PREDICTING FLAMMABILITY OF GAS MIXTURES CONTAINING VOLATILE ORGANIC COMPOUNDS

Kevin Liekhus
Idaho National Engineering and Environmental Laboratory
Idaho Falls, ID 83415

Isaac Zlochower
National Institute for Occupational Safety and Health, Pittsburgh Research Laboratory
Pittsburgh, PA 15236

Sinisa Djordjevic and Cindy Loehr
Benchmark Environmental
Albuquerque, NM 87110

PROCEEDINGS OF THE

International Symposium on Hazards, Prevention, and Mitigation of Industrial Explosions

COLLOQUIUM ON GAS, VAPOR, HYBRID AND FUEL-AIR EXPLOSIONS

Schaumburg, Illinois, 21 – 25 September, 1998

Background

One requirement regarding the transportation of transuranic (TRU) radioactive waste containers currently limits the total concentration of potentially flammable volatile organic compounds (VOCs) and flammable gases in the headspace of the waste container. Typical VOCs observed in the drums include aromatic hydrocarbons, ketones, alcohols, cyclohexane, as well as chlorinated hydrocarbons (alkanes and alkenes). Flammable gases, such as hydrogen and methane, may 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, an effort was also initiated to identify an accurate means for predicting gas mixture flammability.

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 predicting mixture lower flammability limits. The gaseous constituents expected in a TRU waste container fall into one of three compound classes - flammable VOCs, nonflammable VOCs, and flammable gases. Flammable VOCs were categorized by functional groups and pure component LFL. 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 5.6-6.7%. 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:

- Presence or absence of flammable VOCs from one or more of three LFL groups
- Presence or absence of hydrogen
- 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. The experimental test mixtures consisted of hydrogen and the following VOCs: 1,2-dichloroethane (DCA) (flammable chlorinated alkanes); 2-butanone (MEK) (ketones); toluene (aromatic hydrocarbons); and, carbon tetrachloride (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 (on 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 research grade and was analyzed at over 99.8% H_2. The toluene, MEK, DCA, 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 by Aldrich Chemical Co.

Flammability Test Equipment

A heavy-walled, stainless steel test chamber with an approximate volume of 19 L was used for the gas mixture flammability tests. A schematic of the test chamber is shown in Figure 1. The test chamber is a nearly spherical vessel made of 0.013-m thick stainless steel (type 304) with a pressure rating of 21 bar (300 psia). The chamber has been used extensively for dust and gas explosibility measurements at the Pittsburgh Research Center (PRC). This chamber is considerably larger than the 5-L spherical glass flasks specified in the ASTM vapor flammability test procedure[1], but is consistent with the ASTM standard.[2] The larger size of the chamber minimizes wall effects on flammability and allows for the potential use of stronger ignitors to ensure the absence of ignition limitations. An appropriate pressure criterion is used to designate flammability rather than purely visual and subjective criteria.

The chamber is equipped with viewing ports and access ports for pressure and temperature sensors, electronic ignition, evacuation, gas admission, and VOC liquid injection. Ignition was attempted using a 41-joule stored (capacitor bank) energy spark that was discharged through a 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 Baratron temperature-controlled capacitance manometer-type pressure transducer was used to measure component pressures during test 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 Chromel-Alumel (type K) thermocouple. The above instruments were checked against known standards prior to their use in the flammability tests, and pressure transducers with built-in calibrations were checked daily.

