LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-TR-217005

An Improved Analytical Approach to Determine the Explosive Effects of Flammable Gas-Air Mixtures

Joong M. Yang, P.E.

November 2005

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Auspices Statement

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

An Improved Analytical Approach to Determine the Explosive Effects of Flammable Gas-Air Mixtures

Joong M. Yang, P.E.
yang13@llnl.gov
(925) 424-6201
Lawrence Livermore National Laboratory
Livermore, CA 94551

The U.S. Department of Energy (DOE) Complex includes many sites and laboratories that store quantities of low-level, solid nuclear waste in drums and other types of shipping containers. The drums may be stored for long periods of time prior to being transported and final dispositioning. Based on the radioactivity (e.g., Pu^{239} equivalent), chemical nature (e.g. volatile organic compounds) and other characteristics of the stored waste, flammable gases may evolve. Documented safety analyses (DSAs) for storage of these drums must address storage and safety management issues to protect workers, the general public, and the environment. This paper discusses an improved analytical method for determining the explosion effects flammable gas-air mixtures as well as the subsequent accident phenomenology.

EXPLOSIVE REACTION METHODOLOGY

There are two modes of explosive reactions that are determined by the reaction rate for flammable gas-air mixtures, namely detonation and deflagration. The condition and the rate at which the chemical reaction occurs, which is experimentally derived, determine the potential damage to structures, e.g., drums, and the material at risk (MAR). Quantification of the amount of radioactive material subject to accident conditions and potentially made airborne under postulated release conditions are important steps in evaluating impacts for accident analysis. The outcome of this phase of analysis is critical towards determining the type and level of safety controls to be implemented, and is part of the comprehensive DOE-STD-3009-94[1] safety analysis process.

The analytical methodology described here is compared to commonly used explosion assessment techniques. A comparison of this type provides an understanding of the relative merits of the analytical approach.

Although severe physical limitations make a detonation very difficult phenomenon to produce in flammable gas-air mixtures, the analytical method is generalized enough to determine the damage potential from postulated detonations. The approach is discussed along with the physical limitations. In addition, the analytical method to determine the damage potential from potential deflagrations involving flammable gas-air mixtures is also covered. Two mixtures of particular interest in a typical nuclear facility, e.g., hydrogen-air mixtures and natural gas-air

[1] DOE-STD-3009-94, Change Notice 2, "Preparation Guide for U.S. Department of Energy Nonreactor Nuclear Facility Safety Analysis Reports," U.S. Department Of Energy, 2002.

mixtures, are analyzed for various concentrations. Areas of the analysis are described to ensure that conservatism in the analytical results is maintained.

RESULTS

Results of the analysis show that the conventional method using TNT equivalence based on the product yield factor and the heat of combustion may be misleading for predicting the potential damage for the purpose of the accident analysis. The analysis shows that the TNT equivalence depends on the concentration. For example, the conservative TNT equivalence for a potential detonation of the stoichiometric hydrogen-air mixture is 0.82 kg-TNT/kg-mixture and decreases for non-stoichiometric mixtures. Furthermore, the AICC (adiabatic, isochoric complete combustion) pressure from potential deflagrations is only dependent on the concentration and not on the size of the confinement volume.

1.0 Introduction

The fundamentals of the combustion process, whether in an explosion or in a fire, is the same for the given fuel, e.g., a flammable gas such as hydrogen. The only difference is the rate at which the combustion reaction occurs whether that reaction occurs. Physical constraints that must be satisfied for combustion of flammable gases and the method to determine the damage potential expressed in terms of pressure when confined in a volume are discussed to assure that real flammable hazards in DOE nuclear facilities, e.g., TRU waste handling and storage facilities, are addressed effectively with minimal cost. Whether in a deflagration or in a detonation, the pressure increase is significant if the reaction is enclosed in a volume. The discussion is limited to air as the oxidizing agent in the combustion process.

Two common flammable gases of concern will be discussed in detail. The methodology is, however, applicable to all flammable gases, combustion properties of which are known. In addition, an analytical tool will be used to evaluate the damage potential for flammable gas mixtures even in odd concentrations and compositions.

The combustion reaction of a stoichiometric hydrogen-air mixture is shown below:

$$H_2 + 0.5\begin{bmatrix} O_2 \\ 3.76\,N_2 \end{bmatrix} \Rightarrow H_2O + 1.88\,N_2$$

The molar ratio of the stoichiometric mixture would be 1:0.5:1.88 of H_2:O_2:N_2. The volumetric concentration of hydrogen in a stoichiometric mixture is then:

$$\text{mol}\,\%\,H_2 = \text{vol}\,\%\,H_2 = \frac{100\%}{1+0.5+1.88} = 29.586\%$$

The required volume of air for complete combustion of 1 m^3 of hydrogen is 2.38 m^3. Similarly, the combustion reaction can be written for natural gas, which is mostly methane. The combustion reaction of a stoichiometric methane-air mixture is shown below:

$$CH_4 + 2\begin{bmatrix} O_2 \\ 3.76\,N_2 \end{bmatrix} \Rightarrow 2H_2O + CO_2 + 7.52\,N_2$$

The molar ratio of the stoichiometric mixture would be 1:2:7.52 of CH_4:O_2:N_2. The volumetric concentration of hydrogen in a stoichiometric mixture is then:

$$\text{vol}\,\%\,CH_4 = \frac{100\%}{1+2+7.52} = 9.506\%$$

The required volume of air for complete combustion of 1 m^3 of methane is 9.52 m^3. Combustion characteristics of the two flammable gases are listed in Table 1.

Table 1. Combustion characteristics of flammable gases (Reference 1).

	Flammable range, volume %	Laminar burning velocity, m/s	Auto-ignition temperature, °C (°F)	Heat of Combustion, MJ/kg
Hydrogen	4 to 75	3.12	500 (932)	120
Methane	5 to 15	0.45	537 (999)	50.0

One additional term, the equivalence ratio, must be defined before proceeding further. The equivalence ratio is the ratio of the actual mixture to the stoichiometric ratio, defined as follows (Reference 2):

$$\Phi = \frac{\left(\eta_{\text{fuel}} / \eta_{\text{air}} \right)_{\text{actual}}}{\left(\eta_{\text{fuel}} / \eta_{\text{air}} \right)_{\text{stoich}}} \tag{1}$$

where η is the molar concentration of the constituent. For gaseous mixtures, the molar concentration is equal to the volumetric concentration. For Φ less than unity, the mixture is lean and the flammable gas is consumed completely with excess oxygen remaining in the mixture. For Φ greater than unity, the mixture is rich in fuel and oxygen in air is completely consumed.

