

Flammability of gas mixtures containing volatile organic compounds and hydrogen

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Abstract

An experimental program was conducted to evaluate the accuracy of some current methods for predicting the flammability of gas mixtures containing hydrogen and flammable or nonflammable volatile organic compounds (VOCs) in air. The specific VOCs tested were toluene, 1,2-dichloroethane, 2-butanone, and carbon tetrachloride. The lower flammability limits (LFLs) of gas mixtures containing equal molar quantities of the components were determined in a 19.4-l laboratory flammability chamber using a strong spark ignition source and a pressure criterion for flammability. All but one of the LFL values for the individual components were in agreement with earlier literature values. However, the LFL of 1,2-dichloroethane was found to be significantly lower than the range of values reported for previous determinations in smaller chambers. Two methods for calculating the LFL of mixtures were considered. The Group Factor (atomic) Contribution Method was determined to be generally more accurate than the LeChatelier Method for estimating the LFL of the gas mixtures reported here, although the LeChatelier Method was usually more conservative. The Group Factor Method predicted higher values (nonconservative) for the LFLs of several mixtures than were experimentally measured. For the case of a mixture of hydrogen and carbon tetrachloride, the Group Method estimation of the LFL was seriously in error. © 2000 Published by Elsevier Science Ltd. All rights reserved.

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1. Background

One requirement regarding the transportation of trans-uranic (TRU) radioactive waste containers currently limits the total concentration of flammable gases and vapors of potentially flammable volatile organic compounds (VOCs) in the headspace of the waste container (Loehr, Djordjevic, Liekhus & Connolly, 1997). Typical VOCs observed in waste drums include aromatic hydrocarbons, ketones, alcohols, and cyclohexane, as well as chlorinated hydrocarbons (alkanes and alkenes). Flammable gases, such as hydrogen and methane, may also be generated in the containers by radiation-induced decomposition (radiolysis) of water and hydrocarbon waste forms. The paucity of experimental flammability data on gas

mixtures containing the constituents observed in TRU waste containers prompted the establishment of an experimental program to determine the lower flammability or explosibility limit (LFL) for such mixtures. As part of a flammability assessment methodology program at the Idaho National Engineering and Environmental Laboratory (INEEL), efforts were also initiated to test the accuracy of current methods used to predict gas mixture flammability.

The experimental part of this program was conducted by NIOSH at the Pittsburgh Research Laboratory (PRL).¹ Benchmark Environmental prescribed the random order for the tests and calculated the LFLs by the two methods. The INEEL coordinated the research and funded the program. All three groups evaluated the data

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¹ The Pittsburgh Research Laboratory was part of the US Bureau of Mines before transferring to the National Institute for Occupational Safety and Health (NIOSH) in October 1996.

and compared the calculations with the experimental results.

2. Experimental design

The experimental design focused on obtaining data from gas mixtures that contained distinctive and representative components in order to determine the effect of compound classes on actual and predicted mixture lower flammability limits (MLFLs). The gaseous constituents expected in a TRU waste container fall into one of three compound classes: flammable VOCs, non-flammable VOCs, and flammable gases. Flammable VOCs were categorized by functional groups and component LFL values. The functional groups considered were aromatic hydrocarbons, ketones, alcohols, and chlorinated alkanes and alkenes. The flammable VOC LFLs considered were divided into three distinct groups designated by LFLs of 0.9–1.3%, 1.4–2.6%, and ~5%. The nonflammable VOCs observed in TRU waste containers consist of highly halogenated VOCs. Hydrogen is the primary flammable gas. Test mixtures for flammability testing were determined based on the following factors:

- the presence or absence of flammable VOCs from one or more of three LFL groups;
- the presence or absence of hydrogen;
- the presence or absence of a nonflammable VOC.

The VOCs selected to represent the compound and flammability classes were chosen based on their relative prevalence in the TRU waste drums (Loehr et al., 1997). The experimental test mixtures consisted of mixtures of hydrogen (H_2) and/or various VOCs in air. The following VOCs were considered: 1,2-dichloroethane (DCE) (representing the class of flammable chlorinated alkanes); 2-butanone or methyl ethyl ketone (MEK) (representing the class of ketones); toluene (Tol) (representing the class of aromatic hydrocarbons); and carbon tetrachloride (CT) (representing nonflammable VOCs).

