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An improved test method for refrigerant flammability limits in a 12 L vessel

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The current study presents an improved test method for refrigerant flammability limit measurements. Such measurements are essential for determining refrigerant safety classifications. Predicated on expert interviews and experiments, several changes to ASTM E681 and related standards are recommended, as follows. The 12 L glass vessel should be replaced with transparent polycarbonate. The orientation of the electrode supports and the temperature probe should be changed from vertical to horizontal. All penetrations should be removed from the rubber stopper, it should be weighted for a total mass of 2.5 kg, and the initial pressure should be 90 kPa absolute. The flame angle should be plotted versus refrigerant concentration to obtain flammability limits. Finally, the vessel pressure should be measured during each test. These changes are relatively easy to implement and they will improve the test precision and reproducibility without significantly changing previously established flammability limits.

Introduction

An international drive toward improved sustainability of refrigeration systems (Brown 2013a; Kujak 2017) is motivating the adoption of refrigerants with low global warming potential (GWP) and low ozone depleting potential (ODP). Most of these refrigerants are mildly flammable, which is the main impediment to their adoption. As engineers balance refrigerant performance against sustainability and flammability, safety is always an important factor (Brown 2013b; Kujak and Schultz 2016; Tsai 2005).

ANSI/ASHRAE 34 (2016) establishes refrigerant flammability classifications based in part on the ASTM E681 (2015) standard test method. These standards use visual observations of flame propagation in a 12 L spherical glass vessel to measure the lower flammability limits (LFLs) of refrigerants. Flammable conditions are defined as those for which a flame propagates outside a 90° cone angle, measured from the ignition point. This angle was chosen because it corresponded with refrigerant flammability limits in a 200 L cylindrical vessel (Richard 1998). The LFL measurements of ASTM E681 are essential in determining whether refrigerants or their blends are Class 1 (no flame propagation), Class 2 or 2L (LFL > 0.1 kg/m^3), or Class 3 (LFL < 0.1 kg/m^3). The ISO 817 (2014) standard replaces the 0.1 kg/m^3 threshold with a refrigerant concentration of 3.5 vol. %.

Unfortunately, ASTM E681 suffers from limited precision and reproducibility. For example, it has led to published LFLs of R-32 (difluoromethane) in air of 13.48 vol. % (Kondo et al. 2012), 14.4 vol. % (ASHRAE 34 2016; Wilson and Richard 2002), 14.73 vol. % (Kul et. al 2004), and 14.8 vol. % (McCoy 2016).

Expert interviews

Eight experts with extensive ASTM E681 refrigerant flammability experience were interviewed. They expressed several key concerns about this standard, as follows.

- Etching of the 12 L glass vessel requires frequent replacement and can obscure the flame behavior. Most A2L refrigerants contain hydrofluorocarbons (HFCs) and/or hydrofluoroolefins (HFOs), for which gaseous hydrogen fluoride (HF) can be the dominant product following combustion or heating (Feng et al. 2017; Moghaddas et al. 2014; Womeldorf and Grosshandler 1999). Even with rapid flushing with air after each test, HF etching of the vessel interior is apparent after one or two tests and requires vessel replacement (at a cost of US $240) after about 10 tests.

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Additionally, it is difficult to modify glass walls for vessel penetrations.

- Electrode supports and the temperature probe in the flame path disturb the flames. These quench the flames where they would otherwise be their strongest, contributing to poor agreement between laboratories. The quenching distances of 2L refrigerants are typically far larger than those of hydrocarbons (Kul et al. 2004), for example, 7.55 and 24.8 mm for R-32 and R-1234yf (Takizawa et al. 2015).
- Existing E681 apparatus have different venting behavior. Many laboratories consider flame observations after the onset of venting and/or after the flame completes its upward propagation to determine the LFL. The E681 standard requires at least four penetrations in the stopper: two electrode supports, a temperature sensor, and a plumbing connection. These are connected to wires and tubes whose mass and balance are different in each apparatus.
- The sample size is small in the pass/fail flammability criterion. Flammable conditions are defined as those that exceed the 90° cone angle in two out of three tests.