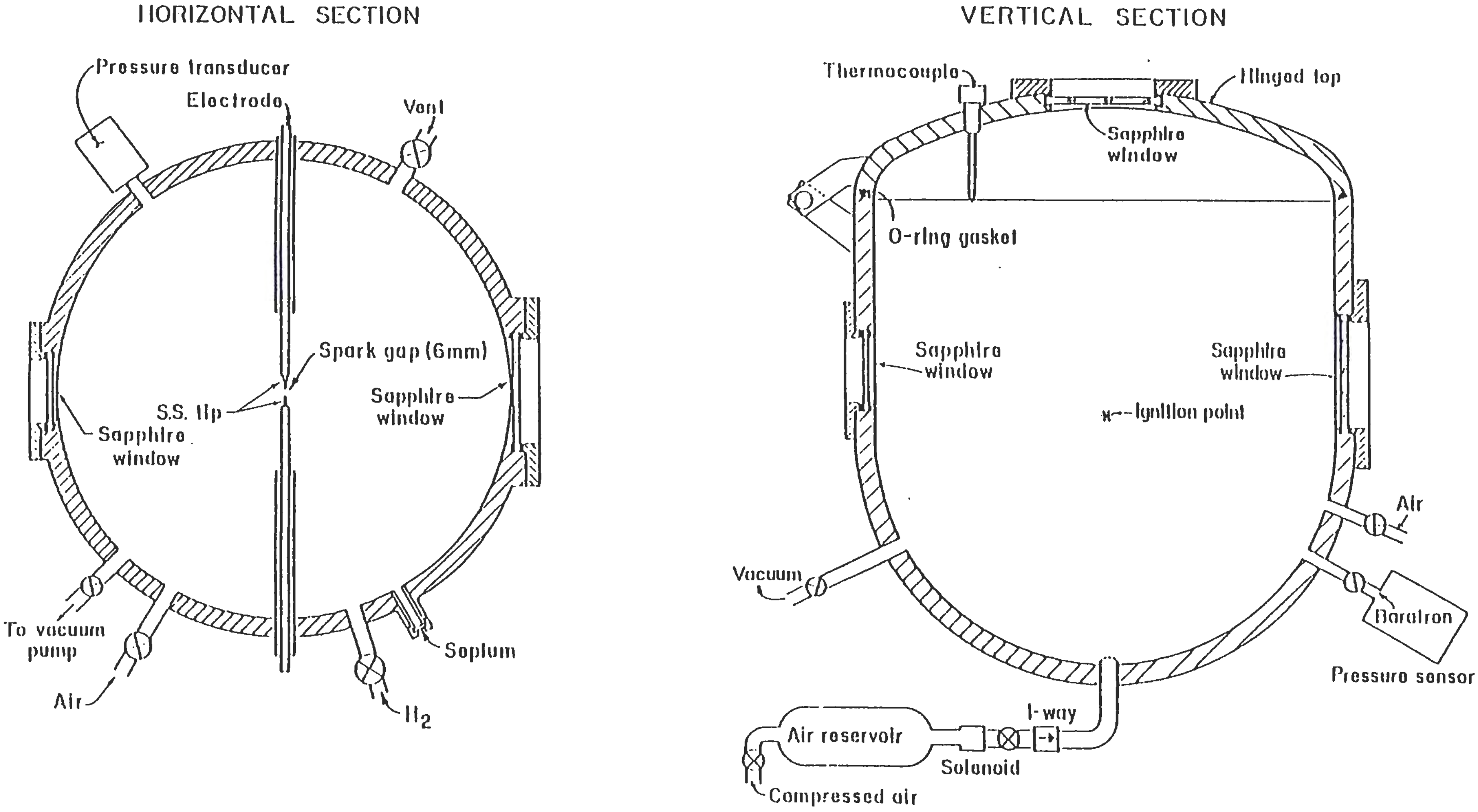

Figure 1. Schematic of 19-L test chamber.

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 equimolar quantities before being mixed with air. Once the appropriate components were introduced into the chamber and 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 first 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 one minute of the initial air blast.

Flammability Testing

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 toluene, DCA, carbon tetrachloride, H_2, and air, in that order. 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 septum was changed and the test chamber was cleaned, sealed, and filled with cylinder air.