All VOCs and gases used for these tests were supplied as high purity materials (>99%) by the manufacturers. The cylinders of purified, dried compressed air that were used in the test program were analyzed by gas chromatography and were found to have very low concentrations of organic and carbon monoxide impurities (of the order of parts per million). The oxygen content was also consistent with that of standard dry air (20.96%). The hydrogen (H_2) cylinder used was analyzed at over 99.8% H_2 . The toluene, MEK, DCE, and carbon tetrachloride that were used in the flammability tests were anhydrous, high purity chemicals that had been packaged under nitrogen in sealed glass containers.

2.1. Flammability test equipment

A heavy-walled, stainless steel test chamber (Cashdollar & Hertzberg, 1985) with a volume of 19.4 l was used for the gas mixture flammability tests at the PRL. Cross sections of the test chamber are shown in Fig. 1. (Note that the 16-l air reservoir is not shown to scale.) The test chamber is a nearly spherical vessel made of 13-mm thick stainless steel (type 304) with a pressure rating of 21 bar (300 psi). The chamber has been used extensively for dust and gas explosibility measurements at the PRL. This chamber is considerably larger than the 5-l spherical glass flask specified in the ASTM E-681 vapor flammability test procedure (ASTM, 1999). The larger size of the chamber minimizes wall effects on flammability and allows for the potential use of stronger igniters to ensure the absence of ignition limitations. An appropriate pressure criterion is used to designate flammability rather than the purely visual criterion used in the ASTM method.

The chamber is equipped with viewing ports and access ports for pressure and temperature sensors, electric spark ignition, evacuation, gas admission, and VOC liquid injection. Ignition was attempted using a 41 J stored (capacitor bank) energy spark that was discharged through a high-voltage transformer, and the resulting pressure trace was monitored to determine flammability or nonflammability for each test. A computer-controlled data acquisition system was used to record and display pressure and temperature data versus time. A high-accuracy Baratron² temperature-controlled, capacitance-manometer type pressure transducer was used to measure component pressures during the mixture preparation, and two Viatran strain-gauge type pressure transducers were used to measure system pressures after ignition. Chamber temperature near the top was monitored by a 130- μ m (5-mil) Chromel-Alumel (type K) thermocouple. The above instruments were checked against known standards prior to their use in the flammability tests, and the pressure transducers with built-in calibrations were checked daily. The VOCs were injected as liquids into the chamber through a rubber septum, using a hypodermic syringe.

2.2. Flammability testing procedures

Each VOC was injected as a liquid into the evacuated test chamber in order to ensure complete volatilization. Each test mixture was prepared so that the specified compounds were present in equal molar (equimolar) quantities before being mixed with air. Once the appropriate components were introduced into the chamber and

² Mention of any company name or product does not constitute endorsement by NIOSH.

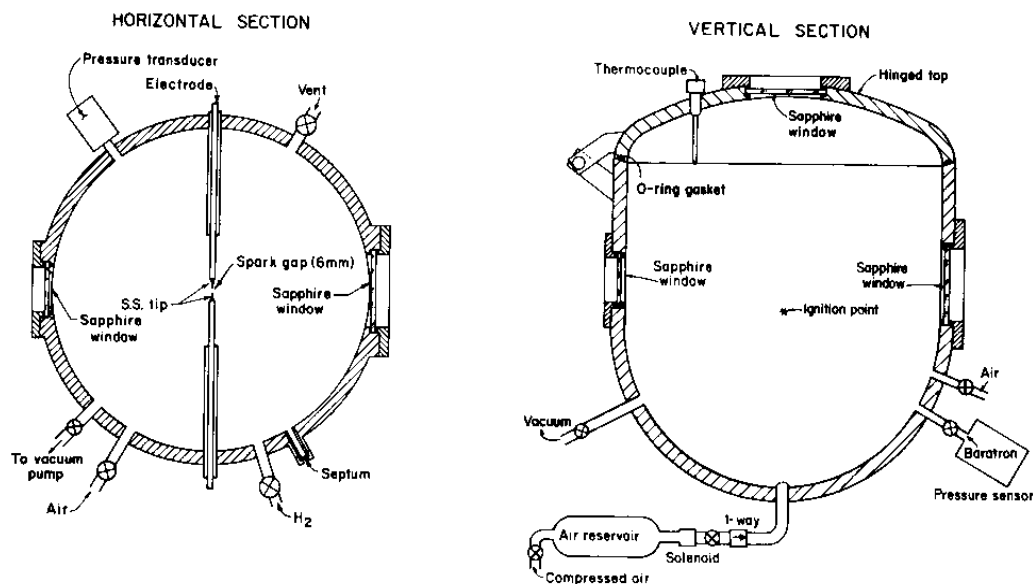


Fig. 1. Flammability test chamber, with horizontal and vertical cross sections.

