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REFRIGERANT FLAMMABILITY TESTING IN LARGE VOLUME VESSELS

FLAMMABILITY CRITERION DETERMINATION FOR ASTM E681

VISUAL OBSERVATIONS

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EXECUTIVE SUMMARY

Refrigerant flammability testing has been plagued with difficulties due to the low combustibility of these materials. The ASTM E 681, 5 and 12 liter flask observations are hindered due to cooling effects of the vessel walls, limited distance for observations and the requirement of an energetic ignition source. A large volume 200-liter vessel can be used to eliminate most of these effects and to examine the true ignition and flame propagation behavior. The validation of the flame cap angle criteria in the proposed ASTM E 681 for determining flame propagation was obtained from a comparison of the results from the 12 and 200-liter vessels. The transition from no flame propagation to true flame propagation in the large 200-liter vessel appears as a 90° fan flame cap in the 12 liter vessel. This criterion was proposed in ASTM E 681-proposed (97) test method for halogenated materials. These experimental observations were determined for two blends of varying flame-suppressing capability: R134a/R152a and R125/R152a.

INTRODUCTION

OBJECTIVE

Investigate the determination of true flame propagation for difficult to ignite refrigerants by studying the effect of combustion vessel volume on the appearance of the flame.

The questions to be answered are: what is the proper criteria for determining whether a flame will propagate throughout a uniform medium?, what does a mixture that just propagates a flame look like in ASTM E 681 - proposed (97) test apparatus, and what is the angle or size of the flame?

OVERVIEW

The flammability phenomenon is an oxidation reaction. A consequence of this fact is that the energy release is directly related to the quantity of material reacting, i.e., the larger amount of material the greater the hazard. Other important outcomes of this chemical nature are effects related to the ratio of reactants, the presence of catalyst (or any thing that changes the chemistry) and the reaction activation energy. Flame propagation is an energy balance: The energy from the heat of reaction is used to initiate the next layer of gases and accommodate any losses. The losses are minimized to enhance the energy available to propagate the reaction. A gas mixture is used so no energy is needed to vaporize liquid and the material can produce a homogenous mixture with air. The most conservative situation will be the unhindered case (i.e., no energy loss, all the energy produced by the combustion is used to propagate the reaction). This leads to a definition for flame propagation as the self-sustained flame front moving through a homogenous mixture. The conservative and most realistic simulation is upward flame propagation that occurs in a quiescent mixture in a large volume vessel, since we want to know the widest concentration range or if at any concentration the flame would be self-sustaining.

Notice that we have two phenomena occurring, first initiation (ignition) and second propagation. To initiate the oxidation reaction we must ensure sufficient energy is present. For difficult to ignite materials, like halocarbons this has been a problem, as seen historically by laboratories having difficulty using sparks, arcs or exploding wires as igniters for R142b and R141b. The match head was adopted because of its reliability in igniting these materials. However the match head caused overdriven reactions that interfered with the visual observance of the flames. So, the spark has been revisited. It can be reliable and allows better flame observations if properly setup.

The flammability dilemma we face is that: just about anything can burn, if the conditions are harsh enough. For example, to initiate combustion the harsh conditions at the igniter causes decomposition and reactions, which are not capable of sustaining themselves once the added ignitor energy ceases. This is where flame propagation becomes important. At some distance from the ignition source all effects of the igniter will have dissipated. At that point the, determination of whether the flame propagates is independent of the ignition. Prior to that point the reaction is overdriven, as the ignition source was large enough to initiate a flame front, i.e., the flame front is propagating due partly to the energy from the ignition source. Therefore, true flame propagation (self-sustaining) must be observed far away from the ignition source.

The potential energy release is directly proportional to the amount of gas used, so to reduce the hazard we need to test on a small scale. Also, the cost and complexity of testing goes up with scale. Large scale tests are needed to obtain realistic conservative flammability determinations but the scaling up of small size testing to real world circumstances is difficult due to energy losses, confinement, slow flame speeds, high minimum ignition energy (MIE), long dissipation lengths, gravity, etc. We needed a real world conservative test. An ASTM E 681 test apparatus is needed that is larger than 12 liters. We chose a 200 liter vessel that gives the equivalent of a 48 liter sphere with extra room above the ignition source. Also, it was believed to be necessary to perform measurements at the proposed flammability test conditions: 100°C, visual observation, have good mixing and use of air at 50 % RH when at room temperature.