The rate at which the chemical reaction takes place determines the potential damage to the structures, e.g., drums, and the material at risk to pose an undue risk to the health and safety of the public and the workers. There are two modes of reactions that are determined by the reaction rate. They are detonation and deflagration. Each mode of reactions and the damage potential are discussed.

2.0 Detonation

Detonation refers to a process in which a shock-induced combustion wave is propagating through a reactive mixture at speeds exceeding the speed of sound. There are severe physical limitations that make detonations very difficult phenomenon to achieve for fuel-air mixtures, in particular, in an accident. First, the concentration limit for detonation, or detonable limit, is narrower than that of the flammability limit for a specific gas. For hydrogen, for example, the flammability limit ranges from 4% to 75% in air in ambient conditions. The detonable limit ranges from 18.3% to 59% for hydrogen. The detonable range of a selected set of flammable gases is provided in Table 2.

Second, there are physical limitations consisting of spatial and initiation energy requirements. Spatial and minimum initiation energy requirements are shown in Figure 1 and Figure 2, respectively, for flammable gas mixtures as a function of concentration. For instance, the minimum initiation energy (MIE) for detonation of a stoichiometric hydrogen-air mixture is approximately 4.0 kJ. This is 2.1×10^{8} times higher than the minimum deflagration initiation energy of 0.019 mJ for the same stoichiometric hydrogen-air mixture. For the stoichiometric methane-air mixture, the detonation initiation energy is off the chart in Figure 2.

Table 2. Detonable limits of selected flammable gases (Reference 3).

Mixture	Lower limit, per cent fuel	Upper limit, per cent fuel
$H_2 - O_2$	15	90
H_2 – air	18.3	59
$CO - O_2$, moist	38	90
$CO - O_2$, well dried	–	83
$(CO + H_2) - O_2$	17.2	91
$(CO + H_2)$ – air	19	59
$NH_3 - O_2$	25.4	75
$C_3H_8 - O_2$	3.2	37
i-$C_4H_{10} - O_2$	2.8	31
$C_2H_2 - O_2$	3.5	92
C_2H_2 – air	4.2	50
$C_4H_{10}O$(ether) – O_2	2.6	>40
$C_4H_{10}O$ – air	2.8	4.5

Figure 1. Measured detonation cell size, λ, for various fuel-air mixtures (Reference 4).

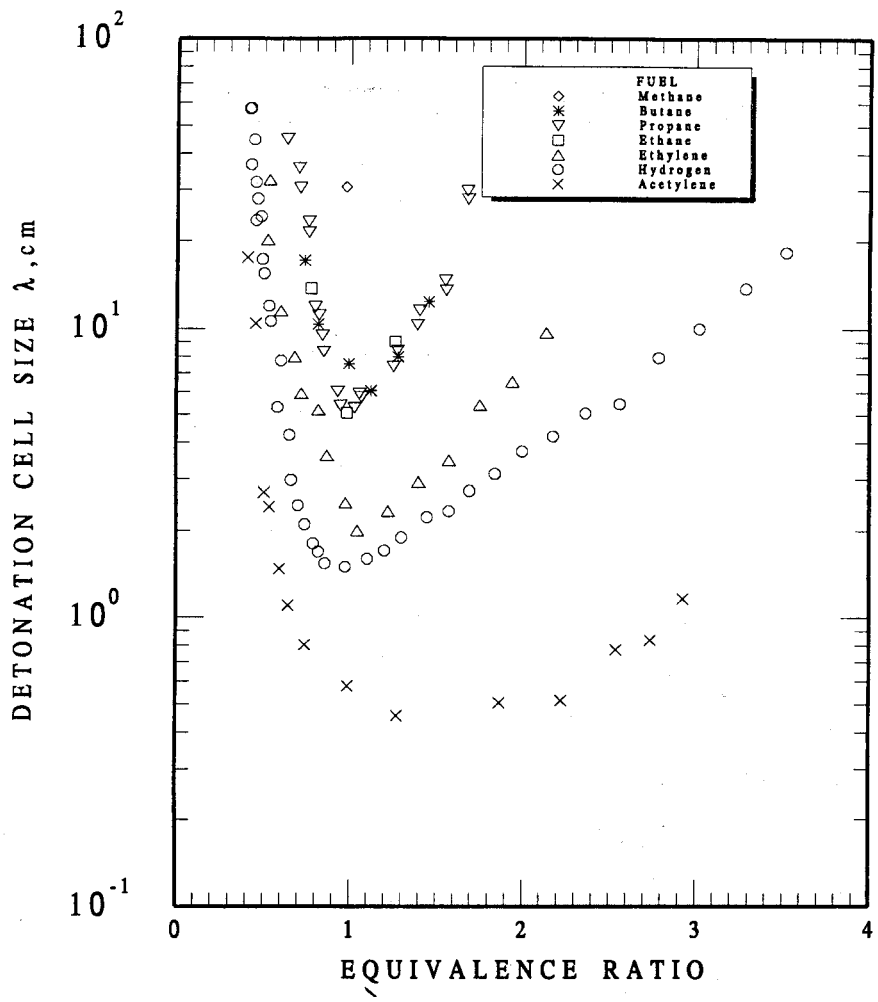
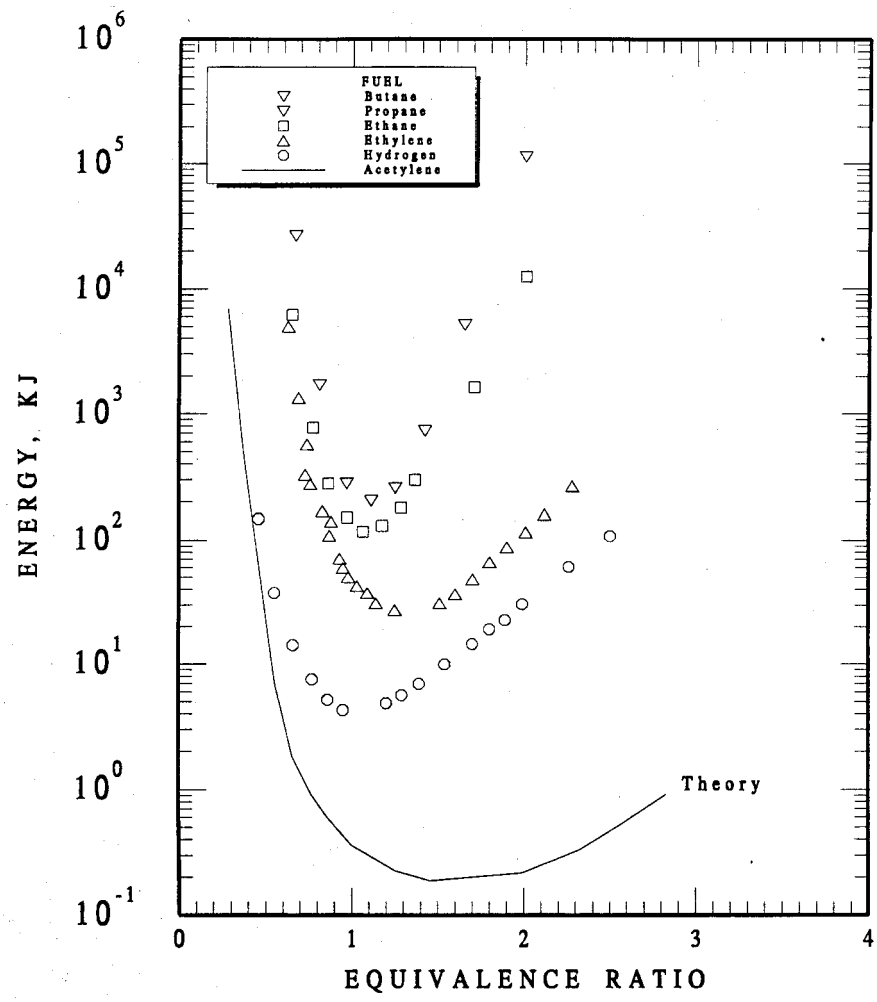