partial pressures were checked to ensure proper component concentrations, the chamber was brought to atmospheric pressure (~1 bar) using the dry air. The bulk of the air was added rapidly through a solenoid-controlled valve at the bottom of the chamber. The controls were designed to discharge enough air in 0.3 s to bring the chamber from near vacuum to near atmospheric conditions. The objective of this method of air addition was to create adequate turbulence to ensure good mixing of mixture components. Final air addition was made manually through a side port to achieve the desired system pressure, and occurred within 1 min of the initial air blast.

At the start of the daily testing, the chamber was evacuated and the pressure transducers were calibrated. With the vacuum pump isolated from the chamber and shut down, the Baratron pressure reading was monitored for several minutes to confirm the vacuum tightness of the chamber. After recording the initial chamber pressure, the first VOC was metered into the chamber by careful liquid injection to achieve the desired component pressure. It was observed during the addition of MEK that the system pressure slowly decreased due to possible absorption inside the chamber. Therefore, the MEK was injected first and care was taken to insure that the desired steady-state vapor pressure reading was attained before the next component was introduced. This injection was followed by that of the other components in order of increasing volatility. The temperature inside the chamber (after each component addition) was read from the digital thermocouple output meter together with the chamber

pressure reading from the Baratron meter. At the end of each test day, the injection septum was changed and the test chamber was cleaned, sealed, and filled with cylinder air. Additional details of the test chamber, instrumentation, and procedures are in the PRL Final Report to INEEL (Zlochower, Cashdollar & Green, 1997).

Mixture flammability was identified by the pressure rise in the test chamber vessel after the ignition of the gas mixture. The LFLs of individual components were determined and compared with values previously determined at the PRL for hydrogen (Cashdollar, Hertzberg, Zlochower, Lucci, Green & Thomas, 1992) and with the values for VOCs that were reported in the literature (Coward & Jones, 1952; Zabetakis, 1965; Kuchta, 1985). A pressure rise of 3.5% or 0.035 bar (0.5 psi) was chosen as the LFL criterion based on these preliminary tests. This pressure rise criterion produced results for hydrogen (LFL ≈ 5%) that were consistent with earlier data from larger closed systems; this is also the LFL value accepted by the Nuclear Regulatory Commission (NRC 1984, 1996). At this pressure criterion, a rising "fireball" was observed that lingered briefly at the 19.4-l chamber top. The more commonly used pressure rise criterion of 0.07 bar (1 psi) would have resulted in an LFL value of 6% for hydrogen. The choice of criterion produced little effect on the measured mixture LFLs except for hydrogen and some mixtures of H₂ with the halocarbons. A more conservative limit is thereby produced for the latter mixtures by using the 0.035-bar criterion. The appropriate pressure criterion for identifying flammability is somewhat system specific

(Cashdollar, Zlochower, Green, Thomas & Hertzberg, 1998) and should be based on reproducing the accepted values for well-studied fuels such as methane and hydrogen.

For the flammability limit measurements, the overall test mixture concentrations were varied, starting with an estimated limit concentration, while keeping the components at equal molar concentrations. Subsequent tests were performed to identify at least two flammable and two nonflammable mixture concentrations near the LFL. The experimental pressure rise results versus mixture concentration in air were plotted for each mixture, and the best measured LFL was determined.

3. Experimental flammability data

A total of 31 unique gas mixtures and seven replicate mixtures were tested to assess experimental error. Table 1 lists the relative percentages of the five components for each of these 38 mixtures. In addition, two blank tests (mixtures 32 and 37) were made of just the igniter in air, as a further check on equipment and procedures. The 40 mixtures were tested in a prescribed random order for statistical reliability.