METHOD

The ideal test requires a large volume vessel that can be controlled at the desired conditions of 100°C, use 50% RH @ room temperature air, operate at 1 atmosphere pressure and allows visual observations. Visual observation is the detection method that is currently required by ASTM E 681-94 as adopted by ASHRAE 34 and UL 2182. Our solution was to construct a temperature-controlled chamber that could contain a 200 liter glass reaction vessel (see Figure 1).

We do not recommend using a large vessel for routine testing. The approach we chose is to use a large vessel to determine the scale up conditions for small vessel results, i.e., interpretation of small-scale results. This allows for an energetic ignition source in a small volume, yet gives the results for an unhindered flame. We compared the videos from mixtures that just propagate and do not propagate a flame in the large vessel to the videos of the same materials in a 12 liter flask as specified in the proposed revisions of ASTM E 681 (annex A1). This direct side by side comparison gives the proper criteria to use in E 681.

EXPERIMENTAL DETAILS

For small scale testing, the tests were performed per ASHRAE's proposed test protocol (conditions and apparatus). In accordance with ASTM E 681-94 spark from 1 mm tungsten wire with ¼ inch gap was used. The apparatus was modified by using a 12 liter flask. The test conditions were 100°C and 0.0086 ± 0.0004 grams water per gram dry air. The ignition source was positioned at 1/3 the diameter of the flask from the bottom.

The large volume vessel has a 450 mm I.D. and is 1500 mm long (see figure 1). This allows the ignition source to be placed 22.5 cm from the walls and the bottom of the vessel. The dissipation of ignition energy, that can produce flame caps of 2 to 3 ft, has plenty of room to be observed. This also allows time for them to produce a propagating flame or merely dissipate. The relative sizes of 5, 12, 22, and 48 liter spheres relative to the 200 liter tube are shown in (figure 2).

Humidity can influence the chemical reaction of combustion particular when halides are present. Therefore, the humidity of the air used was controlled. More precisely the humidity was set as per UL 2182 specifications: the inlet air into the flask shall be 0.0086 grams water per gram dry air. The means, which we employed to achieve this, is shown in figure 4.

The expected worst case flammable concentration in air was tested. This is above the stoichiometric concentration and was determined from the data obtained from first testing in ASTM E 681 apparatus.

Ignition of a uniform mixture of a gas or vapor with air was attempted and the upward and outward propagation of the flame away from the ignition source was noted by visual observation and recorded on videotape.

MATERIAL

The material used was 99.9+% pure and was degassed until no evidence of air was seen. The liquid phase was flashed into the vessel until the desired pressure was obtained, then air was added to bring the pressure up to 1 atmosphere. The range of mixture compositions in air tested was such that if it were possible flame propagation would occur.

To obtain mixtures that could be changed gradually in flammability, we used mixtures of a flammable and nonflammable halocarbons. The flammable component was R-152a, which has flame limits 3.7 to 20.4 vol%. The characteristics of the blend were widely varied by choosing two different nonflammable components. One nonflammable component was R125, which is a good flame suppressant, and the other nonflammable component was R134a, which is a much less effective flame suppressant. Therefore, if the criteria or appearance of the flame were material dependent, different results would be obtained in 12 liter vessel and in the large vessel.

EXPERIMENTAL RESULTS

Initially the thermal and pressure controls were validated. Then we needed to answer the preliminary questions: 1) What does a true flame look like in the big tube? 2) What is a flame cap? 3) How big and where? True flame propagation was clear. There was no ambiguity in the results, the flask filled with fire or the flame caps died away. A flame cap appeared as a mushroom shaped flame front that moved up and grew as long as the ignition source was feeding it energy but died quickly once this extra energy from the igniter stopped. Flame caps rose about 0.5 m directly above the ignition source and grew to about 30 cm in diameter.

