PROPER APPLICATION OF FLAMMABILITY LIMIT DATA IN CONSEQUENCE STUDIES

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Flammability limit data are used in consequence studies to estimate the size, shape, mass, and explosion energy of a flammable cloud formed during the accidental release of a fuel. Thus the flammability limits of a fuel are critical parameters in consequence and risk analyses. However, significant discrepancies often exist between experimental flammability limit data for a fuel. The proper application of flammability limit data in consequence studies requires understanding the causes of discrepancies among data as well as the ability to interpret and extrapolate laboratory results to potential large scale accidental release scenarios. In this study, the impact of using Bureau of Mines or EN 1839(t) flammability limit data to predict resulting explosion consequences is illustrated by comparing predicted dispersion distances, flammable mass, and source energy of several real facility siting studies. The results of the study vary greatly depending on fuel and other model input parameters, but in general using EN flammability limit data resulted in larger predicted dispersion distances and flammable mass, increasing by as much as 200% and 400%, respectively, when compared to predictions generated using US Bureau of Mines flammability limit data.

1. INTRODUCTION

Consequence studies are required in some countries as part of a governmental regulation and are often performed for petrochemical, chemical, and other facilities to estimate potential hazards upon accidental release of a material. These studies also provide much of the input needed for quantitative risk analyses, and are therefore widely used in the field of process safety. A key aspect of consequence studies is the dispersion analysis, which is used to estimate the location, shape and size of a flammable cloud formed by a hypothetical release scenario. The size and shape of a flammable cloud are typically defined using the reported flammability limits of the fuel. For example, many consequence analysis software packages consider the lower flammability limit (LFL) isopleth (or some fraction of it) as the border of the flammable cloud. It is frequently assumed that beyond this boundary little or no significant flammable consequences will occur. Similarly, the flammable mass of the cloud is frequently calculated based on the cloud mass between the upper (UFL) and lower flammability limit isopleths (Hansen et al., 2011; Epstein and Fauske, 2007; van den Bosch and Weterings, 2005), and this mass (or some derivative of it) is used to estimate the blast energy and resultant overpressure and impulse from an explosion.

It is clear that the flammability limits are critical parameters in consequence studies. However, a recent review by DIPPR indicated wide disparity between reported values of flammability limits, largely dependent on the measurement methodology used in obtaining the data (Rowley, 2010). In this work we summarize the differences in two widely accepted methodologies used to measure flammability limit data, and provide a discussion on proper interpretation and application of reported flammability limits. We then illustrate the impact of differences in reported flammability limits on predicted consequences for several real consequence studies. Finally, we provide guidance in selecting proper flammability limit data for use in consequence studies.

2. BACKGROUND

2.1 FUNDAMENTALS OF FLAMMABILITY LIMITS

DIPPR® defines the upper and lower flammability limits as the maximum and minimum concentrations of fuel in air (vol%) that will support flame propagation (Rowley et al, 2011). In other words, above the UFL the fuel-air mixture has insufficient oxygen and below the LFL the fuel-air mixture has insufficient fuel to propagate a flame. This concept is typically visualized as shown in Figure 1.

There have been numerous studies regarding the theory and measurement of flammability limits. For a more detailed literature review see the dissertation of Rowley (2010). Table 1 provides a summary of the standardized methods for measuring flammability limits; however, this work focuses on data from the Bureau of Mines and EN tube methods as they represent the two largest and most widely cited sets of flammability data.

US Bureau of Mines Tube Method

In the US, data measured using the US Bureau of Mines tube apparatus have long been considered the standard for flammability limits. Thus, although reported LFL values for methane range from 4.4 vol% to 5.3 vol%, a large number of data compilations and Material Safety Data Sheet cite the US Bureau of Mines value of 5 vol%.

Flammability measurements at the Bureau of Mines spanned over several decades and consequently the data represent the largest available set of experimental flammability data from a single method, though the apparatus did evolve during that time (Coward and Jones, 1952). Flammability limits were determined in narrow tubes, 2 to 7.5 cm in diameter and 1 to 1.5 m high. A flammable mixture was defined as one that could support flame propagation through a theoretical infinite tube. However, practicality required the Bureau to consider any mixture that propagated a flame to the top of a 1–1.5 m tube as flammable. Recent evidence indicates that the requiring the flame to propagate to the top of the tube through such a narrow diameter resulted in

