlled and reported.⁷ In the case of fluorinated refrigerants, when the number of fluorine atoms exceeds the number of hydrogen atoms, the flammability limits typically widen as the humidity condition of the air increases.¹⁹ Standard humidity is defined as 50% relative humidity (RH) at 23 °C and 101.325 kPa.⁷ This corresponds to an absolute humidity of 0.0088 g of water vapor per gram of dry air⁵ (0.0089 according to ASTM E681), or stated here as 8.8 g/kg.

Two methods have demonstrated success in achieving this degree of control: septum injection and double bucket humidification. Septum injection incorporates a rubber septum on the test vessel cover that facilitates the injection of liquid water while maintaining the pressure seal. The liquid water slowly vaporizes depending on the vacuum and temperature condition of the test vessel, which can take 30 min to ensure complete evaporation.¹⁹ Prior to each test, the amount of water must be calculated according to the volume of air charged to the test vessel.¹⁷ Considering the tolerance provided by ASHRAE 34 (± 0.5 g/kg), typical injections require a precision of approximately 5 to 10 μ L.

Implementation of Double Bucket Humidification Method

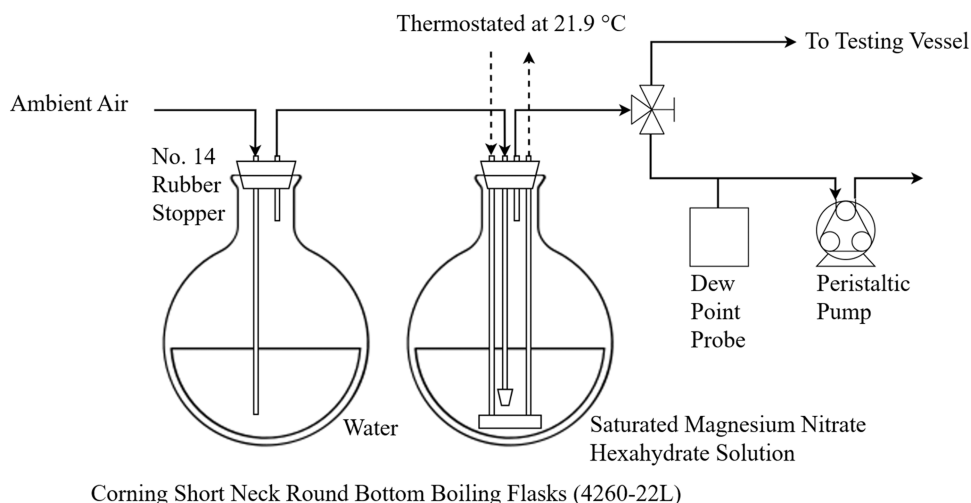


Figure 5. Air humidifier setup.

As recommended by ASTM E681, humidification can also be accomplished by bubbling air through a saturated salt solution, as shown in Figure 5. Air of different relative humidities can be obtained depending on the salt selection. The humidity condition can be further tuned by modulating flow rate and temperature. The degree of humidity control was improved by incorporating a gas sparger and disk heat exchanger (see Supporting Information for details). This process works well in raising the humidity of relatively dry ambient air, but challenges are encountered if the ambient humidity is higher than the test requirements. Dew point measurements were made using a DewTrak II Chilled Mirror Hygrometer with a stated accuracy of ± 0.2 °C, corresponding to an estimated uncertainty of ± 0.15 g/kg near the target absolute humidity condition. Two measurements were sampled, before and after air was added to the test vessel, to confirm that the humidity remained within 8.8 ± 0.5 g/kg.

2.2.7. Flame Propagation Criteria. Recording flames in near-limit mixtures can be challenging, particularly near the LFL, where flames tend to be cooler and dimmer than those near the UFL. To compensate for insufficient luminosity, exposure time and gain were adjusted accordingly. For example, captures of flame propagation near the LFL required longer exposure times, higher gain, and lower frame rates. Flame propagation was analyzed frame by frame using a high-speed camera, with details provided in Table 4. Typical values for the exposure time, gain, and frame rate were 10,000 to 40,000 μ s, 2 to 12, and 20 to 40 fps, respectively.

