Confined After-Burning of Display Pyrotechnics and Explosives

E. Salzano, A. Basco, F. Cammarota

Istituto di Ricerche sulla Combustione - C.N.R., Via Diocleziano 328, 80124 Napoli - ITALY

1. Introduction

Display pyrotechnics are 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. They are intended to be used mainly for entertainment industry in open environment and are classified as UN 1.3 or 1.4, i.e. substances and articles which give rise only to considerable radiant heat and minor or no blast or projection effects. These classifications and definitions seem to assure that they cannot behave as explosives. However, a recent experimental campaign [1] has recently demonstrated that when large amount of fireworks are stored in closed environment, explosive behavior can be observed, thus confirming the en mass explosion behavior already described by McIntyre & Rindner [2] for pyrotechnics.

These aspects are particularly important in Europe, after the accident of Enschede in the Netherlands, because the Seveso Directive (Directive 96/82/EC) [3] and Directive 2007/23/EC [4] have focused the local authorities to be aware of pyrotechnics storage plants other than manufacturing installations. Hence, safety report and design considerations on reinforced structures adopted for firework storage are now mandatory.

Despite the wide interest in pyrotechnics safety, scientific and technical publications are mainly available for high-energy explosives whereas less data are available for low-energy pyrotechnics. Also important worldwide references for the use of flammable and explosive materials such as NFPA 1124, 1123 and NFPA1126 [5-7] give several information on safety distances and recommendation for the manipulation of explosives and fireworks whereas storage design guidelines are neglected. Neither public military guidelines (TM 5-1300 and TM 9-1300-214 [8-9]) are really useful for the producers and design engineers when safety of large storage of low-energy pyrotechnics in reinforced structures are considered.

In this framework, for the aims of risk assessment and safe design, an important issue regards the maximum pressure which can be reached by large amounts of pyrotechnics when ignited in closed storage container. Indeed, as for solid high-energy explosives, non-ideal behavior and complex reaction schemes may occur.

2. Explosion and afterburning of high-energy solid explosives and pyrotechnics

The overall reaction of high energy explosives or pyrotechnics in large atmospheric container, after ignition, is due to primary reactions between the oxygen-donor (oxidizer) and fuel and by secondary reactions (afterburning) of the un-reacted fuel or partially oxidized products with surrounding air.

The afterburning phenomena in large-scale test have been analyzed for explosives as TNT or other high-energy explosives [10-11]. As expected, the energy release of the primary (detonation) explosion is followed by the energy given by the complete combustion with air of reaction products, thus producing an added energy which is typically twice to four times the primary combustion energy, and finally resulting in more severe hazards than expected. Kuhl et al. (1998) [10] have also demonstrated that TNT gaseous products burns under well distributed reaction regime in closed vessel for the afterburning rather than typical convetional/diffusive mechanism typically observed in flammable gaseous/air mixture in the
same conditions.
The same phenomena (primary reaction and afterburning) can also apply for any display pyrotechnic. However, very few references have been found in the open literature. An important text is the large database by McIntyre & Rindner (1980) [2], which gives the experimental heat of explosion (the heat of primary reaction) and heat of combustion (the heat produced by overall reaction with air) for several pyrotechnic compositions, measured in detonation calorimeter.

In this work, the explosion course of explosives (TNT, RDX and PETN), black powder, flash powder and a display pyrotechnic (white flare) either in nitrogen or in air atmosphere, have been analyzed.

The course of reactions has been determined by using the CEA thermo-equilibrium code [12-13], which calculates chemical equilibrium product concentrations from any set of reactants and determines thermodynamic and transport properties for the product mixture.

Plots are given in terms of calculated primary reaction energy and afterburning reaction energy for the entire set of reactants cited above. Comparison with experiments and calorimetric studies are given for the sake of validation of methodology.

Finally, the maximum pressure obtained with respect to the ratio given by explosive or pyrotechnic volume to the total room volume is given. These latest plots can be usefully adopted for risk assessment of pyrotechnic storage plants; the methodology can be extended to any other firework composition.

