THEORETICAL AND EXPERIMENTAL STUDY ON THE TRANSITION FIRE-DEFLAGRATION IN PYROTECHNICS

Emilio Palazzi, Renato Pastorino, Fabio Currò, Fabio Palazzi[1] and Bruno Fabiano*

DIChеP – Chemical and Process Eng. Department "G.B. Bonino", Genoa University, Italy
Via Opera Pia, 15 – I-16145 Genoa - brown@unige.it
[1] Setti Fireworks S.n.c,via Camaldoli 21- 16132 Genoa, Italy

Pyrotechnics, often combining technology and art, requires the production of low combustion mixtures that, when stored in large amounts, can give rise to deflagration or even detonation, in the event of an outbreak of fire. In this paper we analyze the transition from low combustion to deflagration in a peculiar case of black powder-based fireworks, by proper experimental runs and developing a simplified modeling approach.

1. INTRODUCTION

Pyrotechnics dates back to the mists of time and in particular the Italian art of fireworks or "feast fire", fragmented into different local artisanal traditions is rather different from the industrial pyrotechnics of the globalized market, mainly manufactured in far East (China). Our "latin" pyrotechnic art is analyzed in this paper, considering in detail its implications for storage safety. The early origins of fireworks are to be associated with the discovery of black powder (gunpowder) in China and India, nearly 1000 years ago. Fireworks mixtures were introduced in Europe by Crusaders on the way back from the territories of the Greek Byzantine Empire and were studied by Roger Bacon in the 13th century. Fireworks were subsequently further developed in Italy in the early 1500s and investigated by Biringuccio Vanoccio (1480-1539) in his treatise "De la Pirotechnia".

The purpose of this study is the investigation of the phenomenological transition low combustion-deflagration in pelletized pyrotechnic mixtures, which, under accident conditions, are suitable to evolve according to deflagration or even detonation scenario.

The approach was developed performing experimental runs addressed to the evaluation of the reacting front speed in scaled firework models and subsequent physical mathematical modelization of the results.

1.1 Explosion and pyrotechnics

As well known, an explosion can be defined as a rapid and abrupt energy release in a fluid medium (usually air), which produces a pressure wave and /or a shock wave with connected acoustic and mechanical effects. Explosions related to pyrotechnics, either required or unwanted, are all chemical explosions resulting from the evolution of reacting systems obtained by a fine mixture of oxidizers and combustibles, individually less dangerous than the mixtures. Their shattering power or brisance is by far lower than that of high explosives. The basic composition of fireworks is fine black powder with addition of chemicals acting either as binders (e.g. polysulphides, polyurethane, PVC), or as burning rate modifiers (e.g. paraffin wax, shellac, pitch), or as visual and acoustic enhancers. In considering the system in which the explosion takes place, we can observe volumes where the reaction completed, volumes where exothermic reactions occur and volumes where non reacted materials is interested by the reaction front and by energy transport. Following the Enschede explosion (NL) with 20 fatalities and 562 injured people, the Directive 2007/23/EC was implemented in addition to the Seveso Directives, addressing the peculiar case of firework storage activity. Design guidelines and correlations for the maximum pressure within the explosion room or outside the vent section are required for a safe storage design (Basco et al., 2010).

In classifying explosions reference is usually made either to the "effects" or to the "causes" of the different explosion regimes; to the purpose of this simplified approach we refer to the second criterion, referring to: deflagrations, as explosions in which the energy transport by heat fluxes is the limiting step of the overall kinetic; detonations, as explosions in which the energy propagation mechanism is due to mechanical shock wave; slow detonation and intermediate cases.

1.2 Fireworks mixture

In this context, we define the pyrotechnic mixture as a fine blend of components in which the individual constituents are by far less hazardous. Pyrotechnics evolves considerable amounts of heat but less gas than propellants or explosive. By proper mixing the pyrotechnic artisan is able to obtain an intense local heat to render component particles incandescent, with subsequent emission of flames, brilliant sparks, noise and colored smoke. Combination of different chemicals are used to obtain colored flames, whistle effect is obtained by ignition of pressed mixture of organic compounds (e.g. gallic acid and sodium sacylate), while "delay effect" is obtained by suitable low combustion devices.

