

# The limiting oxygen concentration and flammability limits of gases and gas mixtures

Isaac A. Zlochower\*, Gregory M. Green

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

## A B S T R A C T

This paper presents data on the limiting (minimum) oxygen concentration (LOC), in the presence of added  $N_2$ , of methane ( $CH_4$ ), propane ( $C_3H_8$ ), ethylene ( $C_2H_4$ ), carbon monoxide (CO), and hydrogen ( $H_2$ ), and some of their binary mixtures. It also addresses the issue of the flammable concentration (flammability) limits of these pure gases in air. The study is based on spark ignited explosions in large, spherical laboratory vessels (120-L and 20-L) using a 7% pressure-rise criterion for explosion propagation. The results of the study are compared with the older values which used long flammability tubes with a diameter  $\geq 5$  cm together with visual evidence of substantial upward propagation. They are also compared to results reported recently using a 12-L spherical flask with a visual flame propagation criterion. Finally, they are compared to results reported in Europe using more modest flammability criteria and smaller chambers.

The findings reported here show excellent agreement between the 120-L and 12-L results, good agreement with the 20-L results, and reasonable agreement with the earlier flammability tube values for the lower flammability limits. They disagree, however, with the more conservative European values. These results and those from the 12-L experiments also feature lower LOCs than are given by traditional flammability tubes. A model for the LOCs of such fuel mixtures based on the Le Chatelier mixture rule for lower flammable limits is seen to reasonably fit the observed results on binary mixtures and can accommodate more complex mixtures as well. One such set of ternary mixtures containing  $CH_4$  and 1:1 CO: $H_2$  is well fitted by the model.

## 1. Introduction

Starting with basic definitions, the lower and upper flammability (or explosibility) limits (LFL and UFL, respectively) are the limiting fuel concentrations in air that can support flame propagation and lead to an explosion. Fuel concentrations outside those limits are non-flammable. The progressive addition of an inert gas to a fuel-air mixture causes the narrowing of the flammability range to the point where the two limits coincide. The limiting oxygen concentration (LOC) is the minimum  $O_2$  concentration in a mixture of fuel, air, and an inert gas that will propagate flame. In this paper, the inert gas will be nitrogen. In practice, the limits (LFL, UFL, and LOC) represent an average between the neighboring concentrations inside and outside the experimental flammability limits (ASTM International, 2008a, 2008b).

There is currently a significant difference of opinion between American and European based standard-setting organizations as to the prescribed test vessels and criteria for flammability and LOC

determinations (ASTM International, 2008a, 2008b; British and European Standard, 2003, 2007). The traditional criterion used in the US, which was the basis of an extensive database of flammability limits, required that flame and explosion propagation be distinguished from ignition phenomena (Coward & Jones, 1952; Kuchta, 1985). In order to demonstrate unambiguous flame propagation, U.S. standards required that flame be observed at some distance from the ignition source and to have traveled through a significant fraction of the enclosed volume. That requirement was relaxed in a more recent US standard that featured the use of a 5-L spherical glass flask, and mandated only that flame propagation be established by evidence of horizontal as well as vertical flame travel (ASTM International, 2008a). Where ambiguity resulted, the standard called for using a larger (12-L) flask with a more extensive flame evolution – a flame cone with an arc spanning at least  $90^\circ$  at the top of the flask, as measured from the point of ignition (ASHRAE, 2007; ASTM International, 2008a). The explosion overpressure in a closed system was, correspondingly, mandated to be 7%,<sup>1</sup> i.e.,

\* Corresponding author. Tel.: +1 412 386 4960; fax: +1 412 386 6595.  
E-mail address: iaz0@cdc.gov (I.A. Zlochower).

<sup>1</sup> A 7% pressure increase represents a 1 psi increase starting at 1 bar (14.5 psia) or 1 atm (14.7 psia).

a significant percentage of the initial value (ASTM International, 2008b). Although the exact flame travel distance or overpressure required for designation as a true flame propagation and explosion is somewhat subjective and apparatus-dependent, any attempt to minimize such requirements will lead to results that are subjective, apparatus-dependent, and overly conservative. Adding further to the problem, the flammability limits and LOCs when traditionally determined have no built-in safety factors. In practice, therefore, such factors must be imposed. For example, NFPA 69 requires that the fuel concentration only reach 25% of the LFL value (or 60% of the LFL for gaseous systems with automated in-line sensors and controls) (NFPA 69, 2008). Imposing these factors has been the long-standing practice in the US (MSHA, 1996; NFPA 69, 2008).

The current standard adopted by the European Union, based on the earlier German standard (DIN 51649, 1986), is a radical departure from the above considerations. In that standard (EN 1839T), a separation of flame 10 cm above the 0.2–0.5 s induction spark in an 8 × 30 cm cylinder defines a flammable mixture. The same is true if the flame extends to 24 cm without separation from the spark electrodes. The result is basically to substitute an ignitability criterion for flammability. For a closed spherical or cylindrical system with a minimum volume of 5-L and using such a centrally located induction spark, or fuse wire of 10–20 J nominal energy (EN 1839T), the corresponding criterion is a 5% pressure rise above that given by the source alone (British and European Standard, 2003). Other European researchers go further and insist that any separation of flame from the ignition spark bespeaks a flammable mixture (meaning ignitable). The same applies to an overpressure that is just measurable (2%) (De Smedt et al., 1999). The LFLs and LOCs resulting from such minimal flame propagation criteria are, understandably, lower than those resulting from the traditional ones since they have a built-in safety factor. Despite these concerns the primary purpose of this article is not to critique the European methodology, but to alert the readers to the current existence of incompatible flammability databases; the US database (Coward & Jones, 1952; Kuchta, 1985; NFPA, 2008; Zabetakis, 1965) and the European one (CHEMSAFE, 2007). More refined techniques often lead to the revision of earlier data and to progress in the field of study. Revisions based on new arbitrary criteria, however, tend to produce confusion. Moreover, the incompatible databases may lead to the misapplication of traditional safety factors to the already conservative European data. This caution has already been issued by Britton (2002) and is echoed in this paper.

