ABSTRACT

Title of Thesis: IMPROVED VENTING FOR FLAMMABILITY LIMIT TESTING USING ASTM E681 APPARATUS

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Directed by: Associate Professor Peter B. Sunderland
Department of Fire Protection Engineering

The literature on the determination of flammability limits was reviewed and experts on the ASTM E681 standard were interviewed to identify new means of improving the reproducibility of the ASTM E681 test. Venting was identified as a variable of flammability limits not yet addressed. Limitations of the current system for sealing and venting (a rubber stopper) were identified and addressed by the development of a custom burst disc. The burst disc was evaluated for its ability to hold and maintain a vacuum, its ability to vent at pressures of interest, and for its venting phenomena. The burst disc was deemed to be a satisfactory alternative to the rubber stopper and is recommended to be included in the ASTM E681 standard.

IMPROVED VENTING FOR FLAMMABILITY LIMIT TESTING USING ASTM E681 APPARATUS

by

Conor G. McCoy

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Advisory Committee:
Professor Peter B. Sunderland, Chair
Professor Emeritus James G. Quintiere
Professor Stanislav I. Stoliarov

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1 Introduction

1.1 Background

Accurate determination of flammability limits is critical for safe practices worldwide. Flammability limits are used to design and enforce safe practices in storage, transportation, and use of all kinds of chemicals. Flammability limits are important for safety in domestic settings as well because of the large presence of refrigerants in domestic appliances. After the phase out of chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) because of their ozone-depleting effects, refrigerants have been replaced with the more flammable hydrofluorocarbons (HFC).

There exist a number of test standards for determining flammability limits. Examples include ASTM E681 (U.S.), DIN 51649 (E.U.), EN1839T (E.U.), EN1839B (E.U.), and GB/T12474 (China). ASTM E681, DIN 51649, EN1839T, and GB/T12474 all use glass vessels and a visual criteria to determine if a mixture is flammable. However, ASTM E681 uses a spherical flask while the rest use a vertical tube. EN1839B is a steel sphere or bomb-type and uses a pressure rise criteria for the determination of flammability.

In general, there are two types of tests for the determination of flammability limits. Tests either rely on visual propagation such as flame detachment or traveling a certain length, or use a pressure rise criteria, often a percentage of the initial pressure. Some researchers have also modified the standard apparatuses or even created their own unique apparatus. Needless to say, there are many different approaches, variables, and configurations in flammability testing. Consequently, there can be significant differences in the results.

This work shall focus on ASHRAE Standard 34, which is a modified version of ASTM E681 specifically for the determination of flammability limits of refrigerants.

1.2 Purpose of this work

This work sought to understand the complications of flammability limit testing and find new, unexplored ways to improve the reproducibility of the ASTM E681 test, following the guidelines of ASHRAE standard 34. The approach adopted was as follows.

First, it was necessary to understand the current knowledge and criticisms on the determination of flammability limits, especially with respect to the ASTM E681 test method and refrigerants. This was accomplished by a literature review in conjunction with interviews of experts. Next, an ASTM E681 apparatus was built and tested for investigating the test and for future evaluation of solutions. Details of the development of the apparatus can be found in the thesis of P. Lomax [2]. After reviewing the findings from the testing of this work, the interviews, and the literature, it was determined that the effects of venting on flammability limit testing has not yet been addressed. Finally, a solution to the complication of venting − in the form of a burst disc − was developed and evaluated.

1.3 Literature Review

A review of the literature was conducted on the determination of flammability limits and on burning velocity measurements. Burning velocity measurements have been used in conjunction with flammability limits to classify flammability. Both theoretical and experimental work have been reviewed. A summary of the work reviewed is given below and sorted by sub-topics. Summaries are in chronological order within their sub-topic.

Before the summaries is a short section containing common equations and concepts used in the literature of flammability. These concepts are mentioned in the summaries so they are included here to aid your understanding.

1.3.1 Common Definitions and Equations

Lower Flammability Limit (LFL):

From the ASTM E681 standard, the LFL is defined as "The minimum concentration of a combustible substance that is capable of propagating flame in a homogeneous mixture of the combustible and a gaseous oxidizer under the specified conditions of the test" [3].

Upper Flammability Limit (UFL):

From the ASTM E681 standard, the UFL is defined as "The maximum concentration of a combustible substance that is capable of propagating flame in a homogeneous mixture of the combustible and a gaseous oxidizer under the specified conditions of the test" [3].

Le Chatelier's formula:

Le Chatelier's formula [4]is a method to predict the lower flammability limit of a mixture given the flammability limits of its components as well as the fraction of each component. Much work in the literature is spent modifying this formula to improve its accuracy. The justification for this formula is assuming the heat of combustion per mol is constant for each component and for the mixture itself.

$$\frac{1}{L} = \sum \frac{c_i}{Li} \tag{1}$$

Where L is the lower flammability limit of the mixture, c_i are the mol fractions of the component gases and L_i are the lower flammability limits of each component gas.

Flame/Propagation Velocity:

Flame or Propagation velocity refers to the linear velocity of the flame front. It can be found by tracking the distance traveled by the flame front over time and calculated accordingly − often done via high speed video.

Burning Velocity:

Burning velocity refers to the velocity of the flame relative to the unburned gas mixture in front of it. It can be found from the linear velocity by

$$S_u = S_s \cdot \frac{a_f}{A_f} \tag{2}$$

Where S_u is the burning velocity, S_s is the propagation velocity, a_f is the cross-sectional area of the flame, and A_f is flame surface area.

F-Substitution Rate:

F-substitution rate [5] is an important parameter of hydrofluorocarbons. It refers to the percentage of fluorine atoms with respect to the total number of fluorine and hydrogen atoms. The equation is given by

$$F - substitutionRate = \frac{n_F}{n_F + n_H} \tag{3}$$

F number:

F number is an important relationship for prediction of flammability limits for hydrofluorocarbons. It is defined as $F = 1 - G$ where G is the geometric mean of the flammability limits $G = \sqrt{UL}$ where U is the UFL and L is the LFL. Making the substitution gives

$$Fnumber = 1 - \sqrt{UL} \tag{4}$$

1.3.2 Flammability Test Methods

H.F. Coward at the Bureau of Mines gave an extensive foundation for flammability limit testing of individual gases (and a few mixtures) using a long tube apparatus [6]. Although his results were later criticized − other researchers argue that the diameter of the tube apparatus used by Coward was too small and led to quenching − his results were widely used for comparison and validation of early experiments and modeling. Coward's work was an early demonstration of the widening of flammability limits from increased pressure and/or increased temperature [6].

G. De Smedt et al. compared experimentally two different tests: the VDI

2263 (20 L bomb-type based using pressure rise) and the DIN51649 (glass tube using visual criteria [7]. It was found that a 2% pressure rise criteria corresponded to flame propagation to the top of the tube [7].

K. Takizawa et al. determined the burning velocity of mildly-flammable refrigerants using both Schlieren photography and the Spherical Vessel (SV) method [5]. They determined that these methods are valid for mildly flammable compounds and that burning velocity strongly depends on the ratio of hydrogen to fluorine atoms. Takizawa et al. continued to conduct their burning velocity measurements and later measured the burning velocity of fluoropropanes using their two apparatuses. They also found that fuels with lower F-substitution rates had higher burning velocities and had higher equilibrium concentration of H and OH species [8]. This led them to believe that the F-atom has an inhibitory effect by reacting with the active H-species forming the stable compound HF, terminating the chain reaction [8]. Measurements were also later done for R-1234yf using the same method but with varied humidity and oxygen-enriched air because of its low burning velocity with normal air [9].

V. Schroder carefully reviewed the standards used worldwide, specifically the DIN 51649-1 (tube), EN1839T (tube), EN1839B (bomb), and ASTM E681(spherical flask) [10]. He concluded that the European standards are more conservative than the American standard in their definition of flammability limits – European flammability limits use the first concentration where flame fails to propagate as the LFL and UFL giving lower LFL and higher UFL. It was also concluded that the visual tests agreed well enough with one another, but the bomb type was deemed unsuitable based on its significant deviations in LFL from the other tests [10].

F. Van den Schoor et al. compared two test methods: the DIN51649, which is a tube method (d=60 mm) using visual propagation, and a closed sphere (bomb-type) using pressure rise [11]. The flammability criteria used are 100 mm flame detachment and 5% pressure for their respective tests. Methane-air and hydrogen-air mixtures were tested. The tube method had wider flammability limits than the bomb-type, suggesting that the tube method is more conservative. Finally, numerical analysis based on either limiting flame speed or limiting flame temperature was conducted assuming either spherical or planar propagation. Their numerical models failed to agree with the UFL measurements, but had slight success for the LFL measurements. The analysis using a limiting flame velocity assuming spherical propagation best fit the data [11].

D. Crowl et al. argued that existing pressure rise criteria in test methods are arbitrary and not “fundamentally-based” [12]. They proposed instead using the second-derivative of pressure rise as it represents an acceleration signifying the reaction. An expression was derived to calculate the second-derivative of pressure rise from the maximum pressure difference, burning velocity, time rate-of-change of flame front area, vessel volume, and density [12]. Pressure-time data was collected using a 20 L bomb-type with wire fusing ignition of hydrogen-air mixtures. The flammability limits were determined as the turning points of the sign of the second derivative where a positive sign indicates growth and a minus sign, extinction. Their results agreed fairly well with published values, but were found to be more conservative giving a wider range of flammability.

I. Zlowchower et al. conducted tests using two spherical bomb-type tests (20 L and 120 L) with a 7% pressure rise criterion for flammability [13]. Fuels tested included methane, propane, ethylene, carbon monoxide, and hydrogen. The results of the 120 L bomb-type were in good agreement with published results using the 12 L flask (visual criteria). This suggests that the 12 L vessel is large enough and that the 7% pressure rise is suitable since it aligns with the visual criteria. Additionally, Zlochower et al. found the Limiting Oxygen Concentration (LOC) for the fuels diluted with nitrogen. Predictions for the LOC using Le Chatelier's rule agreed well with experimental results.

D. Clodic et al. measured ranges of burning velocities for various fuel-air mixtures including R-32, propylene, propane, R-152a, ammonia, and R-143a at varying concentrations [14]. A tube-type apparatus was used. Burning velocity was determined by measuring the flame propagation velocity through video-photography and multiplying by the ratio of effective cross-sectional area (subtracting the dead space) to flame surface area. Flame surface area was found by fitting points to flame images, obtaining a function, and then rotating the function to obtain an area. Ammonia, R-32, and R-143a had significantly lower burning velocities than the other fuels.

1.3.3 Variable Effects on Flammability Limits

M.V. Blanc et al. were some of the first to investigate the minimum ignition energy for flammability limit testing – using methane-air mixtures – by changing the electrode spacing and measuring the voltage and capacitance [15]. Too large of a distance and the energy is lost to the surroundings and if too close, there is quenching between the electrodes.

A.L. Furno et al. investigated the LFL for upward and downward flame propagation for hydrogen-air and butane-air mixtures [16]. They attempted to explain the relationship between the upward and downward limits using preferential diffusion [16]. They found the following expression $(D_o/D_f)^{1/2} \sim LFL_{up}/LFL_{down}$ after comparing the calculation on the left hand side with their collected data. Subscripts o and f refer to oxygen and fuel respectively.

A. Takahashi et al. evaluated different types of wire fusing ignition sources by changing the wire material and supplied power [17]. Methane-air mixtures were tested in a bomb-type vessel and ignition was determined by a pressure rise [17]. They later investigated the effect of vessel size and shape on flammability limits, testing methane-air and propane-air mixtures in eight different cylinders and the 12 L flask [18]. It was determined that the results of the 12 L flask agreed well enough with the 160 L cylinder. They concluded then that the 12 L flask is sufficiently large to minimize the effects of quenching [18]. Finally, they recommended a minimum diameter of 30 mm and a minimum height of 60 cm for tubes used in flammability testing.