All these effects are the result of the correct and in-depth study of the right composition, granulometry and degree of compactness.

In other words, the technological action on these mixture is addressed to the control of the chemical physical mechanism determining the overall kinetics.

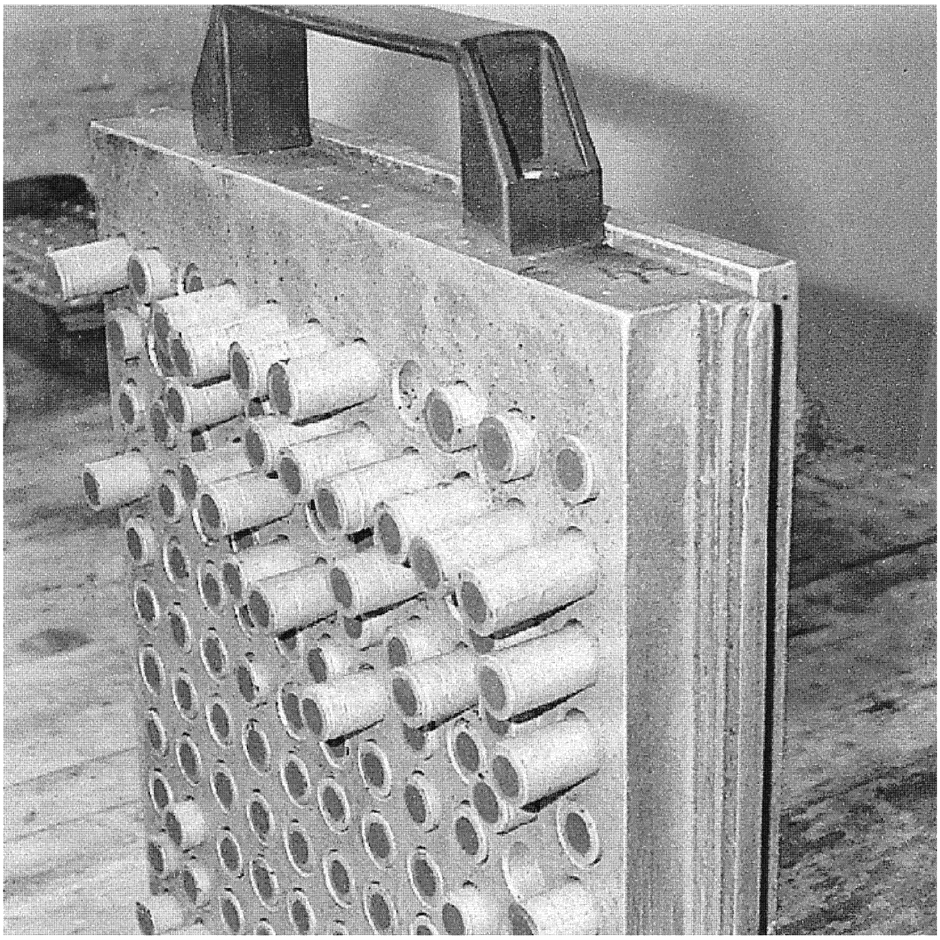

Figure 1: "Delay" firework systems: inert cases filled with highly compacted black powder.

Figure 2: Pelletized pyrotechnic mixture usually adopted for "star" fireworks: they are manufactured to ignite without giving rise to deflagration or detonation, so as to remain suspended for some time in the sky.

In the following, we make reference to micro-granulometry (referred to the particle size distribution of the mixture components), as well as to the macro-granulometry (i.e. the overall granulometry of the pelletized mixture). We can remind to the old black powder (with approximate composition (w/w): 75% salpetre, 15% charcoal and 10% sulphur): it is well-known for its explosive behaviour, for example when utilized as propellants or in mines, but it can also show a low combustion phenomenon, characterized by burning rates of the order of cm s^{-1}, when properly assembled in the so-called "delays" (low combustion elements).
An example of delay devices in provided in Fig. 1.
This evidence clearly shows that for the old gunpowder the energy transport represents the rate limiting step of the ignited system, so that in many cases the thermal flux is not sufficient even to attain the deflagration.
Making reference to luminous systems characterized by low combustion rate phenomena, the intrinsic micro- and macro-granulometry and the high degree of mass compactness suggest a conductive heat transfer phenomenon within the reacting bulk.
On the contrary, real deflagration and possible transition to detonation are expected when experimentally observing the speed of the moving reaction front in pyrotechnic mixtures of similar chemical composition, but different macro-granulometric structure, suitable to enhance convective transport phenomena. An example of pelletized mixture utilized for the artisanal realization of fireworks, according to the Italian tradition, is depicted in Fig. 2.