Motivated by these and other concerns, the objective of the present study is to improve the precision and reproducibility of ASTM E681 for refrigerant flammability limit testing. New hardware and methods are developed and changes are recommended. Despite these changes, the key strengths of the standard are maintained: the test apparatus is relatively inexpensive and easy to fabricate and the flames are observed visually.

Development of the improved method

Polycarbonate vessel design

A standard ASTM E681 apparatus was built (see Lomax 2016; McCoy 2016). R-32 concentrations were established with partial pressures using an Ashcroft DG25 pressure gauge with a range of 0 to 102 kPa_a and a stated accuracy of $\pm$0.5 kPa. Because the calibration was confirmed frequently at vacuum and at atmospheric pressure, the resulting R-32 concentrations have an estimated uncertainty of $\pm$0.1 vol. %.

This apparatus was then modified to replace its glass vessel with polycarbonate. The spherical part of this vessel was a clear polycarbonate lighting globe (Edith Aiken Company, US $45). As shown in Table 1, its capacity and dimensions are similar to those of the standard 12 L glass vessel.

Figure 1 shows a schematic of the polycarbonate vessel design. A 13 mm thick polyvinylchloride (PVC) sheet with a 60 mm hole was attached to the top of the lighting globe with room-temperature-vulcanizing silicone adhesive. A PVC tube

Table 1. Vessel properties.

Material	Capacity L	Outer diameter cm	Wall thickness mm
Glass	12.4	29.5	2–7.6
Polycarbonate	13.9	30.5	3.2–6.4

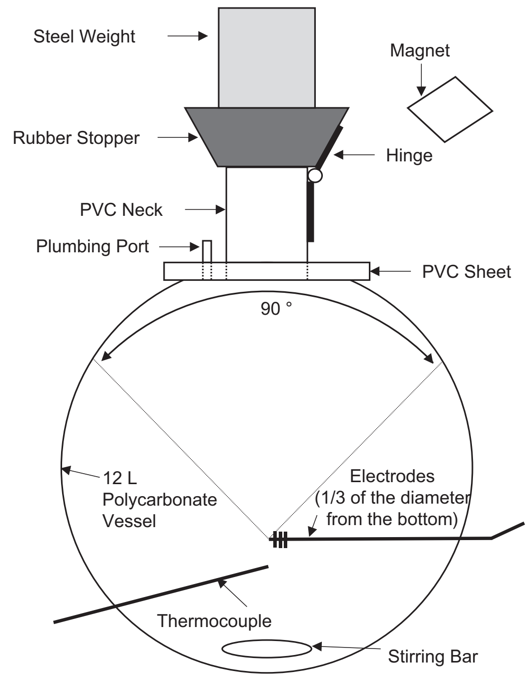

Fig. 1. Schematic of the polycarbonate vessel design. The vessel as tested did not have a thermocouple and used a rope and pulley instead of a magnet and hinge.

with an inner diameter of 53 mm was then attached to the PVC sheet (see Reymann 2017).

A new 12 L glass flask is shown in Figure 2a. Unfortunately, glass is prone to HF etching and is difficult to drill. Glass etching is clearly visible in Figure 2b following 10 tests of R-32 in air near its LFL. The polycarbonate vessel (Figure 2c) is nearly as transparent as a new glass vessel, but showed no signs of etching, bubbling, or discoloration after 68 similar tests. It was readily drilled for gas-tight penetrations for the electrodes and plumbing.