R. Richard sought to determine appropriate small-scale criteria by comparing the flammability of refrigerant blends in large-scale testing with small-scale testing. More specifically, flammability testing in a 200 L cylinder was compared with testing in a 12 L vessel with the same temperature, humidity, and ignition controls [19]. It was determined that flame propagation in the large cylinder corresponded to a 90 ° fan-shape flame front [19]. This is the criteria adopted by the ASHRAE standard 34.

Le Chatelier published later a paper on the flammability limits of carbon monoxide-air mixtures and the effects of tube diameter, pressure, and temperature using a bell-jar apparatus [20]. His results echoed previous findings that high temperature widens flammability limits, low pressure narrows flammability limits, and larger diameters widen flammability limits [20].

G. Ciccarelli investigated the flammability limits of hydrogen-air and ammonia-air mixtures at elevated temperatures $20 - 600\,^{\circ}\mathrm{C}$ in a 12 L cylindrical vessel [21]. Flammability criterion was very conservative, such that any “measurable pressure rise” resulted in being deemed “flammable” [21]. More specifically, Ciccarelli found that flammability limits for these mixtures were linearly dependent on temperature.

Y. Shoshin et al., similar to Takahashi et al., explored the effects of vessel size on flammability limits by changing tube diameter [22]. Tested were methane-hydrogen-air mixtures. Flame speed and position were recorded using a PIV camera. Smaller tube diameters were found to reduce flame speed. The authors attribute this to heat loss and viscous interaction. LFL also decreased with larger diameters.

Z. Li et al. determined the flammability limits of methane-nitrogen-air mixtures at temperatures below atmospheric (150-300K) [23]. The apparatus was a stainless-steel cylinder cooled by a cryostat. Flammability criterion used was an absolute pressure rise of 10 kPa or more. It was found that decreased temperature narrows the flammability limits (higher LFL and lower UFL). They modified Le Chatelier’s formula to include terms for dilution and temperature. Predictions from their modified formula agreed well with their experimental results.

In later work, Z. Li explored the diluting effect of R-134a, a nonflammable refrigerant using a tube apparatus with a visual criterion [24]. R-134a was added to propane and R-152a. It had little effect on the LFL of these mixtures, but significantly decreased the UFL for both mixtures, narrowing the flammable range. Also, their modified version of Le Chatelier's formula was used to predict the flammability limits with dilution. Predictions agreed well with experimental results.

Z. Yang et al. sought to determine the minimum inerting concentration (MIC): the concentration of diluent to make a flammable mixture non-flammable (LFL=UFL) [25]. Experimental work used a vertical tube with R-32 and air mixtures diluted by varying amounts of R-125, R-1227ea, or R-1311. R-1311 was found to have the lowest MIC making it the most effective diluent. The MIC was also calculated theoretically based on a limiting flame velocity and the inhibition coefficient of the fuel calculated by the group contribution method. Inhibition values were taken from previous references. The theoretical predictions however, did not agree well with the experimental results.

Z. Wu et al. conducted extensive work on the flammability limits of ethylene including temperature effects above and below ambient as well humidity effects [26]. Temperatures tested ranged from -5 to 5 °C . The test method employed was based on the Chinese GB/T12474 which is a vertical tube test method. Flammability criteria was propagation to the top of the tube and was recorded by video. Echoing the results of previous work, increased temperature widened flammability limits and decreased temperature narrows flammability limits. They also found that the geometric mean of flammability limits was near constant with temperature. Humidity was found to have little to no effect on the flammability limits of ethylene. Finally, a new expression to predict LFL based on the number of chemical bonds and bond-energies was derived. Their new expression agreed very well with experimental data.

X. Liu et al. investigated the effects of high pressure and temperature on flammability limits of hydrogen-air mixtures using a 5 L bomb-type cylinder [27]. The conditions included 20, 40, 60, 75, and 90 °C as well as 1, 2, 3, 4 atm pressure. The criterion for flammability was 7% pressure rise. Their apparatus was first validated with respect to ambient conditions and was deemed acceptable. It was found that increasing temperature and increasing pressure widened the flammability limits, but pressure had a much greater effect than temperature.

K. Zhang et al. explored the effects of different diluent on the flammability limits of dimethyl ether-air mixtures using an ASHRAE type apparatus [28]. Diluents included N_2, CO_2, R-22, R-134a, and R-227ea. As expected, increased presence of diluents narrowed the flammable range of dimethyl ether. Le Chatelier's formula was modified to include polynomial terms related to the fuel volume fraction. The predictions of the modified Le Chatelier's formula agreed well with experimental results.

R. Tschirschwitz et al. sought to develop flammability criteria for non-atmospheric conditions (high pressure) [29]. A windowed autoclave − made of stainless steel 12 L in size − was used to allow visual observation at high pressure testing. Hydrocarbon-air mixtures were tested and ignited by wire fusing. Their visual criterion for flammability was based on the failure of the flame to reach the vessel walls. A pressure rise of 2% and an optional temperature rise criteria of 100 K was determined to correspond to this visual criteria and became their new flammability criteria. However, it is worth noting that their criteria is much stricter than in other standards.

1.3.4 Theoretical Work

C.K. Law et al. sought to couple the two existing mechanisms for near-limit flames: heat loss balance and the branch chain reaction by comparing the theoretical LFL obtained by each method [30]. For the heat loss analysis, the mass burning rate was found for different equivalence ratio and the point of the lowest mass burning rate to be the LFL. For the branch chain analysis, a "flammability exponent" was defined relating the rates of chain termination to the rate of chain branching [30]. The LFL was said to occur where the flammability exponent is equal to one. The resulting LFL for both analysis was found to be in good agreement with one another.

P. Westmoreland et al. presented early simulations to evaluate the suppressant ability of different fluoromethanes [31]. Westmoreland used the NIST-modified version of Sandia's PREMIX code to evaluate flame temperature and flame velocity for methane-air mixtures with varying percentage of fluoromethanes. [31]. R-32 was found to accelerate the flame (higher burning velocities) but lower flame temperature due to a smaller heat of combustion than methane. CHF_3 (fluoroform) had opposite behavior, it slightly raised the flame temperature but significantly reduced the flame speed − believed to be the result of its chain-terminating reactions. Reaction paths were also presented in detail.

N. Kim et al. conducted numerical simulations of a 1D-flame in small tubes [32]. A finite volume method was used. The conditions simulated included adiabatic and isothermal walls and varied velocity profiles. They were able to obtain the propagation velocity and flame shapes for the different conditions by modeling the heat transfer, momentum of the flow and flame, and chemical species [32].

M. Vidal et al. utilized an algebraic method to predict LFL using the Calculated Adiabatic Flame Temperature (CAFT) [33]. The calculation is based on the assumption that the flame temperature at the LFL is equal to the CAFT. An enthalpy balance is then calculated to determine the mols of oxygen to fuel to then find LFL. Vidal et al. used experimental LFL values to find different CAFT to then use in their model to predict LFL [33]. The predictions based on CAFT agreed well with the experimental data and CAFT were determined for different chemical families; however, to be of use, there needs to be another way to approximate CAFT [33].

C. Chen et al. developed a theoretical model to predict LFL of a diluted mixture given the LFL of the undiluted mixture, properties of the diluent, and amount of diluent [34]. They found that the "inerting ability" of a diluent is thermal in nature and depends most on the mean molar heat capacity (at adiabatic flame temperature). Diluents evaluated included Carbon Dioxide, Steam, Nitrogen, and Helium.

J. Rowley et al. worked to improve the predictions of the Burgess-Wheeler law [35]. They modified the equation to account for heat loss to the products of combustion and allowed for effects of initial temperature on flame adiabatic temperature. Their new formula agrees much better with experimental data than previous models. However, their formula is valid only for basic hydrocarbons.

S. Zhang et al. sought to numerically predict laminar flame speeds of hydrocarbon-air mixtures using CHEMKIN and CANTERA software [36]. They attempted to validate their model experimentally using a vertical tube method. Flame speed was found experimentally from analysis of recorded images. The predictions did not agree well with the experimental data nor other published data. The authors conclude the need to refine their model.

Zlowchower et al. also conducted theoretical work, using a thermodynamic program (CEA code developed by NASA Glenn) to predict flammability limits based on a limiting flame temperature [37]. The calculated adiabatic flame temperature was chosen as the limiting temperature. The program would vary the concentration of fuel (and air consequently) until the limiting temperature is calculated. Results were inconsistent with respect to published experimental data provided by Kondo. The flammability limits agreed well for certain fuels but not others without a noticeable pattern.

T. Albahri et al. developed Artificial Neural Networks to predict the LFL of hydrocarbons based on structural group contributions – 30 structural groups were employed [38]. The model had excellent agreement with published experimental data and proved to be more accurate (smaller error) than previous models.

A. Di Benedetto conducted numerical simulations to calculate LFL based on an energy balance: The energy required to raise the temperature of the burned mixture to the ignition temperature equals the heat released from the reaction minus the heat loss [39]. The heat loss term was a variable parameter and when heat loss goes to zero, the result is the adiabatic flammability limits, they proposed. They argued that because these limits are independent of heat loss, they would be independent of the test method and be a thermodynamic property. The adiabatic flammability limits are much wider than normal flammability limits. However, their work was limited to hydrocarbons only and may carry limited physical significance.

H. Okamoto et al. used CFD (STAR-CD program) to simulate leakage of refrigerants from air conditioners to determine what scenarios would lead to the creation of flammable mixtures [40]. Scenario variables included room size, floor-mounted vs wall-mounted vs ceiling-mounted, different leakage rates, and different room air flows [40]. Cumulative volume fraction of the fuels and flammable volume were tracked over time and used to analyze the hazard of each scenario. It was found that wall-mounted units accumulate significantly lower flammable volumes than floor-mounted units. The concentration of refrigerant did not reach the LFL in the cases of wall-mounted units. Concentrations for floor-mounted units were much higher, but in many cases above the UFL. Finally, it was found that ventilation rate has an enormous impact on the accumulation of flammable volume.

1.3.5 Small-Scale Testing

Maruta et al. examined combustion within 2 mm diameter cylindrical vessel [41]. They were able to create stable hydrocarbon flames, overcoming thermal-quenching by heating the walls with external heaters [41].

N. Kim et al. sought to model stationary flames in small-scale combustors experimentally by using larger vessels at low pressure [42]. The justification for the comparison is by the similarity in flame structure, specifically similar flame sheet thickness [42]. Stationary flames were created by adjusting the flow rate and pressure of pre-mixed propane-air and methane-air mixtures. Finally, through CCD camera, flame thicknesses and dead space − distance between the flame and the tube wall − were directly measured. They argue that most of the heat lost is to the unburned mixture in the dead space and not the walls directly because varied wall temperature profiles had little effect on the observed flammability limits.

B. Bai et al. sought to numerically model the quenching of combustion in small tubes [43]. 1D flame propagation was simulated with species and energy conservation equations. Both thermal and kinetic quenching was evaluated. Two parameters were defined: heat loss coefficient and radical quenching coefficient. Because quenching is inversely related to diameter, quenching effects on negligible in sufficiently large vessels. Additionally, they found that the quenching limits for both thermal quenching and radical quenching are increased with higher wall temperatures. However, changing wall temperature had a much greater effect on thermal quenching than radical quenching. Thus elevated wall temperatures can serve as a solution to quenching in small combustors and allow for smaller diameters.

1.3.6 Work of Shigeo Kondo et al.

Shigeo Kondo et al. have contributed significantly to the study of flammability limits. Their work comprises much of the flammability limit testing and modeling done for refrigerants.

Early work of S. Kondo et al. included investigating the effects of spark duration and spark gap using a tube apparatus and methane-air mixtures [44]. It was determined the optimal ignition conditions are 0.1-0.3 s duration and spark gap of 6-8 mm [44].