Figure 2. Detonation initiation energy of fuel-air mixtures (Reference 4).



Detonations of flammable gas mixtures form distinctive physical structures called “detonation cells” or “cells” shown in Figure 3. The detonation cell size is dependent only on the composition of the mixture, e.g., a hydrogen-air mixture, and its concentration. For example, the detonation cell size for a stoichiometric hydrogen-air mixture, 29.6% hydrogen by volume in air or Φ of unity, is 1.5 cm as shown in Figure 1 (also, refer to Table 9-2, Reference 2). That is, the smallest of the dimensions in the confinement volume in which the stoichiometric hydrogen-air mixture is contained must be greater than the cell size for detonation. The cell size increases significantly for non-stoichiometric mixtures at the flammability limits, including hydrogen, as shown in Figure 1.

For the methane-air mixture, the detonation cell size is 30 cm at stoichiometry. Hence, it can be concluded that the likely mode of combustion for methane-air mixtures for all flammable concentrations is deflagration.

Figure 3. Detonation cells in convergent and divergent flow channels.

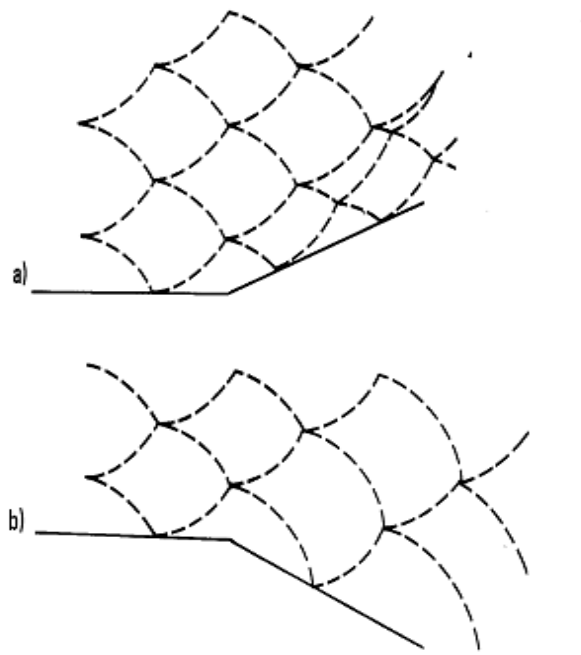


Fig. 1 Sketch of a cellular detonation wave entering a) convergent section and b) divergent section.

Even for the stoichiometric hydrogen-air mixture, the minimum dimension to sustain a planar detonation in a pipe into an unconfined volume is 19.5 cm from a pipe into an adjoining unconfined volume. This is based on the correlation in Reference 5 (Mitrafanov & Soluhkin) for a circular pipe, below:

$$D_{CRITICAL} = 13 \times \lambda \qquad (2)$$

At the upper limit of detonability, i.e., 59% hydrogen by volume or Φ of 3.4 in Figure 2, the detonation cell size is quite large at approximately 20 cm. The minimum pipe diameter for propagation of detonation into an unconfined volume is then 2.6 m (8.5 ft). At the lower limit of detonability, i.e., 18.3% by volume or Φ of 0.53 in Figure 1, the detonation cell size is over 10 cm. Then, from Equation 2, the minimum diameter must be at least 130 cm.

For the stoichiometric hydrogen-air mixture, the total detonation energy of the mixture computed by Cheetah 4.0 (Reference 6) is 0.003 kJ/cm^3. The theoretical maximum density (TMD) calculated by Cheetah 4.0 is 8.57×10^{-4} g-mixture/cm^3. In order to convert to TNT-equivalent, the computed detonation energy must be divided by the mixture density. The result is then divided by the heat of detonation for TNT, as follows:

$$\left[\frac{0.003\,\mathrm{kJ}/\mathrm{cm}^3}{8.57\times10^{-4}\,\mathrm{gr}/\mathrm{cm}^3}\right]\times\left(\Delta H_{\mathrm{detonation}}\right)^{-1} = \frac{3.50}{4.27}\frac{\mathrm{kg\text{-}TNT}}{\mathrm{kg\text{-}mixture}} = 0.820\frac{\mathrm{kg\text{-}TNT}}{\mathrm{kg\text{-}mixture}}$$

where $\Delta H_{detonation}$ is the heat of detonation for TNT, and is quantitatively 4.27 MJ/kg-TNT (Reference 7). This is an extremely conservative estimate since the mechanical detonation energy, which will cause most of the damage to structures and materials at risk, is less than 50% of the total detonation energy. The remaining is released as thermal energy. Even if this is ignored, the TNT equivalence will decrease from the maximum value of 0.82 at stoichiometry, i.e., equivalence ratio, Φ, of unity.

The cell size becomes more significant as a physical constraint for non-stoichiometric mixtures, including hydrogen, as shown in Figure 1. For Φ less than unity, the mixture is lean and hydrogen is consumed completely with excess oxygen remaining in the mixture. For Φ greater than unity, the mixture is rich in fuel and oxygen in air is completely consumed. In both cases, TNT equivalence will decrease from the maximum of 0.82 at stoichiometry to the lower detonability limit of 18.3% or to the upper detonability limit of 59% primarily because of (i) reduction in the total detonation energy and (ii) the change in the mixture density. Analytical results for hydrogen are summarized in Table 3.