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 to values previously determined at the PRC for hydrogen[3] and the values for VOCs that were reported in the literature.[4] Based on preliminary testing, a pressure rise of 0.035 bar (0.5 psi) was chosen as the LFL criterion. Test mixture concentrations were increased in 10% increments, starting with a calculated limit concentration and maintaining the required component ratio, until the chamber pressure increased at least 0.035 bar (0.5 psi) after ignition. After a positive ignition was obtained, subsequent tests were performed to identify at least two additional flammable and nonflammable mixture concentrations both above and below the first composition with positive ignition. These pressure rise results versus mixture composition in air [illegible]ch mixture, and the best estimated LFL was determined to the nearest 0.05%.

Flammability Test Results

A total of 31 unique gas mixtures and seven replicate mixtures were tested to assess experimental error. All tests were performed in a prescribed random order to ensure that experimental errors were properly estimated and not confounded with experimental procedure trends. Figure 2 shows the flammability data for hydrogen. This plot shows the gradual increase in explosion pressure with H_2 concentration. Figure 3 shows the flammability data for the binary mixture of H_2 with carbon tetrachloride. This plot shows an even more gradual increase in pressure with concentration. These figures show that pure hydrogen and some hydrogen

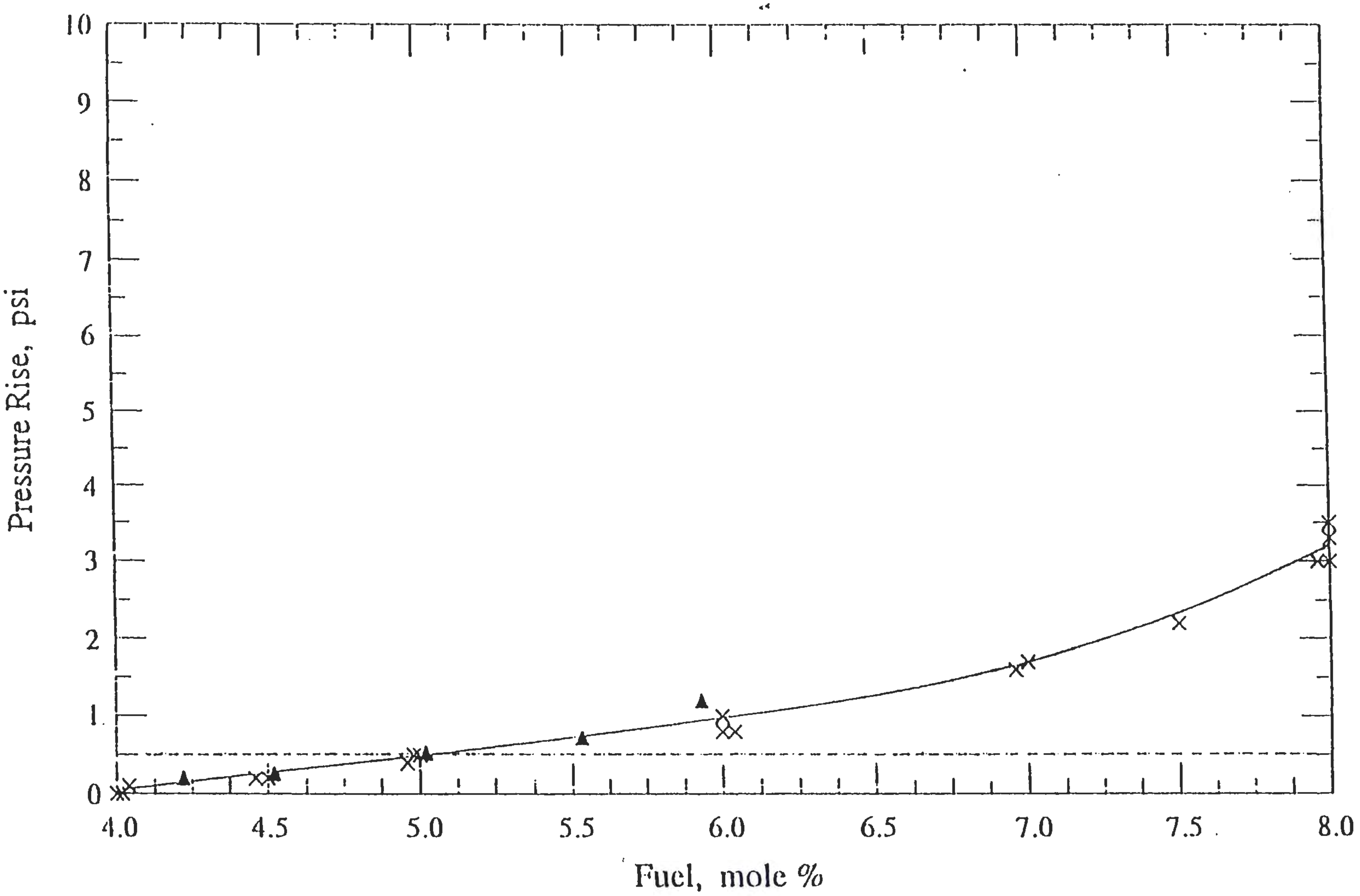

Figure 2. Flammability data for hydrogen.