Fig. 2 shows the flammability data for hydrogen (data ▲s for mixture no. 26 in Table 1) compared with the preliminary data (×s) collected during the evaluation of the test procedures. The vertical axis shows the explosion pressure rise in kPa on the left and psi on the right and the horizontal axis shows the fuel (H_2) concentration. There is good agreement between the preliminary and final data sets. This plot shows the gradual increase in explosion pressure with H_2 concentration. This effect has been attributed to the selective diffusion of hydrogen into the flame front (Cashdollar et al., 1998). As discussed previously, the dashed line at a pressure rise of 0.035 bar (0.5 psi) was selected as the pressure criterion for flammability. Using this criterion, the LFL for hydrogen is $5.0 \pm 0.4\%$, based on the data in Fig. 2. It has already been noted that the more commonly used pressure rise criterion of 0.07 bar (1 psi) would correspond to an LFL of 6% for H_2 , based on the data in the figure.

Fig. 3 shows the flammability data for the binary mixture (no. 27 in Table 1) of H_2 with carbon tetrachloride (CT). In this case, the horizontal axis shows the total mixture concentration (H_2 plus CT). For this graph and the following graphs, the total H_2 and VOC concentration is denoted as "fuel", even though the CT is actually nonflammable. This plot shows an even more gradual increase in pressure with concentration. The best estimate of the LFL for this mixture is $10.8 \pm 0.8\%$, i.e. the decimal value is quite uncertain.

Fig. 4 shows the reasonable agreement of the replicate mixtures (mixture numbers 15 and 35) containing H_2 , DCE, and CT, despite the exhibited gradual rise in

Table 1
Experimental mixture lower flammability limits (MLFL)

| Mixture no. ^a | Proportion of compound in mixture on air-free basis (%) ^b | | | | | MLFL (%) ^c |
|--------------------------|--|-----|-----|-------|-----|-----------------------|
| | DCE | MEK | Tol | H_2 | CT | |
| 1 | 20 | 20 | 20 | 20 | 20 | 3.40±0.10 |
| 2 | 100 | 0 | 0 | 0 | 0 | 4.85±0.05 |
| 3 | 50 | 50 | 0 | 0 | 0 | 2.65±0.05 |
| 4 | 33 | 33 | 33 | 0 | 0 | 1.95±0.03 |
| 5 | 25 | 25 | 25 | 25 | 0 | 2.40±0.05 |
| 6 | 33 | 33 | 0 | 33 | 0 | 3.40±0.07 |
| 7 | 25 | 25 | 0 | 25 | 25 | 5.15±0.05 |
| 8 | 33 | 33 | 0 | 0 | 33 | 4.85±0.10 |
| 9 | 25 | 25 | 25 | 0 | 25 | 2.80±0.05 |
| 10 | 50 | 0 | 50 | 0 | 0 | 2.05±0.03 |
| 11 | 33 | 0 | 33 | 0 | 33 | 3.50±0.05 |
| 12 | 33 | 0 | 33 | 33 | 0 | 2.65±0.05 |
| 13 | 25 | 0 | 25 | 25 | 25 | 3.95±0.05 |
| 14 | 50 | 0 | 0 | 50 | 0 | 5.35±0.20 |
| 15 | 33 | 0 | 0 | 33 | 33 | 9.7±0.5 |
| 16 | 50 | 0 | 0 | 0 | 50 | ND |
| 17 | 0 | 100 | 0 | 0 | 0 | 1.95±0.03 |
| 18 | 0 | 50 | 0 | 0 | 50 | 4.65±0.03 |
| 19 | 0 | 50 | 50 | 0 | 0 | 1.45±0.05 |
| 20 | 0 | 50 | 0 | 50 | 0 | 3.15±0.07 |
| 21 | 0 | 25 | 25 | 25 | 25 | 2.90±0.05 |
| 22 | 0 | 0 | 100 | 0 | 0 | 1.20±0.03 |
| 23 | 0 | 0 | 50 | 0 | 50 | 2.90±0.05 |
| 24 | 0 | 0 | 50 | 50 | 0 | 2.05±0.03 |
| 25 | 0 | 0 | 33 | 33 | 33 | 3.65±0.10 |
| 26 | 0 | 0 | 0 | 100 | 0 | 5.0±0.4 |
| 27 | 0 | 0 | 0 | 50 | 50 | 10.8±0.8 |
| 28 | 0 | 33 | 33 | 0 | 33 | 2.45±0.05 |
| 29 | 0 | 33 | 33 | 33 | 0 | 2.00±0.05 |
| 30 | 0 | 33 | 0 | 33 | 33 | 5.20±0.10 |
| 31 | 0 | 0 | 0 | 0 | 100 | NF |
| 33 | 33 | 0 | 33 | 0 | 33 | 3.45±0.10 |
| 34 | 0 | 33 | 33 | 0 | 33 | 2.35±0.05 |
| 35 | 33 | 0 | 0 | 33 | 33 | 10.1±0.5 |
| 36 | 0 | 33 | 0 | 33 | 33 | 5.20±0.07 |
| 38 | 50 | 50 | 0 | 0 | 0 | 2.70±0.05 |
| 39 | 0 | 0 | 50 | 50 | 0 | 2.05±0.03 |
| 40 | 25 | 25 | 25 | 25 | 0 | 2.40±0.10 |

