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Potential VOC Deflagrations in a Vented TRU Drum

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Abstract

The objective of the analysis is to examine the potential for lid ejection from a vented transuranic (TRU) waste drum due to pressure buildup caused by the deflagration of hydrogen and volatile organic compounds (VOCs) inside the drum. In this analysis, the AICC pressure for a stoichiometric mixture of VOCs is calculated and then compared against the experimental peak pressure of stoichiometric combustion of propane and hexane in a combustion chamber. The experimental peak pressures of propane and hexane are about 12% lower than the calculated AICC pressure. Additional losses in the drum are calculated due to venting of the gases, drum bulging, waste compaction, and heat losses from the presence of waste in the drum. After accounting for these losses, the final pressures are compared to the minimum observed pressure that ejects the lid from a TRU drum. The ejection pressure of 105 psig is derived from data that was recorded for a series of tests where hydrogen–air mixtures were ignited inside sealed TRU drums. Since the calculated pressures are below the minimum lid ejection pressure, none of the VOCs and the hydrogen (up to 4%) mixtures present in the TRU waste drum is expected to cause lid ejection if ignited. The analysis of potential VOC deflagrations in a vented TRU drum can be applied across the DOE-Complex since TRU waste is stored in drums throughout the complex.

Introduction

Recently, the headspace atmosphere of two waste drums at the Savannah River Site (SRS) was found to contain a VOC and air mixture that exceeds the lower flammability limit (LFL) of the VOC. The Documented Safety Analysis (DSA) for the Solid Waste Management Facility (SWMF) at SRS assumes that the TRU waste drums do not have a flammable headspace that could “explode” and cause serious injury to a worker handling the drum (Ref. 1). Therefore, finding VOCs above the LFL value implies the potential for a deflagration event that could compromise both the integrity of the drum and the safety of the worker. At issue is whether or not the deflagration of VOCs and hydrogen at 4% inside a TRU drum would generate sufficient pressure to eject the lid.

The analytical approach taken to resolve the issue of lid ejection is conducted in two steps. In the first step, the minimum pressure that would be needed to eject the lid from a TRU waste drum is determined. In late 1989, SRS conducted a series of TRU drum hydrogen explosion tests (Ref. 3) that involved filling drums with a known concentration of hydrogen in air and then igniting the mixture. All of the drums used in these tests were empty and the vents plugged to prevent any hydrogen from escaping prior to ignition. The minimum pressure that was observed to cause the lid to eject from a TRU drum was measured to be 105.0 psig (119.7 psia) by transducers on the drum. This pressure is selected as a Figure of Merit (FOM) value that is used to determine if lid ejection can take place.

In the second step, the deflagration pressure that results from the combustion of a VOC-hydrogen mixture inside the TRU drum is calculated. An AICC model is used to compute the initial deflagration pressure, which is then corrected using results taken from actual combustion tests. Finally, sources of pressure loss in the drum during the combustion process are identified. The resulting calculated pressure for each VOC/hydrogen mixture is compared against the FOM value to determine if ejection will occur.

Input Data

Table 1 lists the drum physical dimensions and assumed initial conditions with no VOCs present in the drum atmosphere. The inputs in Table 2 are used to calculate the deflagration pressures for the different types of VOCs that are found inside the TRU drums.

Table 1 - Base Input Items

Input Item	Value
Inner diameter of vented TRU drum (Ref. 7)	22.5 inches
Inner usable height of 208L vented TRU drum (Ref. 7)	32.0 inches
Initial pressure	1 atm
Initial temperature	25°C
Oxygen concentration in air (Ref. 4)	21%
Hydrogen combustion energy (Ref. 6)	242.0 kJ/mole (57.8 kcal/mole)
Hydrogen lower flammability limit (Ref. 5)	4%

