CHEMICAL ENGINEERING TRANSACTIONS Volume 19, 2010
Editor Simberto Senni Buratti

DOI: 10.3303/CET1019038

The risk of storage plant of pyrotechnics

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Recent updating of Seveso Directive have made mandatory safety report of storage plants of pyrotechnics (fireworks). However, few guidelines are published in the open literature. The following work deals with the determination of maximum explosion pressures in confined and vented enclosures containing hazardous substances ranging from high-energy explosives to low-energy pyrotechnics.

1. Introduction

Recent accidents involving fireworks, as that occurred in Enschede (NL), have induced important variation in the Seveso Directive (Directive 96/82/EC) and Directive 2007/23/EC, which now include firework storage plants other than manufacturing installations. The most common pyrotechnics used in Europe are called display pyrotechnics, i.e. solid mixtures which react with relative slow rates of reaction with the terminal effect of light, heat, smoke or sound resulting from an exothermic oxidation-reduced chemical reaction.

Despite the low reactivity, recent experimental tests (CHAF, 2002) have demonstrated that large amount of fireworks stored in closed environment may explode with *en mass* behaviour. On the other hand, scientific and technical publications are largely available for high-energy explosives whereas very few data are available for lower energetic pyrotechnics. Also important worldwide references about the use of flammable and explosive materials such as NFPA1124, NFPA1123, NFPA1126 give several information on safety distances and recommendation for the manipulation of explosives and fireworks whereas storage design and risk assessment guidelines are neglected. Neither public military guidelines (TM 5-1300, TM 9-1300-214) are really useful for the producers and design engineers when safety of low-energy pyrotechnics are considered.

In the following, the explosion phenomenon of high-energy explosives and pyrotechnics in closed and vented storage containers is analysed. Plots of pressure with respect to volume ratio V/V° (the room space over the pyrotechnic volume) are shown. These plots can be usefully adopted for engineering practice of storage design of pyrotechnics. Finally, a large set of TNT explosions in vented enclosures have been analysed in order to produce simplified design guidelines and correlations for the maximum pressure within the explosion room or outside the vent section. Furthermore, insights on excess air requirement and vent effectiveness are also given.

Please cite this article as: Basco A., Cammarota F. and Salzano E., (2010), The risk of storage plant of pyrotechnics, Chemical Engineering Transactions, 19, 231-236 DOI: 10.3303/CET1019038

2. Explosion of high-energy explosives and pyrotechnics

The overall reaction of high energy explosives or pyrotechnics may be sketched in two sequential steps: a primary reaction between the oxygen-donor (oxidizer) and fuel and a secondary reactions (after-burning) of the un-reacted fuel or partially oxidized products with surrounding air. As a consequence, the total energy release is the sum of the proper explosion energy and that related to the combustion with air of reaction products, which can be twice the explosion energy, thus resulting in more severe hazards than expected. The same phenomena are also encountered for any pyrotechnic mixture (McIntyre & Rindner, 1980). Table 1 shows the heat of explosion evaluated experimentally by detonation calorimetry and calculated by the use of CEA code (Gordon & McBride, 1994), by means of minimization of Gibbs free energy (chemical equilibrium at constant T,P (25°C, 1 bar). The afterburning reaction energies have been evaluated by CEA assuming the combustion equilibrium at constant internal energy u and volume V, by using large excess of air (ratio of reactant volume to total air volume V/V° = 10^5).

Table 1. Experimental and Calculated explosion energy (kJ/g) for explosives and pyrotechnics mixtures with weight percent composition (in parenthesis). V/V° = 10^5. Experimental data are reported in (Akhavan et al., 2004; Kubota, 2002; Conkling, 1985; Denkevitz & Dorofeev, 2006; Ellern, 1968; Ornellas, 1982).