^a Mixture numbers 32 and 37 were blank tests of the igniter in air.

^b DCE is 1,2-dichloroethane; MEK is methyl ethyl ketone or 2-butanone; Tol is toluene; H_2 is hydrogen; and CT is carbon tetrachloride.

^c ND: not determined because vapor condensed; NF: not flammable.

explosion pressure with concentration. The measured LFLs of these mixtures, 9.7 and 10.1% respectively, still agree within the uncertainty in the measurements, as listed in Table 1.

These figures show that pure hydrogen and some hydrogen mixtures have a fairly large uncertainty in LFL values due to the gradual increase of pressure with concentration. These are the mixtures that are dominated by the flammability of the hydrogen component. Other hydrogen-containing mixtures and the VOC mixtures without H_2 show a sharp discontinuity at the flammability boundary, and, therefore, have more well-defined

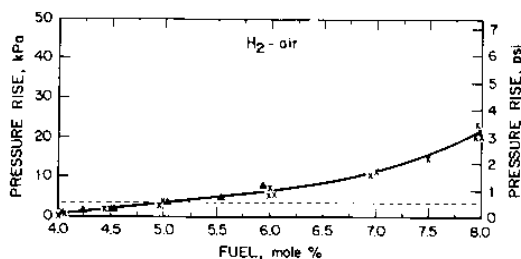


Fig. 2. Hydrogen flammability data, with data ▲ for mixture no. 26 compared to preliminary data ×. The dashed line shows the pressure criterion.

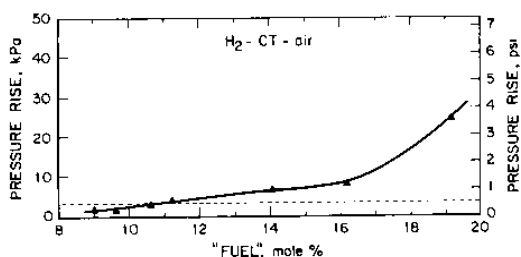


Fig. 3. Flammability data for hydrogen and carbon tetrachloride in air (mixture no. 27).

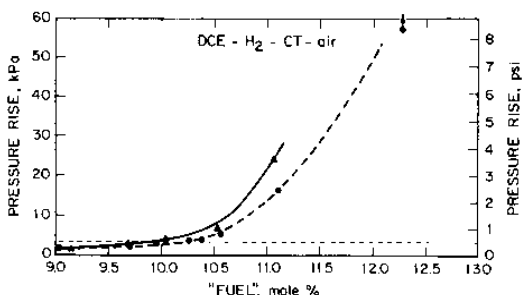


Fig. 4. Flammability data for mixtures of H₂, DCE, and CT in air, with ▲ for mixture no. 15 and ● for mixture no. 35.

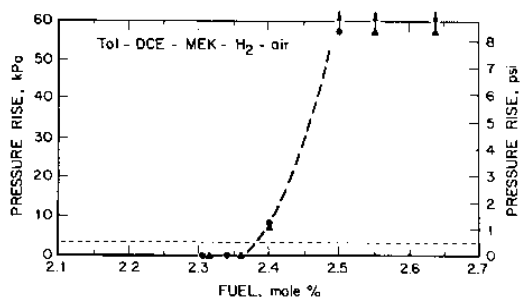


Fig. 5. Flammability data for mixtures of Tol, DCE, MEK, and H₂ in air, with ● for mixture no. 5 and ▲ for mixture no. 40.