Table 2 – Input Items for VOC Deflagration Pressure Calculations

Compound Name	Chemical Formula	C_{ST} (%)	Min. AIT (ºC)	LFL @ 25º C (%)	Molecular Wt.	Molar Heat of Combustion (kJ/mole)
Isopropyl alcohol (2-propanol)	$C_3 H_8 O$	4.45	399	2.5	60.10	1876
Toluene	$C_7 H_8$	2.27	480	1.27	92.14	3775
m, o, p-Xylene	$C_8 H_{10}$	1.96	465	1.10	106.17	4380
Acetone	$(CH_3)_2 CO$	4.98	465	2.6	58.08	1687
Methyl Isobutyl Ketone (MIK)	$CH_3 COC_4 H_9$	2.41	460	1.20	100.16	3425
Methyl Ethyl Ketone (MEK)	$CH_3 COC_2 H_5$	3.67	516	1.8	72.12	2294
1,4-Dimethyl-cyclohexane	$C_8 H_{16}$	1.72	304	1.20	112.21	4421

Analytical Model

An Adiabatic Isochoric Complete Combustion (AICC) model is used to calculate the initial deflagration pressures for different VOCs mixed with hydrogen and air inside the drum; the concentration of hydrogen is set at 4%. The governing equation is the First Law of Thermodynamics for a system (i.e., the drum) as noted below (Ref. 4).

$$Q - W = \Delta U = U_2 - U_1, \tag{1}$$

where Q is the heat released by the hydrogen deflagration, W is the work, and U is the internal energy with subscripts 1 and 2 that designate the initial and final states, respectively.

Since there is no work in the present case due to constant volume, equation (1) can be written as:

$$Q = U_2 - U_1 = \sum_j n_j \int_{T_1}^{T_2} \overline{C}_{V,j}\, dt \tag{2}$$

where $\overline{C}_{V,j}$ is the constant volume specific heat of the jth gas, T is the temperature, and n_j is the number of moles of the jth gas in the combusted gas mixture. Since $\overline{C}_V = \overline{C}_P - \overline{R}$, where $\overline{R}$ is the universal gas constant, Equation (2) can be re-written as follows.

$$Q = \sum_j n_j \int_{T_1}^{T_2} (\overline{C}_P - \overline{R})_j\, dt \tag{3}$$

The total heat resulting from the deflagration of hydrogen and/or a VOC in air is calculated by the following expression, where the parameters for hydrogen/VOCs are set to zero if the two are not combined together in an air mixture.

$$Q = n_h E_h^* + n_v E_v^* , \tag{4}$$

where n_h is the moles of hydrogen combusted; n_v is the moles of VOC combusted; E_h^* is the molar combustion energy of hydrogen (kJ/mole); and E_v^* is the molar combustion energy of the VOC (kJ/mole).

By using the molar form of the Ideal Gas Equation (Ref. 4), the actual moles of hydrogen (n_h) and VOCs (n_v) can be determined by the following relationships.

$$n_h = \frac{C_h P_1 V}{\overline{R} T_1} , \tag{5}$$

$$n_v = \frac{C_{voc} P_1 V}{\overline{R} T_1} \tag{6}$$

where $\overline{R}$ is the Universal Gas Constant; P_1 is initial pressure; $T_1$is initial temperature; V is the volume of the TRU drum; C_h is hydrogen concentration; and C_{VOC} is VOC concentration.

Since the specific heats are temperature dependent, the final temperature T_2 has to be determined iteratively. Once this final temperature is determined, the “raw” final pressure resulting from the constant-volume deflagration process can be calculated using the following expression.

$$P_2 = P_1 \frac{T_2}{T_1} \left(\frac{n_P}{n_R} \right) \tag{7}$$

where n_P and n_R are the number of moles of the products and the reactants, respectively. Physically, the final temperature (T_2) depends on the energy density (energy per unit mass) due to the combustion of the VOC.

Model Results Compared to Experimental Data

The Explosion Dynamics Laboratory of the California Institute of Technology (Cal Tech) performed combustion tests for both propane and hexane (Ref. 8). Cal Tech also used a computer code called STANJAN to calculate the combustion pressures for propane and hexane, and they compared these with the pressure data recorded during testing. Table 3 summarizes the calculated and measured pressures from the Cal Tech work along with pressures from the above AICC model for propane and hexane.