## 2. Experimental

The flammability data reported here were obtained in the spherical 120-L and 20-L chambers used in earlier studies (Cashdollar, Zlochower, Green, Thomas, & Hertzberg, 2000). The internal diameter of the 120-L chamber is 60 cm and its pressure rating is 69 bar. Instrumentation includes a sensitive strain-gauge pressure transducer to measure the partial pressures as the gases are added and mixed, and a higher capacity strain-gauge pressure transducer to monitor the explosion pressure. The strain-gauges have a response time of 1 ms. The pressure transducers were mounted on the top and bottom flanges of the chamber. A fine wire thermocouple near the top of the chamber was used to record the steady-state temperature after the addition of each gaseous component. There were also ports with ball valves for connection to a vacuum pump and vent. An internal non-sparking fan at the bottom of the vessel was used to mix the gases. The gases were added via a manifold and controlled via manual switches in an isolated control room where the additions, pressure monitoring, mixing and spark ignition initiation, and PC recording were conducted.

The spark ignition system consisted of 3-mm diameter metal rod electrodes with a durable plastic spacer for rigidity. The pointed

spark electrodes terminated below the center of the sphere and were bent to face each other with a gap of 6 mm. The electrical energy so delivered came from a 1300  $\mu$ F capacitor charged to 300 V which was then discharged through a transformer to generate a strong spark. This spark was powered by a stored energy on the capacitor of 58 J based on the equation: stored energy =  $1/2CE^2$ , where C is the capacitance and E is the voltage. The actual electrical energy in the spark gap was considerably less, however, because of the low efficiency of the transformer circuit (Hertzberg, Conti, & Cashdollar, 1985).

The calibrations of the pressure transducers were checked daily using the internal shunt calibration resistors provided by the manufacturer. Samples of the gas mixtures could be collected in evacuated test tubes through a sampling needle on the side of the chamber. These samples were then analyzed by gas chromatography (GC). During the initial evaluation of the mixing efficiency in the 120-L chamber, samples of H<sub>2</sub>–air mixtures were collected after the gases had been added to the chamber and after 2 and 5 min of mixing by the fan. There was essentially no difference in the measured concentrations of H<sub>2</sub> for the gas mixtures over this time period, showing that there was good mixing of the gases even before the fan was turned on. The reported concentrations are in mole (volume) percent, based on the partial pressure of the component relative to the total pressure. It was noted that the addition of gas to a fully or partially evacuated chamber led to an increase in temperature due, presumably, to quasi-adiabatic compression of the prior atmosphere. This temperature rise was allowed to fall to a steady-state value. That temperature was then used to correct all the component partial pressures to a common (final) temperature using the ideal gas law.

The 20-L chamber, with a pressure rating of over 20 bar, is nearly spherical, having a diameter of 30 cm and a height of 35 cm. The ceramic encased electrodes were located slightly below the mid-height of the chamber, and the exposed, pointed steel tips were spaced 6 mm apart. The charging circuit was similar to that used for the 120-L sphere except that an 800  $\mu$ F capacitor was charged to 300 V, giving a nominal stored energy of 36 J. The actual thermal energy deposited in the chamber, based on the observed pressure increase due to the spark, was 0.5–1 J. The partial pressures of the gaseous components were measured as above or via a sensitive, temperature-controlled capacitance manometer that had a resolution of 0.1 torr (0.13 mbar) over a range of 1000 torr (1.33 bar). This unit was calibrated by the manufacturer prior to use.

The data from the pressure transducers and the thermocouple were recorded using a high speed analog to digital (A/D) board in a personal computer (PC). This system can sample the data from various instrument channels, usually at speeds less than 20 kHz per channel. An in-house computer software program converted the raw data to engineering units, plotted the data vs. time, and allowed various data smoothing options. Maximum pressure and maximum rate of pressure-rise values were obtained from the pressure vs. time traces. The reproducibility of the flammability data was checked by repeated tests over a period of months and years.

The experimental determination of the flammability limits of the gases studied was done by fully evacuating the chamber and then admitting the fuel gas to the predetermined partial pressure required to produce the desired final concentration in air. Dry, oil-free air was admitted from a compressed gas cylinder to give the desired final pressure of 1 bar (the ambient pressure at the elevation of the laboratory was always less than that final pressure). The temperature in the chamber rose during the addition of both the fuel and air, as previously noted, and the gas was allowed to come to a steady-state temperature and pressure. The temperature of the fuel gas was then used to correct the fuel pressure to that

corresponding to the final temperature of the mixture according to the ideal gas law. The final concentration of the fuel gas was then calculated from its corrected pressure. Next, the non-sparking internal fan was started and run for at least 4 min to fully mix the gases. The fan was shut off and the generated turbulence was allowed to subside for 1 min. The capacitor spark ignition system was then charged to 300 V and discharged through an ignition coil to create the high voltage spark. The series of sparks thereby produced lasted for about 0.1 s.