LFL values. Fig. 5 (mixture numbers 5 and 40) shows the excellent agreement of the replicate mixtures containing H₂, toluene, MEK, and DCE. In this case, there is a sharp distinction between flammable and nonflam-

mable concentrations, and both mixtures gave a LFL of about 2.4%. This is typical of mixtures that are dominated by the flammability of the VOC components.

Fig. 6 shows the excellent agreement and sharp rise in explosion pressure near 3.5% for mixtures 11 and 33 (Tol, DCE, and CT). The pressure rises from near zero at 3.45% fuel to over 350 kPa at 3.5% fuel. Such pressure rise sensitivity to concentration at the LFL value is characteristic of all the non-hydrogen containing mixtures studied. For both mixtures, the measured LFL is between 3.45 and 3.50% H₂, although the LFL values reported in Table 1 are rounded to the nearest 0.05%.

A summary of the measured MLFL values for these and all the other test mixtures is listed in the last column of Table 1. Note that most of the MLFL values are listed to the nearest 0.05% based on the precision of the measurements, although MLFL values to the nearest 0.1% would be sufficient for most practical uses. The estimated error of the MLFL determinations that is reported in Table 1 is based on the number of data points in the near vicinity of the MLFL value, and how close the data points are to the MLFL. The error listed for the MLFL values in Table 1 is a conservative value. A direct measure of the precision of the MLFL values was determined from the replicate runs for seven mixtures. The greatest deviations between replicate trials were less than 5%.

4. Methods for estimating mixture LFLs (MLFLs)

Given the flammability limits of each of the components in a mixture, the lower flammability limit of the mixture may be calculated by LeChatelier's rule (Kuchta, 1985; LeChatelier, 1891):

$$\text{MLFL} = \frac{100}{\sum \left(\frac{C_i}{\text{LFL}_i} \right)} \quad (1)$$

where MLFL is the mixture lower flammability limit (vol%); C_i is the concentration of component i in the gas mixture on an air-free basis (vol%); and LFL_i is the

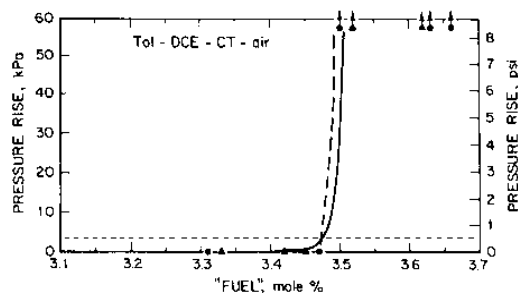


Fig. 6. Flammability data for mixtures of Tol, DCE, and CT in air, with ▲ for mixture no. 11 and ● for mixture no. 33.

lower flammability limit for compound i in the mixture (vol%).

For equimolar mixtures, all values of C_i are equal to $100/N$, where N is the total number of components (other than air). For such mixtures with the nonflammable carbon tetrachloride (CT), $1/LFL_{CT}$ is taken as 0, since the carbon tetrachloride is treated as an inert diluent. Note that for mixtures containing CT, its concentration is included in the C_i values.

The Group Method is based on an extension of a method presented elsewhere (AIChE, 1994). This empirical method predicts the MLFL of a mixture based on the composition of each individual component in the mixture. The LFL values of the individual components are computed by summing the atomic or group contributions to the molecular formula. These atomic or group contributions, in turn, are based on an analysis of experimental LFLs of a large number of compounds.

The MLFL is calculated using the following equation:

$$MLFL = \frac{100}{\sum f_i GCF_i} \quad (2)$$

where MLFL is the mixture lower flammability limit (vol%); f_i is the mole or volume fraction of gas i in the mixture on an air-free basis; and GCF_i is the group contribution factor for compound i .

The group contribution factor for a compound is written as:

$$GCF_i = \sum n_j GF_j \quad (3)$$

where n_j is the number of group type j in compound i ; and GF_j is the group factor for group type j .