Table 3: Summary of Results (psia)

Pressure	Propane	Hexane
AICC Model	150	153
Cal Tech Model	141	142
Measured Data	125	126
Difference	25	27

The AICC model used in this analysis is based on a simple reaction model that assumes 100% conversion of the chemical reactants to the final products. Unlike the Cal Tech model, it does not account for the numerous chemical reactions that occur during the combustion process; thus, it consistently predicts higher combustion pressures. To account for differences in the model and actual measured pressures, the AICC model is corrected in two steps: first, 9 psi is subtracted from the pressures to make them equal to those predicted by Cal Tech; second, an additional 16 psi is subtracted from these results to bring them in line with the measured values. In all, 25 psi is subtracted from each computed pressure value.

Sources of Pressure Reduction for the Drums

Drum Bulging

In viewing a video of the TRU waste drum hydrogen explosion tests (Ref. 9), it was observed that the drum lid undergoes significant bulging in all cases, regardless of whether the lid remains intact or is blown off. Measurements of the drum height for cases where the lid remains intact show that the average volume increase due to the lid bulging is approximately 10%. The time to reach peak pressure (where the lids bulged or blew away) ranged from 5 to 10 msec (Ref. 3 and Ref. 10). It is expected that the drum lid would also bulge during the combustion of VOCs, which have much slower flame speeds than hydrogen. Thus credit was taken for a 10% reduction in final pressure due to the increase in drum volume.

Waste Compaction

The TRU waste drums contain plastic bags filled with items such as coveralls, gloves, shoe-covers, small hand-tools, and cloth/paper wipes impregnated with organic chemicals, which are also the source of the VOCs. Based on results from the first series of drum explosion tests (Ref. 2), it was observed that drums with stoichiometric mixture of hydrogen (~30%) in air did not experience lid ejection as long as they were more than half full of waste bags. Because no effort is made to compact the waste bags before the drum is closed, it is expected that substantial void space exists between the waste bags. These void spaces can provide a significant cushioning effect in terms of waste bag compaction. For example, the typical household garbage compactor provides a compaction pressure of 21 psi that reduces the waste volume by a factor of 10. The pressure rise generated inside a TRU drum due to the deflagration of a VOC-hydrogen mixture is at least 21 psi. Therefore, it is reasonable to assume that the waste volume would be reduced by a factor of two. Data at the 95-percent confidence level for TRU waste drums at SRS show that the void fraction in a TRU drum is 75% (Ref. 11); i.e., the drum has 25% waste. The pressure from a VOC-hydrogen deflagration inside the drum will reduce the 25% waste volume by at least a factor of two, resulting in a new value of 12.5%. The reduction in waste volume increases the vapor volume from 75% to 87.5%; this represents a 16% increase in volume (= 87.5/75). In the analysis, credit for a 10% increase in volume is considered, which translates to a 10% reduction in the final pressure.

Heat Loss

In contrast to the test apparatus used by Cal Tech (Ref. 22), the drums at SRS are never left empty since their sole purpose is TRU waste storage. It is estimated that the additional heat transfer area in a TRU waste drum, due to presence of the bags and waste, is 26% more than the empty Cal Tech test chamber. Referring to Table 3, the 16 psi difference in pressure between the Cal Tech model prediction and the measured data is due to heat loss to the surface of the empty test chamber. The additional heat loss due to the 26% increased heat transfer area from the waste bags in the TRU drums is equivalent to a pressure reduction of 4 psi (26% x 16 psi). When compared to the measured combustion pressure for propane (125 psia) and hexane (126 psia), the 4 psi value represents a 3% reduction in combustion pressure after rounding down. This phenomenon represents a 3% reduction in the final pressure calculation.

Drum Venting

In viewing the video of the TRU drum explosion tests (Ref. 9), it was observed that venting in the form of a puff of smoke occurs when the lid bulges but still remains intact. An explanation for this is that the severe deformation of the lid changes the physical configuration of the drum such that a good contact of the lid with the “lip” of the drum no longer exists. From measurements taken on the TV screen with the video kept still, it was estimated that the puff volume is 5.5% of the drum volume. However, the puff of gas outside the drum has already expanded to atmospheric pressure. The puff volume is reduced by the ratio of the atmospheric pressure (14.7 psia) to the lid ejection pressure of 120 psia to obtain an equivalent in-drum volume; this ratio is ~ 1/8. The 5.5% reduction in volume outside the drum corresponds to a 0.7% reduction in volume inside the drum (5.5% x 1/8) and a 0.7% decrease in drum internal pressure. Therefore, a reduction factor of 1% is used in the analysis.