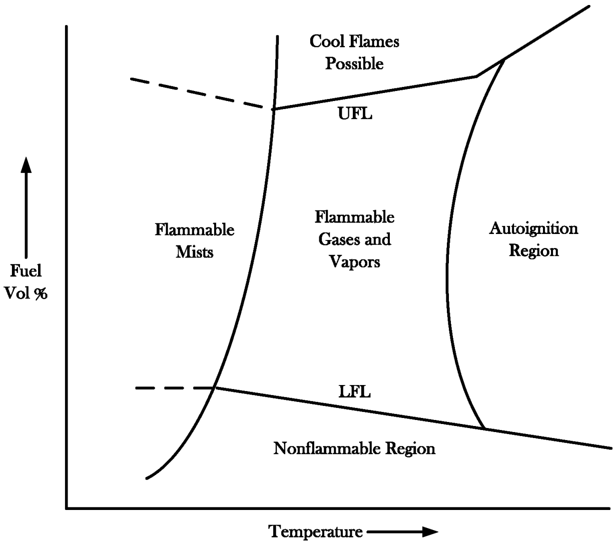

Figure 1. Classical representation of the flammability envelope of a fuel.

excessive heat loss to the tube walls, narrowing the reported flammability limits. This is particularly noticeable when the effect of initial mixture temperature is considered (Rowley, Rowley, and Wilding, 2010).

EN 1839 Tube Method

The European standardized tube method was originally developed in Germany as DIN 51649. Developers of the method took a more conservative approach, considering that any form of flame propagation could potentially result in a hazardous scenario. Flammability limits are measured in a vertical 8 cm diameter tube, 30 cm tall. When the method became European standard EN 1839(t) the propagation criterion was changed to require at least 10 cm of flame propagation. This was thought to account for localized heating of the mixture due to the ignition source.

2.2 UNDERSTANDING REPORTED FLAMMABILITY LIMIT DATA

The term flammability limit, its definition, the graphical representation (Figure 1), and the reported data all may be misleading as they do not specify what is meant by *flame propagation* and therefore imply that a given fuel-air mixture will either ignite or it will not. In reality, for each fuel there is a continuous range of concentrations in air that will support varying levels of flame propagation.

This simple, yet important, concept is rarely discussed in detail in literature, but is readily visible by inspection of reported flammability data and the standardized measurement methods. For example, according to the US Bureau of Mines, ignition of 5 vol% of methane in air will result in a flame that will just propagate for 150 cm in a 5 cm diameter vertical tube (Zabetakis, 1965); meanwhile, data from the EN tube method indicate that ignition of 4.4 vol% of methane in air will, on average, just fail to propagate a flame for 10 cm in a 8 cm vertical tube (Nabert, Schön, and Redeker, 2004). The discrepancy between these reported values can be explained by differences in measurement techniques, and in particular, differences in the required extent of flame propagation. The former measurement method is meant to represent the theoretical threshold between infinite flame propagation and the onset of flame extinction, while the latter measurement method is meant to represent the concentration below which little or no flame propagation will occur. Therefore, although at

Table 1. Standardized methods of measuring the flammability limits of chemicals.

Method	Vessel	Flammability Criterion
US Bureau of Mines	Vertical glass tube 2–8cm × 1–1.5 m	Visual flame propagation to top of tube
ASTM E-681	Spherical glass flask 5 dm^3	Upward and outward flame propagation away from the ignition source
ASTM E-918	Closed vessel $\geq$ 1 dm^3	Pressure rise $\geq$ 7%
ASHRAE	Spherical glass flask 12 dm^3	Continuous flame arc subtending a 90° angle from ignition source
EN 1839(t)	Vertical glass tube 8 cm × 30 cm	Flame detachment and 10 cm of propagation
EN 1839(b)	Closed spherical vessel 14 dm^3	Pressure rise $\geq$ 5%

first glance the two values appear to be at odds with one another, both yield important information regarding the potential flammable hazard of the chemical.

Based on the above discussion, the misconception of a discrete flammability limit should be replaced with a region over which partial to full flame propagation is possible, as visualized in Figure 2. Values measured in the Bureau of Mines apparatus would be located near the transition from infinite to partial flame propagation, while values determined using the EN tube method would be located near the transition from partial to no flame propagation. Viewing the flame extinction phenomena in this manner not only explains many apparent discrepancies among reported data, but also provides further insight into the flame extinction phenomenon, is necessary for proper application of reported flammability data, and may even further the establishment of an internationally accepted measurement method.

