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Improving Refrigerant Flammability Limit Test Methods Based on ASTM E681

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ABSTRACT

An improved test method for refrigerant flammability limit measurements is presented. Such measurements are essential for determining the lower flammability limits of refrigerants, and thus their 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 (or other transparent plastic) to eliminate etching by HF and to facilitate vessel penetrations. The orientation of the electrode supports and the temperature probe should be changed from vertical to horizontal to prevent flame quenching. Venting should not occur before the flame stops propagating near the vessel wall. 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, whereby a least-squares line determines the flammability limit at a flame angle of 90°. Finally, the vessel pressure should be measured during each test to evaluate the pressure rise during flame propagation and to help identify the onset of venting. These changes are relatively easy to implement and they improve the test precision and reproducibility without significantly changing previously established flammability limits.

1. 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 (Tsai, 2005; Brown, 2013b; Kujak and Schultz, 2016).

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. % (Wilson and Richard, 2002; ASHRAE 34, 2016), 14.73 vol. % (Kul et al., 2004), and 14.8 vol. % (McCoy, 2016).

Eight experts with extensive ASTM E681 refrigerant flammability experience were interviewed. Their input is discussed in Kim et al. (2018).

The objective of this 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.

2. Development of the Improved Method

2.1 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 – 102 kPa_a and a stated accuracy of ±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 ±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

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

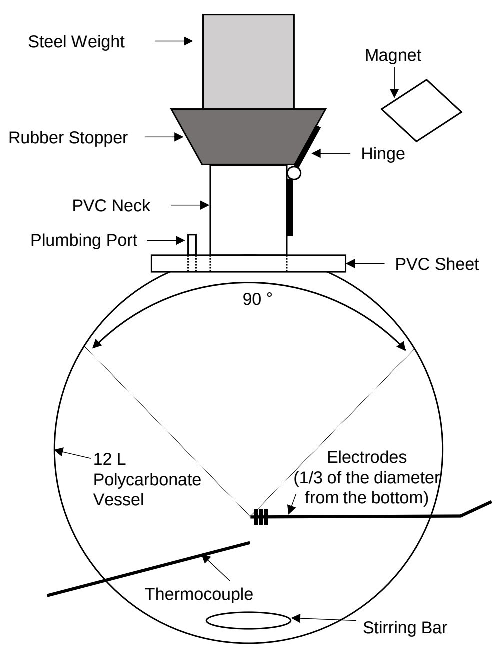

Figure 1: Schematic of the polycarbonate vessel design. The vessel as tested did not have a thermocouple, and used a rope and pulley instead of a magnet and hinge.

globe with room-temperature-vulcanizing silicone adhesive. A PVC tube 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 Fig. 2a. Unfortunately, glass is prone to HF etching and is difficult to drill. Glass etching is clearly visible in Fig. 2b following 10 tests of R-32 in air near its LFL. The polycarbonate vessel (Fig. 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.

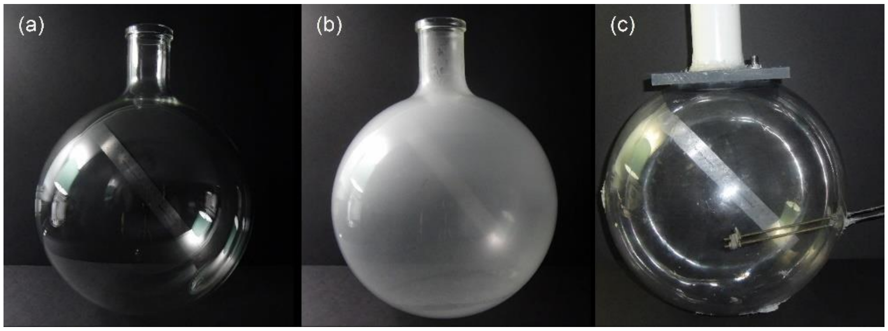

Figure 2: Color images of the vessels used. Shown here are: (a) a new glass vessel; (b) a glass vessel that has been etched by 10 flame tests followed by immediate flushing; and (c) a polycarbonate vessel following 68 similar tests. Behind each vessel is a 30 cm ruler.

2.2 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 here. 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 – 23 °C. The spark parameters were 15 kV, 30 mA, and 0.2 s (Kondo et al., 1999, 2012; Clodic and Jabbour, 2011), 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 Fig. 3, vertical electrode supports cause a large hole in 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.