Name	Composition (%w/w)	ΔH_{expl} Exp	ΔH_{comb} Exp	ΔH_{expl} Calc	ΔH_{comb} Calc
TNT	$C_7H_5N_3O_6$	4.6	15.0	5.4	14.9
RDX	$C_3H_6N_6O_6$	5.4	9.5	6.2	8.6
PETN	$C_5H_8N_4O_{12}$	6.2	8.0	6.9	8.0
Black Powder	KNO_3 (75); C (15); S (10)	2.8	8.7	3.0	8.6
Flash powder	$KClO_4$ (30);Al (40);$Ba(NO_3)_2$ (30)	7.3	11.6	8.3	12.4
Igniter, Sobbe	Zr (40);$Ba(OH)_2$ (30);$Ba(NO_3)_2$ (30)	4.2	*n.a.*	4.7	8.0
Flare	Mg (47);$NaNO_3$ (53);	8.4	11.6	8.4	12.1
Red fountain	$SrCO_3$ (25); $KClO_3$ (57); Shellac (18)	2.6	n.a.	3.6	7.4

The ability of CEA code to reproduce both explosion and combustion mechanism for other explosives and pyrotechnics has been discussed elsewhere, e.g. by predicting the explosion behaviour of black powder when varying composition (sulphur content and KNO_3/C ratio) (Salzano et al., 2009).

3. Explosion pressure in closed system

The maximum pressure obtained in closed environment can be calculated from the reaction energy by means of simple thermodynamic analysis. Furthermore, the CEA code allows the definition of molar fraction of any gaseous by-product, for the following combustion phase. Figure 1 shows the explosion pressure both in nitrogen and air of TNT with respect to the V/V° ratio. By comparing the curves in air and nitrogen, and observing the slope of the same curves, it is clear that afterburning is effective for volume ratio V/V° of about $1 \cdot 10^4$, where correspondingly the CO is completely oxidized to CO_2. On the other hand, its contribution is negligible for V/V° values smaller than $5 \cdot 10^3$, due to lack of oxygen, and larger than $1 \cdot 10^6$, due to volume effects. Comparison with experimental data are also showed for validation purposes.

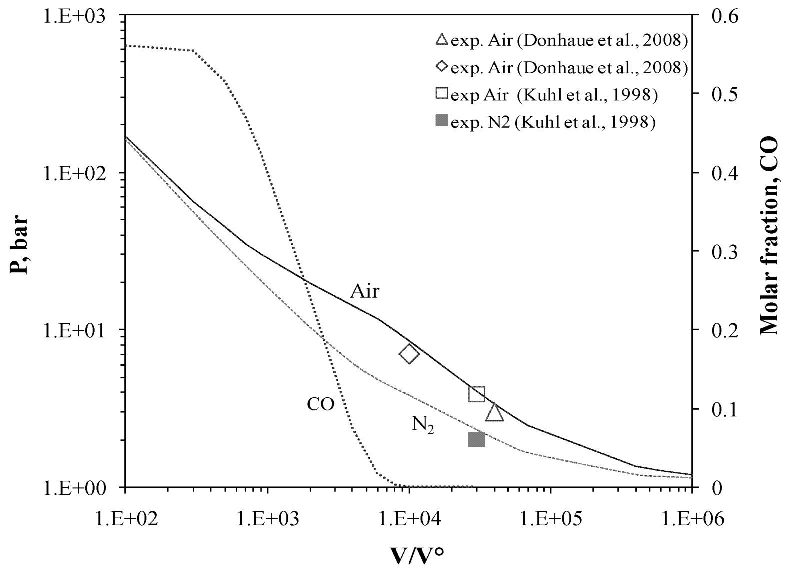

Figure 1. Maximum pressure for TNT vs V°/V, in nitrogen and air. Molar fraction of products in the gaseous products (no air) are showed for excess air evaluation.

