FOCUS ARTICLE

Flammability Testing of Refrigerant Blends

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Improving efficiency, lowering ozone depletion (ODP), lowering contribution to global warming (GWP) are the driving forces behind new chemicals and new formulations being brought to the market by industry.

After banning production of chlorofluorocarbons (CFC), phasing out (underway) hydrochlorofluorocarbons (HCFC), the most recent international agreement (2016 Kigali Amendment to Montreal Protocol) established a time frame for reducing use and phasing out some hydrofluorocarbons (HFC) with higher GWP. As a result, EPA started to list certain HFC refrigerants as unacceptable for use.

The search for suitable replacements (zero ODP, low GWP) is underway and looks complicated. CO_2, NH_3, HC-hydrocarbons, HFO-hydrofluoroolefins and some HFCs are considered as potential substitutes, or blend components. In a recent NIST study on refrigerant substitutes in AC systems, all 27 fluids considered were at least slightly flammable. While the final refrigerant substitutes are still debated, two groups are in the forefront of the search: hydrocarbons like propane, isobutene, propylene, and synthetic chemicals – hydrofluoroolefins (R1234yf, R1234ze(E)), mostly due to their desirable ODP, GWP values. Unfortunately, current codes (ASHRAE Std. 15, UL equipment related standards), severely restrict the use of both HFOs and HCs due to their flammability.

For a wider use and adaptation in industry of these environmentally friendly refrigerants, some of the codes restrictions may have to be relaxed in the future, e.g. propane (A3 flammable) total charge in a closed system is restricted to 150 grams, which limits the size of the appliance. It would have to be increased to 1 kilogram to allow use in larger refrigeration units (European standards allow use of 1.5 kilograms in certain configurations).

No matter what will be the final group of refrigerant replacements, they will certainly have to deal with flammability determination and this is where ASHRAE Std. 34 comes into play.

ASHRAE Standard 34 -2016 "Designation and Safety Classification of Refrigerants" specifies rigorous testing, modeling and data collection process to which any newly formulated blend brought to the market must be subjected. The result of this process is assignment of the "R" number (designation) to the given blend, certifying that the safety classification of the blend was based on the standard required data.

A part of this process is flammability determination which includes fractionation analysis and flammability testing. Multi-component blends (some components are flammable), even if initially non-flammable, may become flammable as the composition of vapor phase and liquid phase constantly changes during a slow leak. Standard 34 defines the way to determine and confirm WCF (worst case formulation) and WCFF (worst case fractionated formulation) of the given blend.

It identifies seven refrigerant leak scenarios for which data should be analyzed. With temperature ranging from (-40)°C to 60°C, and tank fills from 15% to 90%, the leak simulations will correspond to typical storage, or transportation conditions. The data can be acquired either by computer simulation or by running fractionation tests. If the data comes from computer modeling, the leak scenario that yields WCFF must be verified by experiment. Standard 34 determines how to run the fractionation test (isothermal leak, leak rate, GC analysis) and how frequent data acquisition should be (an ASHRAE Guideline 39 detailing how to run fractionation test is also available).

The fractionation analysis yields WCFF(s), the worst composition(s) from flammability (LFL) standpoint of either vapor or liquid phase of the blend. In the same analysis, WCFF(s) for the worst composition for burning velocity (BV) may be also determined.

These compositions have to be tested for flammability (according to Annex of ASTM 681 – 09 (2015) "Test method for materials with large quenching distances, which may be difficult to ignite") with some additional requirements stated in Standard 34. For refrigerants with flammability class 1 and 2 testing has to be done in 12L flask, for class 3 in either 5L of 12L flask. Both WCF and WCFF composition test temperature is set to 60ºC. If any flammability is observed at 60°C, the tests will be re-run at 23°C. For the test to yield a "Burn" result, the flame front has to cross a boundary of a 90° angle anchored at ignition point (between electrodes). The blend concentration with air testing range has to cover from 1 to 30%vol in 1% increments. The typical "Burn" and "No Burn" result in 12 L flask is shown in Figure 1.

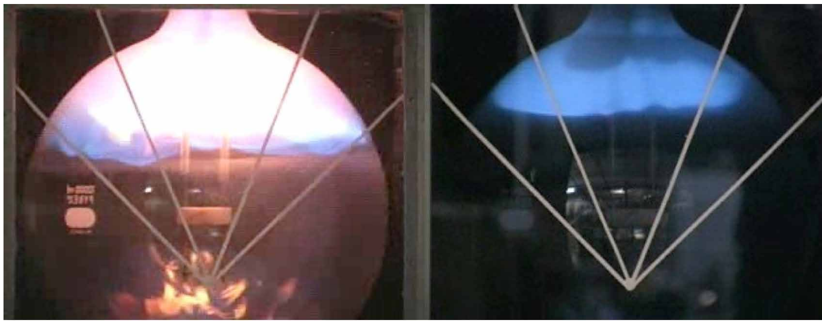

Figure 1: "Burn" and "No Burn" flammability test result in 12L flask.