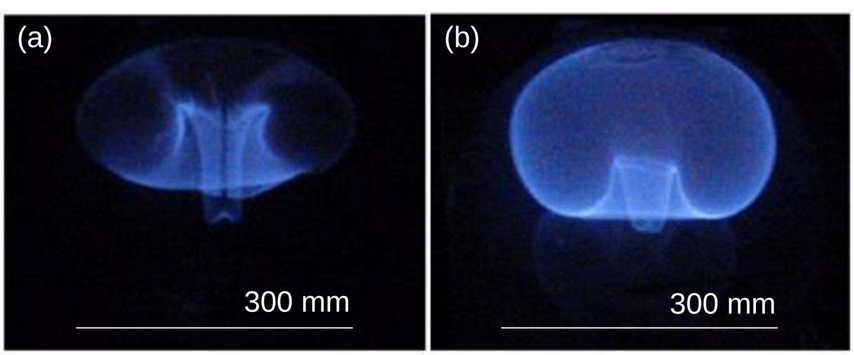

Figure 3: Effects of electrode support orientation, namely (a) vertical and (b) horizontal. The initial composition was 14.8 vol. % R-32 in air at 101 kPa_a. The images were recorded 0.35 s after ignition.

The tests of Fig. 3 were performed with a thin-film pressure transducer connected to a pressure tap in the vessel wall. The transducer was a PCB 1501B02EZ100psig with a response time of 1 ms, a stated range of 0 – 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 Fig. 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.

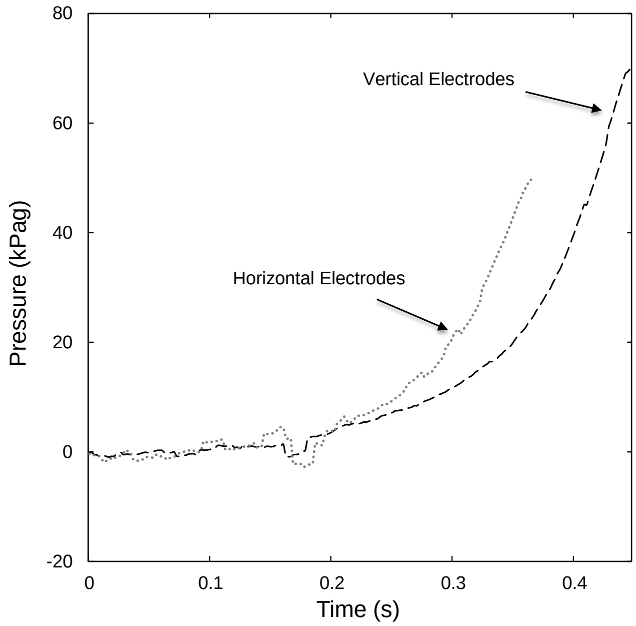

Figure 4: Vessel pressure plotted with respect to time after ignition for the tests of Fig. 3.

2.3 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 higher 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 Fig. 4. Flame propagation was observed in the video record, and venting was identified using the pressure transducer and a microphone near the stopper. 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). The test at a pressure of 91 kPa_a is shown here because 81 kPa_a is far below atmospheric pressure and 101 kPa_a is too close to the laboratory pressure to avoid venting during flame propagation.

ASTM E681 stipulates an initial pressure of 101 kPa_a. However, this has 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. This is the pressure of Fig. 5 rounded to the first significant digit in metric units.

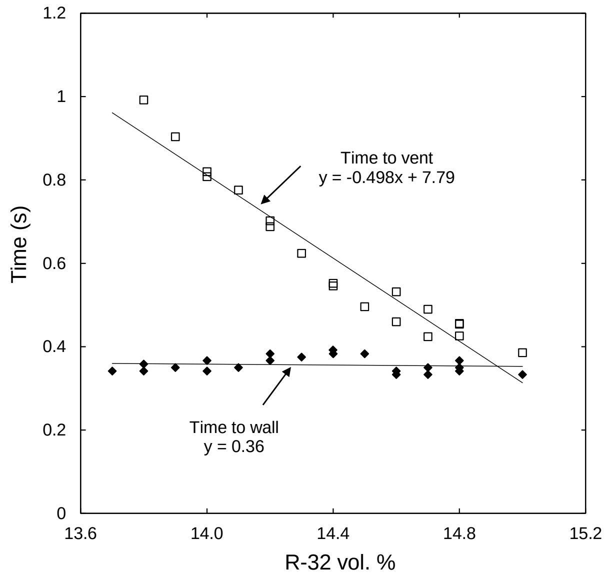

Figure 5: Measurements of when the flame reached the wall and when venting started. The initial pressure was 91 kPa_a.