Electrode support orientation

Two resealable holes were drilled in a rubber stopper, and two others in the wall of the polycarbonate vessel, to introduce the electrodes vertically or horizontally. The location, spacing, and orientation of the tungsten electrode tips were the same in both cases. Glass sheaths surrounding the stainless steel electrode supports are specified in E681, but these complicate the sealing and were not used in the current study. These were not necessary because no electrical current was observed except between the electrode tips. Tests were performed with R-32, whose LFL is not sensitive to humidity (Kondo et al. 2012), in dry air at 21 °C to 23 °C. The spark parameters were 15 kV, 30 mA, and 0.2 s (Clodic and Jabbour 2011; Kondo et al. 1999, 2012), where the duration was reduced from 0.4 s in accordance with ASHRAE 34 (2016).

Figure 3 illustrates the effects of electrode support orientation on two representative flames just before they reached the vessel wall. All other conditions were matched. As seen in Figure 3, vertical electrode supports cause a large hole in the

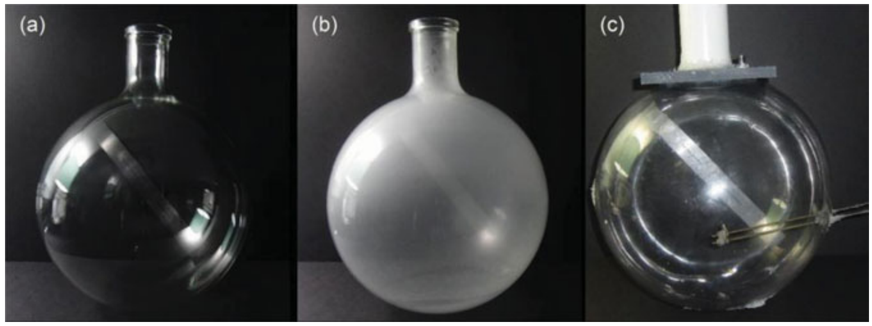

Fig. 2. Color images of the vessels used. Shown here are: (a). a new glass vessel; (b). a glass vessel that has been etched by 10 flame tests followed by immediate flushing; and (c). a polycarbonate vessel following 68 similar tests. Behind each vessel is a 30 cm ruler.

top of the flame, a dimmer and less symmetric flame, and a reduced flame angle (defined below). Such disturbances can change the LFL determination and impair the test precision and reproducibility.

The tests of Figure 3 were performed with a thin-film pressure transducer connected to a pressure tap in the vessel wall. The transducer was a MTS Systems Corp. 1501B02EZ100psig with a response time of 1 ms, a stated range of 0 to 690 kPa_g, and an accuracy of ±1.7 kPa. It was found to maintain this accuracy for pressures as low as –34 kPa_g. The measured pressures are shown in Figure 4, where the time datum corresponds to the first video frame for which a spark was visible. With horizontal electrode supports the pressure increased faster, which confirms that vertical electrode supports weakened the flame.

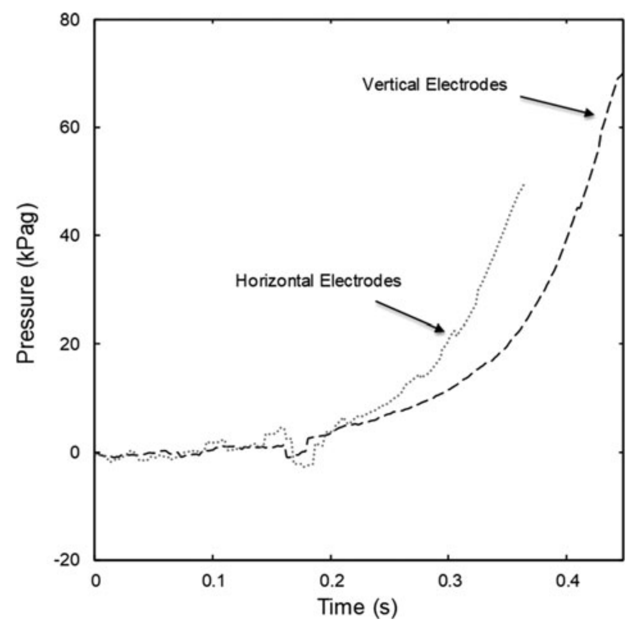

Fig. 4. Vessel pressure plotted with respect to time after ignition for the tests of Figure 3.