2.3 APPLICATION OF REPORTED FLAMMABILITY LIMITS TO CONSEQUENCE STUDIES

Unlike the fuel-air mixtures used in laboratory test to determine flammability limits, dispersing clouds of fuel are not uniform in concentration. Therefore, a flame that is initiated at a location in the cloud with a concentration below the reported Bureau of Mines LFL could propagate into a region of higher concentration, resulting in full flame propagation back to the cloud source and potentially a severe explosion event. Evans and Puttock (1986) performed a short series of tests on propane clouds, attempting to ignite the clouds at locations of varying concentration. They indicated that ignition at a location with a concentration approximately 0.6 times the Bureau of Mines LFL resulted in "small" localized flames (4 to 16 m diameter hot gas zone), while ignition at concentrations 0.9 times the Bureau of Mines LFL resulted in full flame propagation back to the fuel source.

For the sake of conservatism and to account for temporal fluctuations in concentration, it has been suggested to consider the $\frac{1}{2}$-LFL isopleth as the boundary of the flammable cloud (Department of Transportation, 1980; Webber, 2002). Although such an approach is meant to add a measure of conservatism to the predicted results, it is flawed for a number of reasons:

1. It neglects consideration of the region near the UFL where changes in the isopleth result in larger changes in the calculated flammable mass due to the relatively high fuel concentration.
2. It assumes the same "safety-factor" is applicable to all chemicals.
3. The value of the $\frac{1}{2}$-LFL is dependent on which published flammability data the analyst selects.

Adopting the $\frac{1}{2}$-LFL as the cloud boundary is unnecessary when a short averaging time is used, the proper flammability data are utilized, and the purpose of the study is considered. When considering only the ignitability of a cloud, theory and limited experimental evidence suggest the widely published Bureau of Mines data are under conservative. On the other hand, when considering the explosion effects from a flammable cloud, fuel outside the Bureau of Mines flammability limit data is unlikely to contribute significantly to the overpressure since the flame speed drops significantly as the fuel concentration approaches the reported flammability limits (Liao et al., 2005). Perhaps the best approach would be to use both data sets, the EN flammability limit data to determine the ignitability of the cloud and the Bureau of Mines data to determine the flammable mass. However, since typical consequence analysis software utilizes only a single set of flammability data, we consider now the influence of

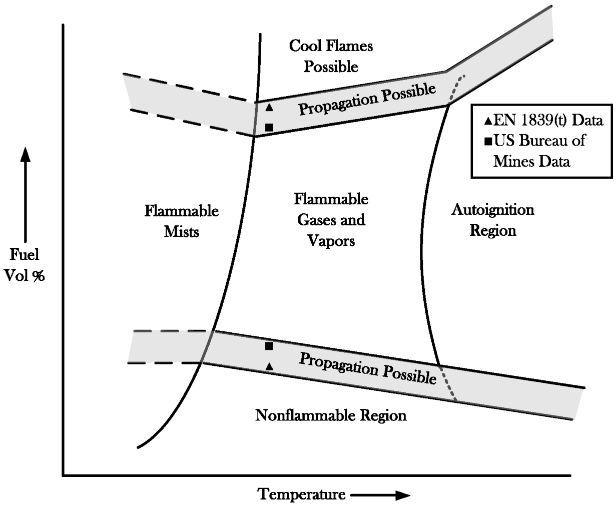

Figure 2. Modified representation of the flammability envelope of a fuel, illustrating the concept of a continuous region of flame extinction encompassing the reported flammability limits.

flammability data on the predicted flammable mass and cloud boundaries.

3. METHODOLOGY

The impact of the selection of flammability limit data on consequence studies was examined for five real consequence studies performed by Baker Engineering and Risk Consultants, Inc. (BakerRisk). Each of the studies was performed using the Bureau of Mines flammability limit data, as reported by Zabetakis (1965) and Kutcha (1985), and then again using the flammability limit data reported by Nabert, Schön, and Redeker (2004). Table 2 lists the reported flammability limit values for the pure components used in the analysis. A summary of the five different consequence studies is provided in Table 3. Where necessary, the flammability limits of mixtures were estimated using Le Chatlier's mixing rule. Discharge and dispersion modeling were performed using BakerRisk's in-house software SafeSite$_{3G}^{TM}$.

4. RESULTS

Results are reported in terms of percent change of flammable mass, distance to UFL, and distance to LFL, with the percent change in this work defined relative to values obtained when the US Bureau of Mines flammability data are used. To avoid reporting large changes corresponding to little practical significance (i.e., predicted flammable mass increasing from 0.001 kg to 0.01 kg corresponds to a 900% change), the percent change in flammable mass was only considered for scenarios with the predicted mass above 1 kg for both the US and EN flammability data.