Kondo et al., after taking new measurements of halogenated hydrocarbons following the ASHRAE Standard, an algebraic model was developed to predict LFL and UFL based on molecular structure [45]. In 2006, they further developed their model specifically for fluorinated compounds. First, they plotted F number versus F-substitution rate and found an F number of zero (meaning LFL=UFL or nonflammable) corresponded to an F-substitution rate $\geqq 0.625$. They developed a numerical model to predict the F number and geometric mean which could then be used to find LFL and UFL. Both expressions consisted of a series of terms relating to the presence of structural groups or other parameters such as saturation. There was good agreement between the predictions of the numerical model and experimental results, except for compounds with F-substitution rates $\geqq 0.625$ where the formula predicted flammability. Their results suggested that F-atoms are not good chain carriers. Compounds with higher F-substitution rates had a lower fraction of active radicals and more free F-atoms.

Kondo next investigated Le Chatelier's formula [46]. Experimental measurements using the ASHRAE method confirmed that Le Chatelier's formula predicts the LFL of hydrocarbon-air mixtures well. Using fitting techniques, they were able to modify Le Chatelier's formula to predict UFL of mixtures. The modified formula agreed well with experimental UFL data. Kondo then investigated the ability of Le Chatelier's equation to predict mixtures with diluents [47]. It was found that Le Chatelier's equation fails for mixtures with nonflammable compounds. The mixtures used were hydrocarbon-air mixtures diluted with R-125. Le Chatelier's equation was modified again, this time to include polynomial terms based on the mol fraction of the diluent. The predictions of the modified equation accounting for diluents agreed well with the experimental data.

Kondo also continued to develop the algebraic prediction of F number for hydrofluorocarbons [48]. Added additional terms to their original expression to account for not just the number of F-atoms, but their distribution as well as the presence of specific structures such as $-O - CF_3$, $O - CF =$ and $-O - CF_2-$ which were found to reduce flammability, have no effect, and have no effect, respectively.

In 2011, Kondo et al. departed from previous work to conduct tests at non-atmospheric conditions, specifically high pressure [49]. A 5 L stainless steel sphere bomb-type was used to test R-1234yf, R-32, and methane-air mixtures. The flammability criterion was 20% pressure rise. The justification of this criterion was their theoretical calculation of a 30% pressure rise for a cone of burned gas at 1500 K. It was found that increasing pressure widens the flammability limits. Pressure dependence of flammability limits was found to be logarithmic. However, R-32 had a sudden change in behavior at 1500 kPa, suggesting a change in combustion mechanism.

The following years, 2011-2014, Kondo et al. thoroughly investigated the effects of temperature and humidity on flammability limits using their ASHRAE-based apparatus. In 2011, they first tested with simple hydrocarbons with dry air [50]. Temperature was controlled via an air bath. Flammability limits were found to be linearly dependent on temperature. Expressions based on White's rule were developed to make predictions of the limits. Their expression was in excellent agreement with the experimental data. In 2012, Kondo et al., using the same apparatus, tested 2L refrigerants [51]. However, the air was no longer dry but with varied levels of humidity. Both temperature and humidity widened the flammability limits. In 2014, they published their work on high humidity testing [52]. The same test apparatus was used, but this time the temperature was kept at 60 °C and the humidity was varied. Again, increased humidity widened the flammability limits. The fuels tested − R-410A, R-410B, R-134a, and R-125 − were nonflammable without sufficiently high humidity. Humidity provides hydrogen atoms to react with the excess F-atoms.

1.3.7 Literature Review Conclusions

With respect to the goal of improving the accuracy and reproducibility of the determination of flammability limits, the following are the key ideas gained from the literature review.

Variables such as temperature, pressure, humidity, ignition source, vessel size, and criteria, and their effects on flammability limits have already thoroughly been investigated. The 12 L spherical flask has been found to be of sufficient size to minimize the effects of wall-quenching, although tests in smaller chambers can be possible if the vessel walls are heated. There exist many algebraic methods to predict the LFL (and UFL) of mixtures from data of its individual components and to predict the LFL and UFL of a pure substance based on its molecular structure. These predictions have aligned well with experimental data (for most compounds and blends). However, these has been no work done yet on venting nor any new solutions either.

2 Interview Results

Experts on the ASTM E681 standard, research scientists and engineers, were interviewed. A copy of the interview questions can be found after the below discussion. The results of the interviews can be summarized as follows.

Experts praise the test for its simplicity and low cost; however, they have a number of criticisms of the test, especially in the context of mildly flammable substances such as Class 2L refrigerants. There is concern that the 90 degree criteria − used to determine if a concentration is flammable − is not physically justified. Additionally, results can depend on the recording equipment, settings and positioning, and operator's judgment. There are no recommendations or controls for the recording of test results to address these variables. The standard should include sample images so that recording is consistent and interpretation of results is reproducible.

Another concern is on the creation of flammable blends. Operators can use different mixing speeds − only a minimum RPM is specified − which can result in different levels of turbulence. Additionally, the standard has no verification of the homogeneity of the blend.

Finally, the majority of the experts expressed concern about the rubber stopper and venting effects. The rubber stopper can have difficulties in maintaining a seal during testing, especially at pressures close to atmospheric. Venting pressure is not consistent because the weight of the stopper with the inlet components − electrodes, sensors, gas controls, etc. − is not standardized. Also, tipping may occur which can also hurt the consistency of the venting pressure. Early venting interferes with the flame structure, invalidating the test. Late venting poses an explosive hazard to safety and the delayed evacuation of gaseous products can damage the flask, one of the more expensive pieces of equipment. From what was seen in the literature, this issue has not yet been addressed and will be the end goal of this work.

Interview Questions

1. What is the nature of your experience with E-681?

2. If you have an E-681 facility, how did you acquire it?

3. What do you think are the strengths of E-681?

4. What do you think are the weaknesses of E-681?

5. Do you find E-681 to be repeatable and operator independent?

6. What changes would recommend to E-681?

7. Can you recommend other interviewees?

3 Experimental Apparatus

3.1 ASTM E681 Apparatus

The experimental apparatus was developed according to ASHRAE Standard 34, which is a slightly modified version of the ASTM E681 test, using a 12 L spherical flask instead of a 5 L spherical flask. Below is a schematic of the experimental apparatus. Ignition is accomplished by an electric spark.

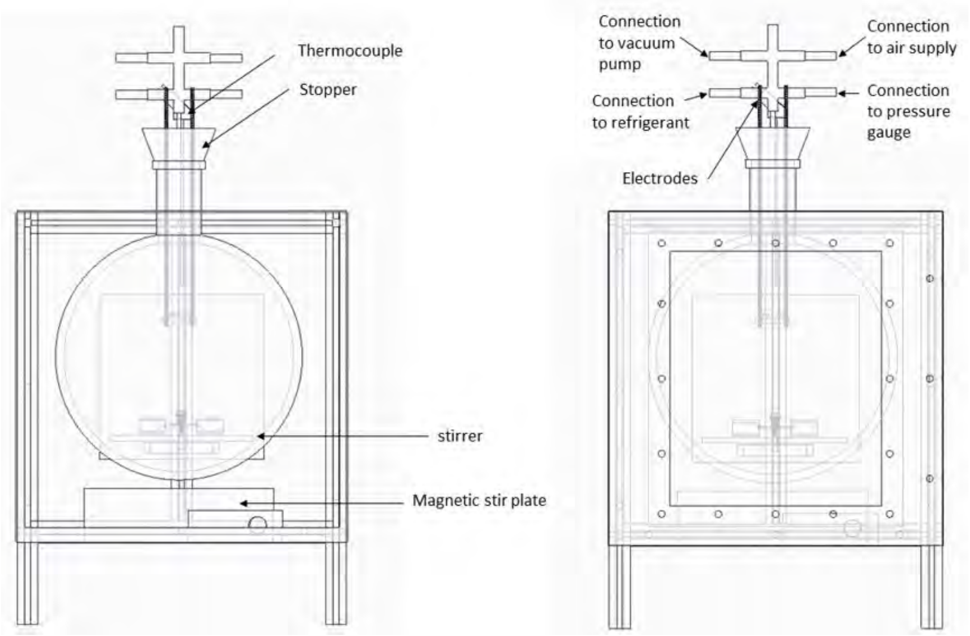


Figure 1: Schematic of Experimental Apparatus

It is worth noting that the duration of the spark was reduced from 0.4 s to 0.2 s because the spark was seen during flame propagation. Tests were conducted at room temperature and atmospheric pressure. R-32 (CH_2F_2) and air mixtures were tested. Gas mixtures were created using the partial pressure method. Flame propagation was recorded using a high-speed video camera. High speed video (120 fps) was also taken of the rubber stopper to better understand its venting. Flammability was assessed using the 90 ° criteria – to be discussed further in section 4.3. The element of greatest interest is the rubber stopper which seals the flask and supports all of the inlet components.

3.2 Burst Disc Development

To address the problems of venting, a burst disc was designed and built as an alternative to the rubber stopper. The goal of the burst disc is for consistent venting pressure, even across laboratories. The burst disc design has the weight of the inlet components rest on the glass and so that they do not affect venting pressure.

The burst disc consists of the following parts: Attached to the neck of the flask is an aluminum clamp, lined with gasket to protect the glass. Bolts attach a nylon block with a hole in the center to the aluminum clamp. There is also a thin sheet of gasket between the aluminum clamp and the nylon block to prevent leaks between the two surfaces. All the components – the electrodes and tubing for the gases and vacuum – are supported by the nylon block. A small 3.75 x 3" sheet of heavy-duty aluminum foil is placed on top of the nylon block, covering the hole. Vacuum grease is also used between the foil and the nylon block. Finally, the cover plate (also made of aluminum) is placed on top of the foil sheet and secured by bolts into the threaded inserts of the nylon block.

Another part of the burst disc system is the adjustable knife edge to break

Figure 2: Burst Disc Without and With Cover

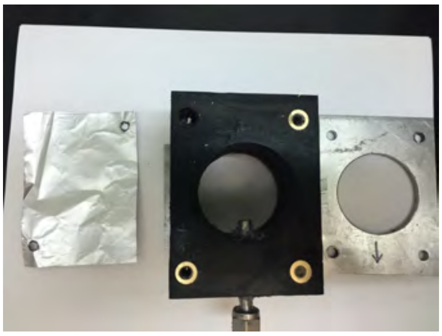


Figure 3: Burst Disc Foil Sheet and Cover Plate Separated

the foil. The knife edge itself consists of four utility blades that are held by a 3D-printed “blade holder”. The knife edge is connected is to a metal sheet that is connected to a micrometer so that the height of the knife edge can be controlled precisely.

Please see the following page for photos and diagrams of the burst disc. Design drawings can be found in Appendix A.

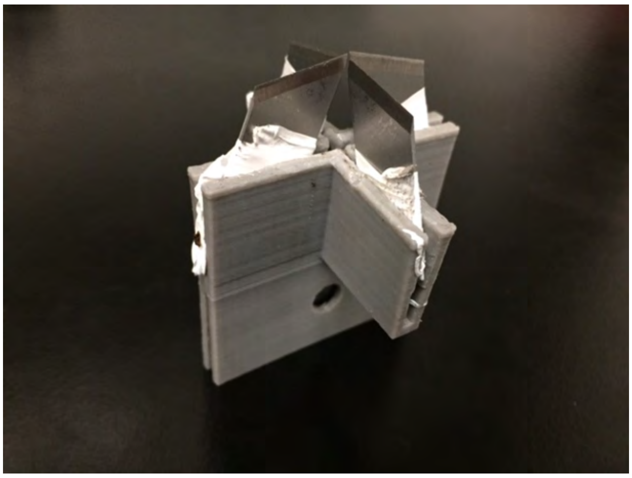


Figure 4: Knife Edge

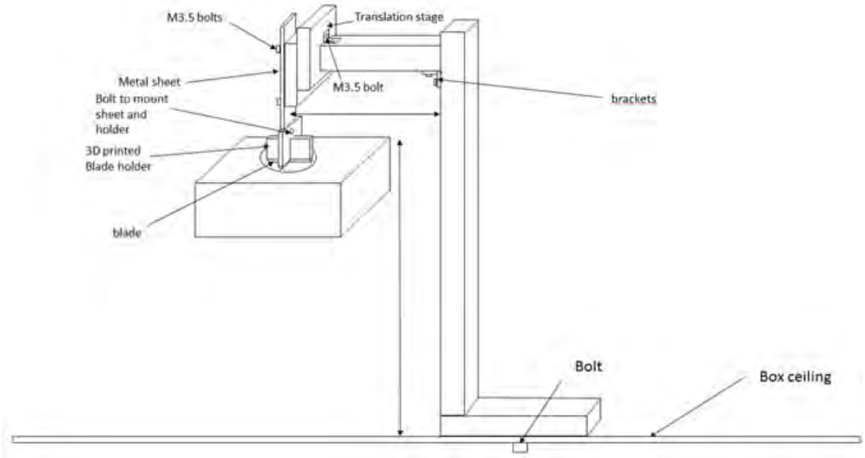


Figure 5: Diagram of Knife Edge and Micrometer Station

4 Results and Discussion

4.1 Vacuum and Leak Testing

If the burst disc design is to be an alternative to the rubber stopper, it must meet, if not exceed all the functions of the original rubber stopper. Of critical importance, is the ability to achieve and maintain a vacuum. Leaks of any nature can greatly affect the mixture composition being tested and can lead to wasted tests and invalid results.