The initial concentrations of fuel gas chosen were based on the literature values for the flammability limits or on prior determinations using such chambers. Once marginal explosion pressures were produced, the concentrations were changed in small steps (0.1–0.2%) for the LFL and UFL measurements of methane, propane, ethylene, and CO. The concentration step for the LFL of hydrogen was 0.5–1% owing to the low sensitivity of the explosion pressure to concentration near the LFL (Cashdollar et al., 2000).

The LOC measurements were made starting at fuel concentrations near the LFL and using oxygen concentrations (from the air and nitrogen additions) that were near the LFL multiplied by the stoichiometric oxygen/fuel ratio (the “R” column in Table 1). The oxygen concentration was varied in steps of 0.2% until the marginal explosion conditions were delineated and verified. Then the fuel concentration was changed and the minimum oxygen concentration again determined. The process was repeated until a global minimum oxygen concentration (LOC) with added N<sub>2</sub> was established.

### 3. Results and discussion: single fuels

Previous results (Cashdollar et al., 2000) for the LFL of H<sub>2</sub> in the 120-L sphere using spark ignition showed a slow, linear increase in explosion pressure with concentration below 7%, followed by an accelerated increase above 7%. The pressure rise became steep at 8% H<sub>2</sub>. The LFL of H<sub>2</sub> is thus quite sensitive to the pressure criterion for explosion propagation. The 7% pressure-rise criterion for spark ignition yielded an LFL of 7% in this chamber. The explosion pressure rise also occurred gradually with low H<sub>2</sub> concentrations in the 20-L chamber (below 8% H<sub>2</sub>), but with a steeper slope. In the 20-L chamber, the 7% pressure-rise criterion was satisfied at 6% H<sub>2</sub> in air. With a meter-long upward flame propagation criterion in vertical flammability tubes, the LFL was found to be 4%. The much shorter 30 cm tubes used in the EN 1839 (T) method gave an LFL of 3.6%

(Schroder & Molnarne, 2005). The tube values are based on the buoyant rise of small flame kernels which represent only a small fraction of fuel consumed and a correspondingly minimal pressure rise. Measurements in a 14-L closed sphere gave an LFL of 4.2% (Schroder & Molnarne, 2005), but the use of fuse wire ignition rather than the weaker and more localized spark ignition is believed to have unduly influenced the pressure rise associated with partial propagation (5%). A more robust explosion pressure-rise criterion (7%) for hydrogen in larger chambers would appear to be better correlated with actual explosion hazards.

There is less data for the UFL in the 120-L sphere. However, the sharp drop in explosion pressure beyond 75.7% hydrogen (the pressure rise is near zero at 76%) argues against a significant dependence of UFL on the above pressure criterion. The UFL is estimated as 75.9% H<sub>2</sub>, the midpoint between these values. Previously, a value of 76.8% was reported by Cashdollar et al. (2000), but that value was obtained in an 8-L chamber. The LFL in that chamber was also found to be lower (5%) than in the larger (20-L and 120-L) chambers. Similarly high UFLs were given in the tests run according to the EN 1839 standard (76.6%, tube and 77.0%, closed sphere). Given the sensitivity of hydrogen flammability to the experimental conditions and chamber volume, the above relative difference of 1% for the UFL is not surprising.

The data on explosion pressures at different oxygen vs. hydrogen concentrations in air–nitrogen mixtures is given in Fig. 1, where the legend symbols represent pressure-rise ranges. In other words, Fig. 1 and the subsequent figures for LOC data are pressure parameter plots for given O<sub>2</sub> and fuel concentrations, with the different symbols representing different pressure-rise levels. Fig. 1 shows a minimum oxygen concentration (LOC) of 4.6% that is independent of hydrogen concentration in the range of 10–30%. More typically, however, the minimum oxygen concentration for an inert fuel–air mixture occurs at a narrow range of fuel concentrations. Those “worst-case” fuel concentrations define the LOC for the fuel–air mixture containing the inert gaseous additive (e.g. N<sub>2</sub>).

The results for the LFL of CO are similar to that of H<sub>2</sub>, but feature a steeper rise in pressure with concentration. They are also dependent on the amount of water vapor present in the mixture. In contrast to the ordinary behavior of water as an effective inhibitor of explosions due to its large heat capacity, here it is an accelerant – at least at low concentrations. It functions, presumably, by supplying the H and OH free radicals for the branching chain reactions needed