If not carefully defined, visual criteria can be subjective, leading to inconsistencies across laboratories. From the benchmark testing used to establish the visual criteria,¹⁵ it is unclear whether the determination was made before or after the flame contacted the vessel walls. This ambiguity is demonstrated by Figure 6.

If the flame angle were measured at (c), it would not be considered flammable, whereas the propagation after (e) exceeds the 90-degree criterion for flammability. Conceivably, the uncertainty due to interactions with the flame front may be avoided by considering flame propagation before contact with the vessel walls.

Table 4. Camera Specifications

equipment	supplier	product number	critical specifications
Basler Ace USB 3.0 Camera	Upstate Technical Equipment Co.	acA640-750uc	frames per second: 751 max resolution: 672 $\times$ 512 image type: color
Basler Camera Lens	Upstate Technical Equipment Co.	C125-0418-5M	focal length: 4 mm working distance: 35.6 cm aperture range: F1.8 to F22

Likewise, it remains unclear whether venting should be considered as part of the visual criteria. A comparison of Figure 6e,f reveals changes in the flame's behavior and luminosity following the onset of venting. During preliminary tests using HFC-32, it was determined that venting hindered flame development that would have otherwise propagated beyond 90°. As a result, the springs on the test vessel cover were left slightly tensioned to ensure that venting did not occur until after the visual criteria were met. Based on rudimentary deflagration pressure observations, an internal pressure-rise of roughly 30% (~ 300 mbar) was witnessed prior to venting.

2.2.9. LFL and UFL Calculation. Assuming ideal vapor phase behavior, the flammability limits can be expressed in mole or volume percent using a method of partial pressures. Three pressure measurements were routinely performed to calculate the sample concentration: P_{vac} (after vessel evacuation), P_{ref} (after sample introduction), and P (final test pressure after air introduction). The sample partial pressure, L_p , used to calculate the LFL was determined by subtracting the absolute vacuum pressure from the pressure following sample introduction, as shown in eq 1:

$$L_p = P_{\text{ref}} - P_{\text{vac}} \quad (1)$$

The corresponding sample concentration is calculated as

$$L = (L_p/P) \times 100\% \quad (2)$$

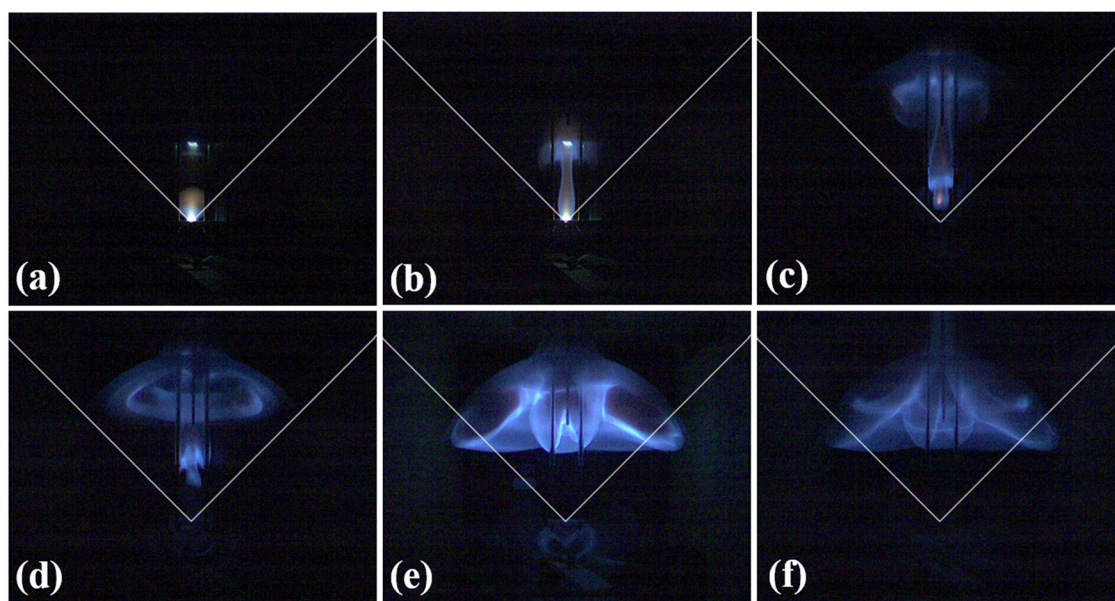


Figure 6. Sequence of flame propagation in a near-limit mixture of HFC-32 and air. (a) Ignition. (b) Flame cap formation. (c) Upward and outward propagation immediately before contact with the vessel wall. (d) Flame propagation after contact with the vessel wall. (e) 90-degree criterion is met. (f) Onset of venting.