Once any of the tested compositions turns out to be flammable, LFL data (Lower Flammable Limit) at 23ºC for these compositions needs to be determined.

The full application seeking "R" number from SSPC 34 needs to include flammability and fractionation data, as well as administrative data, properties of the blend and components, toxicity data, SDS for components and the blend.

Several years ago (upon introduction of slow burning HFOs), the standard was updated to include an additional subclass of flammability that was added to the existing three: 1-nonflammable, 2-lower flammability, 3-higher flammability (see Table 1). The additional subclass divides the lower flammable class into 2 and 2L (2L-burning velocity of less than 10cm/s). This subclass, 2L, was recently voted to become a full flammability class, thus in the future there will be four classes of flammability.

Increasing ↑	Higher flammability	A3	B3	Propane, isobutane...
	Lower flammability	A2	B2	R152a, ammonia
		A2L	B2L	R1234yf, R454B
	Non-flammable	A1	B1	R134a, R410A
		Lower toxicity	Higher toxicity	
		Increasing →		

Table 1: ASHRAE flammability/toxicity classes.

A measurement of burning velocity of the blend is required to have subclass 2L assigned. The standard references the method used for this flammability testing. In Figure 3, an example of a test bench (vertical tube-yielding good results from 4cm/s to 30 cm/s) suitable for this test is shown together with the picture of the R32 flame propagating upwards. The benchmark refrigerants for this test are R32 and R152a. The results of the burning velocity measurements for these two chemicals must fall within ±10% range of established values. The analysis of videotaped test yields a value of linear flame front velocity, as well as, flame front surface area needed to determine burning velocity S_u.

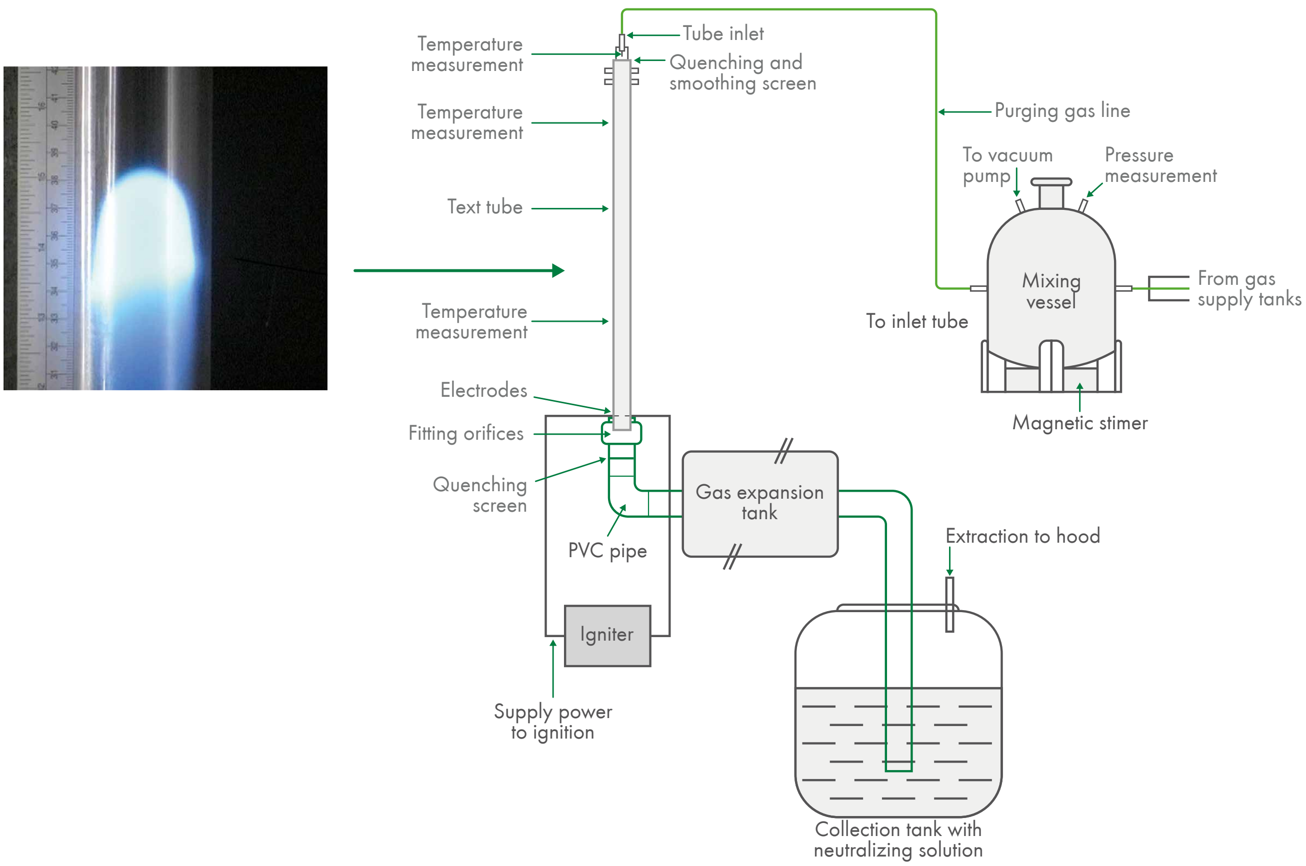

Figure 2: An example of the test setup for burning velocity test. (Insert – R32 flame upward propagation).