**Table 1**  
Flammability/LOC: 120-L and 20-L closed vessel results vs. 12-L glass sphere and flammability tube.

Fuel (F)	Vessel	Stoichiometric equation	Mole ratio (R) (O <sub>2</sub> /F)	LFL (mol%)	UFL (mol%)	LOC (N <sub>2</sub> ) (mol%)	Explosion criterion
Hydrogen (H <sub>2</sub> )	120-L	2H <sub>2</sub> + O <sub>2</sub> = 2H <sub>2</sub> O	<b>0.5</b>	<b>7</b>	<b>75.9</b>	<b>4.6</b>	Pressure
	20-L			<b>6</b>		<b>4.7</b>	Pressure
	Flam. <sup>a</sup> tube			<b>4</b>	<b>75.0</b>	<b>5.0</b>	Visual
Carbon monoxide (CO)	120-L	2CO + O <sub>2</sub> = 2CO <sub>2</sub>	<b>0.5</b>	<b>12.2</b>	<b>72.0</b>	<b>5.1</b>	Pressure
	12-L <sup>b</sup>			<b>12.2</b>	<b>72.5</b>		Visual
	Flam. <sup>a</sup> tube			<b>12.5</b>	<b>74.0</b>	<b>5.5</b>	Visual
Methane (CH <sub>4</sub> )	120-L	CH <sub>4</sub> + 2O <sub>2</sub> = CO <sub>2</sub> + 2H <sub>2</sub> O	<b>2</b>	<b>5.0</b>	<b>15.8</b>	<b>11.1</b>	Pressure
	20-L			<b>4.9</b>	<b>15.9</b>	<b>10.7</b>	Pressure
	12-L <sup>b</sup>			<b>4.9</b>	<b>15.8</b>	<b>11.3</b>	Visual
	Flam. <sup>a</sup> tube			<b>5.0</b>	<b>15.0</b>	<b>12.0</b>	Visual
Ethylene (C <sub>2</sub> H <sub>4</sub> )	120-L	C <sub>2</sub> H <sub>4</sub> + 3O <sub>2</sub> = 2CO <sub>2</sub> + 2H <sub>2</sub> O	<b>3</b>	<b>2.7</b>	<b>31.4</b>	<b>8.5</b>	Pressure
	12-L <sup>b</sup>			<b>2.7</b>	<b>31.5</b>	<b>8.6</b>	Visual
	Flam. <sup>a</sup> tube			<b>2.7</b>	<b>36.0</b>	<b>10.0</b>	Visual
Propane (C <sub>3</sub> H <sub>8</sub> )	120-L	C <sub>3</sub> H <sub>8</sub> + 5O <sub>2</sub> = 3CO <sub>2</sub> + 4H <sub>2</sub> O	<b>5</b>	<b>2.0</b>	<b>9.8</b>	<b>10.7</b>	Pressure
	12-L <sup>b</sup>			<b>2.0</b>	<b>10.0</b>	<b>10.5</b>	Visual
	Flam. <sup>a</sup> tube			<b>2.1</b>	<b>9.5</b>	<b>11.5</b>	Visual

<sup>a</sup> Flammability tube data summarized by Kuchta (1985).

<sup>b</sup> The data from a 12-L spherical flask by Kondo et al. (2006, 2008).

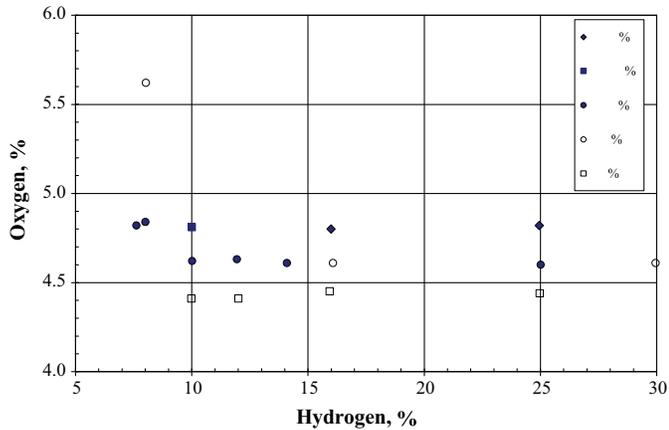


Fig. 1. LOC data on H<sub>2</sub> in air with added N<sub>2</sub> that was obtained in the 120-L sphere. Parametric pressure plot at different O<sub>2</sub> vs. H<sub>2</sub> concentrations, with the symbols representing different pressure-rise ranges.

for combustion and for rapid flame propagation. The measured LFL is 12.2% when the mixture is nearly saturated with water. Similarly, the UFL is 72% for near saturation. The results in the 12-L glass sphere for CO in moist air with added N<sub>2</sub> (LFL = 12.2%, UFL = 72.5%) that was reported by Kondo, Takizawa, Takahashi, Tokuhashi, and Sekiya (2008) agrees with the 120-L values (based on their listed uncertainty of 0.5% for the UFL). Fig. 2 shows an LOC in the 120-L sphere of about 5.1% O<sub>2</sub> for gas mixtures nearly saturated with water vapor. That LOC occurs near a 20% CO concentration.

The above results represent atypical fuels that are lighter and more diffusive than O<sub>2</sub> (H<sub>2</sub>), or have branching chain reactions associated with flame propagation that are more difficult to establish (CO). Hydrogen, for example, is more concentrated at the flame front (i.e., the real fuel concentration at the flame front is higher than the nominal value) which clearly impacts the LFL value (Cashdollar et al., 2000; Hertzberg, 1989). More typical flammable gases – namely, the common hydrocarbons: methane (CH<sub>4</sub>), the primary constituent of natural gas; propane (C<sub>3</sub>H<sub>8</sub>), the popular cooking and heating fuel; and ethylene (C<sub>2</sub>H<sub>4</sub>), a basic chemical feedstock for polyethylene and other plastics – were studied as well.

Cashdollar et al. (2000) have reported 120-L data on the LFL of methane in air which show a gradual increase in pressure from 4.6 to 5.0%. There is little reason, however, to dispute the choice of 5.0%

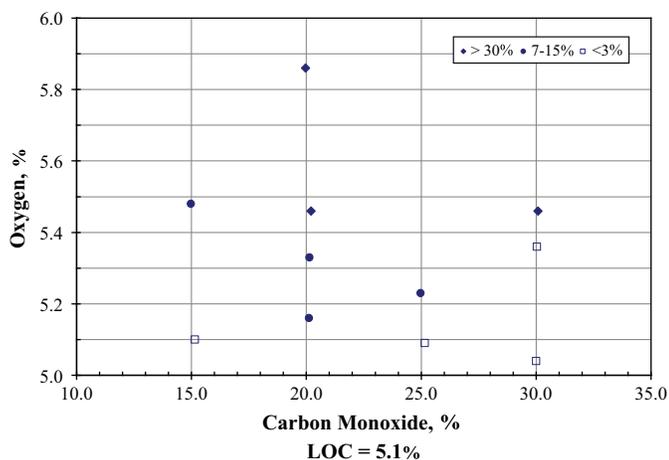


Fig. 2. 120-L data on the LOC of CO in nearly saturated moist air with added N<sub>2</sub>. Parametric pressure plot at different O<sub>2</sub> vs. CO concentrations, with the symbols representing different pressure-rise levels.

