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Lower Flammability Limit of Difluoromethane and Percolation Theory[1]

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Measurements of flammability limits by the ASTM E 681 method are believed to be affected by vessel size. In order to investigate the effect of volume on measured lower flammability limits in air, experimental measurements of the lower flammability limit of difluoromethane (R-32) are made at 21°C using 3, 5, 12, and 20 L vessels. A spark ignition source is used with the voltage adjusted to the value where dielectric breakdown just begins to occur (approximately 7–12 kV). The results demonstrated a higher concentration for the lower flammability limit for the vessels smaller than 5 L suggesting that wall effects quench the flame propagation. The lower flammability limit for vessels with a 5 L or greater volume are in good agreement with those obtained in earlier investigations. For 5 L and larger vessels the lower flammability limits systematically shift to higher concentrations of difluoromethane with increasing vessel size which is consistent with a percolation model for spatial flame propagation. Extrapolation of the data to infinite vessel size using a percolation model yielded a lower flammability limit of 15.2 vol.%. The results are consistent with the work of Richard for refrigerant mixtures, R134a/R152a and R125/R152a, in large volume vessels (200 L) where effects of vessel walls are negligible.

KEY WORDS: ASTM E 681 method; difluoromethane; flammability; percolation theory; R-32.

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1. INTRODUCTION

The need to replace nonflammable chlorofluorocarbon refrigerants for protection of stratospheric ozone has raised concern about flammability of proposed alternatives. Generally if the sum of the number of C–C bonds and C–H bonds in a hydrofluorocarbon (HFC) refrigerant alternative exceeds the number of C–F bonds, one can expect the proposed refrigerant to be flammable [1]. Marginal flammability, such as is the case for 1, 1, 2, 2, 3 pentafluoropropane (R-245ca), is expected if the number of C–F bonds equals the sum of the number of C–C bonds and C–H bonds [1]. These considerations have increased interest in studying refrigerant flammability in recent years and has resulted in several reviews and investigations of methods used for flammability measurements [2–4].

Vapor flammability is defined as the ability to propagate a flame spatially without limits away from a flame initating source like a spark, hot wire, or small match flame. The lower limit concentration of vapor in air where the onset of flammability begins to occur is called the lower flammability limit and the upper limit concentration of vapor in air where the initiated flame just begins to be extinguished is referred to as the upper flammability limit. A concentration gap between lower and upper flammability limits would mean that the vapor is flammable.

The accepted and most widely used method for experimental studies of flammability is the ASTM E 681 method using an apparatus shown in Fig. 1 [5]. This method contains the vapor–air mixture inside either a 5 or 12 L round bottom flask. The flame is initiated at 1/3 of a diameter from the bottom of the vessel by a spark, hot wire or match flame. The lower flammability limit (LFL) is the lower limit concentration where the flame is propagated upward into a volume above a 45° conical angle measured from a vertical axis whose apex is at the center of the flask. A similar criterion is used to determine the upper flammability limit. The ASTM method also suggests types of ignition sources (spark, hot wire, and match), temperature control of the vapor–air mixture, and moisture content of vapor–air mixture. Nevertheless, recent reviews have noted significant variations [4] in flammability measurements of various workers in different laboratories [2, 3]. Also differences between the ASTM E 681 method and the early measurements of Coward and Jones [6], who studied upward flame propagation in a tube rather than in a round bottom flask, have been noted. In view of the variations in flammability measurements by different laboratories, an ingenious counterflow burner method has recently been developed by Womeldorf and Grosshandler [4] which is very reliable and provides for very accurate and reproducible results.

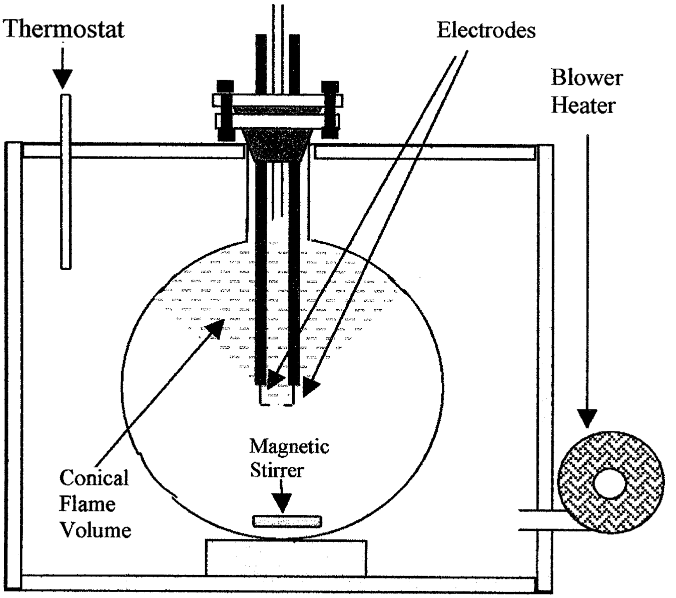

Fig. 1. Sketch of the flammability apparatus.