The other method acceptable for burning velocity measurement is a constant pressure vessel (using Schlieren visualization method) shown in Figure 4.

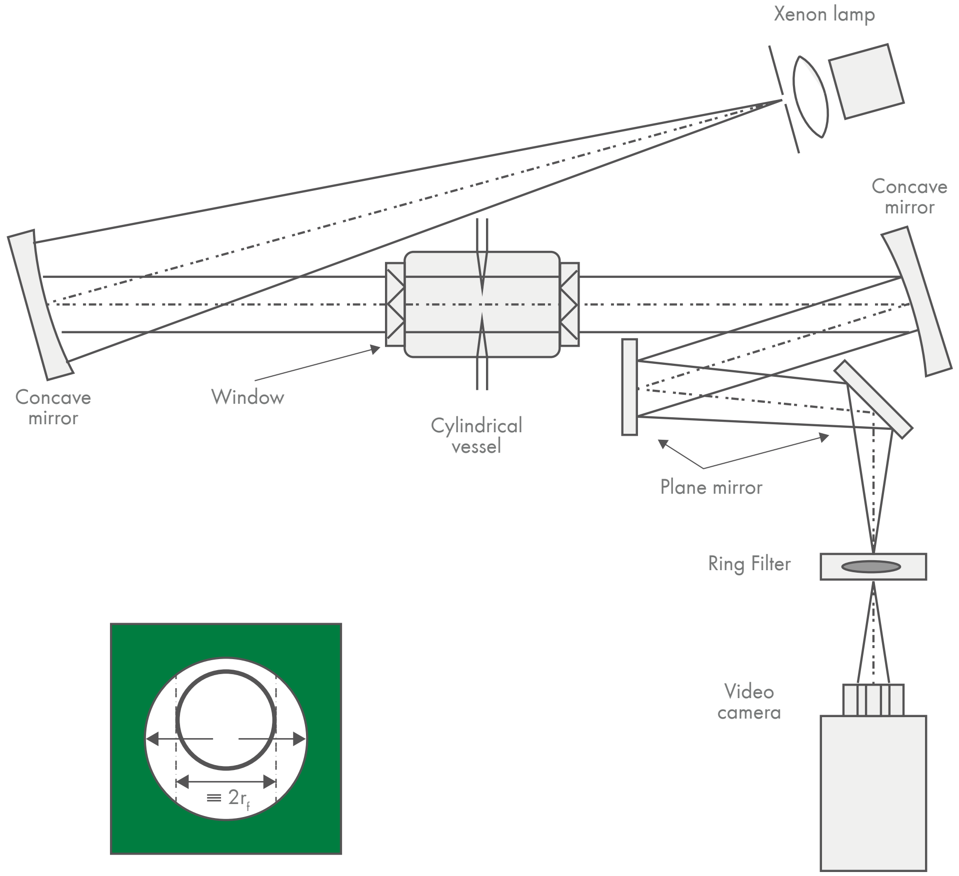

Figure 4: Constant pressure vessel with Schlieren optical system (insert-flame propagating from center outward and upward).

High speed camera video acquisition allows to measure linear flame velocity (in horizontal direction) and the flame bubble growth resulting in burning velocity calculation. This method allows to measure burning velocity as low as 1.5cm/s. Flammability parameters that ASHRAE Std. 34 requests: LFL/UFL, S_u, and HOC (heat of combustion) will help to classify the refrigerant, but if assisted by knowledge of MIE (minimum ignition energy) they will enable performing a hazard assessment of a specific equipment. Typical risk trends to expect in function of variability of flammability parameters are shown in Table 2.

Flammability Parameter		Expected Risk Trend
LFL	↓	↑
MIE	↓	↑
S_U	↑	↑
HOC	↑	↑

Table 2: Risk trends

In general, DEKRA Process Safety provides the entire process of ASHRAE application preparation that would include flammability and fractionation testing, blend property calculations and analysis, as well as toxicity analysis for the components involved.

For more information regarding flammability testing of refrigerant blends, process hazards analysis, system safety, material characterization, DOT and other regulatory compliance, and any associated testing, please contact us at 847-925-8100 or email us at process-safety-usa@dekra.com

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