ASTM E681 requires a vacuum of -100 kPa and a maximum leak rate of 0.1 kPa/min or less [3]. Table 1 below compares the performance of the rubber stopper and the burst disc at vacuum pressure (-100 kPa or less). Although the burst disc has a slightly higher leak rate than the rubber stopper, it still exceeds the requirements of the test standard. The burst disc is also able to reach a vacuum faster than the rubber stopper. So although the rubber stopper may create a better seal, it takes longer to do so.

Type	**Time to Vacuum [min]**	**Leak Rate [kPa/min]**
Stopper	3:03	0.0051
Stopper	3:22	0.0049
Stopper	5:01	0.0032
Burst Disc	2:22	0.0062

Table 1: Performance at Vacuum Pressure

The leak rates of Table 1 were obtained from linear fitting of the pressure-time history. Pressures were recorded every three minutes for a duration of

30 minutes.

The pressure-time history at vacuum are shown below in Figure 6. The solid line of the pressure profile of the burst disc performs satisfactorily with respect to the rubber stopper.

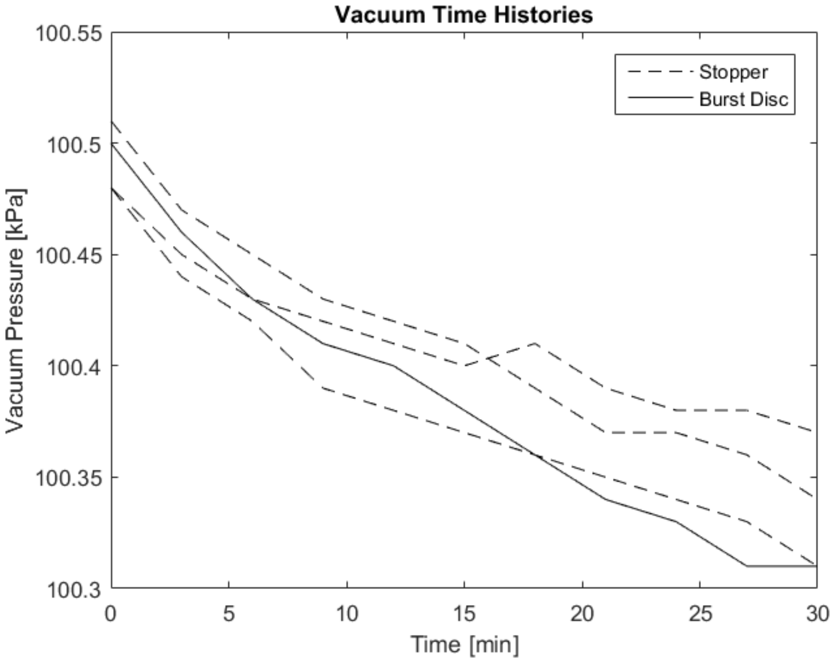


Figure 6: Pressure Time Histories at Vacuum

Additionally, leak testing was performed at other pressures because it was determined that the rubber stopper could only be safely filled to -2 kPa before a leak path was generated evident by a sudden gain in pressure. These leak rates were also found by fitting tools of pressure-time data. Figure 7 shows the leak rates vs different pressures for the stopper and for the burst disc.

As shown, the burst disc allows for filling up to and past atmospheric pressure. Given that the burst disc does not break at vacuum pressure, it is

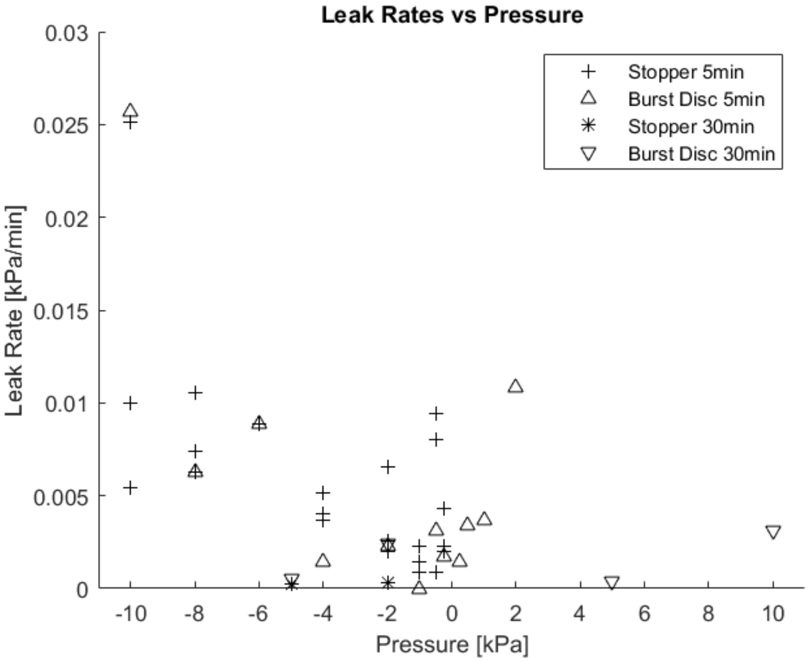


Figure 7: Leak Rates for Different Pressures

likely the burst disc could be filled to 100 kPa above atmospheric. This is another advantage to the burst disc design.

4.2 Venting Pressure Testing

4.2.1 Burst Disc

It was found that the burst disc has two stages of venting. There is an initial puncture pressure at which the aluminum foil deflects upwards to the knife edge, creating a hole. If the pressure is allowed to continue to rise, the aluminum foil will burst open and its edges unfold. See Figures 8 and 9 for results of a completed burst test.

Most importantly, burst disc has reproducible venting. It has been found

Figure 8: Front View of a Successful Burst

Figure 9: Side View of a Successful Burst

to consistently puncture at 7 kPa with the use of the knife edge. As seen in Figure 10, multiple tests all punctured near 7 kPa. Changing the position of the knife edge (relative to the foil sheet) was unable to change this pressure, although. However, adjusting the position of the knife edge did adjust the burst pressure and appears to be linearly related. The burst pressure results do have greater deviations however.

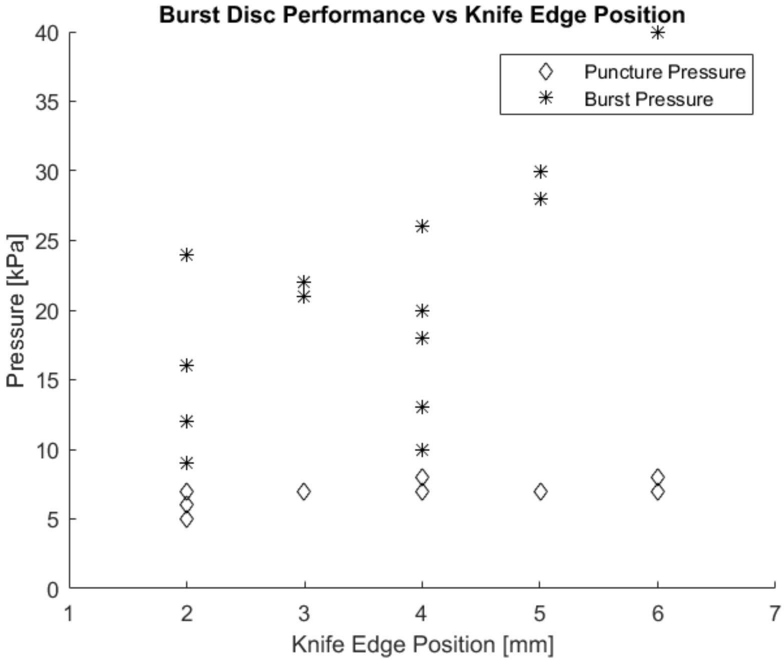


Figure 10: Burst Disc Venting Pressures

4.2.2 Rubber Stopper

The rubber stopper does not have a clear venting pressure. All that is known is that the rubber stopper loses its seal between -2 kPa and 0 kPa. However, there is venting phenomena still to discuss.

High speed images have revealed that the rubber stopper ejects violently when it vents at the conclusion of the test. Note that the concentration (14.8%) used to generate these images is near the LFL and not near stoichiometric (17.3%). R-32 is considered a mildly flammable substance and yet produces violent ejection. Image analysis has also revealed that the stopper can have the issue of re-sealing. After the initial ejection, the stopper can potentially re-assume its position. This presents another advantage of the burst disc: prevention of re-sealing.

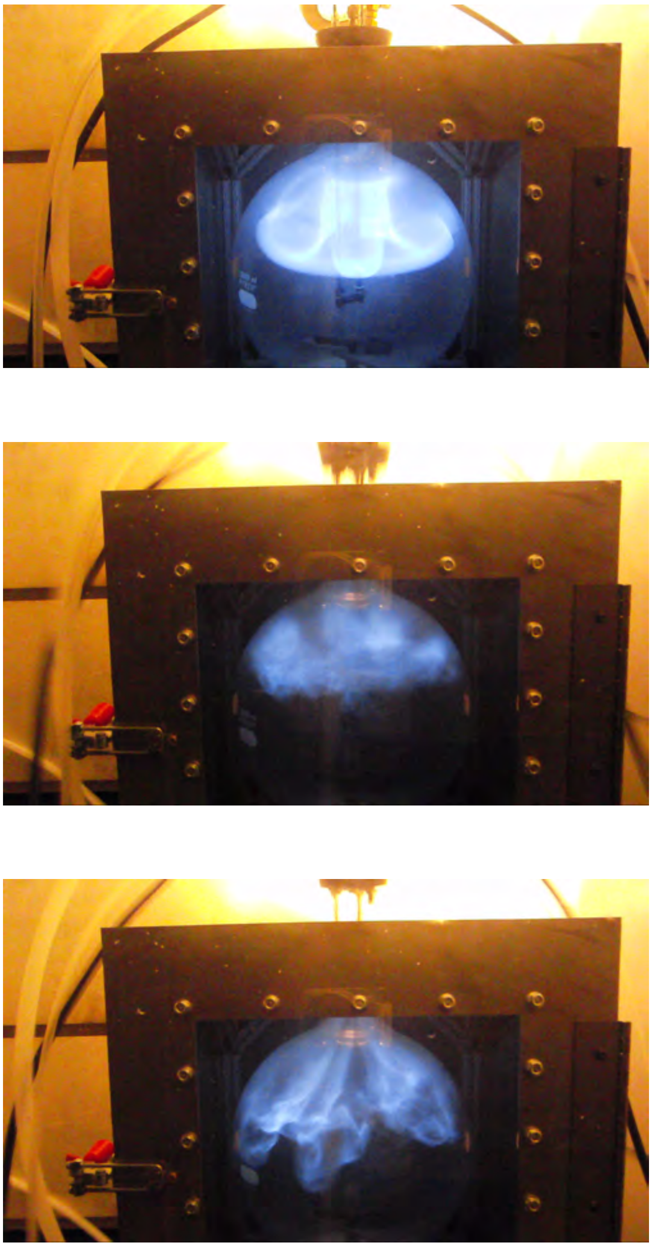


Figure 11: 14.8% Test Showing Stopper Displacement

4.3 Determination of the LFL of R-32

The conditions of the test can be summarized as follows: relative humidity of the supplied air was 11% – Humidity was not a concern because it has shown to have no effect on compounds where $n_h = n_f$ such as R-32. Temperature was ambient (23 °C).