2.4 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 (Takizawa et al., 2009; McCoy, 2016, Reymann, 2017). 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. % (Wilson and Richard, 2002; ASHRAE 34, 2016). The method of Fig. 6 incorporates several flame angle measurements into the determination of the LFL, compared to only two out of three tests above 90°, according to

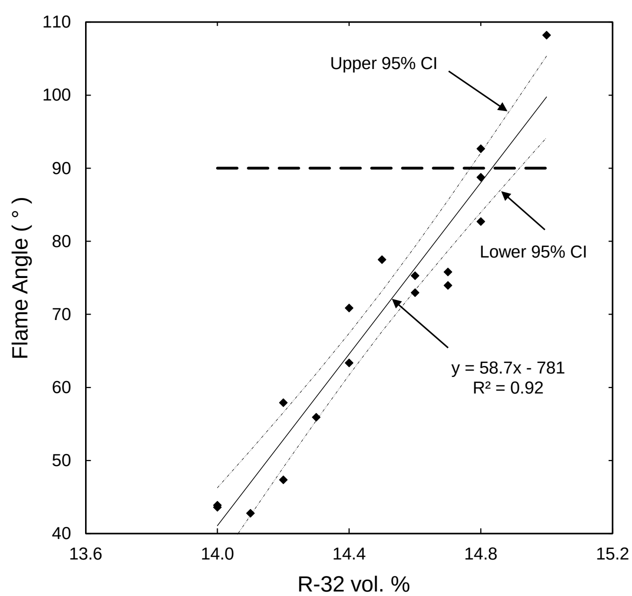

Figure 6: Flame angle plotted with respect to R-32 concentration. The initial pressure was 91 kPa_a.

ASTM E681. Additionally, it yields a 95% confidence interval on the LFL. Based on these observations, it is recommended here that the flame angle should be plotted versus refrigerant mole fraction for at least 6 mole fractions within 1% 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.

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

2.5 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 5-7% (Schroder and Molnarne, 2005; Van den Schoor et al., 2008; Zlochower and Green, 2009) to 20% (Kondo et al., 2011). One disadvantage of pressure-based tests is that they require a constant-volume chamber that can withstand high pressures, which complicates optical access and visual observations.

Tests were performed here in which the vessel pressure was measured with the PCB 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 owing 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 Fig. 6, and corresponds to a flame angle of 35°. Owing to the simplicity of the visual method, its advantage of allowing visual observations of the flames, and complications of revisiting well established flammability limits, the visual method should be maintained in E681. Furthermore, the recommendations above will drastically reduce the subjectivity in the visual method.

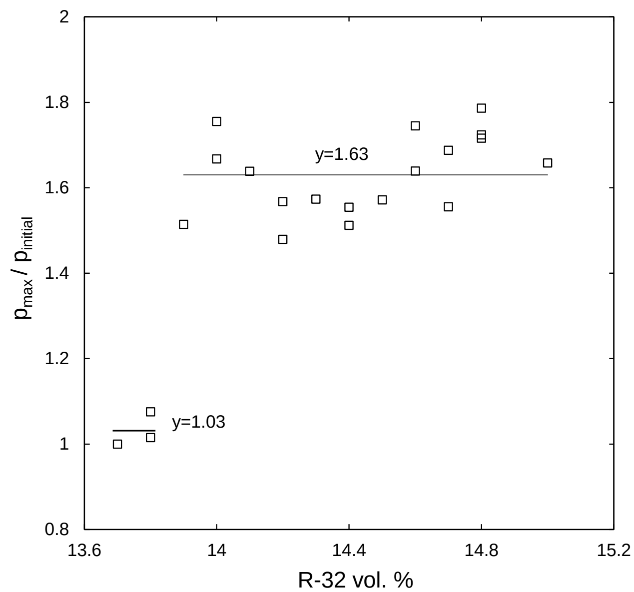

Figure 7: Maximum pressure observed during a test divided by initial pressure (91 kPa_a) plotted with respect to R-32 concentration.

3. CONCLUSIONS

Predicated on expert interviews and experiments, this study recommends several changes to the ASTM E681 standard, as follows:

- The vessel material should be changed from glass to polycarbonate (or other transparent plastic) to eliminate etching and to facilitate penetrations.

- The electrode supports and temperature probe should be oriented horizontally instead of vertically to minimize flame quenching.
- Venting should not occur before the flame stops propagating near the vessel wall. This can be accomplished with an initial pressure of 90 kPaa and by having a stopper with no penetrations and a mass of 2.5 kg.
- The flame angle should be plotted versus refrigerant mole fraction for at least 6 mole fractions within 1% 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.
- 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 1.6 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.

It is recommended that additional work be performed to examine the behavior of other refrigerants, especially those (such as R-1234yf and R-1234ze) that are tested at 60 °C with added water vapor.

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