Table 4 summarizes the percent change in predicted flammable mass and distances to UFL and LFL. Use of the EN flammability data resulted in an average increase in predicted flammable mass by 52%, with the distance to UFL decreasing by 10% and the distance to LFL increasing by 20%. Histograms of the percent change are given in Figure 3 through Figure 5 with frequencies normalized to the number of points per consequence study to account for the large differences in points between studies. Thus an

Table 2. US (Zabetakis, 1965; Kutcha, 1985) and EN (Nabert, Schön, and Redeker, 2004) flammability limit data used in the consequence analyses.

		LFL			UFL		
Material	CASN	US	EN	% Diff	US	EN	% Diff
1,3-Butadiene	106-99-0	2	1.4	30.0	12	16.3	−35.8
Acetylene	74-86-2	2.5	2.3	8.0	100	100	0.0
Ammonia	7664-41-7	15	15.4	−2.7	28	33.6	−20.0
Benzene	71-43-2	1.3	1.2	7.7	7.9	8.6	−8.9
Carbon Monoxide	630-08-0	12.5	10.9	12.8	74	76	−2.7
cis-2-Butene	590-18-1	1.7	1.6	5.9	9.7	10	−3.1
Ethane	74-84-0	3	2.5	16.7	12.4	15.5	−25.0
Ethanol	64-17-5	3.3	3.1	6.1	19	15	21.1
Ethyl Acetate	141-78-6	2.2	2	9.1	11	12.8	−16.4
Ethyl Chloride	75-00-3	3.8	3.6	5.3	15.4	14.8	3.9
Ethylene	74-85-1	2.7	2.3	14.8	28.6	32.4	−13.3
Hydrogen	1333-74-0	4	4	0.0	75	77	−2.7
Isobutane	75-28-5	1.8	1.3	27.8	8.4	9.8	−16.7
Isopentane	78-78-4	1.4	1.3	7.1	7.6	7.6	0.0
Methane	74-82-8	5	4.4	12.0	15	17	−13.3
Methanol	67-56-1	6.7	6	10.4	36	44	−22.2
m-Xylene	108-38-3	1.1	1	9.1	6.4	7	−9.4
n-Butane	106-97-8	1.8	1.4	22.2	8.4	9.3	−10.7
n-Hexane	110-54-3	1.2	0.92	23.3	7.4	9.18	−24.1
n-Nonane	111-84-2	0.85	0.7	17.6	2.9	5.6	−93.1
n-Octane	111-65-9	0.95	0.8	15.8	6.5	6.5	0.0
o-Xylene	95-47-6	1.1	1	9.1	6.4	7.6	−18.8
Propanal	123-38-6	2.9	2.3	20.7	17	21	−23.5
Propane	74-98-6	2.1	1.7	19.0	9.5	11	−15.8
Propylene	115-07-1	2.4	2	16.7	11.1	11.1	0.0
p-Xylene	106-42-3	1.1	1	9.1	6.6	7	−6.1
Styrene	100-42-5	1.1	1.1	0.0	6.1	8	−31.1
Toluene	108-88-3	1.2	1.1	8.3	7.1	7.8	−9.9

Table 3. Summary of the five Consequence Studies performed.

	Study 1	Study 2	Study 3	Study 4	Study 5
Pure Materials	5	8	10	4	12
Mixtures	2	31	41	2	47
Process Pressure (barg)	1.5 to 200	0.1 to 60	0 to 90	0.1 to 37	0 to 103
Process Temperature (^{o}C)	−5 to 100	−40 to 100	−165 to 400	−102 to 98	−37 to 613
Hole Size (mm)	13 to 150	4 to 150	10 to 150	13 to 152	13 to 152
Weather Conditions	B3, D4, D8, F2	B2, D3, D7, F2	B2, D3, D7, F2	D4, F2	D4, F2
Total Number of Scenarios	466	1978	1862	468	2768

Table 4. Average, maximum, and standard deviation (σ) of the percent change in consequence results when EN 1839(t) flammability limit data are used instead of US Bureau of Mines data.

	Flammable Mass			UFL			LFL		
Study/Material	Average	Max	σ	Average	Max	σ	Average	Max	σ
1	38	187	24	−5	−87	8	17	165	10
2	61	437	48	−6	−87	9	21	216	21
3	42	439	27	−14	−88	14	15	162	8
4	29	232	31	−9	−90	31	14	188	15
5	59	200	31	−12	−93	10	23	134	12
Ethylene	39	164	21	−13	−42	8	17	47	5
Propane	58	134	23	−14	−90	11	23	43	6
Overall	52	439	36	−10	−93	11	20	216	15