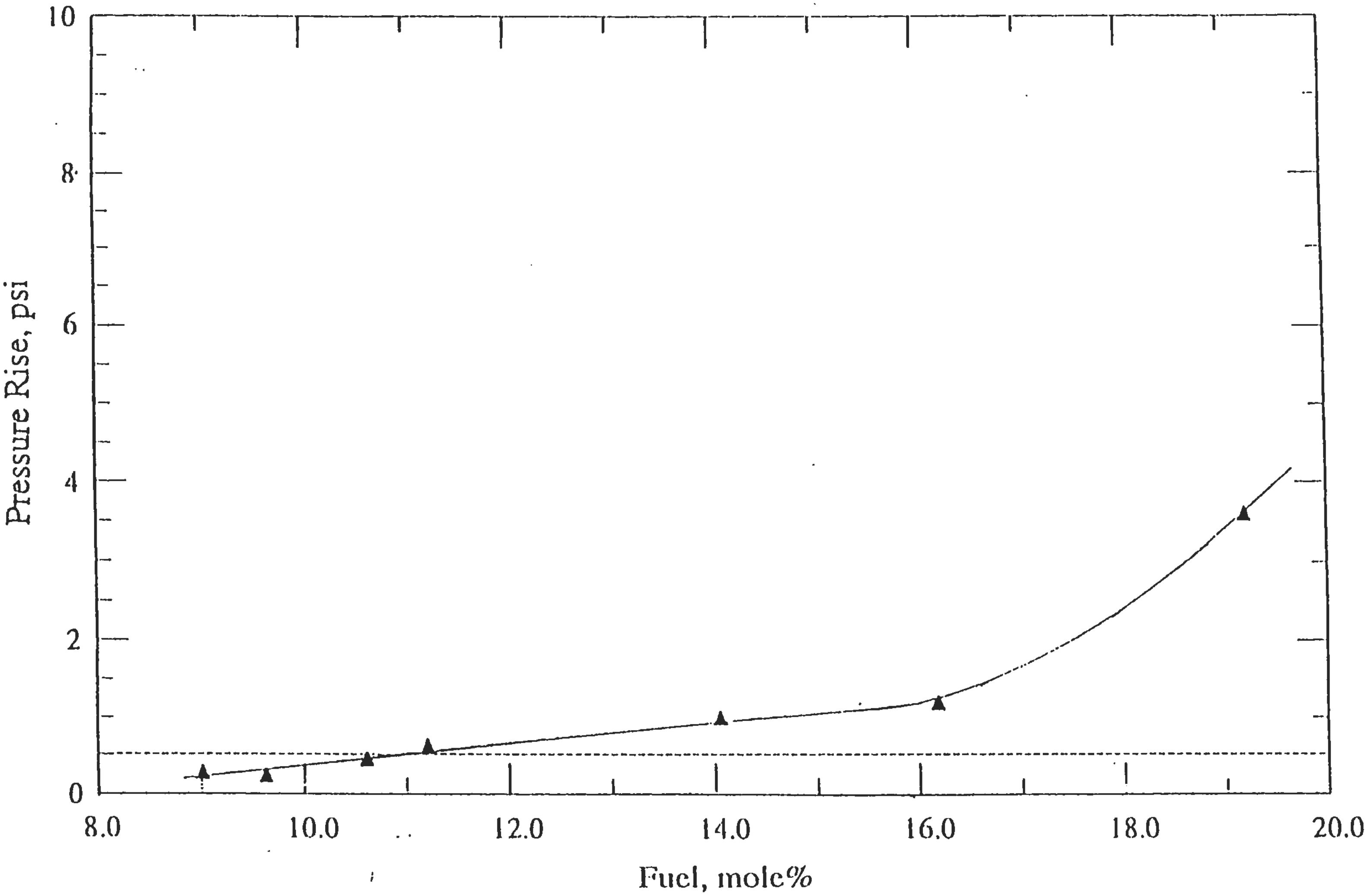

Figure 3. Flammability data for gas mixture containing 50% hydrogen:50% carbon *tetrachloride.*

mixtures have a fairly large uncertainty in LFL values due to the gradual increase of pressure with concentration. Other hydrogen-containing mixtures and the VOC mixtures show a sharp discontinuity at the flammability boundary and therefore have more well-defined LFL values. Figure 4 shows the excellent agreement of the replicate mixtures 13 and 23 containing H_2, toluene, MEK, and DCA. A summary of the measured LFL values for all the test mixtures are listed in Table I.

Methods for Estimating Mixture LFLs (MLFLs)

Given the flammability limits of each of the components in a mixture, the MLFL may be calculated by LeChatelier's rule:[5]

$$MLFL = \frac{100}{\sum\left(\frac{C_i}{LFL_i}\right)} \tag{1}$$

where $MLFL$ = mixture lower flammability limit (vol%)

C_i = concentration of component i in the gas mixture on an air-free basis (vol%)

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

For equimolar mixtures, all values of C_i are equal. For such mixtures with the non-flammable carbon tetrachloride (CCl_4), $1/LFL_{CCl_4}$ is taken as 0, since the CCl_4 is treated as an inert diluent. The Group method is based on an extension of a method presented elsewhere.[6] This method predicts the MLFL of a mixture based on knowledge of the chemical structure of each individual component in the mixture. The LFL values based on the group contribution method are calculated by the following equation:

