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course "Emergency Relief System Design Using DIERS Technology". Since 1987 this course has had approximately 650 students in 56 offerings, which include several in-house courses held at domestic and international (Mexico and Canada) companies.

DIERS' technology has been adopted worldwide with many domestic and international standards and recommended practices having incorporated elements of the original sponsored research and contributions of member company representatives. The efforts of the original DIERS research program, the DIERS Users Group, and company representatives over the years have changed a chemical engineering paradigm – the methodology used to size emergency relief systems for runaway reactions involving two-phase, vapor-liquid venting. The DIERS Users Group has truly been a forum for development and dissemination of the technology used to design emergency relief systems.

For membership information, contact Harold G. Fisher, Chair of the DIERS Users Group, 229 Brookhaven Drive, Nitro, WV 25143. Phone: 304-776-6371, Fax: 304-776-1076 or E-mail at fisherhg@suddenlink.net.

Fauske & Associates, LLC was the DIERS contractor. The DIERS technology manual, computational techniques and SAFIRE computer program, large-scale runaway reaction and blowdown validation experiments, and the runaway reaction and two-phase flow onset / disengagement bench-scale apparatus were all written, conducted, or developed by FAI.

Hans K. Fauske and the staff of FAI and affiliated consultants, Harold G. Fisher of FisherInc, and Joseph C. Leung of Leung, Inc, are available as consultants to support your emergency relief system design and experimental requirements involving runaway chemical reactions and two-phase vapor-liquid flow, litigation support, and training requirements. Several computer programs are also available for sale that can be used to support your in-house emergency relief system design calculations. Please contact Sales and Business Development Leader Russell Lee at rlee@fauske.com or 630-887-5285, to discuss your specific needs.

Flammability Testing at FAI

By Paul Osterberg, Chemical Engineer

Explosions or fires occur frequently in many process vessels or storage tanks that contain flammable chemicals. This frequent occurrence of explosions in the process industries is due to an explosive mixture being present in the vapor space and either the lack of knowledge about the inherent safety implications or inadequate safety procedures. In order to minimize the risk/prevent an explosion, it is important to evaluate the flammability characteristics of gas/vapor mixture such as the lower flammability limit, the upper flammability limit, the limiting oxygen concentration, and the deflagration index.

The resulting phenomenon of an explosion or fire arises when the following three components, shown in Figure 1, are present: fuel, oxidizer, and ignition source.

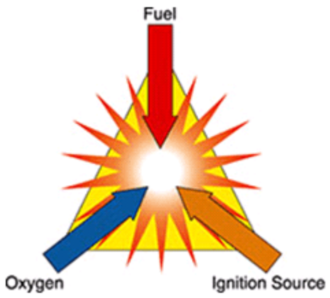

Figure 1: Fire/Explosion Triangle

It is a common practice for many industries to minimize/prevent the formation of explosion hazards in their process by removing one of these components. This may be accomplished through activities such as inerting or suppression mitigation procedures to remove oxidizer and fuel or grounding & bonding of the vessel (or other ignition source controls such as electrical sources, hot work, mechanical sparks etc). However, it is not always applicable or economical to remove the oxygen or the fuel from the process. Grounding and bonding are useful ways to minimize an ignition source; although, it is difficult to say that prevention of the formation of static electricity could always be achieved (Kletz, 1999). Therefore, a process or storage tank may need to contain an explosive mixture in the vapor space at some time that only needs an ignition source to produce an incident. For these reasons, it is important to understand the flammable nature of the chemical(s) that are being used in order to implement the proper safety procedures and design.

Flammable materials are hazardous under certain conditions and the determination of these conditions is essential to understanding the importance of proper safety practices. The region under which a material/mixture is flammable is known as the limits of flammability, shown in Figure 2, where the lower bound limit is the lower flammability limit or lean flammability limit (LFL) and the upper bound limit is the upper flammability limit or rich flammability limit (UFL or RFL).