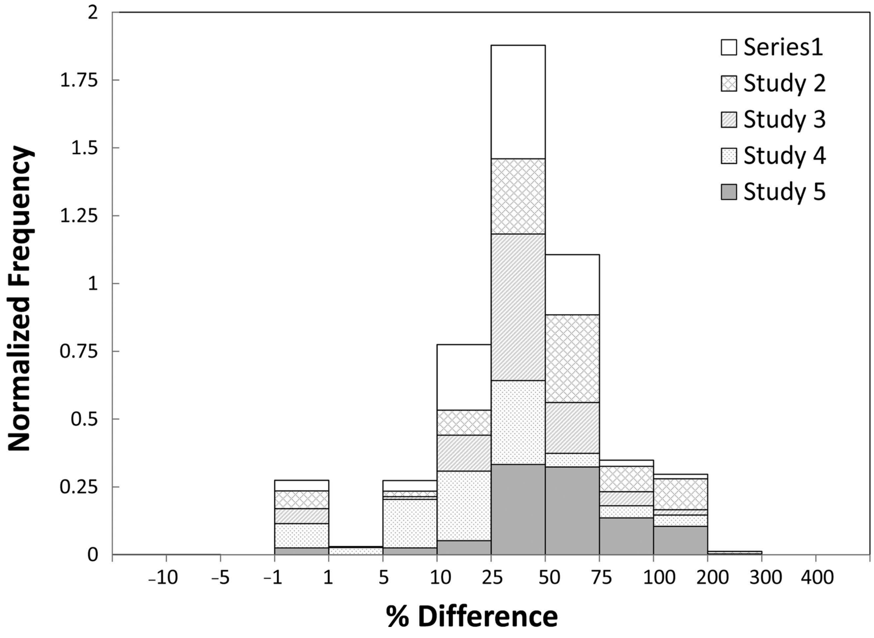

Figure 3. Histogram for percent change in predicted flammable mass when EN flammability data are used instead of US Bureau of Mines data.

individual bar represents the fraction of points from a study falling within the specified range of percent change, the sum of each type of bar being 1 and the sum of all bars being 5. The majority of scenarios resulted in a 25% to 75% change in the predicted flammable mass, though several scenarios resulted in a change in predicted

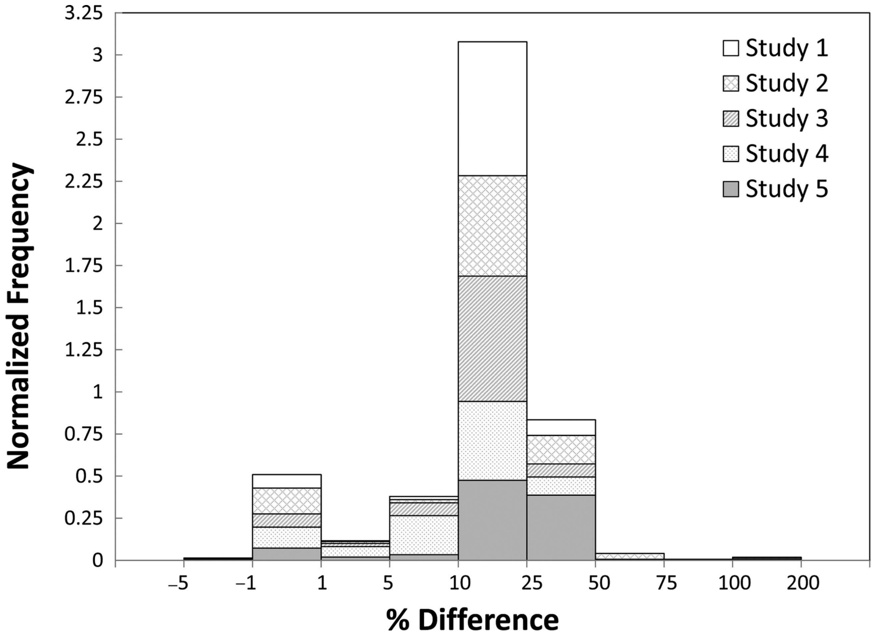

Figure 4. Histogram for percent change in predicted distance to LFL when EN flammability data are used instead of US Bureau of Mines data.

flammable mass exceeding 400%. The distance to LFL preponderantly increased between 10% to 25% when the EN flammability data were used, corresponding closely with the differences in the reported lower flammability limits. Similarly, the majority of predicted distances to UFL decreased by 10% to 25%, but a large number of scenarios also exhibited little change. Many of these scenarios correspond to scenarios with identical US and EN flammability data.