The potential for damage from detonations would be substantial. It can be quantitatively determined by the peak quasi-static pressure calculation using FRANG/SHOCK or BlastX.

As stated previously, for detonation of a flammable gas-air mixture, the initiation energy requirement must be satisfied. The minimum detonation initiation energy for a stoichiometric hydrogen-air mixture is approximately 4.0 kJ, as shown in Figure 3. The experiment in Reference 6 was actually carried out with tetryl, a type of explosives with the heat of detonation of 4.56 MJ/kg (Reference 7). Again, this is 2.1×10^{8} times higher than the minimum deflagration energy of 0.019 mJ.

For non-stoichiometric mixtures, the detonation initiation energy is higher than that required for detonation of a stoichiometric mixture. As shown in Figure 3, at the lower limit of detonability, i.e., the equivalence ratio of 0.53, the detonation cell size and the detonation initiation energy are approximately 50 cm and 150 kJ, respectively. The minimum detonation energy of 150 kJ is in fact over 30 g of tetryl. The critical dimension for deflagration detonation transition (DDT) into an unconfined volume would be 6.5 m (21 ft) using the correlation by Mitrafanov and Soluhkin in Equation 2 (Reference 4).

Table 3. Predicted TNT equivalence from detonation of hydrogen-air mixtures.

Vol. % H_2	Φ	Mixture TMD, g/cc	Total detonation energy		TNT equivalent, kg/kg-mixture
			kJ/cc	MJ/kg	
20	0.59	9.58×10^{-4}	0.002	2.09	0.489
29.586	1.0	8.57×10^{-4}	0.003	3.50	0.820
50	2.4	6.31×10^{-4}	0.002	3.17	0.742

Hence, it is doubtful that detonation of flammable gas-air mixtures within the detonable range can be initiated with just ordinary ignition sources, e.g., an electrical short, postulated in accident conditions in DOE nuclear facilities, e.g., TRU waste storage and handling facilities.

For postulated accidents in DOE nuclear facilities, detonations are unlikely, especially because of the initiation energy requirement. The preferred mode of reaction for a hydrogen-air mixture, in particular, for non-stoichiometric mixtures, is deflagration. This is discussed below.

3.0 Deflagration

In order to determine the effect from a postulated deflagration, the conventional analytical technique requires the total heat of combustion of the flammable gases and vapors that is equated to the equivalent quantity of TNT using an yield factor, typically on the order of 0.1. The TNT equivalence would then be used in a correlation similar to the Weibull correlation (Reference 8) shown below to determine the quasi-static peak pressure within the confinement volume:

$$P_{QS} = 166 \times \left(\frac{w_{TNT}}{V} \right)^{0.72} \text{ bar}, \quad \frac{w_{TNT}}{V} \leq 5 \, \text{kg}/\text{m}^3 \tag{3}$$

where w_{TNT} is the quantity of TNT in kg, and V is the confinement volume in m^3.

However, the TNT equivalence method can be misleading for the following reasons:

- Detonation is not the same type of physical phenomena as deflagration.
- The method does not account for the concentration dependence. That is, the maximum pressure is attained at or just above stoichiometry, and decreases for lean and rich mixtures. The TNT equivalence method would predict higher pressures above the maximum pressure at stoichiometry with increasing hydrogen concentrations.
- Because the total combustion energy is dependent on the concentration, the yield factor must also depend on the concentration as shown in Table 3. However, the concentration is ignored in assumed yield factors.
- With an assumed yield factor of 0.1, the detonation energy associated with 1 kg of hydrogen, equal to 12 MJ, is higher regardless of concentrations than that of 1 kg of TNT, equal to 4.27 MJ. Similarly, the detonation energy associated with 1 kg of methane, which has the least detonation potential, is higher at 5 MJ with an yield factor of 0.1 than that of 1 kg of TNT.

The peak pressure attainable from a potential deflagration in a sealed enclosure, e.g., 55-gal TRU waste drums, with a given quantity of flammable gases can be more physically represented by the correlation provided in Reference 3 (Lewis and Von Elbe), as follows:

$$\frac{P_f - P_0}{P_M - P_0} = \frac{m_b}{m_0} \tag{4}$$

where P_f is the peak deflagration pressure involving a specific quantity of a hydrogen-air mixture consumed in the reaction represented by m_b. The variable m_0 denotes the total mass of gases in an enclosure, including unburned air in a lean mixture or hydrogen in a rich mixture.

For 50% hydrogen-air mixture in a unit volume, for instance, the total and consumed quantities of the mixture must be calculated to determine the AICC pressure from a potential deflagration. Densities of air and hydrogen at 300°K and 101.3 kPa are 0.8497 m^3/kg and 12.22 m^3/kg (Reference 9), respectively. The total quantity of the mixture is then:

$$m_0 = 0.5 \times \left(12.22\ \mathrm{m}^3/\mathrm{kg}\right)^{-1} + 0.5 \times \left(0.8497\ \mathrm{m}^3/\mathrm{kg}\right)^{-1} = 0.629\ \mathrm{kg}/\mathrm{m}^3$$

In this case, the mixture is fuel-rich. Oxygen in air would be totally consumed and hydrogen would be left. The amount of unburned hydrogen is calculated by dividing the available volume of air by the required air volume of 2.38. The mass of the consumed mixture is then calculated by adding the two components, as follows:

$$m_b = 0.5/2.38 \times \left(12.22\ \mathrm{m}^3/\mathrm{kg}\right)^{-1} + 0.5 \times \left(0.8497\ \mathrm{m}^3/\mathrm{kg}\right)^{-1} = 0.606\ \mathrm{kg}/\mathrm{m}^3$$

From Equation 4, the AICC pressure from a potential deflagration of a 50% hydrogen-air mixture is then:

$$P_f = \frac{m_b}{m_0}\left(P_M - P_0\right) + P_0 = \frac{0.606}{0.629} \times \left(6.8 - 1.0\right) + 1.0 = 6.58\ \mathrm{bar} = 95.4\ \mathrm{psig}$$

Results of the calculations for other compositions are provided in Table 4.

It should be noted that the values computed above are *theoretical* maximum pressures for a deflagration, i.e., adiabatic isochoric conditions. An experiment by Whitehouse *et al*. (Reference 10) in Figure 4 showed that hydrogen in hydrogen-air mixtures with Φ less than unity is not completely consumed in combustion reactions. The actual pressure would thus be much less than the theoretical AICC pressure. This is shown in Figure 5 and Figure 6.

Table 4. Predicted AICC pressures from deflagration of hydrogen-air mixtures in varying concentrations using Equation 4.