as the LFL of methane. Both the pressure criterion of 7% and the existence of a discontinuous change in slope yield the same LFL value. The corresponding UFL is 15.8% based on the newer data. The same value is the average of the values reported by Cashdollar et al. (2000) for the 120-L and 20-L chambers (15.7 and 15.9%, respectively), while the LFL was 5.0% for both chambers. The 12-L glass sphere gave an LFL of 4.9% and a UFL of 15.8% (Kondo, Takizawa, Takahashi, & Tokuhashi, 2006).

Fig. 3 shows an LOC of 11.1% O<sub>2</sub> for 5.2–5.8% CH<sub>4</sub> in air–N<sub>2</sub> mixtures in the 120-L sphere, but the LOC was found to be 10.7% O<sub>2</sub> in the 20-L chamber. The 12-L sphere gave a value of 11.3%, as reported by Kondo et al. (2006). The lower value given by the 20-L chamber may indicate the need for a higher pressure-rise criterion in chambers appreciably smaller than 120-L (Brandes & Ural, 2008).

Past work (Cashdollar et al., 2000) gave an LFL value for propane of 2.05% with a sharp rise in pressure with concentration. The pressure drop with concentration near the UFL was more gradual. It was found to be 9.8% for the 7% pressure criterion. Current results in the 120-L sphere are consistent with the earlier findings. The LOC of propane is seen to be about 10.7% at 2.5–2.7% propane (Fig. 4). The 12-L glass sphere results of Kondo et al. (2006) gave an LFL of 2.0%, a UFL of 10.0%, and an LOC of 10.5%, again in agreement with the 120-L results.

Ethylene also features a sharp rise in pressure with concentration at low concentrations and a slower decline in pressure near the UFL. The LFL is found to be 2.7% and the UFL is 31.4% using the 7% criterion. The LOC is seen to be 8.5% O<sub>2</sub> at 2.9–3.2% ethylene (Fig. 5). The 12-L results of Kondo et al. (2006) yielded an LFL of 2.7%, a UFL of 31.5%, and an LOC = 8.6%.

The 120-L and 20-L data are summarized in Table 1 together with the reported results from the 12-L sphere (Kondo et al., 2006, 2008) and flammability tubes (Kuchta, 1985). The reported results from the 12-L glass sphere are essentially identical to the results obtained here in the 120-L sphere despite the great difference in volume and propagation criterion.

A good reflection of the difference between the US and European standards is given by the LFLs of methane in air. Traditionally, this value has been listed as 5.0% based on the results of flame propagation studies using a large upward propagation distance in tall, wide containers (Britton, 2002; Coward & Jones, 1952), in closed, larger spherical vessels (120-L and 20-L), and in a very large spherical vessel (Cashdollar et al., 2000). The European Standard (Annex E) using a 5% pressure-rise criterion in a small vessel (EN 1839B) gave 4.6% as the LFL. Using the flame detachment criterion in a small

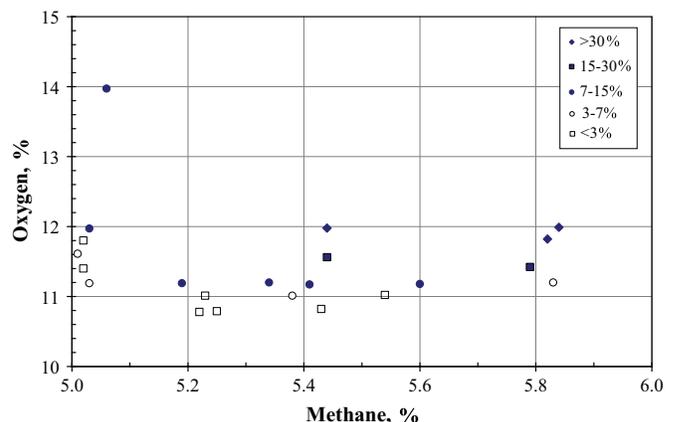


Fig. 3. 120-L data on the LOC of CH<sub>4</sub> in air with added N<sub>2</sub>. Parametric pressure plot at different O<sub>2</sub> vs. CH<sub>4</sub> concentrations, with the symbols representing different pressure-rise ranges.

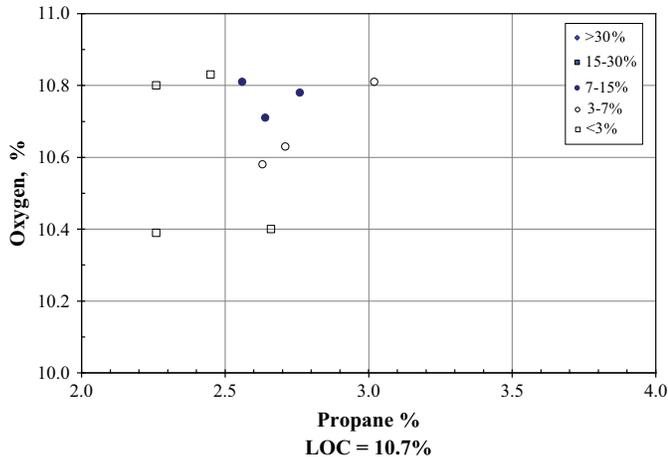


Fig. 4. The LOC of propane in air with added N<sub>2</sub>; 120-L data. Parametric pressure plot at different O<sub>2</sub> vs. C<sub>3</sub>H<sub>8</sub> concentrations, with the symbols representing different pressure-rise ranges.