Reproducible venting

The polycarbonate vessel facilitates moving all penetrations from the rubber stopper to the vessel walls. However, the 270 g mass of the size 14 rubber stopper without these attachments is too low to prevent venting before the flames reach the vessel wall. It was found that a weighted stopper with a total mass of 2.5 kg was ideal. For typical refrigerant test conditions, this resulted in venting that occurred soon after the flame reached the vessel wall. The 2.5 kg mass also prevented leakage during hold times near atmospheric pressure. For tests at high elevation, a larger mass would be necessary.

Figure 5 shows measurements of when flame propagation stopped near the vessel wall and when venting started. The time datum is the same as in Figure 4. Flame propagation was observed in the video record, and venting was identified using the pressure transducer and a microphone near the stopper.

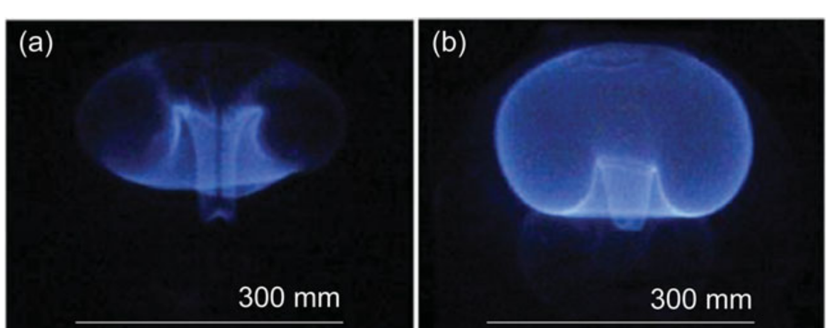

Fig. 3. Effects of electrode support orientation, namely (a). vertical; and (b). horizontal. The initial composition was 14.8 vol. % R-32 in air at 101 kPa_a. The images were recorded 0.35 s after ignition.

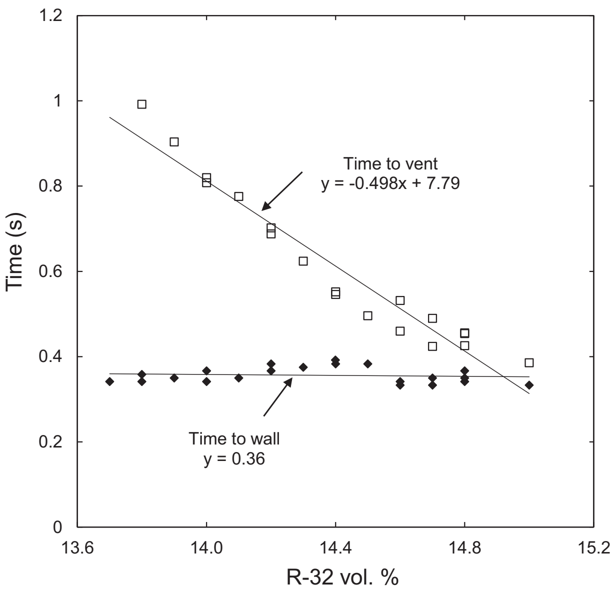

Fig. 5. Measurements of when the flame reached the wall and when venting started. The initial pressure was 91 kPa_a.

The flames reached the wall after approximately 0.36 s regardless of R-32 concentration, but venting started earlier with increasing R-32 concentration. In all cases flame propagation stopped before venting started. Similar behavior was observed at initial pressures of 81 and 101 kPa_a (Klieger 2017).