Vol. % H_2	Φ	m_b, kg	m_0, kg	P_f	
				bar	psig
4.0	0.10	0.115	1.133	1.6	23.1
10	0.26	0.288	1.067	2.6	37.2
20	0.59	0.577	0.958	4.5	65.1
29.586	1.0	0.853	0.853	6.8	98.6
50	2.4	0.606	0.629	6.5	95.4
75	7.1	0.303	0.356	5.9	86.1

Figure 4. Fraction of consumed hydrogen as a function of hydrogen concentrations and ignition configuration (Reference 10).

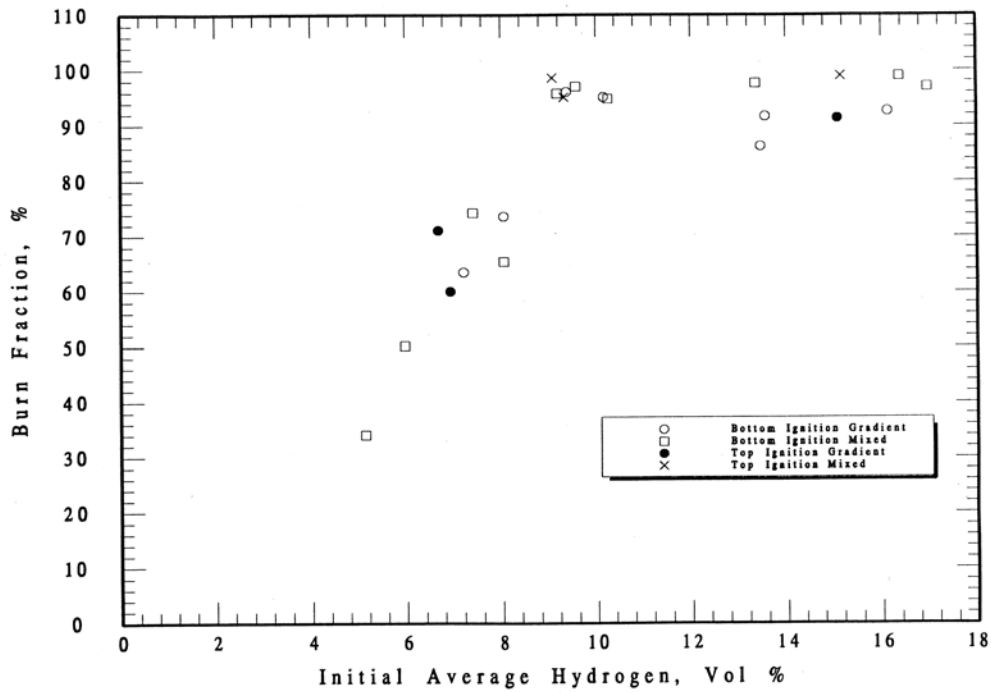


Figure 5. Measured maximum pressure as a function of hydrogen concentrations and ignition configuration (Reference 10).

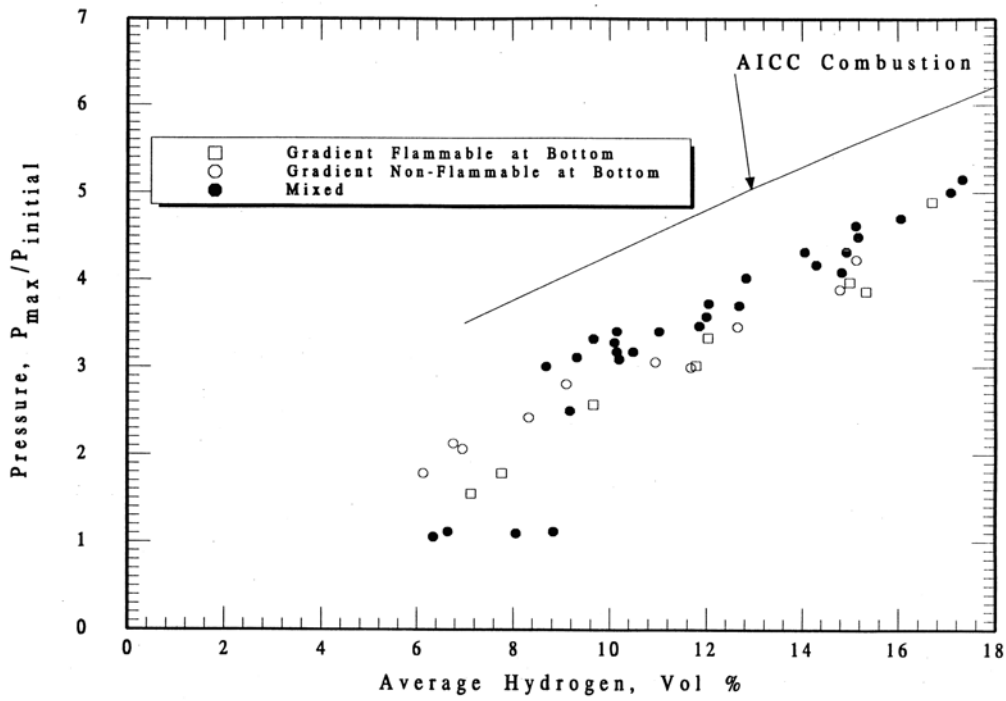
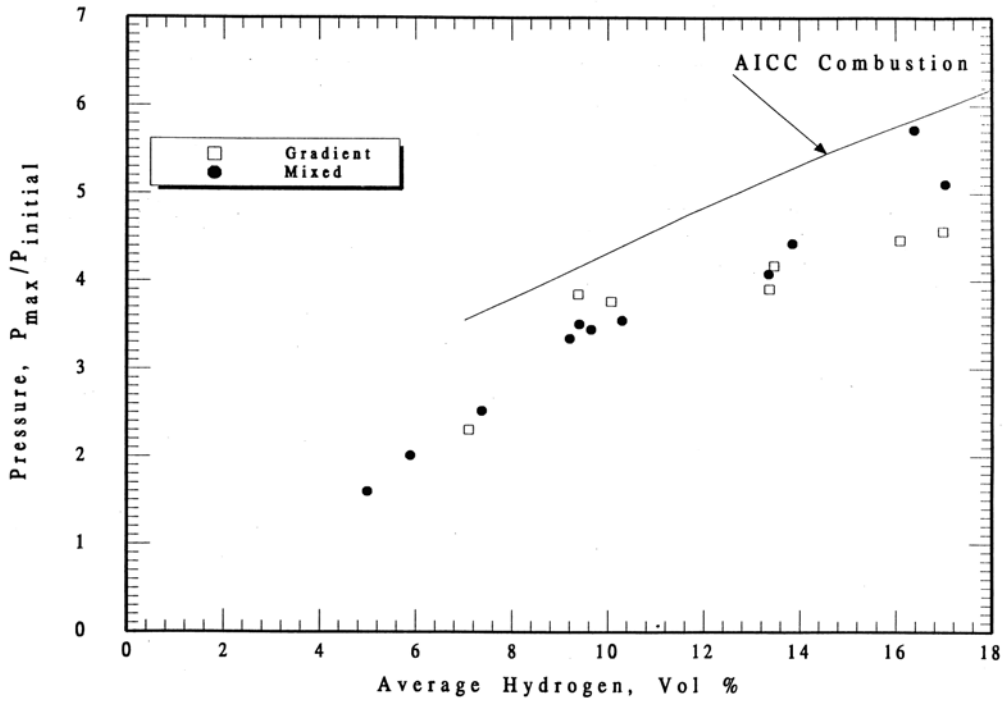