Figure 6 shows the histograms of percent changes in flammable mass for scenarios involving ethylene and propane, two fuels commonly evaluated during consequence

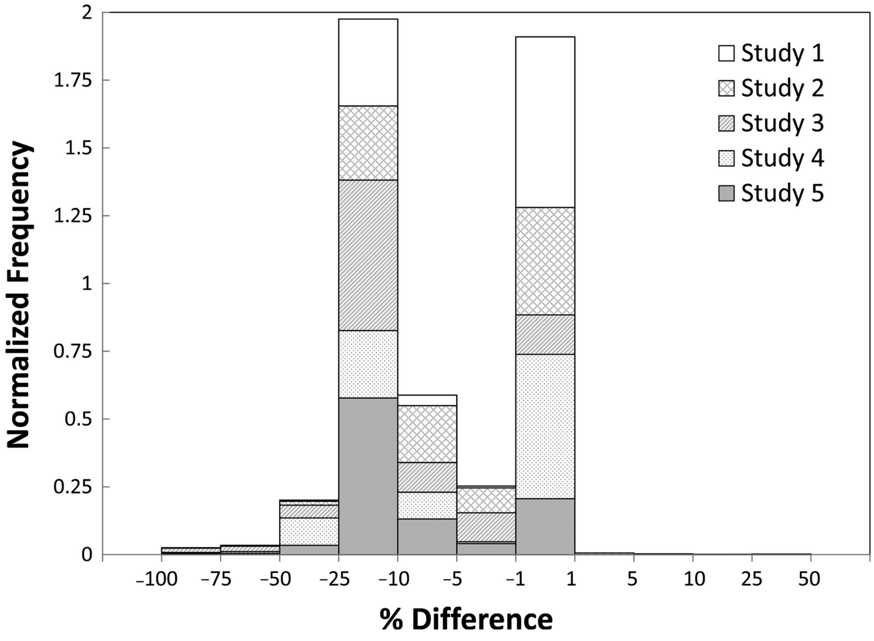

Figure 5. Histogram for percent change in predicted distance to UFL when EN flammability data are used instead of US Bureau of Mines data.

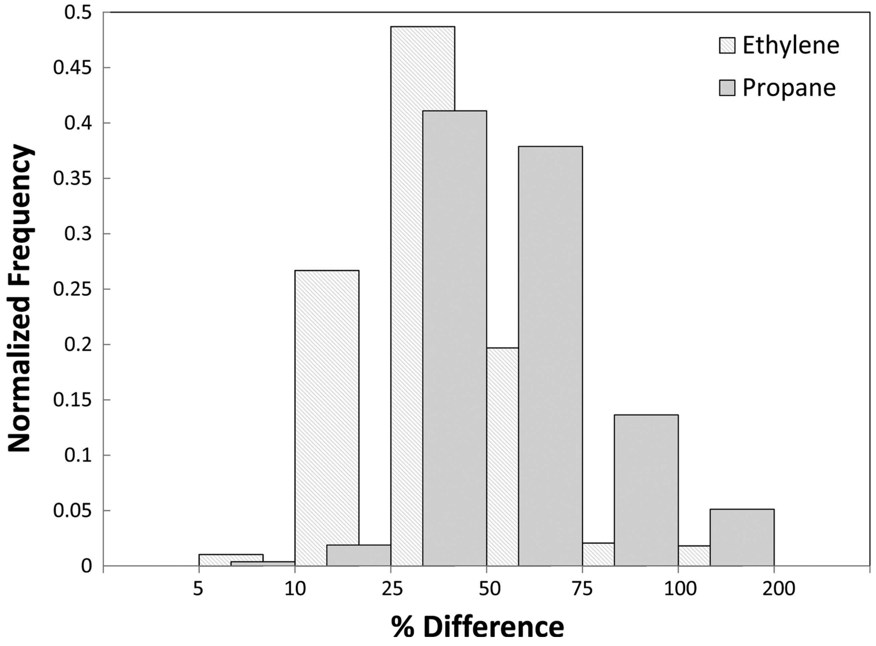

Figure 6. Histogram for percent change in predicted flammable mass for scenarios involving ethylene and propane.

analyses. The distributions of the change in flammable mass for both fuels are approximately the same as the distribution for all scenarios (Figure 3). However, as shown in FigureS 7 and 8, using EN flammability data will nearly always increase the distance to LFL and decrease the distance to UFL between 10% and 25% for these two fuels, corresponding roughly to the percent difference between the US and EN reported flammability limit values. In fact, as shown in Figure 9, for many fuels the change in the distance to UFL or LFL is roughly proportional to the percent difference between the data sets for the reported flammability limits.