ASTM E681 stipulates an initial pressure of 101 kPa_a. However, there are three drawbacks: it can result in venting before the completion of flame propagation; the mean pressure during a test is above atmospheric; and laboratories at high elevations cannot easily follow the standard. Therefore, testing was conducted at initial pressures of 81, 91, and 101 kPa_a. To be close to atmospheric pressure without a risk of venting during flame propagation, an initial pressure of 90 kPa_a is recommended.

Flame angle measurement

Just prior to the end of flame propagation, an image of each flame was used to measure its flame angle—the angle subtended by the flame with respect to the electrode gap. These angles were measured using ImageJ software. Figure 6 shows a plot of flame angle versus R-32 concentration. A linear best fit line is shown and this has a R^2 coefficient of determination of 0.92. This line's intersection with 90º is used here to determine the LFL (McCoy 2016; Reymann 2017; Takizawa et al. 2009). The 95% confidence interval curves are also shown. This yielded an LFL of 14.8 vol. % with a 95% confidence interval of ±0.1 vol. %. This is slightly higher than the generally accepted R-32 LFL of 14.4 vol. % (ASHRAE 34 2016; Wilson and Richard 2002). The method of Figure 6 incorporates several flame angle measurements into the determination of the LFL, compared to only two out of three tests above 90°, according to ASTM E681. Additionally, it yields a 95% confidence interval on the LFL.

The modifications proposed above result in only a small change in the measured LFL of R-32. The vertical electrodes

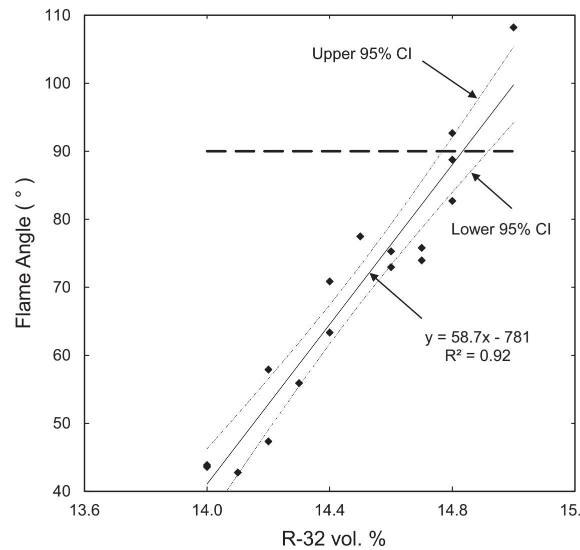

Fig. 6. Flame angle plotted with respect to R-32 concentration. The initial pressure was 91 kPa_a.

decrease the flame angle whereas preventing venting before the flame reaches the vessel walls increases it. At least for R-32, this maintains the agreement between these 12 L tests and the large-scale tests of Richard (1998).

Pressure measurement

Several flammability tests use pressure-based criteria (Pagliaro et al. 2015), which are less subjective than visual criteria. Pressure-rise thresholds have varied from 2% (De Smedt et al. 1999) to 5% to 7% (Schroder and Molnarne 2005; Van den Schoor et al. 2008; Zlochower and Green 2009) to 20% (Kondo et al. 2011).

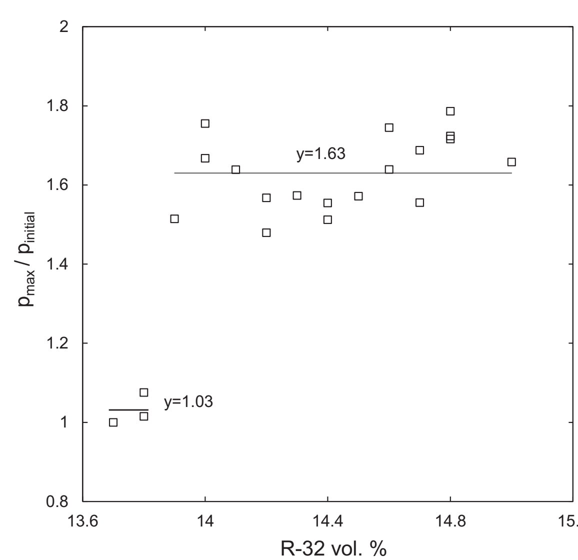

Fig. 7. Maximum pressure observed during a test divided by initial pressure (91 kPa_a) plotted with respect to R-32 concentration.