cylindrical vessel (EN 1839T) yielded a value of 4.4% in this standard (British and European Standard, 2003). A similar difference was observed for the UFL measurements of methane in air. The European standard methods gave 16.6% and 16.8% values for the tube and “bomb” methods, respectively – cited in Annex E, while both the 120-L and 12-L spheres gave 15.8%. A further confirmation of the results reported here is given by the studies of Kondo’s group on the effect of vessel size and shape on the experimental flammability limits of methane and propane. They found that cylindrical vessels did not yield values that were size independent until quite large dimensions were used. Their largest cylinder (45 × 100 cm) with a volume of 160-L gave values quite consistent with those reported here for full upward propagation of a flammable mixture (methane flammability limits = 5.0–15.8%; propane limits = 2.0–9.9%) (Takahashi, Urano, Tokuhashi, & Kondo, 2003).

The different values cited for the LFL of methane in the new databases which are based on the European standards (CHEMSAFE, 2007) should not be interpreted as an argument for the retention of older flammability values if new experiments in larger chambers using comparable flammability criteria produce new values. That is the case with experiments reported here, particularly in regards to LOC values. These experiments now generate systematically lower LOC values, as do the results in the 12-L glass sphere (Kondo et al., 2006). This agreement between the pressure-rise criterion used in

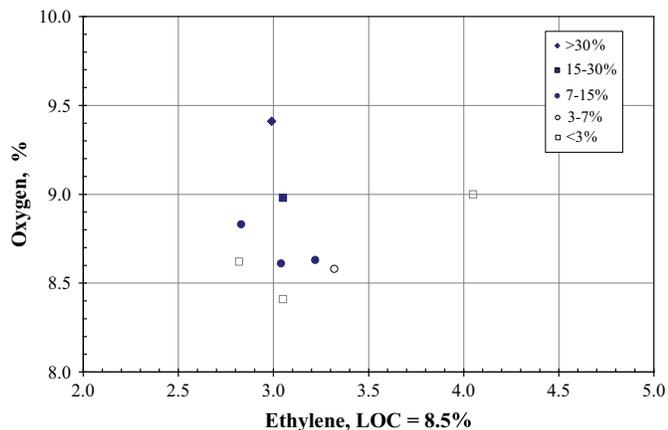


Fig. 5. The LOC of ethylene in air with added N<sub>2</sub>; 120-L data. Parametric pressure plot for different O<sub>2</sub> vs. C<sub>2</sub>H<sub>4</sub> concentrations, with the symbols representing different pressure-rise ranges.

the 120-L sphere and the visual criterion in the 12-L sphere lends encouragement to the assumption that values have been determined that are reasonably independent of vessel size and flame propagation criteria.

The above argument implies that the LOC values in the older literature are not sufficiently conservative and should not be used to generate safety protocols unless conservative safety factors are incorporated. The problem with the older LOC values is also recognized in the 2008 NFPA 69 standard which requires subtracting 2% (abs.) from the old values. While that is probably a conservative stance, it may involve unnecessary expense in the case of hydrogen – based on the results obtained in the 120-L sphere. Additional measurements using large chambers and appropriate flame propagation criteria will be needed to form a reliable database of LOC values.

#### 4. Fuel mixtures

The LFL of fuel mixtures is predicted adequately by the Le Chatelier rule for fuel mixtures (Burgess et al., 1982; Coward & Jones, 1952; Kondo et al., 2008; Liekhus, Zlochower, Cashdollar, Djordjevic, & Loehr, 2000). That rule is less adequate, but still generally conservative, in predicting the UFL of mixtures (Kondo et al., 2008). The LOCs of such mixtures, however, have not been extensively studied. Prior work on mixtures of hydrogen and benzene (Thomas, 1996) established the utility of a calculation scheme that will be derived in this paper and used to compare to the experimental results on binary mixtures of hydrogen, CO, or ethylene with methane. Mixtures of propane and methane are not considered since their LOCs are too close to produce a significant variation with composition. The experimental method chosen was the same as for the single fuels, except that two different fuels were mixed together with air and nitrogen to establish the stated mixtures. Ternary mixtures of 1:1 hydrogen:CO with methane were also studied. Water was not added to the mixtures containing CO since the other fuel(s) had the H species needed for efficient CO combustion. The results are summarized in Table 2.

Table 2 shows the experimental and calculated values of the LOC of CH<sub>4</sub> mixtures with H<sub>2</sub> and/or CO, or with C<sub>2</sub>H<sub>4</sub>. The predicted LOCs involving mixtures of H<sub>2</sub> and/or CO with CH<sub>4</sub> follow the experimental values but fall to a maximum of 0.9% (abs.) below them. The calculations to be described in the next section are therefore seen as realistic but conservative. H<sub>2</sub> and CO are unusual fuels, however (high diffusivity or low reactivity) as noted earlier. The deviation of the experimental results from the derived formula is, therefore, not surprising. The one clear example of a mixture of more typical fuels with widely different LOCs is the mixture of methane and ethylene. The calculated values are very close to the experimental ones with a maximum difference of 0.15% (abs.).

#### 5. LOC of fuel mixtures

As noted previously, the lower flammability limit (LFL) for mixtures of fuels is adequately given by the Le Chatelier rule:

$$L_{\text{mixt.}} = 1 / \sum x_i / L_i \quad (1)$$

Where  $L_{\text{mixt}}$  is the LFL of the fuel mixture,  $L_i$  is the LFL of fuel component  $i$ ,  $x_i$  is the mole fraction of the fuel component.