The following table presents the results of the testing on R152a/R134a and R152a/R125. 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 E 681 test apparatus. These tests were made using the same 15 lb. jugs of the mixtures that were carried from one unit to the other and run using identical protocols. This method was used to eliminate as many variables as possible except for the volume of the vessel.

The flammability testing conditions and procedures are those prescribed in the addendum ASHRAE 34p (second public review draft). Testing was performed at 100°C in a 12 liter flask, with a 0.4 second spark and using air at 0.0086 ± 0.0004 grams water/gram dry air. The spark was generated from the secondary of an illumination transformer rated 12,000 V @ 30 mA. The spark gap was positioned 1/3 above the bottom of the flask and made using ¼ inch gap between 1 mm tungsten wires.

The very same ignition circuit was used when testing in the 200 liter chamber. These tests were also run at 100°C and the air was conditioned by the same humidity procedure and equipment as was used for the 12 liter vessel used.

The accompanying video records the visual observation for the following data. The video starts with footage of a flame cap. This was the largest flame cap observed that did not develop into a self-propagating flame front. Next the video shows the unambiguous case where the true self-propagating flame developed. The videotape proceeds through side by side comparisons of the 12 liter ASTM E681 test versus the big tube test observations.

The less effective flame suppresser R134a results

Material	wt% of Flammable R152a	12 liter Angle	Bigtube 200 liter
R134a/R152a	8.6	60°	No
	9.6	90°	No
	10.1	110°	Burnt
	10.6	120°	Burnt
	11.1	120°	Burnt

The more effective flame suppresser R125 results

Material	*wt% of Flammable R 152a*	*12 liter Angle*	*Bigtube 200 liter*
R125/R152a	20.0	100°	Burnt
	19.5	90°	Burnt
	19.0	90°	Wave No Burn

VALIDATION

After construction, the oven temperature control, vessel mixing device and the ability of the vessel to hold full vacuum were tested. The in tube thermometer varied ±2°C while controlling at 100°C. The system held 1 torr for more than 10 minutes. The mixing pump circulated 25 liter/minute and ran for a minimum of 15 minutes.

The ASTM E 681 method and apparatus were tested using R32/R134a flammability characterization as a comparison with other laboratories. A CFR of 32.5 wt% R32 was found. The round robin testing result was 33.4±1.2 wt%.

CONCLUSIONS

Test methods have undergone substantial improvements in accuracy and repeatability in recent years. Many parameters for testing and methods have changed. Some of these include vessel volume, ignition source and flame propagation criteria. Due to the difficult to ignite nature of halocarbon refrigerants, a high-energy ignition source had to be employed. It has since been found that these ignition sources overdrive combustion in the 5 liter flask and may also influence flame propagation in the newly adopted 12 liter flask. This overdriving means there are flames observed in the 12 liter flask that will not develop into self-propagating flames. The 200 liter vessel allowed us to relate the appearance of a flame event in the 12 liter flask to true self-propagation. This data is not available for any other condition than the 12 liter and spark ignition. The other extremely important factor learned is that these materials are humidity sensitive and even small uncertainties, can be important. For good laboratories that do not specialize in humidity control, great care must be excised to avoid problems.

Considering data generated, the 90° fan flame propagation criterion is appropriate for determining whether true flame propagation will occur in less hindered situations than the 12 liter vessel with the spark ignition under the modified E 681 procedure, i.e., most conservative conditions. Figure 3 shows this flammability criterion. The length of the hashed area must be filled with a flame that is continuous from one end to the other for the mixture to be deemed flammable. The range of uncertainty in the ASTM E 681 fan angle is estimated to be ± 5°.

Much progress has been made in standardizing and improving small-scale flame limit measurement methods to represent real world flammability.