Figure 6. Measured maximum pressure as a function of hydrogen concentrations and concentration gradient (Reference 7).



In the case of a 55-gal drum, there will be heat transfer to the surrounding and the volume will not remain constant. That is, the content of the drums would be compressible in most cases. When the consideration is given to the dynamic nature of the deflagration in a 55-gal TRU waste drum, the pressure developed in an accident condition may not lead to breach of the structural integrity of the drum, which is typically hydrostatically tested for integrity up to 20 psi.

4.0 Practical application of the flammability data to DOE sites

The conventional analytical technique relies only upon the flammable gas concentrations. One additional concept must be considered to determine the real flammability hazards to assure that the effective means are applied to those that present a real potential for deflagration or detonation. That is the concept of the lower oxygen limit (LOL), the concentration of oxygen in the confinement volume below which combustion cannot be sustained. This can be illustrated with the upper flammability limit (UFL) of hydrogen in air.

Above 75% hydrogen in air, i.e., UFL for hydrogen, the mixture is not flammable. Stated differently, if the maximum oxygen concentration in a hydrogen-air mixture is limited to 5% by volume, the mixture is not flammable and the deflagration potential does not exist. With carbon dioxide as the diluent, the maximum safe oxygen concentration is 5.9%. This is called the lower oxygen limit (LOL). This is graphically illustrated in flammability charts for hydrogen and methane in Figure 7 and Figure 8 (Reference 12), respectively. For common flammable gases, the LOL with CO_2 the diluent and N_2 as the diluent are provided in Table 5.

Again, the oxygen concentration is just as significant in determining whether the mixture in a vessel is flammable as shown in Table 5. If the maximum oxygen concentration in the methane-air mixture is limited to 12.1% by volume, the deflagration potential is eliminated. With carbon dioxide as the diluent, the maximum safe oxygen concentration is 14.6%. In general, carbon dioxide is a more effective suppression agent than nitrogen as shown in Table 5. Therefore, the lower oxygen limit (LOL) must be considered when identifying the flammability hazards in those confinement volumes, e.g., TRU waste drums.

As an example, the flammability data discussed up to now are applied to several TRU waste drums with known concentrations to demonstrate the flammability hazard identification process and the analytical results using the correlation in Equation 4 from Reference 3 (Lewis and von Elbe). TRU waste drums in the Idaho National Engineering and Environmental Laboratory (INEEL) were sampled, concentrations of which are cited in HNF-19492 (Reference 12).

Figure 7. Limits of Flammability of Hydrogen-Carbon Dioxide-Air and Hydrogen-Nitrogen-Air Mixtures at 25°and Atmospheric Pressure (Reference 11).

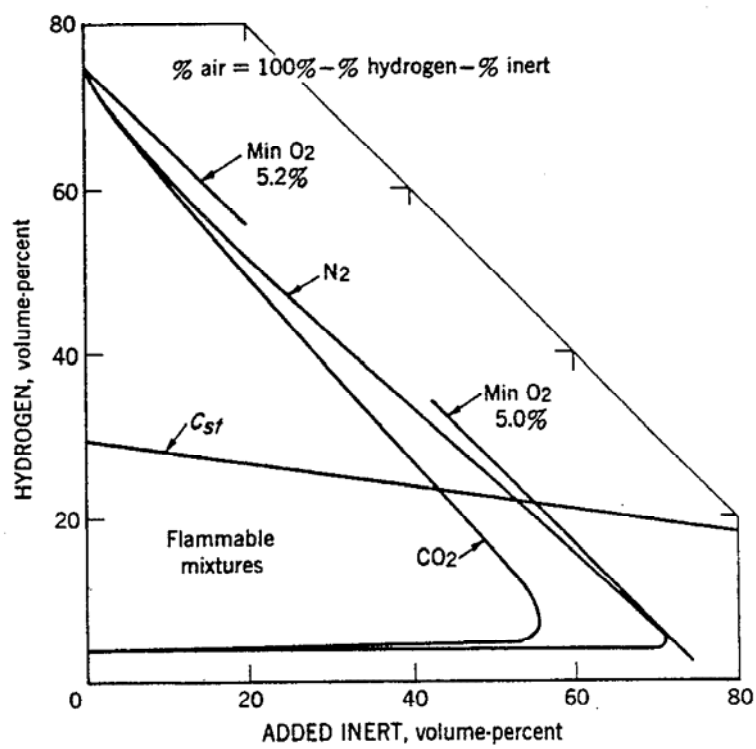


FIGURE 111.—Limits of Flammability of Hydrogen-Carbon Dioxide-Air and Hydrogen-Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure.

Figure 8. Limits of Flammability of Various Methane-Inert Gas-Air Mixtures at 25°C and Atmospheric Pressure (Reference 11).