Results

Combustion of VOCs without Hydrogen

The deflagration pressure for each of several VOCs was calculated based on a stoichiometric concentration of the VOC in air, using the AICC combustion model that was described earlier. Maximum combustion energy is produced when there is no hydrogen present because the VOC undergoes a complete reaction with the oxygen in the air. As shown in Table 4, the *raw* deflagration pressures for the VOCs are calculated directly from the AICC model. Xylene is the most limiting VOC with a *raw* deflagration pressure of 153.4 psia. Subtracting 9 psi from the *raw* pressure corrects it to match the Cal Tech model that accounts for numerous chemical reactions that occur during the combustion process. The *corrected* pressure for xylene is 144.4 psia (153.4 psia – 9 psi). The *adjusted* pressure inside an empty drum is now obtained by subtracting 16 psi from the *corrected* pressure to bring it in line with measured results from the Cal Tech tests; this brings the pressure down to 128.4 psia. Finally, taking into account drum bulging, waste compaction, venting, and the presence of waste in the drums, the *final* pressure reached during VOC combustion is just 99.9 psia or 85.2 psig. The bounding final pressure is below the FOM value of 105 psig.

Combustion of VOCs with Hydrogen

When a VOC is mixed with 4% hydrogen and combusted, the peak deflagration pressure occurs at a VOC concentration that is somewhat less than stoichiometric. This can be seen by comparing the concentration for a VOC such as xylene in Table 4 where no hydrogen is present with that in Table 5 where hydrogen is present. The reason for the lower concentration of xylene in the latter case is that hydrogen burns at a much faster rate than any of the VOCs and consumes some of the oxygen first. This reduced amount of oxygen does not support the complete combustion of xylene at its stoichiometric concentration.

Because the Cal Tech model and combustion chamber tests do not account for the presence of hydrogen (Ref. 8), a conservative approach is used in applying pressure reductions to correct the results from their model. As noted above, the VOC concentrations for mixtures with hydrogen are less than stoichiometric. This lower VOC concentration can be divided by the stoichiometric concentration for the same VOC, and the result used to discount the pressure reductions. For xylene, the concentration is 1.7 with hydrogen present and the stoichiometric concentration is 1.96 with no hydrogen; when 1.7 is divided by 1.96, a reduction factor of 0.867 is obtained.

After examining reduction factors for all of the VOCs, a bounding factor of 0.85 was chosen to make the pressure corrections in Table 5. Xylene is the most limiting VOC with a *raw* deflagration pressure of 150.1 psia. Subtracting 7.7 psi (0.85 x 9 psi) from the *raw* pressure corrects it to match the Cal Tech model that accounts for numerous chemical reactions that occur during the combustion process. The *corrected* pressure for xylene is 142.4 psia (150.1 psia – 7.7 psi). The *adjusted* pressure inside an empty drum is now obtained by subtracting 13.6 psi (0.85 x 16 psi) from the *corrected* pressure to bring it in line with measured results from the Cal Tech tests; this brings the pressure down to 128.8 psia. Finally, taking into account drum bulging, venting, waste compaction, and the presence of waste in the drums, the *final* pressure reached during VOC and hydrogen combustion is just 100.7 psia or 86 psig. This bounding final pressure is below the FOM value of 105 psig.

Table 4 – Results for VOCs with no Hydrogen Present

VOC Name	Stoichiometric Concentration (% vol.)	*Raw* Calculated Pressure Inside TRU Drum (psia)	*Corrected* Pressure Inside TRU Drum (psia)	*Adjusted* Pressure in Empty Drums (psia)	*Final* Pressure in Drums with Waste Bags (psia)
Isopropyl alcohol (2-propanol)	4.45	150.0	141.0	125.0	97.3
Toluene	2.27	153.2	144.2	128.2	99.8
m, o, p-Xylene	1.96	153.4	144.4	128.4	99.9
Acetone	4.98	150.0	141.0	125.0	97.3
Methyl Isobutyl Ketone (MIK)	2.41	149.0	140.0	124.0	96.5
Methyl Ethyl Ketone (MEK)	3.67	150.8	141.8	125.8	97.8
1,4-Dimethyl-cyclohexane	1.72	140.1	131.1	115.1	89.6