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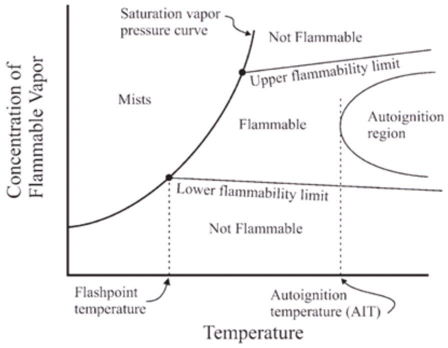

Figure 2: Temperature Effects on a Combustible Mixture (Crowl, 2003)

Inside these limits, a flammable mixture is able to sustain flame propagation even after which an ignition source has been removed. However, the mixture ratios outside of these limits are not able to self-support the flame propagation once the ignition source has been removed. Another important issue with flammable chemicals is the autoignition region. The autoignition temperature is the temperature at which a fuel/air mixture enters the self-explosion regime not requiring an external localized ignition source.

As shown in Figure 2, the LFL and UFL are function of temperature where that the flammability region broadens as the temperature increases. These limits are also affected by pressure. There is little effect on the LFL except at very low pressures; however, the UFL generally increases as the pressure increases. The LFL and UFL for many hydrocarbons can be estimated as follows (Crowl, 2003)

$$\mathrm{LFL} = 0.55C_{st} \qquad (1)$$

$$\mathrm{UFL} = 3.5C_{st} \qquad (2)$$

where Cst is the stoichiometric concentration of fuel in air.

Another important characteristic of flammable chemicals is the limiting oxygen concentration (LOC). This provides the minimum amount of oxygen needed for a flammable mixture to sustain flame propagation. The LOC for a gas or vapor can be estimated by (Crowl, 2003)

$$\mathrm{LOC} = x(\mathrm{LFL}) \qquad (3)$$

where x is the stoichiometric coefficient for oxygen in a balanced combustion reaction equation.

These flammability characteristics (LFL, UFL, and LOC) of gases and vapors are determined at Fauske & Associates using various flammability test chambers; the primary one being a 5-L spherical Parr vessel as shown in Figure 3. This vessel is capable of withstanding pressures up to 10,000 psig with working temperatures of up to 150°C.

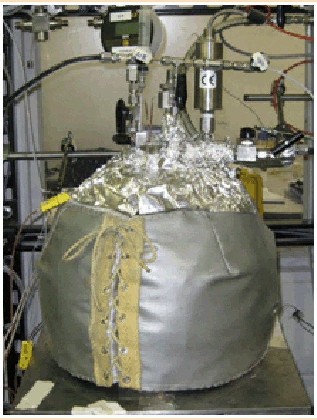

Figure 3 : 5-L Parr Vessel

For example, the combustion reaction for propane is

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad (4)$$

Thus giving a stoichiometric concentration of 4 vol.% propane in air. The LFL, UFL, and LOC of propane were determined in accordance to the ASTM Standards E918 "The Standard Practice for Determining Limits of Flammability of Chemicals at Elevated Temperatures and Pressures" and E2079 "Standard Test Methods for Limiting Oxygen (Oxidant) Concentration in Gases and Vapors". Based on these standards, a positive ignition result is when combustion reaction produces a 7% rise above the initial absolute pressure. Further, a 10 J ignition source was used during these tests. Results obtained for the LFL, UFL, and LOC for propane, shown in Table 1, are compared with other reported literature values and approximations made using equations 1 through 3.

Table 1: Flammability Limits of Propane

	Estimated Values	*FAI Results*	*Literature Values*
LFL	*2.2*	*2.05*	*2.0*[a]
UFL	*14.1*	*10.25*	*10.0*[a]
LOC	*11.0*	*10.75*	*10.7*[b]

a. Data was obtained from Kondo et al. (2008).
b. Data was obtained from Zlochower et al. (2009).

These results are illustrated graphically on propane's flammability envelope, shown in Figure 4, and compare very well with the reported literature values.

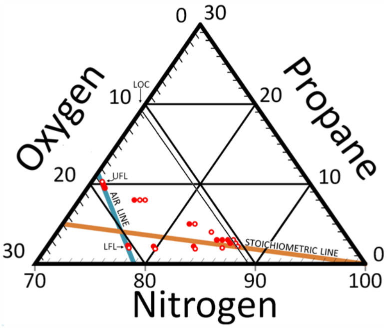

Figure 4 : Flammability Envelope for Propane-Air Mixtures at an Increased Resolution