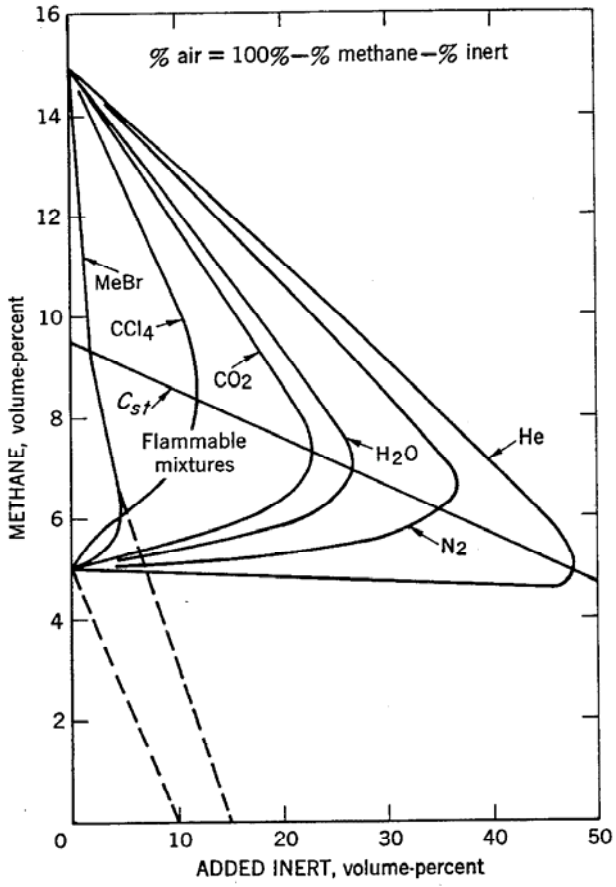


FIGURE 28.—Limits of Flammability of Various Methane-Inert Gas-Air Mixtures at 25° C and Atmospheric Pressure.

Of the 210 drums sampled, reported concentrations in HNF-19492 (Reference 12) were as follows:

- Six drums contained H_2 concentrations exceeding 15%.
  - Five of the six drums contained O_2 concentrations less than 1%.
  - The remaining one drum contained 17.7% H_2 and 11.4% O_2. This mixture is flammable.
- 24 drums contained H_2 concentrations from 1% to 5%.
- 131 drums contained H_2 concentrations less than 1%.
- 49 drums contained H_2 concentrations less than 5%.

Additionally, there were four TRU waste drums from SRS that were discussed in the same analysis. Concentrations and waste drum identification numbers are shown in Table 6.

Table 5. Lower oxygen limit for selected combustibles and flammable gases (Reference 2).

Combustible	Maximum safe percentage of oxygen	
	CO_2 as diluent	N_2 as diluent
Hydrogen	5.9	5.0
Carbon monoxide	5.9	5.6
Methane	14.6	12.1
Ethane	13.4	11.0
Propane	14.3	11.4
Butane and higher hydrocarbons	14.5	12.1
Ethylene	11.7	10.0
Propylene	14.1	11.5
Cyclopropane	13.9	11.7
Butadiene	13.9	10.4
Benzene	13.9	11.2

Table 6. Measured concentrations in TRU waste drums at SRS in DP-1604, "Radiogenic Gas Accumulation in TRU Waste Storage Drums," as cited in HNF-19492 (Reference 12).

	Pu^{238}, Ci	H_2, %	O_2, %	Detonable?	Flammable?
Drum 119	37	5	2 to 7	No	Maybe
Drum 120	113	50	< 5	No	No
Drum 121	47.5	4	< 4	No	No
Drum 122	142	30	< 5	No	No

From the flammability chart for hydrogen in Figure 7, it is determined that nearly all drums do not contain sufficient reactants, either hydrogen in excess of 4% (LFL) or oxygen in excess of 5% (LOL). There are two exceptions in the samples of TRU waste drums reported in HNF-19492 (Reference 12).

For the two TRU waste drums, a consequence analysis must then be performed. Predicted maximum pressure from postulated deflagration of flammable mixtures using Cheetah 4.0 is shown in Table 7. Analytical results show that only the two TRU waste drums present a significant potential for damage. Results are based on the assumption that the remaining volume is occupied by nitrogen. The potential for fires involving waste in TRU waste drums following deflagrations is minimal because of the LOL and the ignition energy requirement as will be discussed subsequently in Section 5.0.

As a verification and validation process for Cheetah 4.0, several flammable gas mixtures were analyzed to determine the AICC pressures for comparison to the measured data reported by Dr. W. Bartknecht in Appendix D of NFPA 68 (Reference 13). Comparison is provided in Table 8.

Table 7. Predicted maximum pressures from postulated deflagrations of flammable mixtures.

	N_2, %	H_2, %	O_2, %	P, psig
INEEL* (1 of 6)	70.9	17.7	11.4	57.5
SRS (Drum 119)	88.0	5.00	7.00	25.2

* The atmospheric pressure is adjusted for the site elevation of 5,000 ft.

Table 8. Comparison of the maximum pressures from postulated deflagrations of selected combustible and flammable gases in air.

Gases or vapors	Maximum pressure at stoichiometry, bar	
	Cheetah 4.0	NFPA 68*
Acetone	8.4	7.3
Acetylene*	10.4	10.6
Ammonia	7.9	5.4
Carbon disulfide	7.0	6.4
Diethyl ether	8.7	8.1
Ethane	8.3	7.8
Ethanol	8.4	7.0
Hydrogen	6.8	6.8
Isopropanol	8.5	7.8
Methane	7.9	7.1
Methanol	8.2	7.5
Pentane	8.6	7.8
Propane	8.5	7.9
Toluene	8.5	7.8

* The pressure is computed for optimum mixtures (Reference 13).

The radiolytic generation rate of carbon dioxide was noted to be on the same order of magnitude in HNF-19492 (Reference 12). Its impact was, however, ignored. Presence of carbon dioxide in significant quantities will reduce the peak deflagration pressure by increasing the unreacted gaseous mass in the 55-gal drum as shown by Equation 4. Again, the theoretical maximum pressure can be obtained simply by adjusting the total gaseous mass to include the quantity of radiolytic carbon dioxide in Equation 4 *after* the identified mixture satisfies the flammability limit and the lower oxygen limit (LOL).

The range of flammability for flammable gases, such as those in Table 1 for hydrogen and methane, is specified for ambient conditions. Pressure and temperature have an effect on the flammability limit and the deflagration effect, as listed below:

- Significant increase in temperature will increase the flammability limits of flammable gases.
- Significant increase in pressure will increase the flammability limits of flammable gases.

- The lower oxygen limit, i.e., the maximum safe oxygen concentration, will decrease with increasing pressure and temperature.

Hence, caution is necessary in conditions that are significantly different from the standard atmospheric conditions when applying the flammability limits to determine the potential for combustion reaction, whether the concern is detonation or deflagration. The effect of pressure and temperature on flammability is discussed in Reference 11.