Figure 2 reports the comparison of TNT pressure curve reported in Figure 1 for air and pressure curve fitted over more than 177 vented explosion for different explosives (RDX, Dynamite, TNT, PETN, PBX, Pentolite, C-4), as reported in Baker et al. (1982). For the aims of discussion, a venting coefficients λ is now defined as the ratio of vent area A_v over $V^{2/3}$, where V is the room volume.

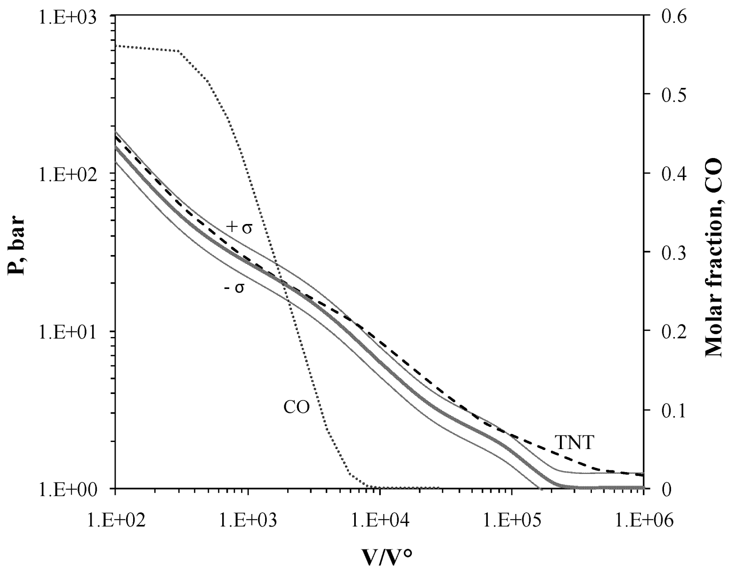

Figure 2. Maximum pressure vs V°/V for TNT explosion (as in Figure 1) and for 177 experimental vented explosion (Baker et al., 1982) of high-energy explosives. σ is the standard deviation. Vent area coefficient λ (=$A_v/V^{2/3}$) < 0.325.

The experimental data in Figure 2 have been produced for λ values lower than 0.325. Hence direct comparison with closed systems is not proper. However, the full curve is actually over-imposed with the TNT pressure curve due to low effectivness of vent, showing that TNT can be approximately adopted for any explosive, thus including display pyrotechnics though on the conservative option. Furthermore, the slope variation is still encountered at the same values of V/V° as in Figure 1, despite the different explosives. Finally, vent is effective for V/V° > 10^5, for the given value of λ.

Similar analysis can be produced for any pyrotechnic. For black powder (Figure 3), molar ratio of CO/CO_2 in the gaseous products and K_2S/K_2SO_4 (liquid) are also showed in order to evaluate excess air evaluation. The reaction of K_2S to K_2SO_4 is indeed often indicated as the main chemical difference for afterburning. In this case, excess air threshold is however found at V/V° ≈ 1000, which is smaller than high energy explosives.

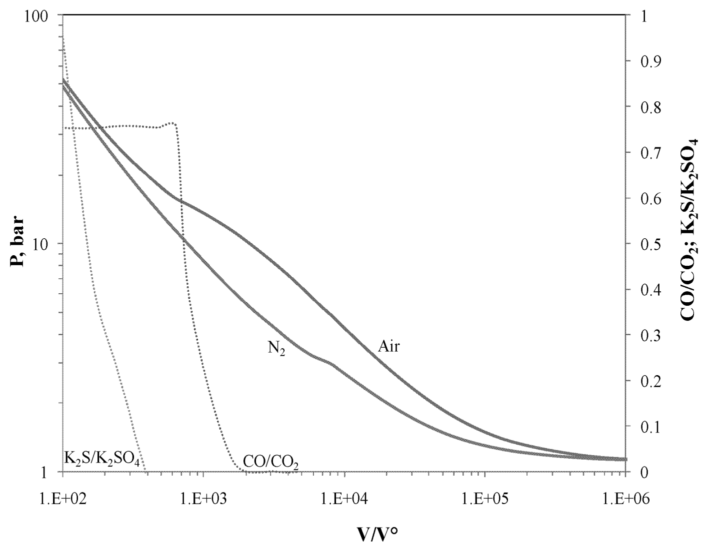

Figure 3. Maximum pressure vs V°/V for black powder, in nitrogen and air atmosphere. Molar fraction of products in the gaseous products (no air) and K_2S/K_2SO_4 (liquid products) are also showed for excess air evaluation