This flammability data can be used to help minimize the chance of an explosive mixture resulting when a process vessel is brought into service or taken out of service. For example, when a vessel that contains a flammable gas or liquid needs to be removed. If air is introduced to the vessel, a flammable mixture will exist between the LFL and UFL; thus, presenting a safety hazard. In order to safely decommission a process vessel, the flammability zone could be avoided through diluting the fuel vapor with an inert to below the out-of-service fuel concentration (OSFC). The OSFC is given by (Mashuga & Crowl, 1998)

$$\mathrm{OSFC} = \mathrm{LOC}/z(1-\mathrm{LOC}/21) \qquad (5)$$

On the other hand, flammability data also needs to be used when a process vessel is being commissioned to contain a flammable mixture. Consider a vessel that needs to be filled with a flammable gas or liquid. If the flammable liquid is introduced to the vessel containing air, a flammable mixture will exist between the LFL and UFL; thus, presenting a safety hazard. In order to safely add this liquid, the oxygen concentration in

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the tank must be lowered to a certain level. The in-service oxygen concentration (ISOC0 is given by (Mashuga & Crowl, 1998)

$$ISOC = (LOC*z)/((z-LOC/100)) \qquad (6)$$

When using data obtained for the flammability characteristics of an explosive mixture, it is important that the data models the specific process as close as possible. Slight variations could have a drastic impact on the flammability parameters, thereby, possibly underestimating the potential hazards of a mixture. For instance, inert diluents are not all equal and do not have the same effectiveness in extinguishing flame propagation in a flammable mixture. The reason for this is the molar specific heat of the diluents. The higher the specific heat the more effective the inertant is at removing heat form the system and lowering the final temperature. Figure 5 shows how different diluents change the flammability region of methane.

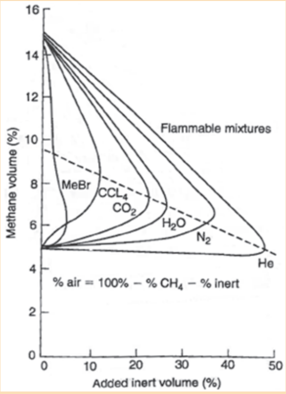

Figure 5: The Effect of Inertants on the Flammability Envelope of Methane (Glassman & Yetter, 2008)

It is important to know whether a gas and/or vapor mixture lies within the flammable region; however, it is more important to understand its explosion severity potential. The explosion severity of a mixture changes depending on where the mixture lies within the flammable region. Determination of the potential hazards of an explosion (i.e. the maximum overpressure and the maximum rate of pressure rise during a deflagration event) allows for the proper design for pressure relief vents as well as pressure ratings on vessels. This is done through measuring the deflagration characteristics of a specific mixture over a range of concentrations. The deflagration index is the normalization of maximum rate of pressure rise to the apparatus' test volume which is given by

$$K_G = (dP/dt)_{max} V^{(1/3)} \qquad (7)$$

For example, take hydrogen which has a LFL of approximately 4% and a UFL of 75% in air with a stoichiometric concentration of 29.5% in air. Inside its flammable region, the violence of a hydrogen deflagration varies significantly as shown in Figure 6.

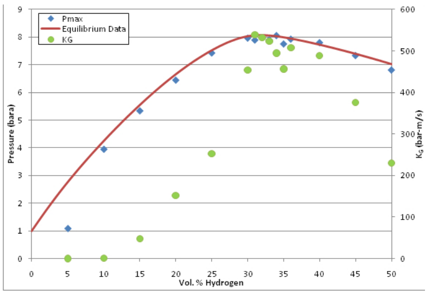

Figure 6: Pressure and K^G Results as a function of Hydrogen Concentration

Typically, near the stoichiometric concentration the most violent deflagration events will result. The KG value, summarized in Table 2, was determined for hydrogen and is compared to other literature values.

Table 2: Deflagration Data of Hydrogen

	FAI Results		*NFPA*[c]	
Gas	P_{MAX} (bar g)	K^G (bar-m/s)	PMAX (bar g)	K^G(bar-m/s)
Hydrogen	7.1	540	6.8	550

c. Data was obtained from Bartknecht (NFPA, 2007).

At this time there is no standard method for the determination of the maximum rate of pressure rise and the maximum pressure for gases and vapors. Also, it seems that the deflagration index for an explosive mixture is a function of the vessel volume. Furthermore, it has been shown that the deflagration index is sensitive to small changes in the experimental procedure (Mashuga & Crowl, 2000). For these reasons, there is much variability between reported literature values.

Gaining an understanding of the flammability characteristics of a hazardous material can greatly assist in the assessment and mitigation of fire and explosion hazards in the process environment. For additional information, please contact Fauske & Associates, LLC.

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