Nevertheless, the question of how experimental data obtained in a small scale experiment (5 or 12 L flask) will carry over to the appraisal of a fire hazard in real large-scale application remains [2]. In a finite vessel rather than flame propagation proceeding spatially to an infinite range, it is redirected at the vessel walls. The redirection results in a convective velocity field or vortex ring with a mixing action that accelerates the flame. The vortex ring is clearly visible and it gradually settles to the bottom of the vessel until the combustion is complete over a time scale of seconds as compared with the time scale of 0.1–0.2 s for the flame propagation to the vessel wall. Since the convective velocity field has no effect other than to complete the combustion of the contents of the vessel, it is rarely discussed. It occurs subsequent to propagation of the flame front, and for that reason, it is believed it has no effect on flame propagation to the vessel wall. Only the length of upward propagation of the flame front which determines the magnitude of the conical volume of the flame front above the electrodes affects the measured lower flammability limit.

A wall effect that may impact the lower flammability limit is quenching of the flame because the wall serves as a heat sink. This quenching effect can be minimized and hopefully rendered negligible by using flasks of sufficiently large volume so that the quenching effect does not extend from the wall to a significant portion of the interior volume of the flask. Generally lower flammability limit measurements conducted under the same conditions for the two flask sizes used in the ASTM method (5 and 12 L) yield small differences, which is an indicator that quenching effects in the ASTM method are small [2]. Although the effect of quenching is often discussed in the literature, there have been very few reported experiments which are specifically designed to assess the impact of quenching. Therefore, measurements were conducted in this work on the 3 L vessel. The 3 L vessel measurements are expected to have greater contributions from quenching than the 5 or 12 L vessels and would provide additional information to what extent quenching is minimized by increasing vessel volume to 5 L or greater.

If one assumes quenching can be minimized to a point where it is negligible, one would expect an increased lower flammability limit for larger vessels in order to support a flame front that will propagate the greater distances to the wall and into a larger conical volume above the electrodes with a specified conical angle (45° for our measurements). For example, if one attempts to use a concentration equivalent to the lower flammability limit in a 5 L vessel for an experiment with a 12 L vessel, the flame front will either extinguish before reaching the upper wall, or after reaching the upper wall, will subtend a cone of a smaller conical angle than specified (45° in this work).

In a benchmark experiment Richard [7] studied the lower flammability limit of refrigerant mixtures, R134a/R152a and R125/R152a, in very large volume vessels of 200 L, providing a direct measure for effects of flame propagation to a virtually infinite range. He found the lower flammability limit increased by 0.5 mass percent of the flammable component, R152a, (9.6–10.1 mass % for R134a/R152a and 19.0–19.5 mass % for R125/R152a) using the 200 L vessel as compared with the 12 L vessel which is in agreement with expectations.

In this work a percolation theory [8] is proposed to explain the effect of vessel size and the theory is used to extrapolate the lower flammability limit of R-32 to an infinite volume. The refrigerant R-32 is selected for this purpose because it has marginal flammability characteristics (i.e., a high concentration for the lower flammability limit), and the effect of vessel size on the lower flammability limit is greatest for such chemicals. Lower flammability limit measurements are reported for vessel sizes of 3, 5, 12, and 20 L.

2. EXPERIMENTAL METHODS AND RESULTS

The apparatus used for the lower flammability limit measurements is constructed according to the design for the ASTM E 681 method (see Fig. 1). The round bottom flask containing the vapor/air mixture was contained inside an insulated box with a plexiglas door to observe the flask contents as shown in Fig. 1. The temperature could be controlled at temperatures above room temperature using a blower which contained a heating element. The temperature was controlled via a trimmer heater and a thermostat. Often flammability measurements are conducted at both room temperature and at 100°C. However, for purposes of this work, we only report results at room temperature, i.e., 21± 1°C. The temperature was measured with a thermocouple to within ± 0.1°C and the measured temperature was used to calculate the molar concentration of each gas in $\mathrm{mol \cdot m^{-3}}$ from the measured partial pressure.