Tests were performed in the current study in which the vessel pressure was measured with the MTS pressure transducer. Figure 7 shows the maximum pressure divided by the initial pressure plotted with respect to R-32 concentration. The pressure ratio has a plateau at 1.63 due to venting behavior, thus a flammability threshold of 1.3 is recommended here. The sharp increase from a negligible pressure rise (at an R-32 concentration of 13.9 vol. %) is the best indication of LFL available with a pressure measurement. This LFL is lower than that obtained in Figure 6, and corresponds to a flame angle of 35°. Due to the simplicity of the visual method, and complications of revisiting well established flammability limits, the visual method should be maintained in E681.

Conclusions

Predicated on expert interviews and experiments, this study recommends several changes to the ASTM E681 standard test method for refrigerants, as follows.

1. The vessel material should be changed from glass to polycarbonate (or other transparent plastic) to facilitate vessel penetrations and to eliminate etching and frequent vessel replacement.
2. The electrode supports and temperature probe should be oriented horizontally rather than vertically to minimize flame quenching.
3. Venting should not occur before the flame stops propagating near the vessel wall. This can be accomplished with an initial pressure of 90 kPa_a and by having a stopper with no penetrations and a mass of 2.5 kg. A larger mass will be needed at high elevations.
4. The flame angle should be plotted versus refrigerant concentration for at least six concentrations near and on both sides of the LFL. The measurements should be fit with a least-squares line. Where this line intersects a flame angle of 90° is the LFL.
5. A pressure transducer with a response time of 1 ms or faster may be used to evaluate the pressure rise during flame propagation and to help identify the onset of venting. A final pressure greater than 1.3 times the initial pressure indicates flammable conditions. Although both determinations can be reported, the LFL determination based on a flame angle of 90° should take precedence.

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References

ASHRAE 34. 2016. *ANSI/ASHRAE Standard 34–2016, Designation and Safety Classification of Refrigerants*. Atlanta: ASHRAE.

ASTM. 2015. *ASTM E681-09, Standard Test Method for Concentration Limits of Flammability of Chemicals*. West Conshohocken, PA: American Society of Testing and Materials.

Brown, J.S. 2013a. Fourth ASHRAE/NIST refrigerants conference: "Moving towards sustainability". *HVAC&R Research* 19: 101–12.

Brown, J.S. 2013b. Introduction to hydrofluoro-olefin alternatives for high global warming potential hydrofluorocarbon refrigerants. *HVAC&R Research* 19:693–704.

Clodic, D., and T. Jabbour. 2011. Method of test for burning velocity measurement of flammable gases and results. *HVAC&R Research* 17:51–75.

De Smedt, G., F. de Corte, R. Notele, and J. Berghmans. 1999. Comparison of two standard test methods for determining explosion limits of gases at atmospheric conditions. *Journal of Hazardous Materials* 70:105–13.

Feng, B., Z. Yang, and R. Zhai. 2017. Experimental research on the concentration characteristics of R32 and R161 combustion product HF. *Energy* 125:671–80.

ISO 817. 2014. *Refrigerants—Designation and Safety Classification*. Geneva: International Organization for Standardization.

Klieger, A.E. 2017. Pressure measurements for flammability limit testing using ASTM E681 apparatus, M.S. Thesis, University of Maryland, Department of Fire Protection Engineering.

Kondo, S., A. Takahashi, K. Takizawa, and K. Tokuhashi. 2011. On the pressure dependence of flammability limits of $CH_2 = CFCF_3$, CH_2F_2 and methane. *Fire Safety Journal* 46:289–93.