To illustrate that the above results are likely applicable to studies performed with other consequence analysis

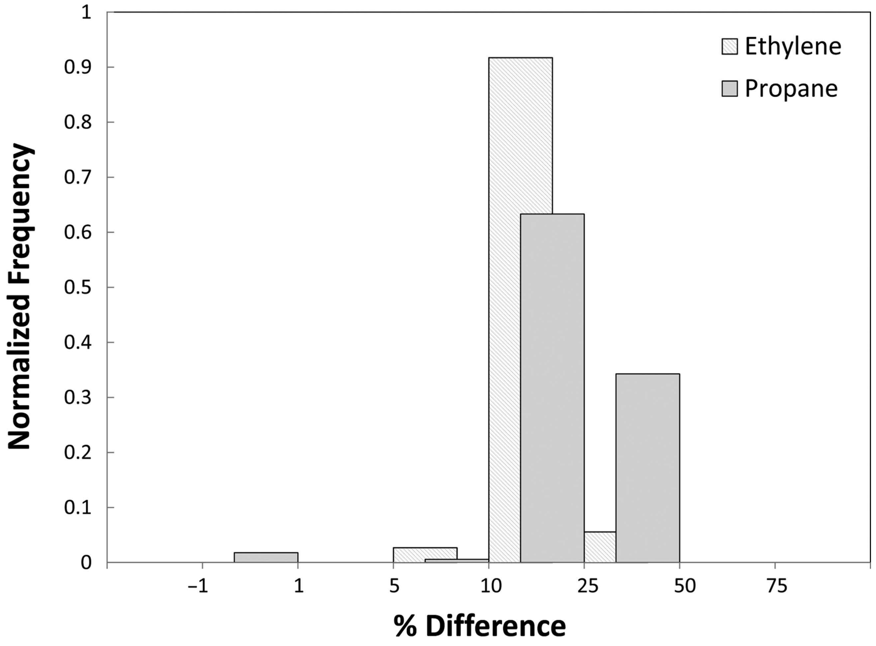

Figure 7. Histogram for percent change in predicted distance to LFL for scenarios involving ethylene and propane.

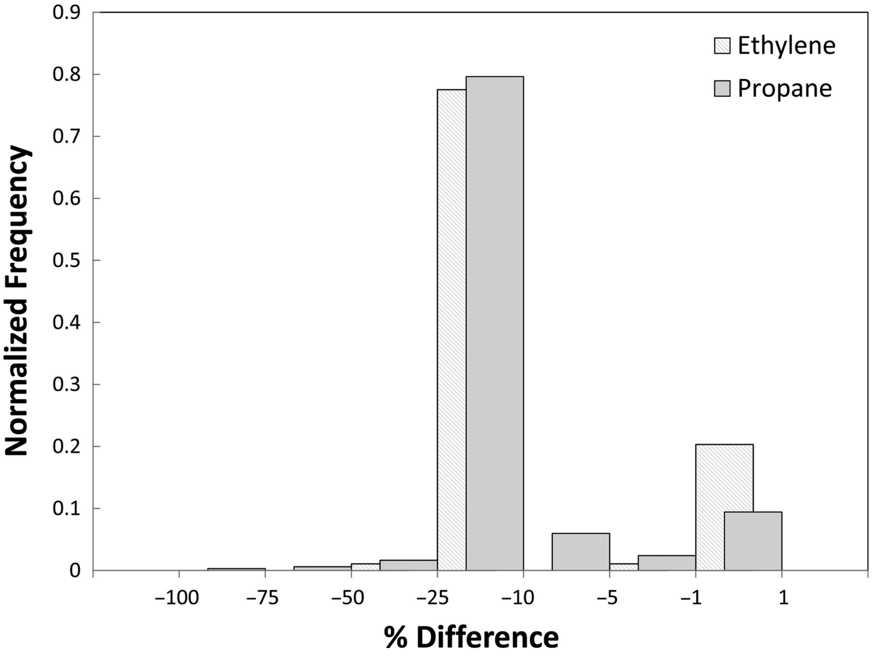

Figure 8. Histogram for percent change in predicted distance to UFL for scenarios involving ethylene and propane.

software, 20 scenarios were randomly selected and modeled in DNV's PHAST software. A comparison of the results is given in Figure 10. Although there are differences in the results, particularly for the predicted flammable mass, the scatter in Figure 10 appears to be randomly distributed on both sides of the 45^o parity line.

5. CONCLUSIONS

It has been shown that the flammability limit data used in consequence analyses can significantly impact the results, with the EN (t) flammability limit data leading to increases in predicted flammable mass and cloud size when compared to predicted results with the US Bureau of Mines data in use.