Table 5. Select Testing Data Used to Calculate the LFL and UFL for HFC-32

	concentration (vol %)	temperature (°C)	pressure (mbar)	absolute humidity (g water/kg dry air)	flammable
LFL	14.29 ± 0.15	23.0 ± 2.2	960.4 ± 1.0	8.8 ± 0.5	no
	14.21 ± 0.15	23.4 ± 2.2	960.0 ± 1.0	8.8 ± 0.5	yes
UFL	26.83 ± 0.15	22.8 ± 2.2	961.6 ± 1.0	8.8 ± 0.5	no
	26.73 ± 0.15	22.8 ± 2.2	959.3 ± 1.0	8.8 ± 0.5	yes

Starting from a composition below the LFL, the sample concentration was varied to find the minimum concentration, L_1 , that supported the propagation of flame beyond the required flame angle, and the largest discernible concentration, L_2 , that does not give flame propagation. The difference between L_1 and L_2 provides a measure of variability for the material being studied, and the arithmetic mean is calculated to provide a representative LFL value between the two sample concentrations:⁷

$$\text{LFL} = \frac{1}{2}(L_1 + L_2) \quad (3)$$

Conversely, upper limit tests begin at a composition above the UFL. The sample concentration is varied to find the greatest concentration, U_1 , that will propagate a flame, and the least quantity, U_2 , above U_1 , that does not give flame propagation:

$$U = (U_p/P) \times 100\% \quad (4)$$

$$\text{UFL} = \frac{1}{2}(U_1 + U_2) \quad (5)$$

where U_p is the sample partial pressure used to calculate the UFL. Pressure measurements were made using a Fluke 700GA5 digital pressure gauge with a stated accuracy of ± 0.001 bar. This corresponds to an uncertainty of ± 0.15 vol % for both of the calculated HFC-32 concentrations near the LFL and UFL. Accounting for additional sources of uncertainty, such as slight temperature fluctuations during mixture preparation, an uncertainty of ± 0.2 vol % is assigned to the refrigerant vol % used to report the final LFL and UFL values.

3. RESULTS

The lower flammability limit (LFL) for HFC-32 was determined to be 14.2 ± 0.2 vol %, calculated from the average of the minimum flammable concentration (14.29 vol %) and the maximum nonflammable concentration (14.21 vol %). Similarly, the UFL was determined as 26.8 ± 0.2 vol % based on the average of the highest flammable concentration (26.73 vol %) and the lowest nonflammable concentration (26.83 vol %). The uncertainty in HFC-32 concentration, as shown in Table 5, was derived from pressure gauge accuracy and propagated calculation errors.

Tests were conducted using an absolute humidity of 8.8 g water/kg dry air with an average temperature of 23.0 ± 2.2 °C and average pressure of 960.3 ± 1.0 mbar. For each test, dew point measurements taken before and after air introduction ensured that humidity remained within ± 0.5 g/kg, and a 0.3 s spark was delivered using a 15 kV, 30 mA transformer. Flammability was confirmed through visual observation criteria and considered upward and outward flame propagation beyond the required 90-degree flame angle. The flammability assessment was made after contact with the vessel walls but before the onset of venting. A complete set of the HFC-32 test results is available in the Supporting Information. For halogenated materials, the repeatability within a single laboratory considered by ASTM E681 is 0.2 vol % for the LFL and 0.8 vol % for the UFL.⁷ The precision of the LFL measurement aligns well with the uncertainty derived from the pressure gauge resolution and partial pressure method. However, a larger deviation for the UFL (0.8 vol %) suggests