Kondo, S., K. Takizawa, and K. Tokuhashi. 2012. Effects of temperature and humidity on the flammability limits of several 2L refrigerants. *Journal of Fluorine Chemistry* 144:130–6.

Kondo, S., Y. Urano, A. Takahashi, and K. Tokuhashi. 1999. Reinvestigation of flammability limits measurement of methane by the conventional vessel method with AC discharge ignition. *Combustion Science and Technology* 145:1–15.

Kujak, S. 2017. Flammability and new refrigerant options. *ASHRAE J.* 59:16–24.

Kujak, S., and K. Schultz. 2016. Insights into the next generation of HVAC&R refrigerant future. *Science and Technology for the Built Environment* 22:1226–37.

Kul, I., D.L. Gnann, A.L. Beyerlein, and D.D. DesMarteau. 2004. Lower flammability limit of difluoromethane and percolation theory. *International Journal of Thermophysics* 25:1085–95.

Lomax, P.Q. 2016. Development of the ASTM E681 standard. M.S. Thesis, University of Maryland, Department of Fire Protection Engineering.

McCoy, C. 2016. Improved venting for flammability limit testing using ASTM E681 apparatus, M.S. Thesis, University of Maryland, Department of Fire Protection Engineering.

Moghaddas, A., C. Bennett, E. Rokni, and H. Metghalchi. 2014. Laminar burning speeds and flame structures of mixtures of difluoromethane (HFC-32) and 1,1-difluoroethane (HFC-152 a) with air at elevated temperatures and pressures. *HVAC&R Research* 20:42–50.

Pagliaro, J.L., G.T. Linteris, P.B. Sunderland, and P.T. Baker. 2015. Combustion inhibition and enhancement of premixed methane-air flames by halon replacements. *Combustion and Flame* 162:41–9.

Reymann, J. 2017. Improvements to refrigerant flammability testing through use of a polycarbonate apparatus, M.S. Thesis, University of Maryland, Department of Fire Protection Engineering.

Richard, R.G. 1998. *Refrigerant flammability testing in large volume vessels*. ARTI Report 665–52400. Arlington, VA: Air-Conditioning, Heating, and Refrigeration Institute.

Schroder, V., and M. Molnarne. 2005. Flammability of gas mixtures Part 1: Fire potential. *Journal of Hazardous Materials* 121: 37–44.

Takizawa, K., K. Tokuhashi, and S. Kondo. 2009. Flammability assessment of CH2=CFCF3: Comparison with fluoroalkenes and fluoroalkanes. *Journal of Hazardous Materials* 172:1329–38.

Takizawa, K., N. Igarashi, S. Takagi, K. Tokuhashi, and S. Kondo. 2015. Quenching distance measurement of highly to mildly flammable compounds. *Fire Safety Journal* 71:58–68.

Tsai, W.-T. 2005. An overview of environmental hazards and exposure risk of hydrofluorocarbons (HFCs). *Chemosphere* 61:1539–47.

Van den Schoor, F., R.R.E. Hermanns, J.A. van Oijen, F. Verplaetsen, and L.P.H. de Goey. 2008. Comparison and evaluation of methods for the determination of flammability limits, applied to methane/hydrogen/air mixtures. *Journal of Hazardous Materials* 150:573–81.

Wilson, D., and R. Richard. 2002. Determination of refrigerant lower flammability limits in compliance with proposed addendum p to standard 34. *ASHRAE Transactions* 108:739–56.

Womeldorf, C., and W.L. Grosshandler. 1999. Flame extinction limits in CH2F2/air mixtures. *Combustion and Flame* 118:25–36.

Zlochower, I.A., and G.M. Green. 2009. The limiting oxygen concentration and flammability limits of gases and gas mixtures. *Journal of Loss Prevention in the Process Industries* 22:499–505.