5.0 Potential for fire in TRU waste drums following deflagration

TRU waste is commonly stored in 55-gal drums in the DOE nuclear facilities, in anticipation of shipment to WIPP. A volume of 55 gal is equivalent to 208.2 liters. Assuming a void fraction of 0.2, radiolytic hydrogen accumulation in a 55-gal drum to the lower flammability limit (LFL) of 4% by volume is 1.67 liters (208.2×0.2×0.04). Using the volumetric heat of combustion for hydrogen from Table 1, the total potential combustion energy from a deflagration of a hydrogen-air mixture at the LFL is then:

$$\Delta h = 12.1\frac{\text{MJ}}{\text{m}^3}\times 1.67\times 10^{-3}\,\text{m}^3 = 20.2\,\text{kJ}\times 0.9478\frac{\text{Btu}}{\text{kJ}} = 19.1\,\text{Btu}$$

The potential combustion energy from a deflagration is small. A fire following the postulated deflagration will be sustained only if significant decomposition of polyethylene (PE) or cellulosic materials occurs. The exothermic pyrolytic decomposition temperature for cellulosic materials exceeds 280°C; the 1% thermal decomposition temperature of PE is 548°K (275°C, 527°F) (Reference 1), which is not sufficient to sustain a fire.

To determine whether a potential deflagration can lead to a fire involving the waste, the potential temperature increase can be conservatively calculated assuming an *adiabatic* condition. Using cork with the specific heat of 0.485 Btu/lb-°F (2.02 kJ/kg-°C) at an ambient temperature, the maximum temperature rise is:

$$\Delta h = mc_p\Delta T \Rightarrow \Delta T = \frac{\Delta h}{mc_p} = \frac{20.2\,\text{kJ}}{m\times 2.02\,\text{kJ}/\text{kg-°C}} = \frac{10\,\text{kg-°C}}{m}$$

For example, with 1 lb (0.454 kg) of contaminated cellulosic materials, e.g., paper or cork, the adiabatic temperature increase is less than 22°C. In the ambient condition, the temperature increase is not sufficient to reach the exothermic pyrolytic decomposition temperature of 280°C. Even at the stoichiometric concentration, the potential combustion energy from a deflagration, equal to 150 kJ (142 Btu), is not sufficient to bring contaminated cellulosic materials to the exothermic pyrolytic decomposition temperature of 280°C or a small quantity of PE to the 1% thermal degradation temperature of 275°C.

Furthermore, after a reaction of the stoichiometric mixture is completed, oxygen is completely consumed. The enclosed gaseous constituents cannot sustain a combustion process because it contains less than the lower oxygen limit (LOL) shown in Table 5. Without additional flow of air to replenish oxygen in the confinement volume, a fire following a hydrogen deflagration is not consistent with the chemical, i.e., the lower oxygen limit, and thermal limitations.

6.0 Recommendation

For the flammable gas-air mixture analysis, the potential for detonations in accident conditions should be ruled out with spatial and initiation energy requirements as appropriate in addition to the narrower concentration limits. For hydrogen as an example, the detonability limit ranges from 18.3% to 59% by volume as shown in Table 2. In comparison, the flammability limit for hydrogen is from 4% to 75%.

Based on the physical data, it is reasonable to conclude that a potential combustion reaction involving natural gas, most of which is methane, is deflagration.

As a practical matter, headspace gas sampling of TRU waste drums should monitor oxygen concentrations in addition to the flammable gas concentrations to determine the potential for deflagration. The flammability or detonability determination must consider the oxygen concentration information above the lower oxygen limit (LOL) for various flammable gases listed in Table 5. In the event a confinement volume such as a 55-gal drum is found to contain potentially flammable mixtures in the headspace, the most effective way to preclude the potential reaction is to add diluents, e.g., CO_2 or N_2, to limit the oxygen concentration below the LOL in Table 5. For most volatile organic compounds (VOC) in confined volumes, the appropriate quantities of diluents, either CO_2 or N_2, would render the oxygen concentration below 10% by volume. This is the most effective solution to minimizing the risk of potential reaction that may lead to uncontrolled releases of radioactive materials and pose undue occupational concerns to workers in the vicinity.

For a mixture in a confinement volume, the flammability hazard is established if (i) the flammable gas concentration is within the flammability limit and (ii) the oxygen concentration is above the lower oxygen limit. Once the flammability hazard is established, the potential damage as expressed by the AICC pressure from a potential deflagration can be estimated. It was shown that the conventional TNT equivalence method is not a good predictive tool because it requires use of assumed, non-physical yield factors. Through a thermochemical analysis using Cheetah 4.0, it was shown that the yield factor is very much dependent on the mixture concentration.

For the purpose of performing the consequence analysis from a postulated deflagration, it is recommended that the correlation in Equation 4 from Reference 3 (Lewis and von Elbe), or other thermo-chemical analytical codes based on JANAF tables, be used to determine the peak AICC pressures.

7.0 Reference:

1. *The SFPE Handbook of Fire Protection Engineering*, 2nd Edition, National Fire Protection Association, Quincy, Massachusetts, 1995.
2. *Combustion Fundamentals*, Roger A. Strehlow, McGraw-Hill, 1984.
3. *Combustion, Flames and Explosions of Gases*, Lewis and Von Elbe, 1986.
4. "Measurements of Cell Size in Hydrocarbon-Air Mixtures and Predictions of Critical Tube Diameter, Critical Initiation Energy, and Detonability Limits," R. Knystaustas, C. Guirao, J.H. Lee, and A Sulmistras, Progress in Astronautics and Aeronautics, Volume 94, American Institute of Aeronautics and Astronautics (AIAA), 1984.
5. "The Diffraction of Multifront Detonation Waves," V.V. Mitrofanov and R.I. Soloukhin, Hydrodynamic Institute, Siberian Division of the Academy of Sciences of the USSR, Translated from Doklady Akademii Nauk SSSR, Vol. 159, No. 5, June 1965.
6. UCRL-CODE-155944, Cheetah 4.0, Lawrence Livermore National Laboratory, L.E. Fried *et al*., October 2004.
7. UCRL-52997, "LLNL Explosives Handbook; Properties of Chemical Explosives and Explosive Simulants," Dobratz, B.M., and P.C. Crawford, Lawrence Livermore National Laboratory, January 1985.
8. "Pressures Recorded in Partially Closed Chambers at Explosion of TNT Charges," Hans R.W. Weibull, Annals NY Academy of Sciences, 1968.
9. "Thermodynamic Properties in SI," W.C. Reynolds, Stanford University, 1979.
10. "Combustion of stratified hydrogen-air mixtures in the 10.7 m^3 Combustion Test Facility cylinder," Whitehouse, D.R., D.R. Grieg, and G.W. Koroll, *Nuclear Engineering and Design*, Vol. 166, p. 453, 1996.
11. "Flammability Characteristics of Combustible Gases and Vapors," Michael G. Zabetakis, Bulletin 627, Bureau of Mines, Washington, D.C., 1965.
12. HNF-19492, "Revised Hydrogen Deflagration Analysis," Revision 0, January 2004, Fluor Hanford.
13. NFPA 68, "Guide for Venting of Deflagration," National Fire Protection Association, 1998.