4.3.1 Flammability Criteria

This work used the same criteria as ASHRAE Standard 34 [1]. A mixture is considered flammable if the flame font forms a continuous, 90 ° arc - measured from the ignition point (electrodes) to the vessel walls - when the flame front reaches the vessel walls. To aid your understanding, Figure 12 shows the positioning of the angle measurement.

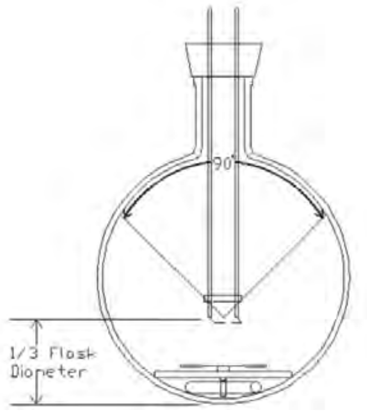


Figure 12: Diagram showing the proper location for the apex of the angle measurement [1]

4.3.2 Rubber Stopper

Flammability was assessed by image analysis of the flame. The procedure was as follows:

1. Convert the video file into a series of images
2. Select the images of interest: One frame of the ignition and one frame of the flame front reaching the vessel walls
3. In any software with image editing (this work used MS powerpoint), place the images side-by-side.
4. Place a horizontal line such that it passes through the point of ignition and marks it on the other image of interest
5. Place a 90 ° angle with its vertex aligned with the previously placed horizontal line
6. Examine the image and decide if the flame angle equals or exceeds the arc.

Figures 13 and 14 show two sample images analyzed from testing using the rubber stopper.

4.3.3 Burst Disc

The image analysis of the burst disc used the same method. Figures 15 and 16 show two analyzed images

The flames produced with the burst disc seem much more uniform and nearly perfectly symmetrical. This is valuable for the reproducibility of

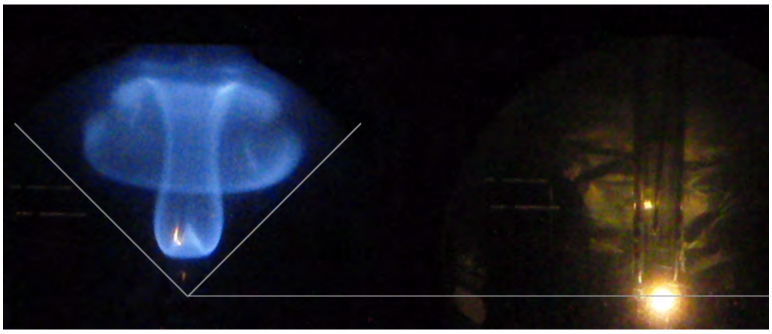


Figure 13: An example of a “Nonflammable” result with the stopper at 14.7%

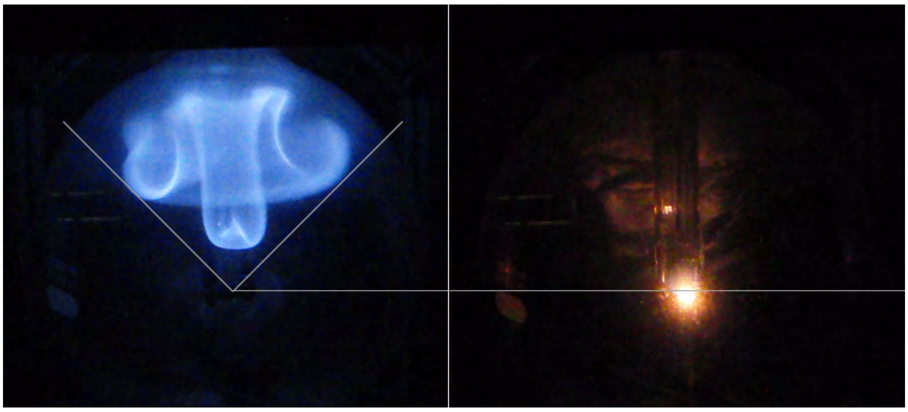


Figure 14: An example of a “Flammable” result with the stopper at 14.8%

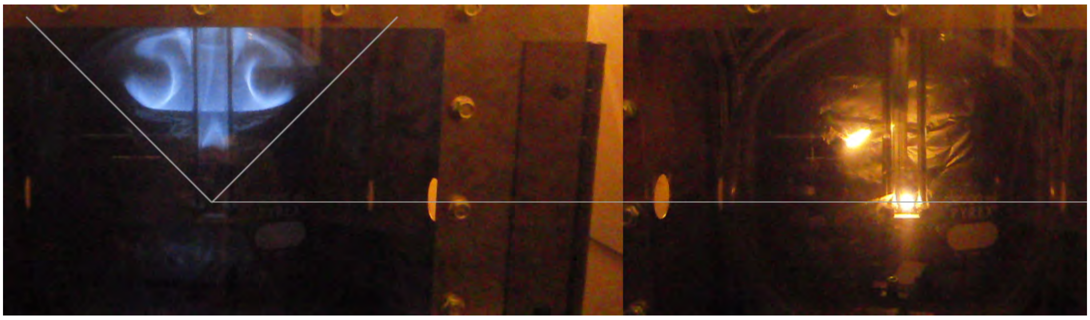


Figure 15: An example of a “Nonflammable” result with the burst disc at 14.6%

flammability testing using the flame angle criteria, especially because of the requirement that the flame front be continuous.

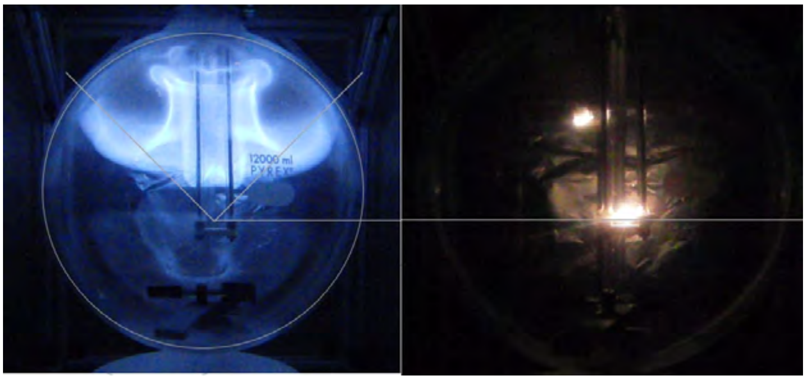


Figure 16: An example of a “Flammable” result with the burst disc at 14.7%

4.3.4 Comparison With Past Data

Table 2 contains many different LFL values for R-32 as well as the test method and the references.

LFL (%)	Method	Reference	Notes
13	Reported	[53]	Airgas MSDS
13.5	ASHRAE	[51]	-
14	Reported	[54]	Linde MSDS
14	Reported	[55]	Hynote Gas MSDS
14.4	ASHRAE	[56]	-
14.7	ASTM E681-12L	[57]	Reduced spark power
14.7	ASHRAE, Burst Disc	This work	Reduced spark duration
14.8	ASHRAE, Stopper	This work	Reduced spark duration

Table 2: LFL values for R-32

Compared to previously published data for the LFL of R-32, the results of this work are higher. There are two possibilities for this deviation. One possibility is that our ignition source is weaker (reduced duration) and so a more flammable (less lean) mixture is required to compensate. The fact that Kul’s value of 14.7% agrees with this work also used a weaker ignition (same duration but lower power) supports this notion. Another possibility is that this work's criteria is not conservative enough and instead of the initial flame angle, the maximum flame angle should be used.

4.4 Burst Disc Venting Performance

One of the most important things for the burst disc (and the stopper) is the time difference between the flame front reaching the vessel walls and the start of venting.

Through image analysis, the delay between the flame reaching the vessel walls and venting by displacement of the rubber stopper has been quantified. The approach was to identify the frame where the flame reached the vessel walls – which was the frame used to evaluate the flame angle – and to identify the frame where venting first occurs. Then this difference in frame number can be divided by the frame rate (120 fps) to obtain seconds, see the below equation

$$\Delta t = \frac{\Delta frame}{120 fps} \tag{5}$$

Venting is identified by the onset of turbulence and destruction of the initial flame cap. Below is an example of the frame when a flame vented.

In Table 3, are the data used to find the time difference.

Concentration (%)	Flame Angle Frame	Venting Frame	Frame Difference	Time Difference (ms)
14.4	654	658	4	33.3
14.5	163	167	4	33.3
14.6	654	659	5	31.7
14.7	367	369	2	16.7
14.8	692	695	3	25

Table 3: Stopper Venting Time

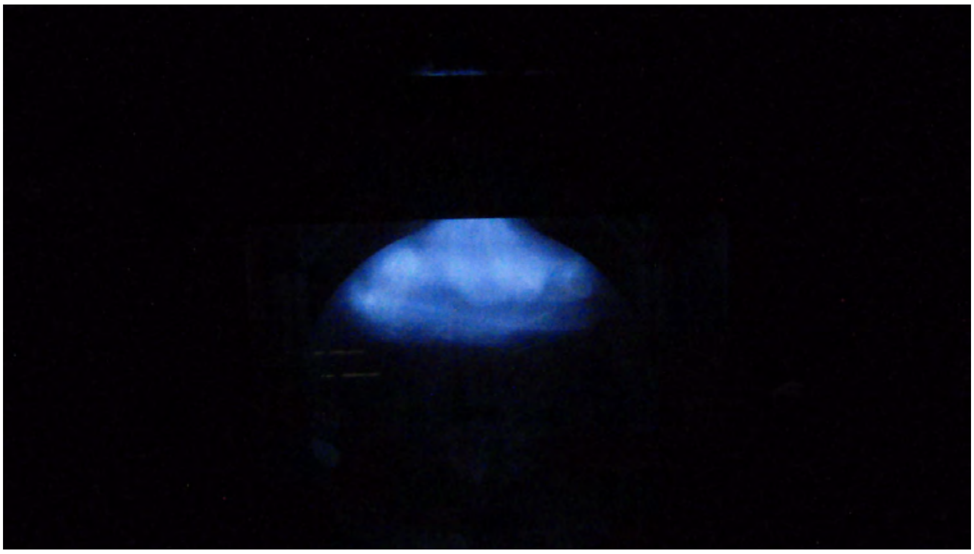


Figure 17: Flame during venting (14.8%)

It appears that it takes about 16-34 ms for the stopper to vent, with shorter times at higher concentrations. This is reasonable because it has been shown by Takizawa that as the concentration of fuel increases, burning velocity increases until a maximum value at stoichiometric before decreasing [5].

Regarding the burst disc, image analysis is not an option to determine time to venting because the camera does not have a direct view of the foil disc itself. Installing a camera in the fume hood was not an option because of the effect of the gaseous HF products (from the combustion of R-32) on glass. However, audio analysis can be used to identify the onset of venting. The action of the burst disc was identified by the sudden increase in sound. The timestamp of venting was recorded and compared with the time at which the flame struck reached the vessel walls. The smallest unit of the time stamp is frames, which can be converted into ms as done previously.