2. EXPERIMENTAL

As already remarked, the purpose of the model is to identify the conditions suitable to enhance or inhibit the deflagration transition within pyrotechnic storage systems that are individually characterized by possible low combustion phenomena.
As an applicative case-study, we can consider the already mentioned “circle stars” (see Fig. 2 for their hand-manufacture), consisting of spherical pellets obtained by proper color–light compressed mixtures. Each pellet is designed to leave a luminous trace in the sky for nearly one second, once ignited on contact with air and producing for example a fountain display. They cannot be considered as explosive systems: the heat transport phenomenon within each spherical pellet can be considered of predominant conduction, due to the negligible void degree of the medium.
On the contrary, generally speaking, this configuration can’t be applied when large amount of “star” fireworks are stored in silos, or other packages, in which the content can be considered as a granular bed with a high void degree.
Bearing in mind these considerations, we developed a preliminary modeling approach to shed light, in view of future theoretical insight, on the physical variables determining the mentioned transition fire-explosion.

2.1 The model mixture

The possible formulations of pyrotechnic mixtures are too different to allow the attainment of general results covering all possibilities, at a preliminary research level. Therefore, we refer to the mixture that is associated to the origins of fireworks, i.e. black powder, for which there is a large availability of statistical significant data.
Gunpowder shows low combustion rate in the “delay” devices, as well as when packed and compressed in pelletized form in a cylindrical case. On the contrary, a deflagration can be obtained when it is stored in granular form, within suitable containers, i.e. in the peculiar case of large “stars” storage.
A standardized methodology was developed in the experimental work to allow for a high reliability and comparability of experimental results. In order to define a physical model, we refer to a cylindrical non deformable container in which it is possible to select the reaction regime by the control of parameters referring only to the pyrotechnic mixture: micro and macro granulometry, composition and void degree of the granular bed. According to this approach, it is possible to analyze the dependence of the reacting front, u, on the geometrical characteristics, separately from the dependences of different origin. In order to develop a simplified model under the hypothesis of one-dimensionality, experimental runs were carried out by means of specimens characterized by overall length of at least 2 m. All data obtained in the transient phase (i.e. those obtained in the transition regions at the inlet and outlet of the container) were excluded from the modeling verification.
The schematization of the testing model is depicted in Fig. 3, representing a cylindrical case, with ignition device at the left end and equipped with thermocouples and optical probes equispaced along the longitudinal axis and connected to a transducer, suitable to detect the velocity of the reacting front.
The basic composition of tested black powder was the standard one (KNO_3 75% C 15% and S 10% w/w) and two types were tested, namely the “superficial graphitized” and the “non graphitized” one. Experimental characteristics of both types were obtained as follows:

ρ_s = $1.95\cdot10^3$ [$kg\cdot m^{-3}$];
ΔH_{expl} = $-2.8\cdot10^3$ [$kJ\cdot kg^{-1}$];
T_R = 507 [K];
$\hat{c}_p$ = 0.9 [$kJ\cdot kg^{-1}\cdot K^{-1}$] (weighted average of the components);
K_{cond} = 0.4 [$W\cdot m^{-1}\cdot K^{-1}$] (weighted average of the components).

Starting from the experimental value of density (which is comparable with the theoretical one obtained by weighted average on the elemental composition $\rho_t \approx 2\ 10^3$ [$kg\ m^{-3}$]), the void rate, ε ,was easily calculated.