The LOC of fuel mixtures can be derived from (1) by defining  $L_{\text{mixt}}^*$  and  $L_i^*$  as,

$$L_i^* = (\text{LOC})_i / R_i, \quad L_{\text{mixt}}^* = (\text{LOC})_{\text{mixt}} / R^* \quad (2)$$

Where  $(\text{LOC})_i$  is the experimental value for LOC of component  $i$ ,  $(\text{LOC})_{\text{mixt}}$  is the calculated LOC for the fuel mixture,  $R_i$  is the

**Table 2**

LOC: fuel mixtures containing methane: CH<sub>4</sub>-H<sub>2</sub>; CH<sub>4</sub>-CO; CH<sub>4</sub>-C<sub>2</sub>H<sub>4</sub>; CH<sub>4</sub>-1:1 CO:H<sub>2</sub>; experimental vs. calculated.

Fuel: % CH <sub>4</sub>	Methane-H <sub>2</sub>		Methane-CO		Methane-ethylene		CH <sub>4</sub> -1:1 CO:H <sub>2</sub>	
	(LOC) <sub>exp</sub>	(LOC) <sub>calc</sub>	(LOC) <sub>exp</sub>	(LOC) <sub>calc</sub>	(LOC) <sub>exp</sub>	(LOC) <sub>calc</sub>	(LOC) <sub>exp</sub>	(LOC) <sub>calc</sub>
0	4.6	4.6	5.1	5.1	8.6	8.6	4.8	4.8
10	6.5	5.6	6.1	6.1	8.6	8.7		
20							7.3	6.7
25	7.7	6.9	7.8	7.4	8.9	9		
35	8.3	7.65						
40							8.7	8.2
50	9.1	8.64	9.5	9.0	9.3	9.45		
60							9.7	9.4
75	10.3	10	10.9	10.2	10.05	10.1		
80							10.5	10.3
90	10.9	10.7	11	10.8				
100	11.1	11.1	11.1	11.1	11.1	11.1	11.1	11.1

stoichiometric molar ratio of oxygen to fuel  $i$  (see Table 1),  $R^*$  is the stoichiometric ratio of oxygen to the fuel mixture, as given by  $\sum x_i R_i$ .

For  $L_{\text{mixt}}^* = 1 / \sum x_i / L_i^*$  (modified Le Chatelier rule), substituting (2) into the modified Le Chatelier and rearranging terms gives

$$(LOC)_{\text{mixt}} = \sum x_i R_i / \sum x_i / L_i^* = \sum x_i R_i / \sum x_i R_i / (LOC)_i$$

For a 2-component mixture (a,b):

$$(LOC)_{\text{mixt}} = (x_a R_a + x_b R_b) / [(x_a R_a / (LOC)_a) + (x_b R_b / (LOC)_b)]$$

For binary mixtures of methane (m) and hydrogen (h):  $R_m = 2$ ,  $R_h = 0.5$ ,  $x_h = 1 - x_m$ ,  $LOC_m = 11.1$ ,  $LOC_h = 4.6$ . The result is:  $LOC_{m-h} = (1.5x_m + 0.5) / (0.0715x_m + 0.109)$ .

For binary mixtures of methane and CO:  $R_{CO} = 0.5$ ,  $x_{CO} = 1 - x_m$ ,  $LOC_{CO} = 5.1$ . The result is:  $LOC_{m-co} = (1.5x_m + 0.5) / (0.0821x_m + 0.0980)$ .

For binary mixtures of methane and ethylene:  $R_{et} = 3$ ,  $x_{et} = 1 - x_m$ ,  $LOC_{et} = 8.6$ . The result is:  $LOC_{m-et} = (3 - x_m) / (0.349 - 0.169x_m)$ .

For ternary mixtures of methane with 1:1 CO:H<sub>2</sub>,  $x_{CO} = x_h = (1 - x_m) / 2$ . The result is:  $LOC_{m-co:h} = (1.5x_m + 0.5) / (0.0768x_m + 0.1034)$ .

The above equations lead to the calculated LOC results shown in Table 2. As noted previously, the calculated results for the mixture of hydrocarbons accurately predict the experimental values. The results for the unusual fuels, H<sub>2</sub> and CO, are below the experimental values, but barely outside experimental error. In any case, the calculated results are conservative. It remains to be seen how this calculation scheme will fit data on oxygenated and other non-hydrocarbon fuels.

## 6. Conclusions

The primary finding reported here is that the traditional flammability tube values for the LOCs are too high – at least for N<sub>2</sub> inerting that was the subject of this study. The differences from the 120-L results are typically less than 1% (e.g. 12 vs. 11.1% for CH<sub>4</sub>, 11.5 vs. 10.7 for C<sub>3</sub>H<sub>8</sub>), but the difference is 1.5% for ethylene (10 vs. 8.5%). These results should be taken into account by the standard-setting organizations – or at least be subject to independent verification. A start in this direction is currently being made by standards committees based in the US (NFPA 69, 2008).

This study also generally confirms the results of the flammability tube measurements on the LFLs of these fuels (hydrogen being exceptional). The excellent agreement between the 120-L

results using a 7% pressure-rise criterion with the reported results in the 12-L glass sphere which uses a visual criterion supports the contention that these results are realistic. The issue of the conflicting American and European flammability standards needs to be resolved so as to provide a consistent and reliable database for flammability.