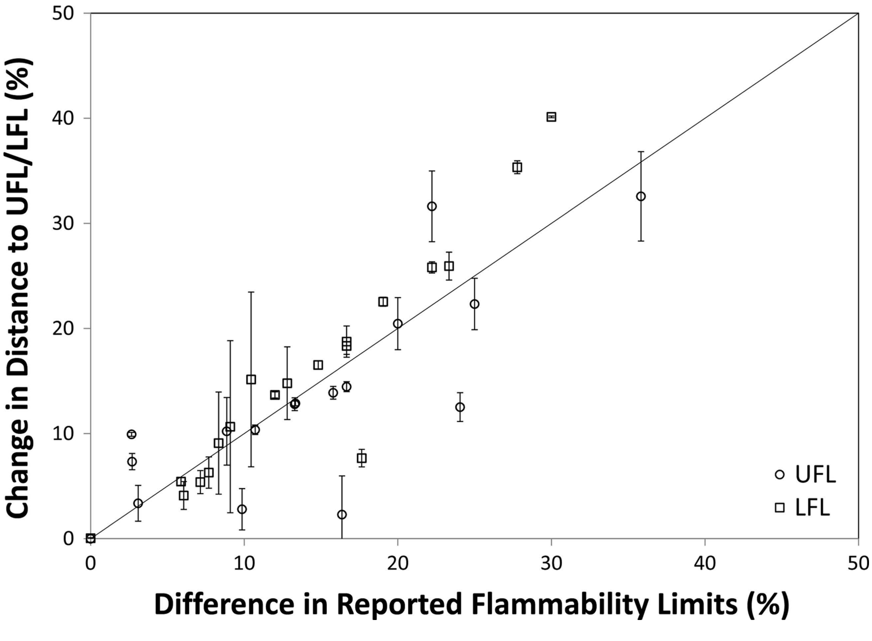

Figure 9. Average impact of using EN instead of US Bureau of Mines flammability data on predicted distance to UFL/LFL for pure fuels.

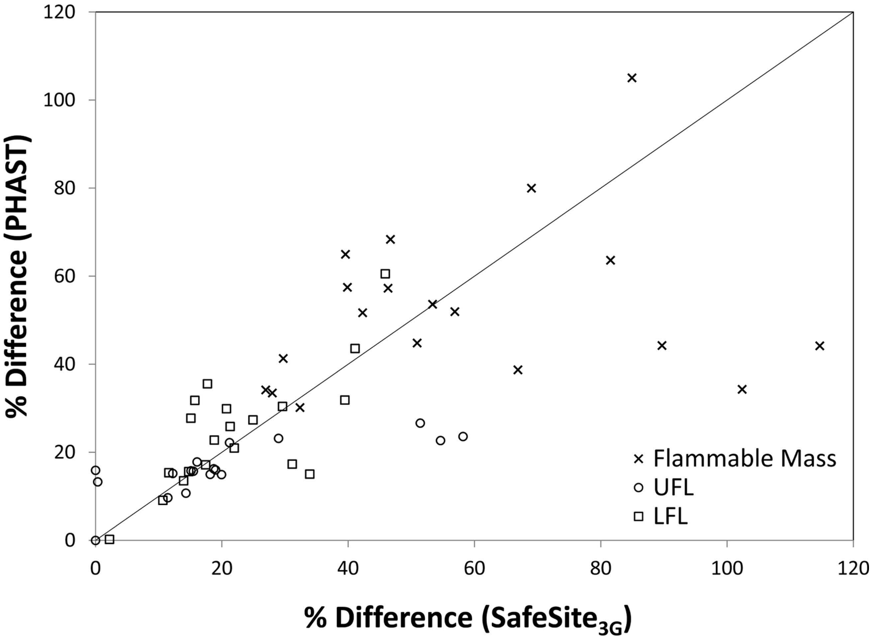

Figure 10. Comparison between PHAST and SafeSite$_{3G}$ of the impact of flammability data on predicted results for flammable mass, distance to UFL, and distance to LFL.

Because the US Bureau of Mines data are meant to represent the fuel concentrations that will propagate a flame infinitely away from the ignition source, using the Bureau of Mines data set will result in under prediction of the flammable cloud size. The EN data, on the other hand, correspond to incipient flame propagation and will yield a more accurate, if not slightly conservative, picture of the region in the plume where flame propagation is possible.

Therefore, if the purpose of the consequence analysis is to determine the shape and size of the flammable cloud, we recommend use of flammability data obtained using the EN 1839(t), when possible. Flammability data obtained using the US Bureau of Mines method are possibly suitable when estimating the flammable mass for explosion overpressure calculations because the flame speed drops significantly as the fuel concentration approaches the reported flammability limits. However, use of the EN 1839(t) flammability data will lead to more conservative results.

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