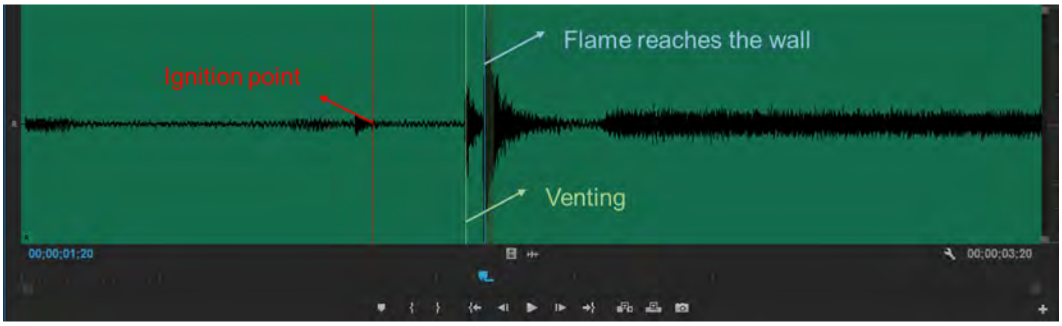


Figure 18: Audio of 14.5% Test

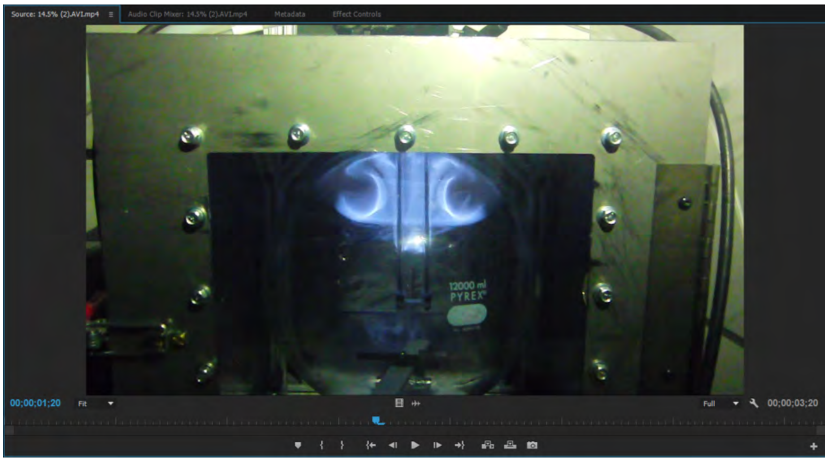


Figure 19: Flame of 14.5% Test

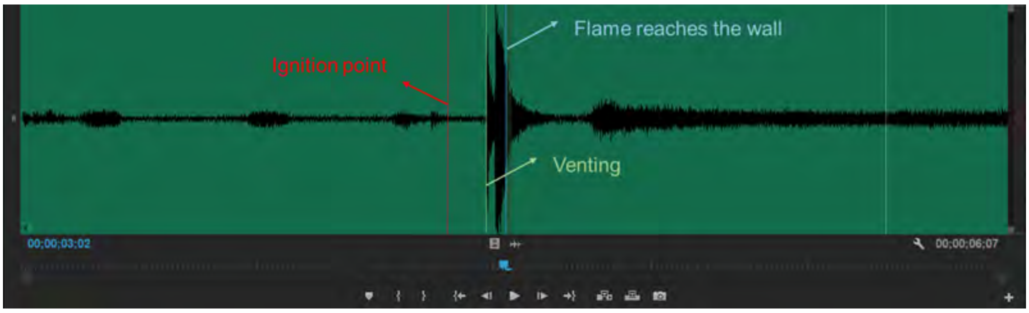


Figure 20: Audio of 14.8% Test

As seen above, the burst disc starts slow venting (the first peak marked “venting”) before the flame reaches the vessel walls, but this has been found

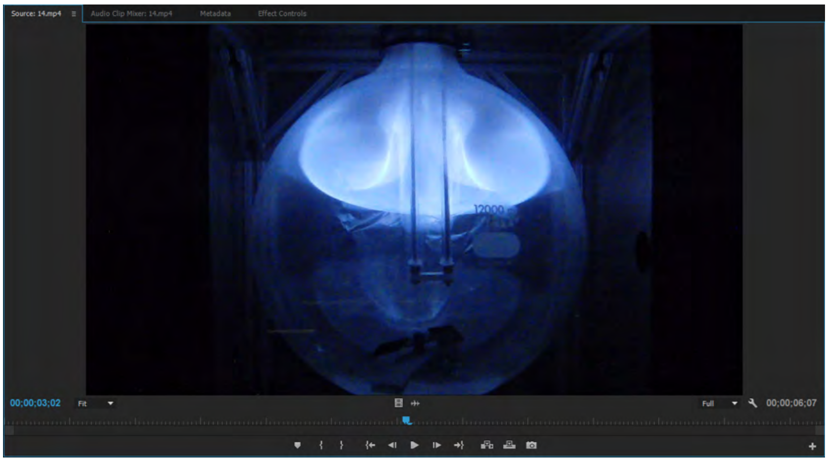


Figure 21: Flame of 14.8% Test

Concentration (%)	Frame Difference	Venting Time Difference (ms)
14.5	4	33.3
14.8	2	16.7

Table 4: Burst Disc Venting Time

not to affect flame structure. Immediately after the flame reaches the vessel walls, the burst disc breaks open and vent completely shown as the largest peak in the audio file. In Table 4 are the time differences for the two tests with analyzed audio.

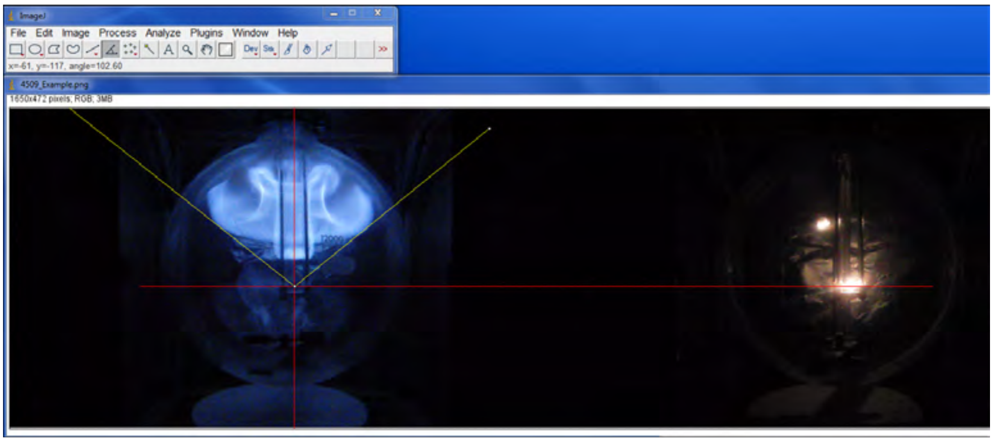
Comparing the venting time difference, the Burst Disc is able to vent as rapidly as the rubber stopper. The time difference is equal. This presents further proof that the burst disc is a reliable alternative to the rubber stopper.

4.5 Direct Flame Angle Measurement

As an alternative to the simple 90 ° assessment with binary “Flammable” or “Nonflammable” checks, a method to measure the flame angle was developed and carried out. A summary of the method is given below:

1. Identify the frame when the flame front has reached the vessel walls
2. Arrange the frame of interest next to the ignition frame to determine ignition point.
3. Using ImageJ software, draw an angle and adjust it until:
    (a) Its apex is at the ignition point
    (b) The left arm is tangent to the left edge of the frame front
    (c) The right arm is tangent to the right edge of the frame front
4. Record the degrees of the angle given by the ImageJ software
5. Repeat 10 times for each test
6. Calculate the average of the 10 measurements

Figures 22 and 23 show examples of the new method.



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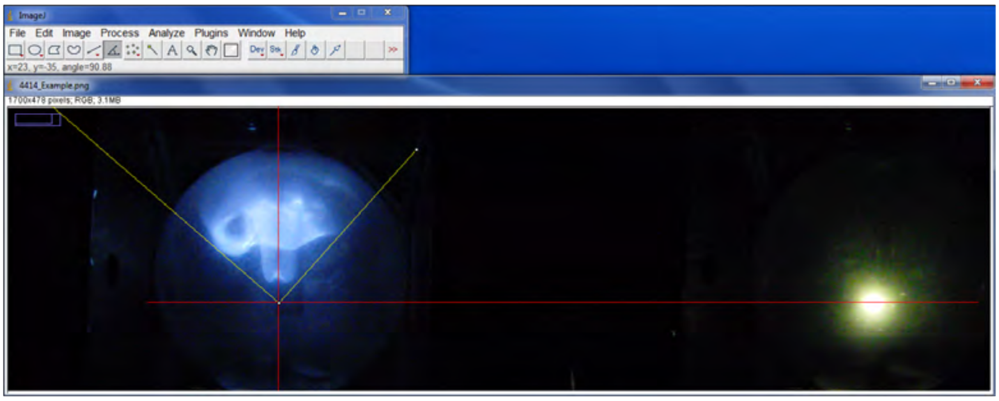
x=-61, y=-117, angle=102.60
1650x472 pixels; RGB; 3MB
```

Figure 22: Direct Angle Measurement for a Flame with the Burst Disc (14.3%)