Table 6. Flammability Limits of HFC-32 Reported in Literature

source	LFL (vol %)	UFL (vol %)	initial pressure (kPa)	initial temperature (°C)	humidity ^b	transformer rating/spark duration
ASHRAE ^a	14.4		ambient	23	8.8 g/kg	15 kV, 30 mA 0.2–0.4 s
Kondo et al. 2012 ²⁰	13.48 ± 0.15	27.7 ± 0.5	ambient	20 ± 2	dry air	15 kV 0.4 s
Kim et al. ¹⁶	14.8 ± 0.1		91 ± 0.5	21–23	dry air	15 kV, 30 mA 0.2 s
Bellair and Hood ²¹	13.3	28.6	ambient	25	50% RH	15 kV, 30 mA 0.4 s
Lv et al. ²²	14.8 ± 2.78	28.9 ± 3.21	ambient	25 ± 1	15–17% RH	15 kV 0.4 s
reported	14.2 ± 0.2	26.8 ± 0.2	96 ± 0.1	23 ± 2.2	8.8 ± 0.5 g/kg	15 kV, 30 mA 0.3 s

^aWilson and Richard²³ ^b0.0088 ± 0.0005 g water vapor/g dry air = 8.8 ± 0.5 g/kg = 50 ± 5% relative humidity (RH) at 101.3 kPa and 23 °C.

that the upper concentration limit is likely more sensitive to the uncertainty associated with the test conditions.

Between laboratories, some discrepancies in the reported flammability limits of HFC-32 may be explained by differences in the test conditions—initial test temperature, initial test pressure, humidity, and spark duration—as well as the construction of the test apparatus and interpretation of visual criteria. ASTM E681 reports an interlaboratory reproducibility of 0.9 vol % for the LFL and 1.8 vol % for the UFL,⁷ providing a benchmark to evaluate the reliability of the experimental apparatus. The results of this study fall within the expected reproducibility ranges when compared to literature values obtained under similar testing conditions, as summarized in Table 6. In some cases, however, the observed flammability range is slightly narrower. A relatively short spark duration (0.3 s) may be a reason for this difference.

4. CONCLUSIONS

The growing theoretical knowledge base behind fundamental flammability limits provides a useful basis for understanding how the test environment affects measured values. Through a detailed examination of the experimental design described by ASTM E681–09, this study identified several improvements, leading to modifications in the test vessel stopper assembly, testing chamber, ignition system, and humidification system. In particular, the stopper assembly ensured reproducible vessel sealing and venting behavior. The test chamber was constructed to provide adequate protection and temperature control while also facilitating reproducible vessel orientation. Flame propagation was analyzed using high-speed imaging, which highlighted the challenges encountered using visual criteria. Precise humidity control was achieved through double bucket humidification, and the ignition system ensured the spark duration could be reliably controlled.

Flammability testing of HFC-32 in air yielded a lower flammability limit (LFL) of 14.2 ± 0.2 vol % and an upper flammability limit (UFL) of 26.8 ± 0.2 vol % at approximately 23.0 ± 2.2 °C, 960.3 ± 1.0 mbar, and 8.8 ± 0.5 g water vapor/kg of air. These results met the repeatability and reproducibility expected by ASTM E681, and the controls adhered to ASHRAE Standard 34 test condition tolerances. Future testing will include additional refrigerants, especially blends, to assess the performance of the apparatus and provide experimental confirmation for computational methods and predictive modeling efforts.

As mentioned by ASTM E681, the bias for this test method has not been determined, and the results suggest that factors beyond inherent measurement uncertainties may play a role in the differences reported among laboratories. Additional research using HFC-32 as a reference material is needed to isolate and quantify the impact of uncertainty in test conditions. Future tests at various humidities, temperatures, pressures, and spark durations will help quantify these effects. Modifications to the testing apparatus and procedure, such as coupled pressure rise and visual criteria, will also be explored to understand exactly how these variables affect the accuracy and precision of flammability limit measurements.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.5c01453>.