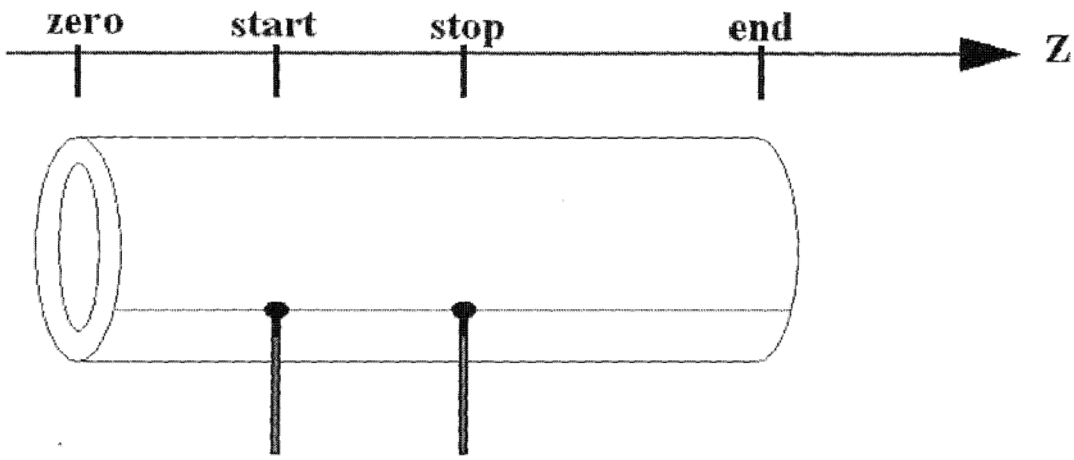

Figure 3: Experimental set-up according to the one-dimensional approach.

The experimental design was realized considering different situations, ranging from the limiting case of void rate → 0 (corresponding to a single cylindrical grain of blackpowder with boundary limits) to a range of different granulometries realizing a given void rate. The reaction velocity u corresponding to the former situation was experimentally evaluated in the range 0.01-0.03 ms^{-1}. Experimental values of u obtained for the macro-granulometry of 16-18 mesh ranged from 15.5 to 17.3 m s^{-1}, while, in connection with the macro-granulometry of 8 mesh , u ranged from 178 to 222 m s^{-1}.

3. MODELIZATION APPROACH

Starting from different studies available in the scientific literature (Frolov and Korostelev, 1989, Boddington et al., 1986 and Goodfield and Rees, 1985), two approaches can be sorted, respectively based on heat conductive transport (Carslaw and Jaeger, 1959) and heat convective transport within the reacting bulk. Results obtained by the former one-dimensional model are integral part of the latter, in which the single explosive grains are subjected to heat transport by conduction from the surface exposed to hot gases towards the inner region.

3.1 Pure conduction model

The simplified physical model corresponds to a cylinder of infinite length filled with black powder characterized by a high degree of compactness and is depicted in graphical form in Fig. 4 .The reference system is coincident with the flame front, corresponding to x = 0. The arrow shows the heat flux by conduction from the reaction zone (x = 0) towards the region containing the unreacted mixture.

Following simplifying hypotheses were assumed: complete reaction in the control volume; adiabatic control volume along the lateral surface; gaseous reaction products at T_0; ideal gas law.

The adiabatic flame temperature T_{ad} in x = 0 was estimated according to a thermodynamic approach. The explosion reaction suitable for our purpose may be written as (Russel, 2000):

$$74KNO_3+30S+96C+16H_2O$$
$$\downarrow$$
$$19K_2CO_3+7K_2SO_4+2K_2S+56CO_2+35N_2+14CO+3CH_4+2H_2S+4H_2+8K_2S_2O_3+2KSCN+(NH_4)_2CO_3+C+S$$

We can notice that at least the following reaction compounds undergo an endothermic transition below 873 K: K_2CO_3, K_2SO_4, KSCN and $(NH_4)_2CO_3$ (Perry and Green, 1998).