4. Explosion pressure in vented systems

Venting is the main technique to mitigate the effects of confined explosions. However, when explosives are of concern, the safety of structure is rarely considered. On the other hand, the prediction of maximum pressure reached at close distance from vent section is essential for safety of personnel or for the prevention of escalation of accidents. Figure 4 reports a large experimental dataset of pressures for explosion of TNT inside vented chamber, for different vent area A_v, with respect to V/V°. The plot shows that venting systems are effective only for V/V° < 1000, at least for the experimental conditions here analysed. This venting effectiveness threshold value is more conservative that V/V° < 5000 as given by Keenan & Tancreto (1975).

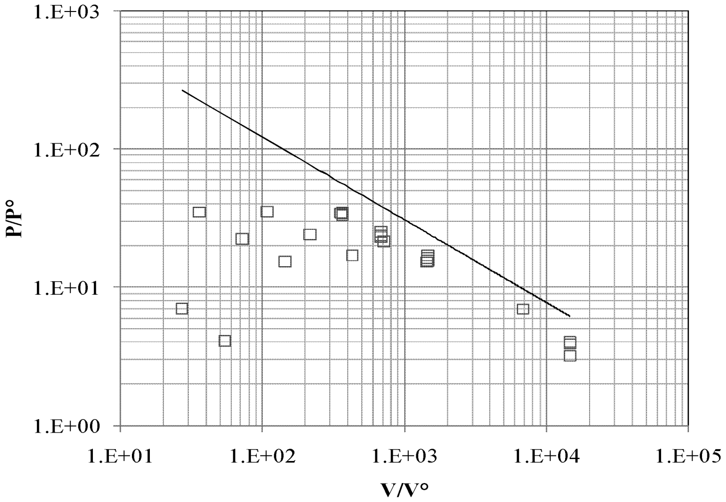

Figure 4. Experimental pressure (Keenan & Tancreto, 1975) measured inside vented chamber with respect to V/V°. Line represents maximum calculated un-vented pressure.

Here it's however worth saying that some difficulties arise when measuring pressure inside explosion chamber, due to shock pressure interferences, whereas more clarity is obtained when analysing the experimental pressure measured at close distance from the vent section. Figure 5 shows the pressure measured in several explosion at respectively 1 m and 10 m from vent section, with respect to a new vent coefficient, Γ, which takes into account the mass, the volume and the vent section of the explosion chamber.

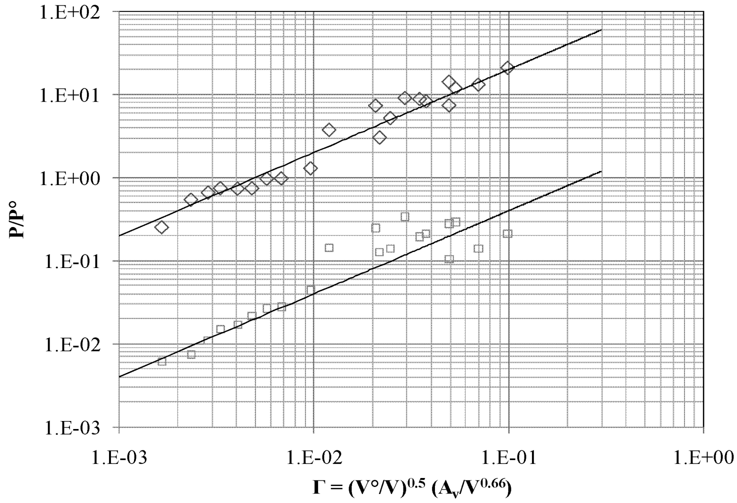

Figure 5. Experimental pressure measured at distance of 1 m (diamond) and 10 m (square) from the vent section with respect to the vent coefficient Γ.