Figure S1. Experimental apparatus. Figure S2. Stirring propeller schematic. Table S1. Stirring System Parts List. Figure S3. Humidification system schematic. Table S2. Humidification System Parts List. Figure S4. Process and instrumentation diagram. Supporting Information S1. Operating procedure. Table S3. HFC-32 Flammability Testing Data. Figure S5. Comparison of flame behavior near the flammability limits of HFC-32 in air (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Mark B. Shiflett — *Environmentally Applied Refrigerant Technology Hub (EARTH), U.S. National Science Foundation Engineering Research Center, University of Kansas, Lawrence, Kansas 66045, United States; Wonderful Institute for Sustainable Engineering and Chemical and Petroleum Engineering, University of Kansas, Lawrence, Kansas 66045, United States; orcid.org/0000-0002-8934-6192; Email: mark.b.shiflett@ku.edu*

Authors

Kevin Turner — *Environmentally Applied Refrigerant Technology Hub (EARTH), U.S. National Science Foundation Engineering Research Center, University of Kansas, Lawrence, Kansas 66045, United States; Wonderful Institute for Sustainable Engineering and Chemical and Petroleum Engineering, University of Kansas, Lawrence, Kansas 66045, United States; orcid.org/0009-0000-8827-8127*

Arthur Benson – Environmentally Applied Refrigerant Technology Hub (EARTH), U.S. National Science Foundation Engineering Research Center, University of Kansas, Lawrence, Kansas 66045, United States; Wonderful Institute for Sustainable Engineering and Chemical and Petroleum Engineering, University of Kansas, Lawrence, Kansas 66045, United States

Michael Lundin – Environmentally Applied Refrigerant Technology Hub (EARTH), U.S. National Science Foundation Engineering Research Center, University of Kansas, Lawrence, Kansas 66045, United States; Wonderful Institute for Sustainable Engineering and Chemical and Petroleum Engineering, University of Kansas, Lawrence, Kansas 66045, United States

Ed Atchison – Environmentally Applied Refrigerant Technology Hub (EARTH), U.S. National Science Foundation Engineering Research Center, University of Kansas, Lawrence, Kansas 66045, United States; Wonderful Institute for Sustainable Engineering and Chemical and Petroleum Engineering, University of Kansas, Lawrence, Kansas 66045, United States

Dave Watson – Hudson Technologies Company, Champaign, Illinois 61822, United States

Steve Campbell – Hudson Technologies Company, Champaign, Illinois 61822, United States

Brian Finney – Hudson Technologies Company, Champaign, Illinois 61822, United States

Glen Khlebutin – Hudson Technologies Company, Champaign, Illinois 61822, United States

Riyaz Papar – Hudson Technologies Company, Champaign, Illinois 61822, United States

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.iecr.5c01453>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the U.S. National Science Foundation ERC Award 2330175 Environmentally Applied Refrigerant Technology Hub (EARTH) and Hudson Technologies Company for their support of this research. The authors would also like to thank Joseph Blanchett, Morela Chapman, Caymen Barnes, Evan Dennard, Raymond Hamilton, and Oluwafemi Odusanya for their assistance with apparatus construction, initial experimental testing, and LabVIEW programming and integration.

REFERENCES

- (1) Calm, J. M. The Next Generation of Refrigerants—Historical Review, Considerations, and Outlook. *Int. J. Refrig.* **2008**, *31* (7), 1123–1133.
- (2) Kujak, S.; Schultz, K. Insights into the Next Generation HVAC&R Refrigerant Future. *Sci. Technol. Built Environ.* **2016**, *22* (8), 1226–1237.
- (3) Heinonen, E. W.; Tapscott, R. E.; Crawford, F. R. *Methods Development for Measuring and Classifying Flammability/Combustibility of Refrigerants: Final Report*; U.S. Department of Energy: 1994. DOE/CE/23810–50.
- (4) World Meteorological Organization (WMO). *Scientific Assessment of Ozone Depletion: 2022*; GAW Report No. 278; WMO: Geneva, 2022; pp 448–483.
- (5) ASHRAE. *Designation and Safety Classification of Refrigerants*; ANSI/ASHRAE Standard, 2023; pp 34–2022.