The corresponding adiabatic flame temperature can be calculated with good approximation as about 2270 K.
We must remark that, since a significant mass of black powder is not converted into gaseous products and consequently much heat is retained in the solid products, the explosive efficiency of black powder is rather limited.
Experimental determination of the velocity u of the reacting front allows the estimation of the global heat transfer coefficient black powder-gas, according to:

$$h_c(T_{ad} - T_R) = \rho_s u\left[\hat{c}_p(T_R - T_0) + \omega_S\lambda_S + \omega_{KNO3}\lambda_{KNO3}\,0.6 + \xi\omega_{KNO3}\lambda_{KNO3}\right] \tag{1}$$

where:
h_c = heat transfer coefficient [J m^{-2} K^{-1} s^{-1}];
T_{ad} = adiabatic flame temperature [K];
T_R = ignition temperature [K];
T_0 = ambient temperature [K];
c_p = thermal capacity of the powder [J·kg^{-1}·K^{-1}];
ρ_s = compressed mixture density [kg m^{-3}];
u = 0.01 m s^{-1};
ξ = 0.44 non dimensional parameter accounting for KNO_3 partial fusion.
The reference stoichiometry corresponds to the thermal decomposition of potassium nitrate in reductant environment:

$2KNO_3 \rightarrow K_2O + N_2 + 3O_2$

The maximum error, in evaluating h_c, connected to the choice of ξ was analytically calculated as 11%.
We calculated a value of $h_c \approx 7\ 10^{-3}$ J m^{-2} K^{-1} s^{-1}, in connection with $T_{ad} \approx 2270$ K .

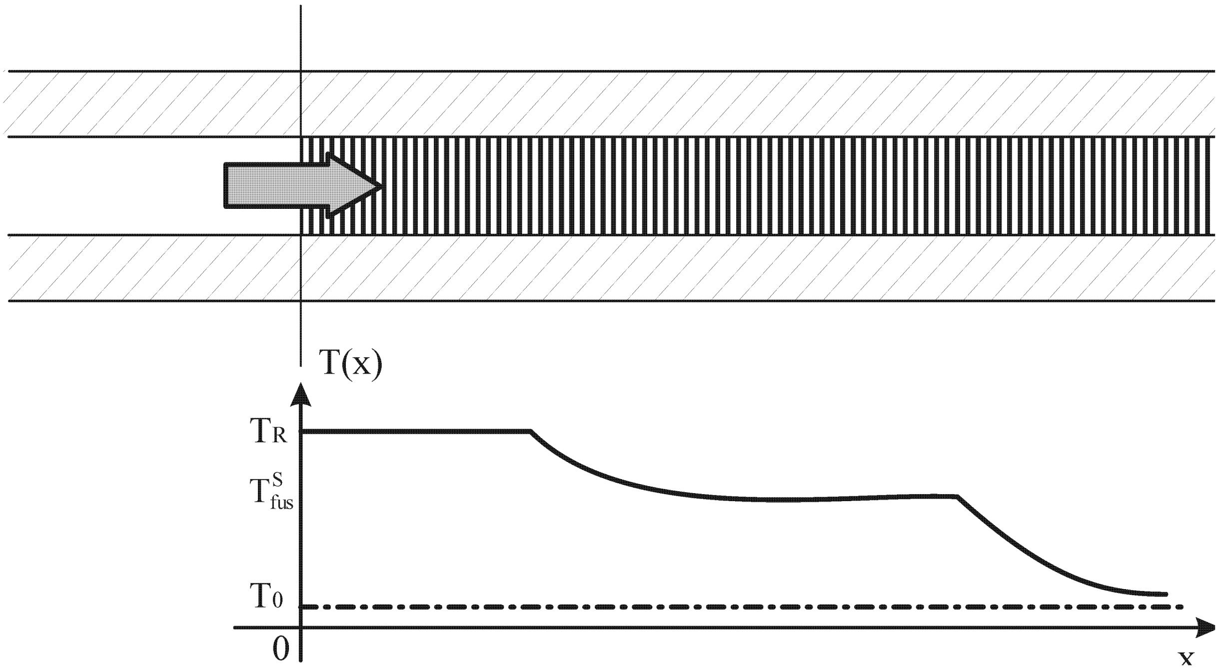

Figure 4: One-dimensional schematization and qualitative thermal profile behaviour, considering phase transitions of sulphur and potassium nitrate.

3.2 Convective-filtration model

When considering the peculiar case of a black-powder granular bed, the energy transport mechanism is obviously rather complicated. In fact:

- starting from x = 0 there is a limited "filtration domain" where the hot gases coming from the reacting zone exchange heat with unreacted pellets;
- owing to the hot gas motion the activation energy of the combustion process can be significantly affected by "mechanical terms";
- the domain corresponding to x >> 0 can be described to the purpose of this approach by proper arrangement of the above-mentioned conduction model.