The functional correlation between the vent coefficient and measured pressure in the combustion chamber is clear, whereas negligible correlation can be found with λ. The dependence of vented pressure could be considered as strictly correlated to the maximum pressure inside the explosive room. Value of pressure is about 200 times or 4 times the value of Γ for distances of 1 m and 10 m, respectively. If personnel safety is considered, negligible values of pressures (<0.07 bar) are found only for 10 m distance, for Γ = 0.01. Finally, it's worth mentioning that Kuhl et al. (1998) have also demonstrated that TNT gaseous products burn under well distributed reaction regime in closed vessel for the afterburning rather than typical convectional/diffusive mechanism typically observed in flammable gaseous/air mixture. Hence, the correlations obtained for venting of TNT can be conservatively adopted for pyrotechnics, which are less reactive and energetic, if considering that production of gases is slower and afterburning phenomena occur within the same regime.

References

Akhavan J., The Chemistry of Explosives, Royal Society of Chemistry (2004).

Baker W.E., Anderson C.E., Morris B.L., Venters D.K., Quasi-static pressure diratopm, and impulse for explosion in structures, Southwest Res. Inst., San Antonio (1982).

CHAF. Quantification and Control of the Hazards Associated with the Transport and Bulk Storage of Fireworks, EC CONTRACT EVG1-CT-2002-00074 (2002).

Conkling J.A., Chemistry of pyrotechnics: basic principles and theory, Marcel Dekker Ed., NY (1985).

Denkevitz A., Dorofeev S., Explosibility of fine graphite and tungsten dusts and their mixtures, Journal of Loss Prevention in the Process Industries, 19, (2006) 174-180.

Directive 2007/23/EC, Placing on the market of pyrotechnic articles. 23 May 2007.

Directive 96/82/EC, The control of major-accident hazards involving dangerous substances. 9 December 1996.

Donhaue L., Pegg M.J., Zhang F., Afterburning of TNT detonation products in air, Seventh International Symposium on Hazards, Prevention, and Mitigation of Industrial Explosions (7th ISHPMIE), St. Petersburg, Russia (2008).

Ellern H., Military and Civilian Pyrotechnics, Chemical Publishing Co., NY (1968).

Gordon S., McBride B.J., Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications. NASA RP 1311 (1994).

Keenan W.A., Tancreto J.E., Blast environmental for fully and partially vented explosion in cubicles, Technical Report R828, Civil Engineering Laboratory, Deparment of the Army, Picatinny Arsenal, Dover, NJ (1975).

Kubota N., Propellants and Explosives: Thermochemical Aspects of Combustion, Wiley-VCG Verlag GmbG & Co. KGaA (2002).

Kuhl A.L., Forbes J., Chandler J., Oppenheim A.K., Spektor R., Ferguson R.E., Confined Combustion of TNT Explosion Products in Air, LLNL, K-131748 (1998).

McIntyre F.L., Rindner R.M., Compilation of Hazard and Test Data for Pyrotechnic Compositions. - Final rept. Jan 69-Mar 79. Computer Sciences Corp., NSTL (1980).

Ornellas D.L., Calorimetric Determination of the Heat and Products of Detonation for Explosives: October 1961 to April 1982, LLNL, UCRL-52821 (1982).

Salzano E., Basco A., Cammarota F., Confined After-Burning of Display Pyrotechnics and Explosives, 32nd Combustion Meeting, Napoli (IT), 2009.