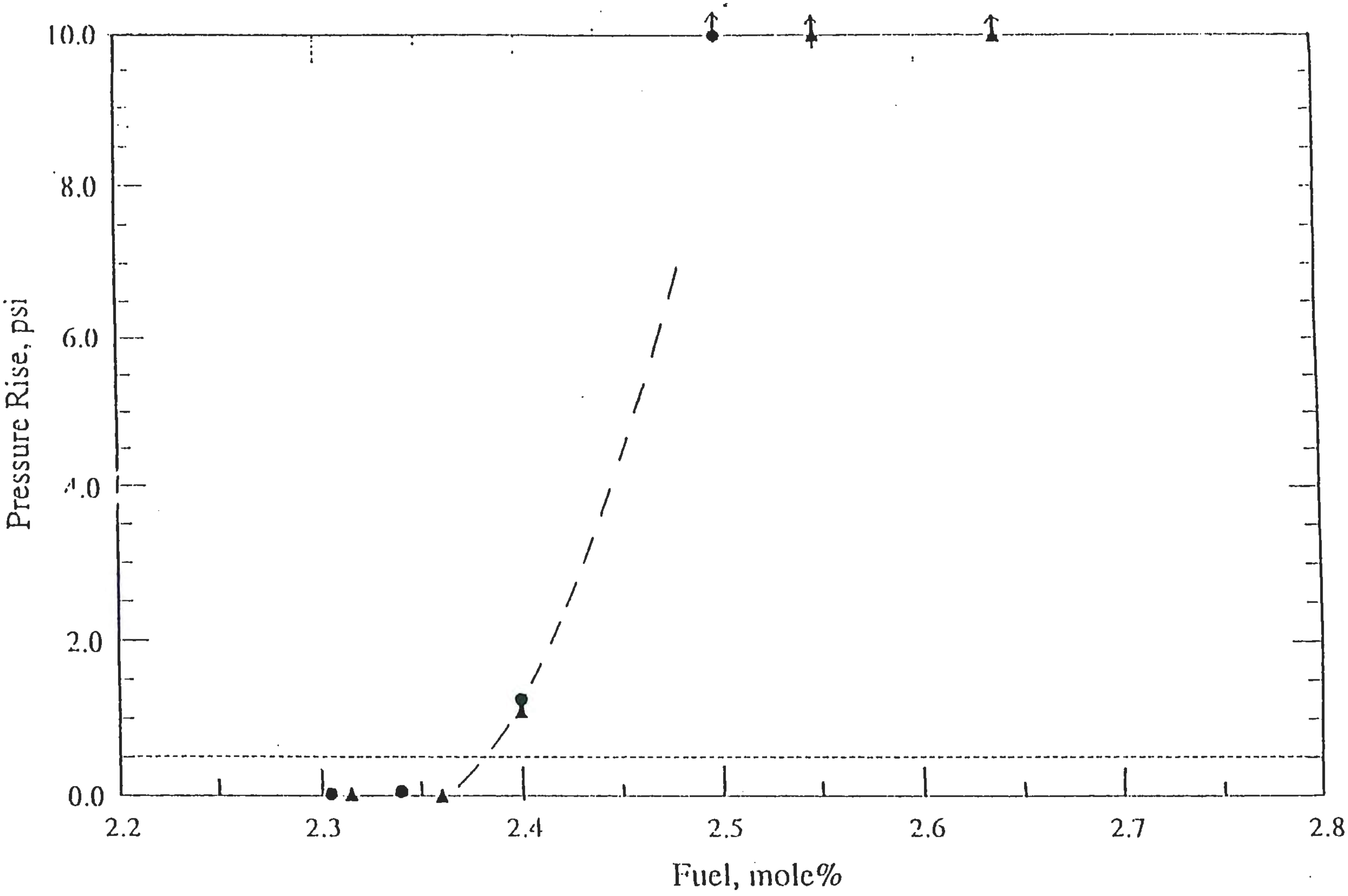

Figure 4. Flammability data for gas mixtures containing 25% by volume each of toluene, DCA, MEK, and H_2.

Table I. Experimental MLFL results for test mixtures.

Mixture No.	Proportion of Compound in Mixture on Air-Free Basis (%)					MLFL (%)
	1,2-Dichloro-ethane	Methyl ethyl ketone	Toluene	Hydrogen	Carbon tetrachloride	
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±0.50
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	5.00±0.40
27	0	0	0	50	50	10.8±0.80
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±0.50
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

ND = Not determined because vapor condensed; NF = Not flammable.

$$MLFL = \frac{100}{\sum f_i \, x \, GCF_i} \qquad (2)$$

where $MLFL$ = mixture lower flammability limit (vol%)

f_i = mole or volume fraction of gas i in mixture on an air free basis

GCF_i = group contribution factor for compound i.

The group contribution factor for a compound is written as:

$$GCF_i = \sum n_j \, x \, GF_j \qquad (3)$$

where n_j = number of group type j in compound i

GF_j = group factor for group type j.

Table II contains the calculated group factor values for the various groups used to determine the GCF for compounds of interest. The comparison of the results of these two methods to experimental determined MLFLs are summarized in Table III.

Table II. Group factor values used in Equation (3).