The electrode assembly was held in place with a rubber stopper which also served to seal the round bottom flask. The stopper also provided entry into the flask for evacuation and introduction of gases at a desired pressure. The pressure was measured with a precision MKS capacitance pressure sensor with an uncertainty of ± 0.1 kPa. The gases, difluoromethane and air, were metered into the flask to a desired pressure via a needle valve. Before introducing gases, the flask was evacuated to about 10^{-4} kPa. After evacuation, there is a 15-minute waiting period to be certain there are no leaks.

The difluoromethane used in the experiments was purchased from PCR with 98 % purity and was used without further purification. Before introduction of gases, water was first introduced into the flask via a septum, using a microsyringe, in order that the relative humidity within the flask would be 50 % when filled with air at 21°C. The R-32 vapor is then introduced into the flask to its desired pressure (ranging from 14.3 to 16.0 kPa). Lastly dry air was then introduced into the flask until the pressure was adjusted to 99 ± 0.4 kPa. Although the variation in final total pressure was ± 0.4 kPa, the uncertainty in the final pressure measurement was ± 0.2 kPa. The magnetic stirrer was turned on to mix the flask contents for about 5 min.

To initiate the flame with a spark, a DEL high voltage power supply is used that is capable of providing voltages up to 20 kV with currents as high as 50 mA. However, the flammability experiments were conducted by adjusting the voltage and current so that the electrodes just begin to generate a spark for 0.2–0.4 s across the electrode gap of 6.4 mm. The voltage ranged from 7 to 12 kV depending mostly on the flask size, the larger flask size requiring the greater voltage. The current was set to 10 mA for all measurements. The observed variation in dielectric breakdown voltage (1.1–$1.9\ \mathrm{kV \cdot mm^{-1}}$) is not unexpected and the range of variation is within that reported for dielectric breakdown voltage of dry air (0.4–$3\ \mathrm{kV \cdot mm^{-1}}$) in the 81st Ed. of the *Handbook of Chemistry and*

Physics [9]. A plausible explanation for variation of voltage with vessel volume is that trace concentrations of suspended particulate matter and free electrons (tend to decrease dielectric breakdown voltage [9]) increases with the increased surface-to-volume ratio for the smaller vessels.

We achieved excellent reproducibility and a very precisely defined flammability limit (to within 0.1 kPa) by this procedure. The ASTM E 681 method calls for 15 kV at 30 mA. However, this would put a very strong spark in our experiments and would result in considerable energy dissipation in the mixture. This would place a strong perturbation on the system, and ideally application of percolation theory would call for a negligible perturbation on the system by the flame initiator.

The flask and its contents were videotaped during the experiment with a Canon video camera, and the tape could be replayed in slow motion with a VHS player. We began with a mixture concentration that was just below the flammability limit. We checked it for flammability by generating a spark. We would add R-32 to the mixture until the flame front would propagate to the upper wall filling the conical volume generated by rotation of a 45° conical angle as illustrated in Fig. 1. We would then evacuate the flask and recharge it with the same partial pressure of R-32 and enough air to produce a total pressure of 99 kPa with an uncertainty of ± 0.4 kPa and determine if the flame propagation is reproduced. We found that the pressure or concentration of flammable component tbat produced the onset of flame propagation was very reproducible to within about 0.5 % excepting for the 3 L flask where the standard deviation is somewhat larger, being 1.3 %. The higher standard deviation for measurements with the 3 L vessel reflects the greater difficulty in reproducing ignition. This is believed to be due to the greater impact of quenching by the vessel walls in the smaller 3 L vessel. The results for the lower limit flammability are presented in units of $\mathrm{mol} \cdot \mathrm{m}^{-3}$ and volume percent for four flask sizes; with nominal volumes of 3, 5, 12, and 20 L in Table I. The estimated percent standard deviation is also given in the last column of Table I.

The lower flammability limit for the 3 L flask is much higher (about 8.5 % higher) than for the larger flasks, indicating quenching had a significantly greater impact on the measurements with the 3 L vessel. The data imply that quenching effects on the measurements decrease rapidly with volume in going from 3 to 5 L vessel. The much smaller change in the lower flammability limit measurement in going from the 5 to 12 L vessel (about 1.8 % increase) and 12–20 L vessel (about 0.95 % increase) would suggest that quenching effects are small for vessel volumes of 5 L or greater. A further indication that quenching is not dominant with vessel volumes of 5 L or greater is that the increase in the lower flammability

Table I. Lower Flammability Limit Expressed as vol.% and mol$\cdot$m^{-3} for Various Flask Sizes