Table 5 – Results for VOCs With 4% Hydrogen

VOC Name	VOC Conc. at Max Pressure (% vol.)	"Raw" Calculated Pressure Inside TRU Drum (psia)	"Corrected" Pressure Inside TRU Drum (psia)	Unadjusted Pressure in Empty Drums (psia)	Final Pressure in Drums with Waste Bags (psia)
Isopropyl alcohol (2-propanol)	3.9	147.2	139.6	126.0	98.5
Toluene	2.0	150.1	142.4	128.8	100.7
m, o, p-Xylene	1.7	150.1	142.4	128.8	100.7
Acetone	4.3	146.9	139.3	125.7	98.3
Methyl Isobutyl Ketone (MIK)	2.1	146.2	138.6	125.0	97.6
Methyl Ethyl Ketone (MEK)	3.2	148.0	140.4	126.8	99.1
1,4-Dimethyl-cyclohexane	1.5	138.6	131.0	117.4	91.8

Conclusions

Two main conclusions are reached at the end of the analysis. First, none of the VOCs is expected to cause the lid to eject from a vented TRU drum if it were ignited along with 4% hydrogen in a mixture with air inside the drum. This conclusion will stand as long as the hydrogen concentration inside the drum is limited to no more than 4%. Second, none of the VOCs is expected to cause the lid to eject from a vented TRU drum, even if it were ignited at the stoichiometric concentration in a mixture with air inside the drum.

The validity of these conclusions is dependent upon the protection of two key assumptions. These are:

1. The TRU waste drums are standard DOE 55-gallon drums with hydrogen vents installed, and
2. All drums are closed using the standard lid bolt and closure ring, and no special efforts are made to seal the drums.

In addition to the main conclusions, several conservatisms were identified in the analysis, and these are described below.

1. Hydrogen combustion: the AICC model is used to calculate the pressure due to the combustion of 4% hydrogen; this is about 20 psi. Based on empirical data, the combustion of hydrogen at this concentration produces a pressure rise that is barely noticeable. If it is assumed that the hydrogen burns first, then there would be a negligible pressure increase before the VOCs start to burn. If the hydrogen and VOCs burn together, then the energy losses considered for VOC combustion alone should apply to hydrogen-VOC combustion as well. Such an approach would produce at least a 10% reduction in the combustion pressure of hydrogen; this equates to a 2 psi reduction in final pressure.

2. Combustion propagation quenching: the placement of waste bags in the drum creates channels that the combustion front must pass through in order to reach flammable vapors in portions (pockets) of the drum. As the flame front passes by, it is directly exposed to the cold surfaces of the package and the drum wall. This could lead to flame quenching and certainly non-ideal behavior, which would result in reduced burn efficiency and lower pressures.

3. Temperature change: the fluctuation of ambient temperature in the field makes the VOC vapor pressure continuously variable. As a result, it is extremely difficult to have a perfect mix of gas concentrations that would yield the maximum deflagration pressure at the instant combustion occurred.

4. Auto ignition: VOCs in any amount inside a TRU waste drum are not expected to ignite automatically and cause a deflagration. As noted in Table 2, the auto-ignition temperature (AIT) of VOCs is typically in excess of 300º C (572º F). Such temperatures would not be reached under normal conditions at SWMF.

5. Ignition energy: the ignition energies of the VOCs are typically in the range of 0.2 to 0.3 mJ and the minimum ignition energy for hydrogen is 0.02 mJ. However, the concentration of hydrogen is limited to 4% and the ignition energy for hydrogen at this concentration is 0.2 mJ. With the hydrogen ignition energy comparable to that of the VOCs and the high relative humidity of South Carolina, the likelihood of combustion in the drum due to static electricity would appear to be very small.

6. Bulging of drum bottom: the video of the TRU drum explosion tests shows significant bulging of the drum bottom and in several cases this caused the drum to fall over on its side. Although not credited, bottom bulging increases the drum volume even further and this reduces the internal pressure.

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