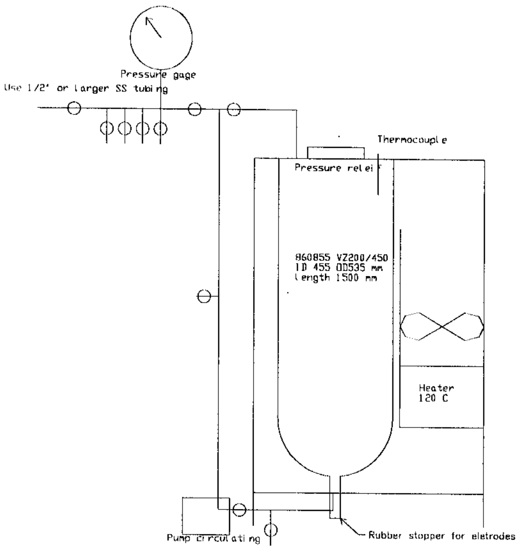

Figure 1: Big Tube Apparatus

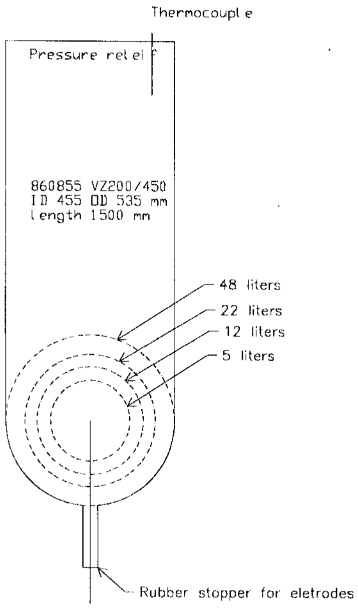

Figure 2: Big Tube relative to 5, 12, 22, 48 liter spherical flask

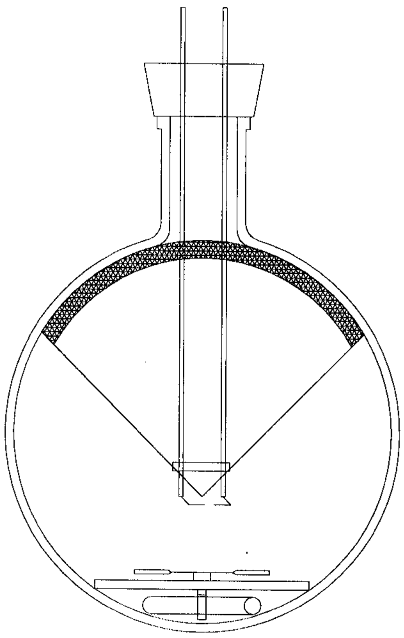

Figure 3: "Fan" Definition of Flame Propagation

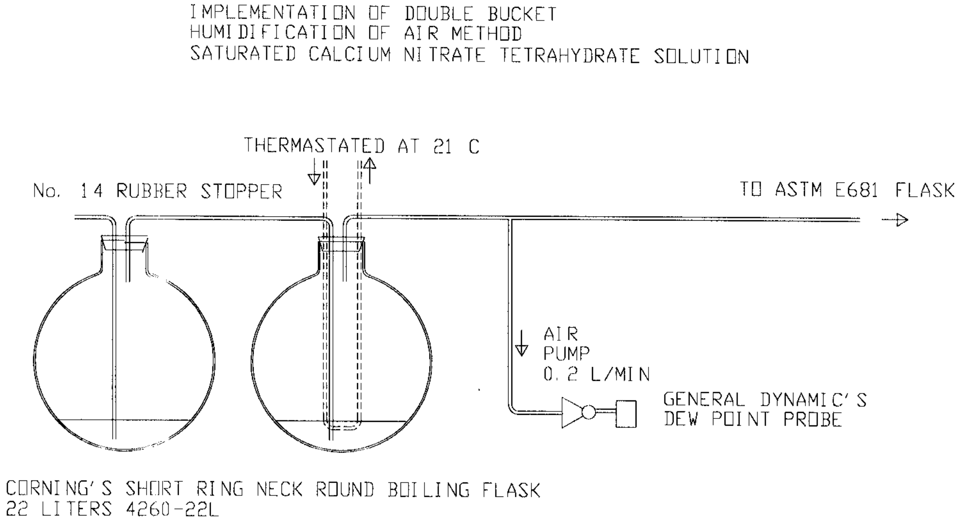

Figure 4: Double Bucket Humidification Method