```
x=23, y=-35, angle=90.88
1700x478 pixels; RGB; 3.1MB
```

Figure 23: Direct Angle Measurement for an Asymmetric Flame with the Stopper (14.9%)

Figure 24 shows the results of the direct flame angle measurement. The markers correspond to the raw data for both the stopper and burst disc. A dashed line at 90 ° shows graphically the criteria for flammability used by ASHRAE. A linear fit (shown as a solid line) was made. Flame angle appears to linearly increase with increasing fuel concentration which is in agreement with test observations.

However, it is important to recall that flame angles should eventually decrease because of the existence of the UFL, past which the mixture is no longer flammable. Thus perhaps a quadratic would better fit the data since the behavior should be close to parabolic when the entire flammable range is considered. Further data is needed before quadratic fitting can be accomplished.

Also plotted are the lines that define the confidence intervals. Using the linear fit and the confidence interval, an LFL of $14.74 \pm 0.12\%$ is reported with 95% confidence using this new method.

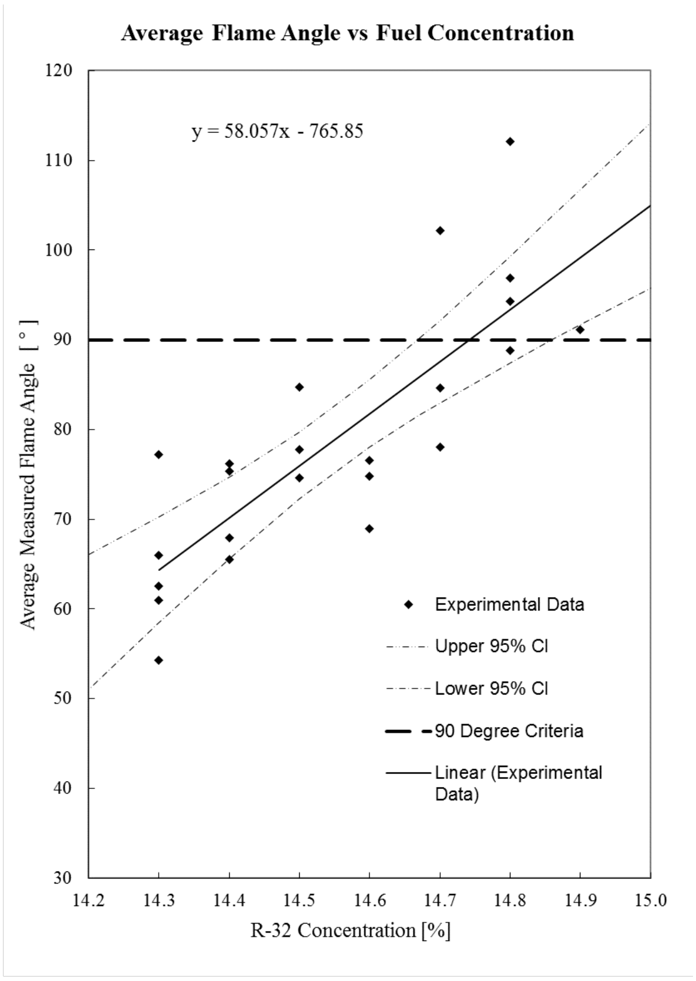


Figure 24: Results of Measured Flame Angles

4.6 Discussion

From the feedback in the interviews and our testing experience with the ASTM E681 standard, a number of limitations of the rubber stopper have been identified.

Use of the rubber stopper can lead to hazardous situations. The rubber stopper – even for mildly flammable substances – can eject violently, potentially damaging the electrodes. The rubber stopper may also re-seal, trapping the gas which can result in re-ignition. Re-sealing can also mean serious etching of the glass flask, the most expensive part of the apparatus.

Additionally, the rubber stopper can interfere with the assessment of flammability. When close to atmospheric pressures, the stopper is known to leak, which can affect the composition of the mixture, ruining the test. The rubber stopper also can tilt, leading to asymmetric flames or patches of flames which interfere with flame angle interpretation.

The burst disc is a viable solution to the problems posed by the rubber stopper. It can hold a vacuum as well as the rubber stopper and even reach a vacuum in a shorter period of time. The burst disc does not leak when close to, and even above atmospheric. Tilting and re-sealing is impossible with the burst disc. The burst disc vents at a consistent pressure. Additionally, the burst disc would allow for testing in other orientations. The rubber stopper requires that the flask is kept upright because it is secured by gravity, but the burst disc does not need this support. Also, the burst disc allows for the use of audio analysis because of its audible pop. All in all, the burst disc makes flammability testing more reproducible.

Finally, direct flame angle measurement is a more objective way of assessing flammability instead of a simple “Flammable” or “Nonflammable”. This new method of assessing flammability should be included in the ASTM E681 standard because it will help address the variable of operator judgment that occurs when using the 90 ° criteria.

5 Conclusions