Volume (L)	Flask radius (cm)	T (°C)	Flammability (mol$\cdot$m^{-3})	Flammability limit (vol. %)	Std. Dev. (%)
3.28	9.22	22.1	6.41	15.70	1.30
5.26	10.79	20.3	5.95	14.47	0.14
12.80	14.51	21.0	6.02	14.73	0.45
21.35	17.21	22.1	6.05	14.87	0.45

limit is opposite in direction to what one would expect from quenching. It is consistent with expectations for the effects of propagation of the flame front and the result of Richard [7] who found for R134a/R152a and R125/R152a mixtures that the lower flammability limit increased by 0.5 mass % of R152a for a 200 L vessel as compared with a 12 L vessel. We would further add that even though the 1.8 % increase and 0.95 % increase are small, the data are sufficiently accurate to establish this trend based on their standard deviations of 0.14%, 0.45% and 0.45% for the measurements with vessel volumes of 5, 12, and 20 L, respectively. It is apparent from the data that one must use 5 L flasks and larger before vessel wall effects that quench flame propagation are no longer dominant and perhaps insignificant. This is consistent with the choice of vessel volumes by the ASTM method.

The results for the lower flammability limit from earlier work vary from 11.5 to 15 vol. % (See Ref. 4 for a review of results of earlier workers). For the 5 L flask our results (14.47 %) agree very well with the hot-wire ignition source 5 L flask results of Richard and Shankland (14.2 %) [2] and Dekleva et al. (14.5 %) [3]. Good agreement for the 5 L flask is also obtained with the very recent results of Womeldorf and Grosshandler [4] (14.1 % after conversion from equivalence ratios to vol. %) who used the counterflow method [4]. Generally our results yield a higher vol. % for the flammability limit than earlier work in which match flame ignition sources were used (Ref. 2 (12.7 %) and Ref. 3 (13.9 %)).

3. PERCOLATION THEORY AND FLAMMABILITY MEASUREMENTS

Propagation of flammability may be viewed as energy release at an initiation site that produces combustion at neighboring sites. The neighboring sites now become new initiation sites for continued propagation of the flame front. Since this process generates numerous pathways for the propagation of the flame throughout an entire volume, a statistical model for generating these pathways provides a starting point for a theory of flammability. Percolation is such a statistical model and percolation theory provides mathematical relations for a network of pathways on a lattice that are generated by a statistical model [8]. The advantage of this theory is that it leads to exponential scaling relations in which the exponents obey the Principle of Universality, i.e., have 'universal' values that are independent of details of the lattice model and depend at most on the dimension or symmetry of the system [8]. Therefore, the exponents can be calculated from a very simple lattice model that reflects the dimension and symmetry (symmetry distinguishes between directed or isotropic percolation) of the system, without explicitly identifying the lattice model with flame propagation or incorporating the complexities of the flame propagation mechanism into the model. The other parameter of the theory, which is a prefactor to the exponential scaling and is dependent on the details of the lattice model, i.e., the mechanism for flame propagation, may then be obtained empirically.

For the fundamentals of percolation theory the reader is referred to the text by Stauffer [8]. Percolation is best illustrated by considering a point lattice and picturing a fraction, p, of randomly selected points to be occupied. Connected clusters of points will be generated by connecting nearest-neighbor occupied points with a bond. In application to flammability theory, the connected clusters of points can represent a network of pathways for flame propagation throughout a volume that is occupied by the cluster. The value of p where the cluster size just begins to grow rapidly to infinite is referred to as the percolation limit. In application to flammability it would be proportional to the lower flammability limit.

The percolation limit as defined above is for propagation throughout an infinite volume, and for application to flammability measurements, we must develop a theory for finite volume. For such applications the vessel size determines the cluster size that would provide for flame propagation throughout the vessel. The smaller is the vessel, the smaller is the cluster. The density of occupied sites that produces the finite cluster size that corresponds to the vessel size is referred to as the effective percolation limit, p_{eff}. The effective percolation limit is related to the infinite volume percolation limit, p_{c}, by the power law,

$$p_{\mathrm{c}} - p_{\mathrm{eff}} \propto L^{-(1/\nu)}, \tag{1}$$

where L is the length of one dimension of the system. The quantity, ν, is an example of a power law exponent which according to percolation theory is postulated to obey universality principles [8], i.e., is independent of the lattice details or physical processes that are involved and is dependent at most on the dimension and symmetry of the system. The parameter, ν, is the power law index for the correlation length, and its value has been calculated to be 4/3 for an isotropic two-dimensional system and 0.9 for an isotropic three-dimensional system [8].