3. Explosion energy of explosives and pyrotechnics

When high-energy charges explode, a detonation occurs. The heat of detonation and product-composition data for high explosive charges may be evaluated by detonating charges in bomb calorimeter [14]. Several attempts by rules of thumb have been proposed in the literature (e.g. [15,16]) to reproduce the chemical reaction occurring along the detonation. These rules are however limited to carbon, hydrogen, nitrogen, oxygen compounds and cannot be applied to more complex substances or mixtures containing sulphur, aluminum or other inorganic salts or organic materials as in pyrotechnic.

As cited above, the CEA code has been used to calculate the total heat of explosion. In Table 1, the heats of explosion evaluated experimentally by detonation calorimetric analysis are compared with the heats calculated from the products of reaction given by CEA by using either the chemical equilibrium reached by freely expanding gaseous products at fixed freezing temperature (constant temperature and volume) by minimizing Helmholtz energy; or the chemical equilibrium at constant temperature and pressure (25°C; 1 bar), by minimization of Gibbs free energy. The use of the freezing temperature is common in thermo-chemical codes for the evaluation of explosives and it is related to the water-gas-shift reaction occurrence. Its use and definition has been fully explained elsewhere [17]. But however different temperatures are given in the literature between 1350 K and 2100 K.

Clear indications are given in Table 1 on the ability of the code when reproducing the data by using both methodologies, even if the explosion heats calculated at atmospheric T,P are slightly in excess. On the other hand, the use of calibration constant (the freezing temperature), is a weak point for the first method. It’s also worth noting that some scatter of experimental values is found in the literature for the heat for explosives due to the strong variability of results with the formulation: density, granulometry, additives, igniters, humidity. The ability of CEA code to evaluate the heat of explosion of non-detonating mixtures is further confirmed for black powder, by varying the sulphur content in the range typically adopted in the pyrotechnic industry, and comparing these data with experimental data (Fig. 1).
Table 1. Calculated results for the explosion energy. $T_f =$ freezing point. Black Powder: KNO$_3$: 75%; C 15%; S 10%. Flash powder: KClO$_4$: 30%; Al 40%; Ba(NO$_3$)$_2$: 30%.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>$\Delta H_{\text{explosion, J/g}}$</th>
<th>$\Delta H_{\text{explosion, J/g}}$</th>
<th>$T_f =$ 1350K, constant V</th>
<th>$T_i =$ 298K; $P_i =$ 1 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT (C$_7$H$_5$N$_3$O$_6$)</td>
<td>4573 [14]; 5070 [14]</td>
<td>4893</td>
<td>5434</td>
<td></td>
</tr>
<tr>
<td>RDX (C$_3$H$_6$N$_6$O$_6$)</td>
<td>5400 [15]</td>
<td>5379</td>
<td>6172</td>
<td></td>
</tr>
<tr>
<td>PETN (C$_5$H$_8$N$_4$O$_12$)</td>
<td>6235 [16]</td>
<td>6332</td>
<td>6889</td>
<td></td>
</tr>
<tr>
<td>Black Powder</td>
<td>2760 [18]</td>
<td>2510</td>
<td>2980</td>
<td></td>
</tr>
<tr>
<td>Flash powder</td>
<td>7348 [2]</td>
<td>9510</td>
<td>not convergent</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1 Comparison of experimental [19] and calculated heat of explosion for black powder (KNO$_3$:C:S = 7:8:x) by varying sulphur content. $T_f$ and $T_i$, $P_i$ refer respectively to the freezing temperature methodology and to the equilibrium at constant atmospheric pressure (1 bar) and temperature (25°C).