Venting effects on flammability limits were identified as a variable not yet addressed in research. The greatest variable affecting venting is the rubber stopper of the ASTM E681 apparatus. Limitations of the rubber stopper have been identified. In response to these limitations, a burst disc was developed. The burst disc has been shown to meet the leakage and vacuum requirements, reaching below -100 kPa in less than 3 minutes and having a leakage rate of only 0.0062 kPa/min. The burst disc also provides great consistency in venting after being found to puncture at 7 kPa for multiple trials. The burst disc avoids the complications discussed in the interviews such as re-sealing, tilting, and leaking. The flames obtained during flammability testing with the burst disc have less instabilities than those obtained from the rubber stopper, which is critical for flammability assessment using a visual criteria. Needless to say, the burst disc meets all the current requirements of the rubber stopper and exceeds the performance of the rubber stopper in many ways. An LFL of 14.8% for R-32 was obtained using the rubber stopper and an LFL of 14.7% was obtained using the burst disc. However, the investigation into the burst disc and venting effects has only just begun. There remain many variables to couple with the burst disc such as temperature, humidity, testing at UFL instead of LFL and other refrigerants and refrigerant blends. Additionally, simulations could help better understand the physics of the flow during venting. The burst disc has great potential in flammability testing and should become part of the standard test method.

Finally, a new method of direct flame angle measurement for assessing flammability is presented. Direct flame angle measurement will result in more objective assessment of flammability than the traditional binary decision, leading to more reproducible results. An LFL of $14.74 \pm 0.12\%$ for R-32 is found when using data fitting with the new method.

A Appendix: Design Drawings for Burst Disc

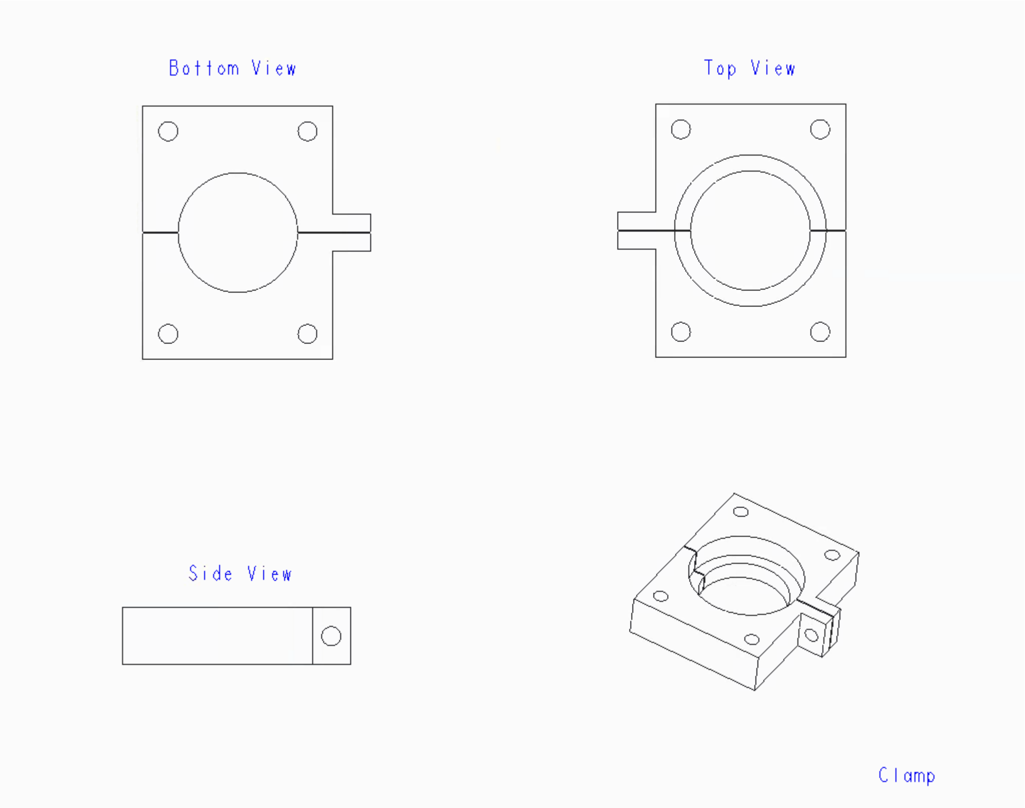


Figure 25: Flask Neck Clamp Drawing

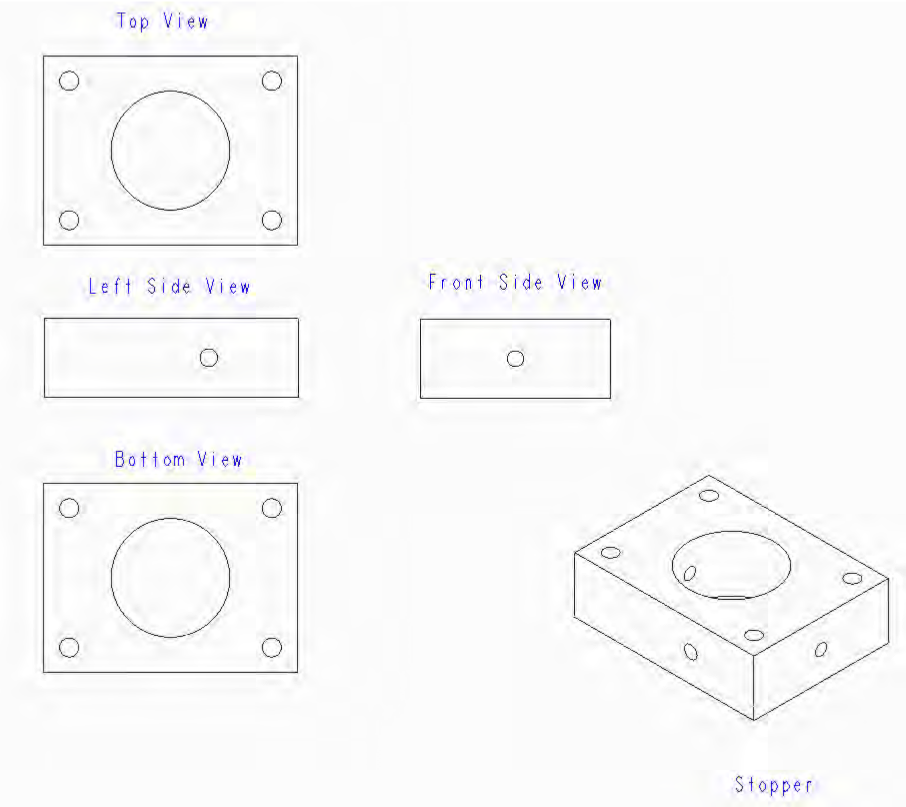


Figure 26: Nylon Block Drawing

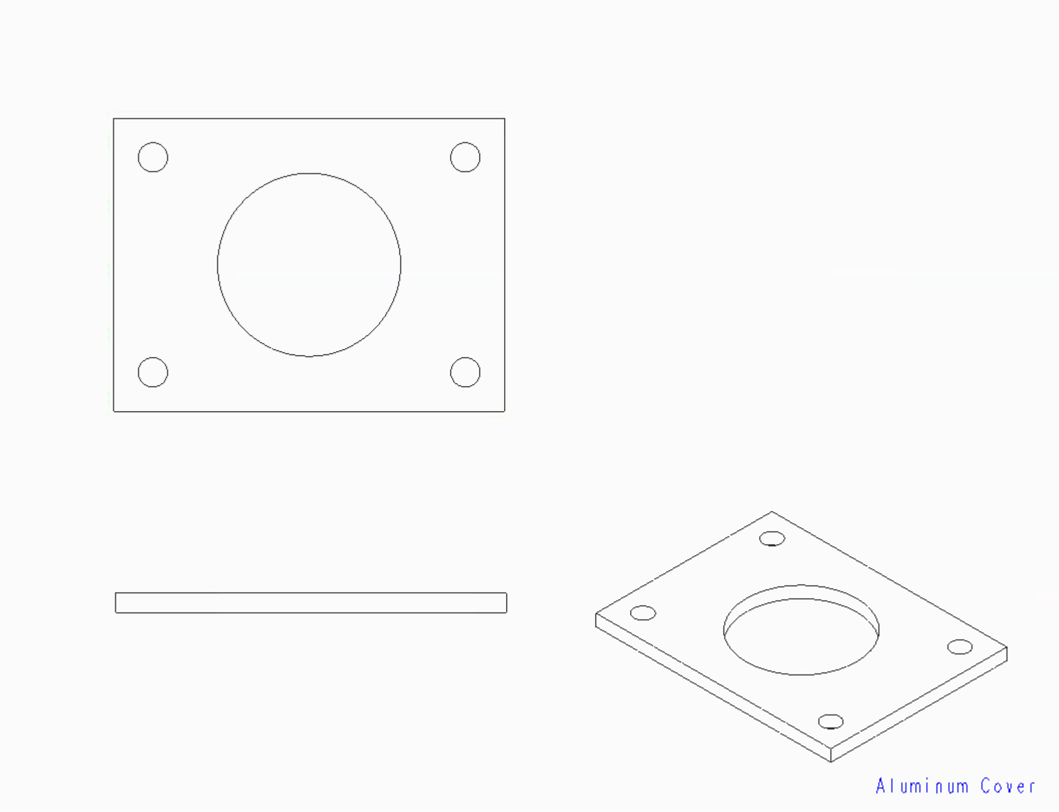


Figure 27: Cover Plate Drawing

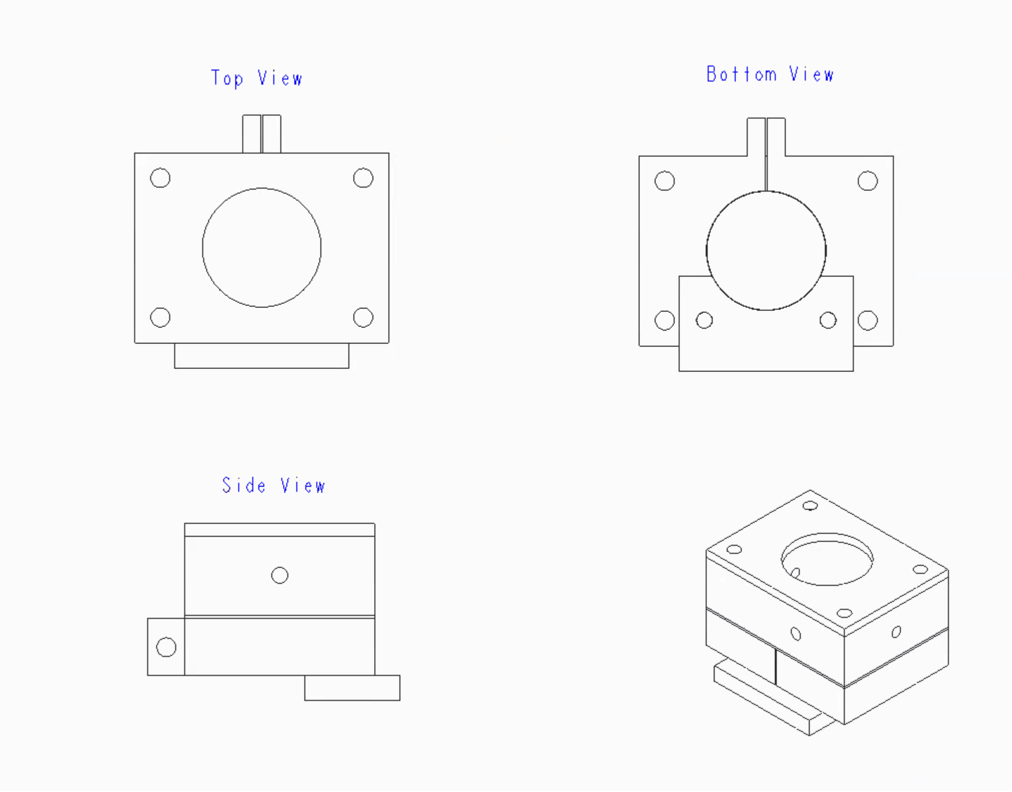


Figure 28: Assembled Burst Disc

B Appendix: Supplementary Flame Images

Figure 29: 14.3% Test with stopper

Figure 30: 14.4% Test with stopper

Figure 31: 14.4% Test with stopper

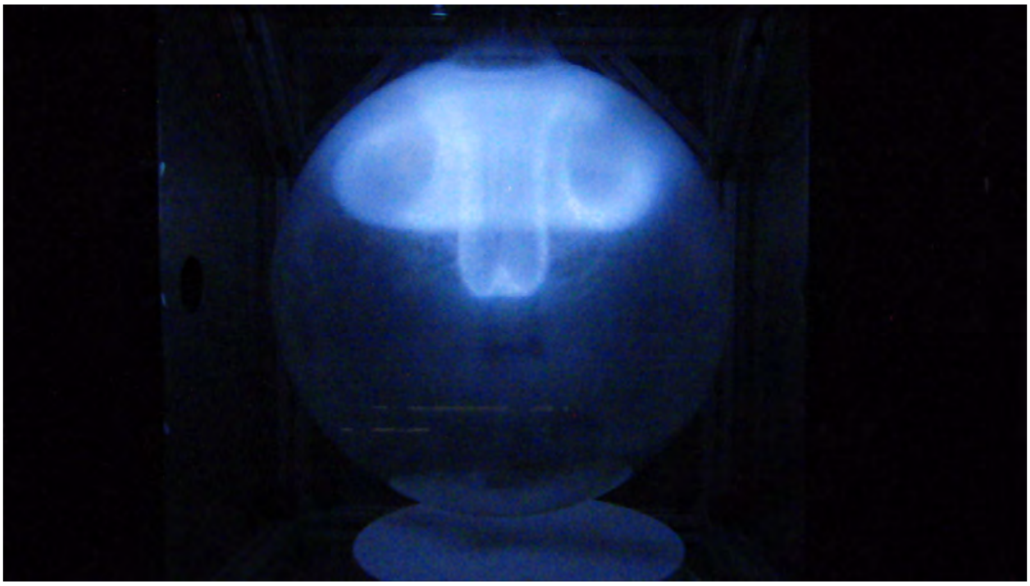


Figure 32: 14.8% Test with stopper

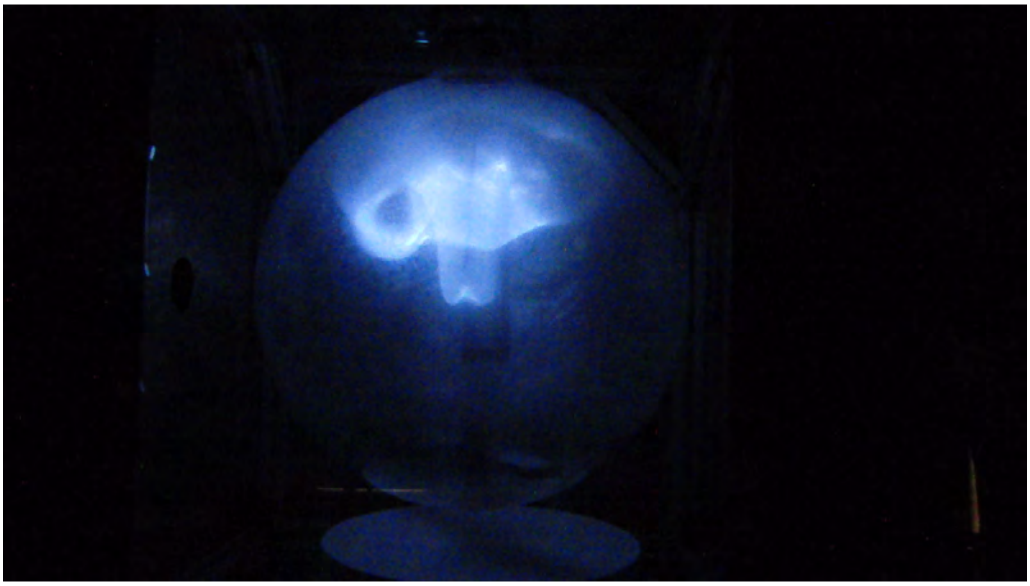


Figure 33: 14.9% Test with stopper

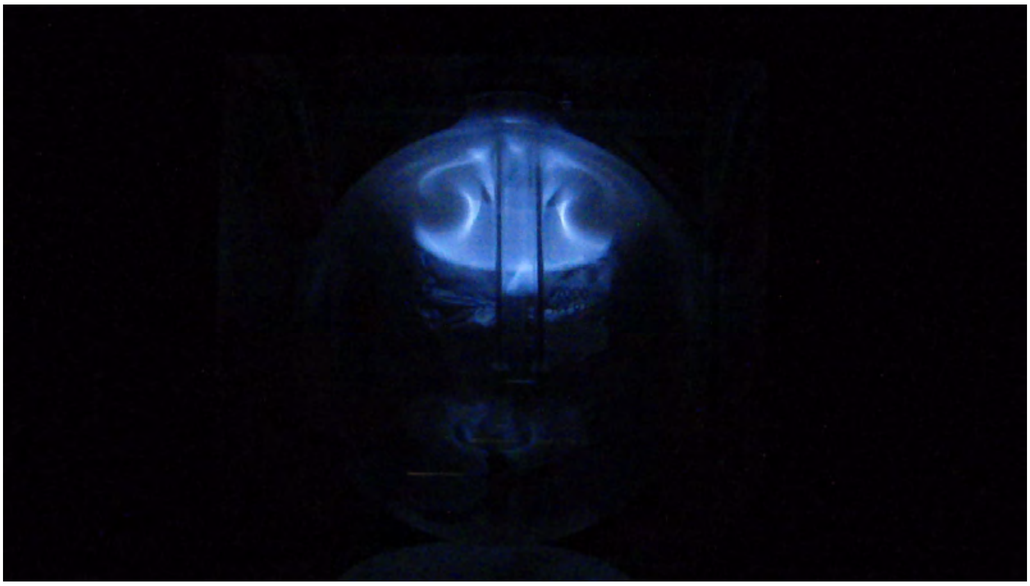


Figure 34: 14.3% Test with burst disc

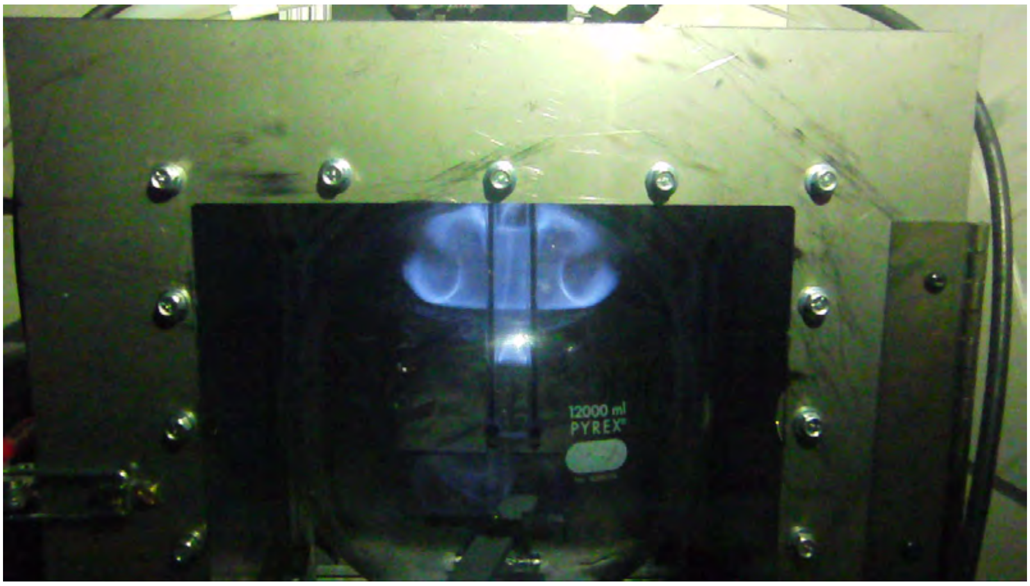


Figure 35: 14.5% Test with burst disc

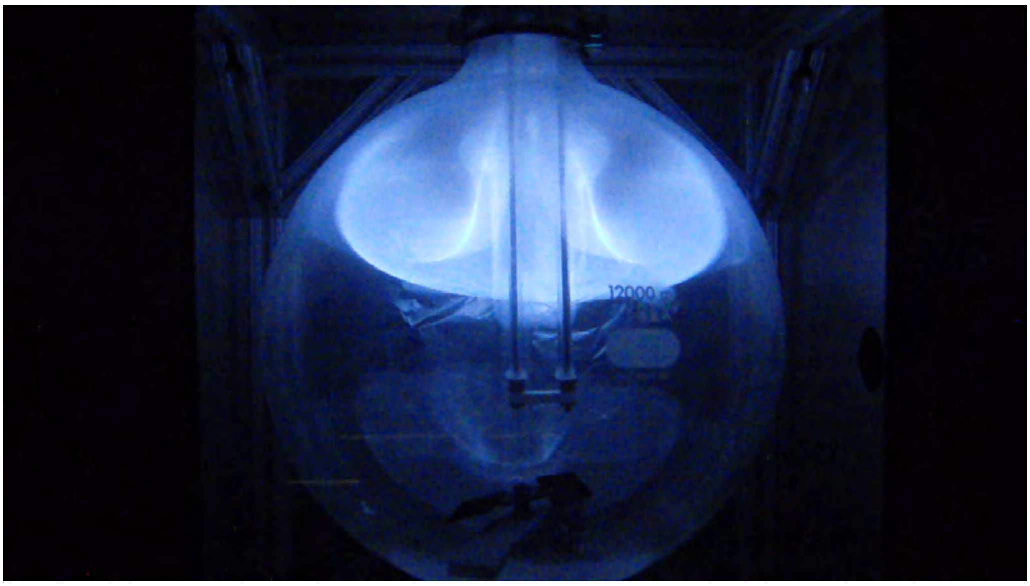


Figure 36: 14.8% Test with burst disc

References

[1] ASHRAE. Standard 34-2013, Designation and Safety Classification of Refrigerants. Technical report, American Society of Heating, Refrigerating and Air-conditioning Engineers., Atlanta, 2013.

[2] Peter Lomax. Development of the astm e681 standard. Master's thesis, University of Maryland, College Park, 8 2016.

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