The fraction of occupied sites may be regarded as proportional to the molar concentration, ρ, of a real system by a simple change of length scales. Thus, we rewrite the above relation in terms of ρ_{eff} and ρ_{c} as

$$\rho_{\text{eff}} = \rho_{\text{c}} - AL^{-(1/\nu)}, \tag{2}$$

where the change in length scale has been lumped into the proportionality factor A. In modeling flame propagation, ρ_{c} would correspond to the flammability limit for an infinite vessel volume.

In contrast to the exponential parameter, ν, the prefactor A and ρ_{c} are dependent on the lattice and, therefore, would embody the detailed physical and chemical aspects of the percolation process which, in our case, is flame propagation. In this work we evaluate A and ρ_{c} empirically. Theoretical prediction of A and ρ_{c} would require identifying the lattice model with the mechanism for flame propagation in a real system. For example the observed flame propagation is upward suggesting convection contributes to flame propagation. A possible way this may be incorporated into the percolation model is including next nearest–neighbor and higher-order neighbor connectivity as well as nearest neighbor connectivity in selected directions in order to bias the percolation or propagation toward those directions. It is beyond the scope of this work to consider such a lattice analysis to predict A and ρ_{c} and we leave such an analysis for future investigations.

Figure 2 provides a plot of ρ_{eff} versus $L^{-(1/\nu)}$ where we set ν equal to its three dimensional value of 0.9 and L was set equal to the vessel radius. The intercept, $\rho_{\text{c}} = 6.21\ \text{mol} \cdot \text{m}^{-3}$, obtained from a linear least-squares fit represents the flammability limit for an infinite volume. This is equivalent to 15.2 % by volume. We have excluded the result for the 3 L flask from the least-squares calculation because we concluded that the vessel walls have affected the 3 L flask results.

Since the flame propagation is directed upward, the model for flammability is directed percolation rather than isotropic percolation. Consequently the value for ν may be intermediate between the value for three dimensions, 0.9, and the value for two-dimensions, 4/3. Lattice methods for percolation processes can be used to investigate if the three-dimensional value of ν is appropriate and may yield a better value for ν [10]. We would point out that the extrapolation to the infinite volume flammability limit is not very sensitive for variations of ν between its two- and

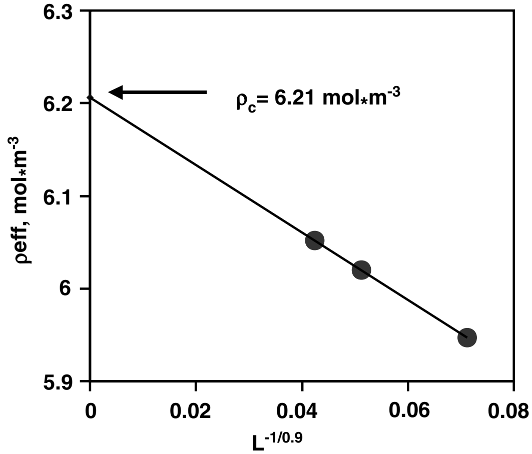

Fig. 2. Plot of the molar density versus $L^{-(1/\nu)}$ for a three-dimensional flame propagation. The length parameter, L, was set equal to the vessel radii. The symbols represent experimental results, and the lines represent results of a linear least-squares fit.

three-dimensional value. Therefore, the extrapolation method should still be useful with the three-dimensional value of v.

4. CONCLUSIONS

The percolation theory is useful to account for volume effects on the lower flammability limit measurements by the ASTM method, for flask volumes of 5 L or more. This is consistent with previous results and is consistent with practice when using the ASTM methods. The volume effect is small for flask volumes of 5 L or more, but nevertheless significant, the infinite volume limit being 15.2 % by volume as compared with 14.47 % by volume for the 5 L flask.

Also in this work we used minimal voltage and current settings to generate a spark, because minimal perturbation on the system to initiate the flame is consistent with the percolation theory approach. However, this should not suggest that minimal current and voltage settings should be preferred over the settings prescribed by the ASTM method where the purpose does not require conformance to theoretical constraints of percolation theory or other theories. If testing of theories or theoretical constraints are not an issue, consistency with other workers and adherence to ASTM requirements should be the primary considerations in choosing current and voltage settings. We would note, however, that the results of this work were in excellent agreement with other workers even though we used minimal values for current and voltage. Nevertheless, the effect of voltage and current settings or an evaluation of optimal current or voltage settings for general applications of the ASTM method were beyond the scope of this work.

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