## Acknowledgement

This is to acknowledge the important contributions of Kenneth L. Cashdollar over the years to the flammability and LOC studies in the 120-L and 20-L chambers, and to his helpful suggestions and advice. Sad to say, Ken recently passed away and we will no longer have the benefit of his leadership, humanity, and superlative experimental and organizational skills. His many contributions to our organization and the field of explosion prevention will be sorely missed.

## References

- ASHRAE. (2007). Number designation and safety classification of refrigerants, ANSI/ASHRAE Standard 34-2007. American Society of Heating, Refrigerating, and Air-conditioning Engineers (ASHRAE), Atlanta GA.
- ASTM International. (2008a). *Standard test method for concentration limits of flammability of chemicals (vapors and gases)*. E681-04. In: *ASTM International annual book of standards, Vol. 14.02*. West Conshohocken, PA: American Society for Testing and Materials.
- ASTM International. (2008b). *Standard test methods for limiting oxygen (oxidant) concentration in gases and vapors*. E2079-07. In: *ASTM International annual book of standards, Vol. 14.02*. West Conshohocken, PA: American Society for Testing and Materials.
- Brandes, E., & Ural, E. A. (2008). Towards a global standard for flammability determination. In *Proceedings of the 42nd annual loss prevention symposium – Global safety congress, paper 2E, April 6–10*. New Orleans, LA: American Institute of Chemical Engineers.
- British and European Standard. (2003). *Determination of explosion limits of gases and vapours*. sections 4.1, Method T (BS EN 1839T) and 4.2, Method B (BS EN 1839B). rue de Stassart, 36, B-1050 Brussels, Belgium: CEN European Committee for Standardization.
- British and European Standard. (2007). *Determination of limiting oxygen concentrations of gases and vapours*. EN 14756. rue de Stassart, 36, B-1050 Brussels, Belgium: CEN European Committee for Standardization.
- Britton, L. G. (2002). Two hundred years of flammable limits. *Process Safety Progress*, 21, 1–11.
- Burgess, D. S., Furno, A. L., Kuchta, J. M., & Mura, K. E. (1982). Flammability of mixed gases. *U.S. Bureau of Mines Report of Investigations*, 8709, 20 pp.
- Cashdollar, K. L., Zlochower, I. A., Green, G. M., Thomas, R. A., & Hertzberg, M. (2000). Flammability of methane, propane, and hydrogen gases. *Journal of Loss Prevention in the Process Industries*, 13, 327–340.
- CHEMSAFE. (2007). *Database of evaluated safety characteristics*. Frankfurt/M, Germany: DECHEMA, BAM, and PTB.
- Coward, H. F., & Jones, G. W. (1952). Limits of flammability of gases and vapors. *U.S. Bureau of Mines Bulletin*, 503, 155 pp.
- De Smedt, G., de Corte, F., Notele, R., & Berghmans, J. (1999). Comparison of two standard test methods for determining explosion limits of gases at atmospheric conditions. *Journal of Hazardous Materials*, A70, 105–113.

- DIN (German standard) 51649-1. (1986). *Determination of the explosion limits of gases and gas mixtures in air*. (Ger.). Berlin, Germany: Deutsches Institut für Normung.
- Hertzberg, M. (1989). Selective diffusional demixing: occurrence and size of cellular flames. *Progress in Energy and Combustion Science*, 15, 203–239.
- Hertzberg, M., Conti, R. S., & Cashdollar, K. L. (1985). Electrical ignition energies and thermal autoignition temperatures for evaluating explosion hazards of dust. *U.S. Bureau of Mines Report of Investigations*, 8988. 41 pp.
- Kondo, S., Takizawa, K., Takahashi, A., & Tokuhashi, K. (2006). Extended Le Chatelier's formula and nitrogen dilution effect on the flammability limits. *Fire Safety Journal*, 41, 406–417.
- Kondo, S., Takizawa, K., Takahashi, A., Tokuhashi, K., & Sekiya, A. (2008). A study on flammability limits of fuel mixtures. *Journal of Hazardous Materials*, 155, 440–448.
- Kuchta, J. M. (1985). Investigation of fire and explosion accidents in the chemical, mining, and fuel-related industries – a manual. *U.S. Bureau of Mines Bulletin*, 680. 84 pp.
- Liekhus, K. J., Zlochower, I. A., Cashdollar, K. L., Djordjevic, S. M., & Loehr, C. A. (2000). Flammability of gas mixtures containing volatile organic compounds and hydrogen. *Journal of Loss Prevention in the Process Industries*, 13, 377–384.
- MSHA. (March 1996). *Safety standards for underground coal mine ventilation: Final rule*. 30 CFR, Part 75, Section 75.323. In: *Federal register, part III*. Department of Labor, Mine Safety and Health Administration.
- NFPA 69. (2008). *Standard on explosion prevention systems* (2008 ed.). Quincy, MA: National Fire Protection Association.
- Schroder, V., & Molnarne, M. (2005). Flammability of gas mixtures. Part I: fire potential. *Journal of Hazardous Materials*, 121, 37–44.
- Takahashi, A., Urano, Y., Tokuhashi, K., & Kondo, S. (2003). Effect of vessel size and shape on experimental flammability limits of gases. *Journal of Hazardous Materials*, 105, 27–37.
- Thomas, J. K. (1996). *Composite minimum oxygen concentrations for benzene–hydrogen–nitrogen–air mixtures*. WSRC-RP-96-619. Aiken, SC: Westinghouse Savannah River Co., Safety Engineering Div..
- Zabetakis, M. G. (1965). Flammability characteristics of combustible gases and vapors. *U.S. Bureau of Mines Bulletin*, 627. 121 pp.