4. Combustion energy of explosives and pyrotechnics

The afterburning products may be also evaluated by using CEA code if adding atmospheric air to the reactants by assuming the combustion equilibrium at constant internal energy and volume, by minimizing Helmholtz energy. Hence, the heat of combustion $\Delta H_{\text{comb}}$ and the afterburning energy ($\Delta H_{\text{comb}} - \Delta H_{\text{explosion}}$) for same substances or mixtures reported in Table 1 can be calculated (Table 2). For this aim, a large excess of air has been considered by using a ratio of reactant volume to total air volume ($V/V^o = 10^5$).

Table 2. Calculated results for the heat of combustion in air excess ($V/V^o = 10^5$) for substances and composition reported in Table 1. *KNO$_3$/C/S ratio unknown.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>$\Delta H_{\text{comb}, J/g}}$</th>
<th>$\Delta H_{\text{comb}, J/g}}$</th>
<th>$\Delta H_{\text{comb}, J/g}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT (C$_7$H$_5$N$_3$O$_6$)</td>
<td>14961 [14]</td>
<td>14900</td>
<td></td>
</tr>
<tr>
<td>RDX (C$_3$H$_6$N$_6$O$_6$)</td>
<td>9460 [14]</td>
<td>8613</td>
<td></td>
</tr>
<tr>
<td>PETN (C$_5$H$_8$N$_4$O$_12$)</td>
<td>8018 [14]</td>
<td>7952</td>
<td></td>
</tr>
<tr>
<td>Black Powder</td>
<td>5963 [20]*</td>
<td>8610</td>
<td></td>
</tr>
<tr>
<td>Flash powder</td>
<td>11584 [2]</td>
<td>24320</td>
<td></td>
</tr>
</tbody>
</table>

Quite clearly, the combustion energy corresponds to that calculated by assuming that carbon and hydrogen oxidize to carbon dioxide and water for high-energy explosives. On the other
hand, large over-prediction is seen for flash powder. Here it’s also worth noting that rules of
thumb cannot be simply adopted for black powder or other pyrotechnics for afterburning.
Figure 2 shows, for the same composition reported in Figure 1, the combustion, explosion and
afterburning heat as calculated by CEA.

![Figure 2](image)

*Fig. 2 Calculated explosion, combustion and afterburning energy for black powder (KNO3:C = 7:8) as function of sulphur content.*

From the data reported, it is easy to note that in closed system the afterburning reaction may
produce larger hazards for less reactive mixtures due to the reaction with air of excess un-
reacted or partially oxidized substances.

### 5. Maximum pressure developed by explosives and pyrotechnics in closed container

The total energy given by CEA for the primary explosion and for the afterburning can be
adopted to calculate the maximum pressure in closed storage container by varying the ratio of
system volume over pyrotechnic or explosive charge volume, either in nitrogen atmosphere
(hence only primary reaction is considered) or in air atmosphere. The pressure is calculated by
constant internal energy for each volume V, by calculating average specific heat of products
and with ideal gas assumption.

Figure 3 reports the calculated pressure curves and comparison with experimental values for
TNT explosion. Good reproduction of experimental data is clear. In the same plot, the molar
fraction of CO in the gaseous products are also showed. Quite clearly, the afterburning
contribution is seen up to volume ratio of $10^4$ where CO is completely oxidized to CO2. After
this point, the slope of curves obtained with air tends to decrease and reaches the nitrogen
curve due to large volumetric effects. Density of TNT is 1600 kg/m$^3$, hence direct
transformation to mass to volume ratio is possible. For very low values of volume ratio, on
the other hand, the effect of afterburning is negligible when air is not available for the full
combustion of CO.

Finally, Figure 4 shows the maximum combustion pressure for black powder explosion
calculated by same procedure of TNT. Similar plot can be produced for any pyrotechnic.
6. Conclusions

The code of CEA has been demonstrated to fully solve either the primary or the afterburning reactions for explosives and pyrotechnics when large values of $V/V^o$ are considered. The plot of pressure with respect to volume ratio can be usefully adopted for engineering practice of storage design of pyrotechnics.
Acknowledgments
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References
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