Group	Group Factor
C	9.10
H	2.17
H_2	20
O	-2.68
N	1.38
Cl	-4.38
C=C	14.07
F (No.H>No.F atoms)	-4.18
F (No.H<No.F atoms)	-2.55
I	17.5
S	10.9
P	9.6

Table III. Predicted mixture lower flammability limits.

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	9.70	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	10.80	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	10.10	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.

Discussion

In order to characterize the accuracy of the two predictive methods, the mean relative percent difference between experimental and method MLFLs was calculated. 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 opposed to 7 tests with the LeChatelier method (excluding duplicate tests). The standard deviation for the Group method was significantly skewed by its inability to accurately predict the LFL for the gas mixture 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 estimated error of the LFL determinations that is reported in Table I is based on the number of data points in the near vicinity of the LFL value, and how close the data points are to the LFL. The error listed for the LFL values in Table I is a conservative value. A direct measure of the precision of the LFL values was determined from the replicate runs for seven mixtures. The greatest deviations between replicate trials were less than 5%.

The actual pressure criterion used to identify flammability is system specific. ~~A~~ pressure rise criterion 0.035 bar (0.5 psi) was chosen that produced results consistent with earlier data from larger closed systems that identified the hydrogen LFL to be 5%. At this pressure criterion, a rising "fireball" and a definite temperature increase (1°C) by the 12.7-mm (5-mil) thermocouple located near the top of the chamber were observed, both indicative of gas flammability.

The LFLs for the pure components toluene and MEK determined from test chamber data were consistent with values reported using flammability tubes data. The DCA LFL of 4.85% determined in this study was considerably less than reported LFL values of 6.2% to 5.4%.[4] The variability in the earlier values is probably a reflection of wall effects and ignition limitation. Most of the earlier determinations were made in U.S. Bureau of Mines type flammability tubes that were 0.05 m in diameter and 1.5 m long.[4] 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. It is recommended, therefore, that the Group Factor contribution 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.

Conclusions

The group factor contribution method was determined to be more accurate than the LeChatelier method for estimating the LFL for gas mixtures containing hydrogen, carbon tetrachloride, 1,2-dichloroethane, toluene, or 2-butanone. The LFLs of gas mixtures containing equimolar combinations from the four specified VOCs and hydrogen were determined in a 19-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.

Acknowledgments

The U. S. Department of Energy, Office of Environmental Management, under DOE Idaho Operations Office Contract DE-AC07-94ID13223 supported this research.

References

1. Standard Test Method for Concentration Limits of Flammability of Chemicals, E681-94, West Conshohocken, Pennsylvania, American Society for Testing and Materials, 1997.

2. *CHETAH, Version 7.1, The ASTM Computer Program for Chemical Thermodynamic and Energy Release Evaluation (NIST Special Database 16)*. 3rd Edition, ASTM Data Series DS51 B. Philadelphia, Pennsylvania, ASTM Subcommittee E27.07 on Estimation Methods of ASTM Committee E-27 on Hazard Potential of Chemicals, American Society for Testing and Materials, 1997.

3. Cashdollar, K. L., M. Hertzberg, I. A. Zlochower, C. E. Lucci, G. M. Green, and R. A. Thomas, Laboratory Flammability Studies of Mixtures of Hydrogen, Nitrous Oxide, and Air. Pittsburgh Research Center, Final Report, WHC-SD-WM-ES-219, Rev 0, June, 1992, 71 pp.

4. Coward, H. F., and G. W. Jones. Limits of Flammability of Gases and Vapors. U.S. Bureau of Mines Bulletin 503, 1952, 155 pp.

5. Kuchta, J. M. Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries - A Manual. U.S. Bureau of Mines Bulletin 680, 1985, 84 pp.

6. *Procedure B: Method for Estimating Lower Flammability Limit of Pure Compounds in the Data Prediction Manual*. New York, New York, American Institute of Chemical Engineers, 1994.

7. Zabetakis, M. G. Flammability Characteristics of Combustible Gases and Vapors. U.S. Bureau of Mines Bulletin 627, 1965, 121 pp.