Table 2 contains the calculated group factor values for the various groups used to determine the GCF for the compounds of interest. The Group Method (AIChE, 1994) also has additional factors for other elements or groups that may be in compounds beyond those considered in this report. It should be noted that a negative value in Table 2 for an element or group implies a negative contribution to flammability; a negative value for a component or mixture implies nonflammability of that component or mixture. Thus carbon tetrachloride (CCl_4) has a GCF value of -8.42 . The factor for H_2 is not 2×2.17 since the H-H bond is very different from the

Table 2
Group factor values used in Eq. (3)

| Group | Group factor |
|-------|--------------|
| C | 9.10 |
| H | 2.17 |
| H_2 | 20 |
| O | 2.68 |
| Cl | -4.38 |

C-H bonds in organic compounds. Instead, the factor of 20 for H_2 is based directly on the experimental LFL of 5% for hydrogen.

The calculated MLFLs of all the studied mixtures using the LeChatelier and Group Contribution methods are compared with the experimental results in Table 3.

5. Discussion

In order to characterize the accuracy of the two predictive methods, the mean relative percent difference between the calculated MLFLs and the experimental MLFLs was computed. A positive value indicates an overall higher mean value for the calculation method compared to the experimental MLFLs. Therefore, a posi-

Table 3
Predicted mixture lower flammability limits (vol%)*

| Mixture no. | Experimental | LeChatelier | Group |
|-------------|--------------|-------------|--------|
| 1 | 3.40 | 2.85 | 3.09 |
| 2 | 4.85 | 4.85 | 5.52 |
| 3 | 2.65 | 2.78 | 2.89 |
| 4 | 1.95 | 1.95 | 2.02 |
| 5 | 2.40 | 2.28 | 2.35 |
| 6 | 3.40 | 3.30 | 3.40 |
| 7 | 5.15 | 4.35 | 4.95 |
| 8 | 4.85 | 4.21 | 4.99 |
| 9 | 2.80 | 2.58 | 2.82 |
| 10 | 2.05 | 1.92 | 2.02 |
| 11 | 3.50 | 2.92 | 3.34 |
| 12 | 2.65 | 2.44 | 2.54 |
| 13 | 3.95 | 3.23 | 3.61 |
| 14 | 5.35 | 4.92 | 5.25 |
| 15 | 9.7 | 7.46 | 10.20 |
| 16 | ND | 9.70 | 20.62 |
| 17 | 1.95 | 1.95 | 1.96 |
| 18 | 4.65 | 3.90 | 4.69 |
| 19 | 1.45 | 1.49 | 1.51 |
| 20 | 3.15 | 2.81 | 2.81 |
| 21 | 2.90 | 2.59 | 2.78 |
| 22 | 1.20 | 1.20 | 1.23 |
| 23 | 2.90 | 2.40 | 2.75 |
| 24 | 2.05 | 1.94 | 1.98 |
| 25 | 3.65 | 2.93 | 3.27 |
| 26 | 5.0 | 5.00 | 5.00 |
| 27 | 10.8 | 10.00 | 17.27 |
| 28 | 2.45 | 2.25 | 2.45 |
| 29 | 2.00 | 1.96 | 1.99 |
| 30 | 5.20 | 4.25 | 4.84 |
| 31 | NF | NA | -11.88 |
| 33 | 3.45 | 2.92 | 3.34 |
| 34 | 2.35 | 2.25 | 2.45 |
| 35 | 10.1 | 7.46 | 10.20 |
| 36 | 5.20 | 4.25 | 4.84 |
| 38 | 2.70 | 2.78 | 2.89 |
| 39 | 2.05 | 1.94 | 1.98 |
| 40 | 2.40 | 2.28 | 2.35 |

* ND: not determined because vapor condensed; NA: not applicable; NF: not flammable.

tive value indicates a lack of conservativeness and a negative value indicates conservative predictions overall. For the Group Method, the mean relative percent difference (using average of duplicate tests and excluding tests with no measured LFL) was calculated to be +0.8% with a standard deviation of 12.6%. With the LeChatelier Method, the mean relative percent difference is -8.5% with a standard deviation of 7.6%. In addition, the Group Method predicted values closer to experimental values in 20 tests as opposed to seven tests with the LeChatelier Method (excluding duplicate tests).