(6) Zabetakis, M. G. *Flammability Characteristics of Combustible Gases and Vapors*; U.S. Bureau of Mines. Bulletin, 1965; Vol. 627, pp 1–121.

(7) ASTM International. *Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases)*; ASTM, 2023; pp E681–09 DOI: [10.1520/E0681-09R23](https://doi.org/10.1520/E0681-09R23).

(8) Coward, H. F.; Jones, G. W. *Limits of Flammability of Gases and Vapors*; United States Bureau of Mines. Bulletin, 1952; Vol. 503, pp 2–6.

(9) Mendiburu, A. Z.; Carvalho, J. A.; Ju, Y. Flammability Limits: A Comprehensive Review of Theory, Experiments, and Estimation Methods. *Energy Fuels* **2023**, *37* (6), 4151–4197.

(10) Zabetakis, M. G.; Scott, G. S.; Jones, G. W. Limits of Flammability of Paraffin Hydrocarbons in Air. *Ind. Eng. Chem.* **1951**, *43* (9), 2120–2124.

(11) Rowley, J. R.; Bruce-Black, J. E. Proper Application of Flammability Limit Data in Consequence Studies. *Inst. Chem. Eng. Symp. Ser.* **2012**, *Hazards XXIII* (158), 443–452.

(12) Linteris, G. T.; Bell, I. H.; McLinden, M. O. An Empirical Model for Refrigerant Flammability Based on Molecular Structure and Thermodynamics. *Int. J. Refrig.* **2019**, *104*, 144–150.

(13) Kul, I.; Gnann, D. L.; Beyerlein, A. L.; DesMarteau, D. D. Lower Flammability Limit of Difluoromethane and Percolation Theory. *Int. J. Thermophys.* **2004**, *25* (4), 1085–1095.

(14) Takahashi, A.; Urano, Y.; Takuhashi, K.; Kondo, S. Effect of Vessel Size and Shape on Experimental Flammability Limits of Gases. *J. Hazard. Mater.* **2003**, *105*, 27–37.

(15) Richard, R. G. *Refrigerant Flammability Testing in Large Vol. Vessels*. Buffalo Research Laboratories; U.S. Department of Energy, 1998. DOE/CE/23810–87..

(16) Kim, D. K.; Klieger, A. E.; Lomax, P. Q.; McCoy, C. G.; Reymann, J. Y.; Sunderland, P. B. An Improved Test Method for Refrigerant Flammability in a 12L Vessel. *Sci. Technol. Built Environ.* **2018**, *24*, 861–866.

(17) Lomax, P. Q. Development of the ASTM E681 Standard. Master's Thesis, University of Maryland, College Park, MD, 2016. ProQuest Dissertations & Theses. (1828001044).

(18) McCoy, C. G. Improved Venting for Flammability Limit Testing Using ASTM E681 Apparatus. Master's Thesis, University of Maryland. College Park, MD, 2016. ProQuest Dissertations & Theses. (1828001002).

(19) Kondo, S.; Urano, Y.; Takizawa, K.; Takahashi, A.; Tokuhashi, K.; Sekiya, A. Flammability Limits of Multi-Fluorinated Compounds. *Fire Saf. J.* **2006**, *41*, 46–56.

(20) Kondo, S.; Takizawa, K.; Tokuhashi, K. Effects of Temperature and Humidity on the Flammability Limits of Several 2L Refrigerants. *J. Fluorine Chem.* **2012**, *144*, 130–136.

(21) Bellair, R. J.; Hood, L. Comprehensive Evaluation of the Flammability and Ignitability of HFO-1234ze. *Process Saf. Environ. Prot.* **2019**, *132*, 273–284.

(22) Lv, Z.; Yang, Z.; Ma, H.; Chen, Y.; Zhang, Y. Flame Retardant Effect of the Halohydrocarbons on the Mildly Flammable Refrigerant Difluoromethane. *J. Fluorine Chem.* **2021**, *248*, No. 109832.

(23) Wilson, D. P.; Richard, R. G. Determination of Refrigerant Lower Flammability Limits in Compliance with Proposed Addendum p to Standard 34. *ASHRAE Trans.* **2002**, *108*, 739–756.