The LeChatelier Method is thus less accurate but slightly more conservative than the Group Method. It must be noted, however, that the mean value and standard deviation for the Group Method was significantly skewed by the large positive error in predicting the MLFL for the binary gas mixture (no. 27) containing hydrogen and carbon tetrachloride. The mean relative percent difference for the Group Method excluding this one test is -1.3% with a standard deviation of 5.5%. The accuracy of the Group Method using the current (AIChE) atomic parameters suffers from inaccurate values of some group factors due to uncertainties in the experimental LFLs of halogenated compounds. In addition, the Group Method does not work well for mixtures dominated by the flammability of hydrogen, because hydrogen flammability at the LFL is dependent on physical (selective diffusion) as well as chemical processes. In particular, the Group Method predicted a MLFL of 17.27% for the binary gas mixture (no. 27) containing hydrogen and carbon tetrachloride, compared to the experimental MLFL of 10.8%.

The inaccuracy of the LeChatelier Method in predicting the MLFLs of these mixtures can be attributed primarily to the lack of an adequate means of treating the effect of a nonflammable component (such as carbon tetrachloride) that is relatively effective as an inerting agent. The mere elimination of a positive contribution to flammability together with a dilution effect does not do adequate justice to a species such as carbon tetrachloride that is a more effective heat sink than nitrogen and that may even exhibit some chemical interference with flame propagation. The LeChatelier Method, as used here, only treats these nonflammable components as inert diluents, equivalent to nitrogen. The Group Method introduces negative contributions to flammability to treat such effects, and that is why it is more accurate for these mixtures.

The LFLs for the pure components toluene and MEK determined here (mixtures 22 and 17, respectively, in Table 1) were consistent with values reported earlier using flammability tubes (Coward & Jones, 1952; Zabetakis, 1965; Kuchta, 1985). The DCE LFL of 4.85% determined in this study (mixture 2) was considerably less than the reported LFL values of 5.4-6.2% (Coward & Jones, 1952). The variability in the earlier

values is probably a reflection of wall effects and ignition limitations. Most of the earlier determinations were made in US Bureau of Mines type flammability tubes that were 0.05 m in diameter and 1.5 m long (Coward & Jones, 1952). However, it was recognized that this tube diameter, although recommended as the minimum acceptable size, was not adequate for all fuels, particularly halogen-containing fuels such as the chlorohydrocarbons. This new experimental value of 4.85% for DCE was used in the LeChatelier Method calculations in this paper. However, no corrections were made for the Group Method. It is recommended, therefore, that the Group Factor value of Cl in such compounds be redetermined from LFL tests in larger test vessels such as that used in this study. It is anticipated that the Group Contribution Method for estimating MLFLs will then become even more accurate. There will, nonetheless, remain such dynamic factors as relative diffusivity of components in the flame zone that will prevent an accurate estimate of MLFL using the above methods in extreme cases of high and low diffusivity, such as hydrogen-carbon tetrachloride mixtures.

In using either the measured MLFLs or the calculated MLFLs by one of these two methods, a safety factor must be included. NFPA 69 recommends (NFPA, 1997) that the combustible concentration be kept below 25% of the LFL. When this safety factor is taken into consideration, either of the two calculation methods would be acceptable, except for the Group Method for the H₂ and CT mixture. In this case, a factor of four safety level based on the Group calculation is 40% of the actual measured MLFL. The latter safety margin may not be adequate, given sampling uncertainties in actual applications.

6. Conclusions

The LFLs of gas mixtures containing equal molar combinations from the four specified VOCs (2-butanone, toluene, 1,2-dichloroethane, and carbon tetrachloride) and hydrogen were determined in a 19.4-l laboratory flammability chamber using a strong spark ignition source. The LFL of 1,2-dichloroethane was determined to be 4.85% which is significantly below the range of values cited in the literature. The measured LFL values reported here are considered more accurate than the previous literature values since a larger chamber was used in combination with a more energetic spark, and it is known that the halogenated species are prone to exhibiting wall effects and ignition limitations. The LFLs of the other flammable VOCs were within the relatively narrow range of values cited in the literature.

The Group Factor Contribution Method was determined to be generally more accurate than the LeChatelier method for estimating the LFL of the above gas mix-

tures. However, the Group Method fails seriously in estimating the mixture LFL of the binary mixture of hydrogen and carbon tetrachloride. It, therefore, can not be used without correction for this mixture. The current Group Factor value for Cl may also be in error due to problems in previous determinations of the LFLs of halocarbons. More accurate values of the LFLs of such compounds will enable a more accurate calculation of the MLFL of mixtures with halogenated species.

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