Making reference to Fig. 5, we can observe a schematization of the here considered situation, where the plane $x = x_F$ allows the delimitation of the here defined "filtration region".

Physical systems of this type are experimentally characterized by transition from low combustion to deflagration and possible low detonation.

By proper arrangement of the conductive model it was possible to evaluate the time t_R required to the single explosive grain to rise its superficial temperature from T_0 to T_R, owing to the convective effect of the hot gases in the filtration region.

Starting from this theoretical estimation, it is possible to obtain on an experimental basis the length of the filtration region, in granular beds of different granulometries, properly packed according to the experimental set-up already depicted in Fig. 3.

The approximated evaluation was obtained by following relation:

$$\frac{x_F}{u} = t_R \qquad (2)$$

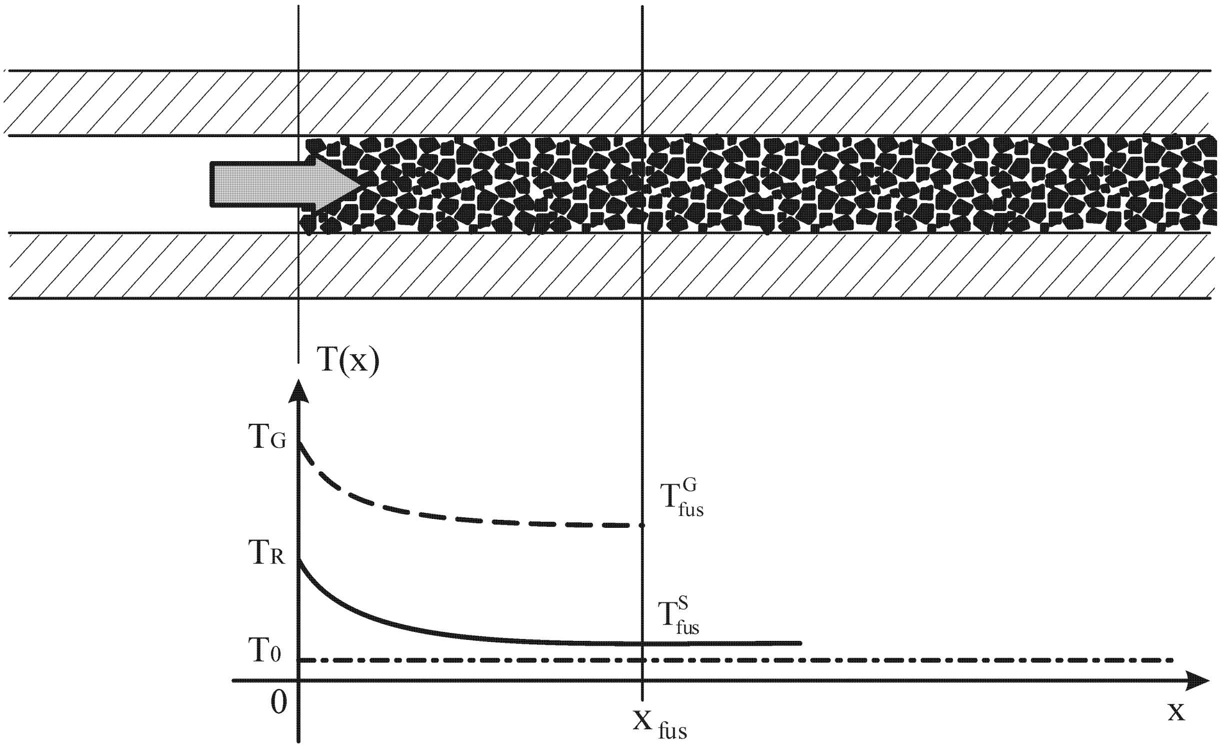

Figure 5: One-dimensional schematization of a black powder granular bed and qualitative thermal profile behaviour of gas(G) and solid(S) phase in the" filtration region".

In connection with macrogranulometry in the range 30-40 mesh, we experimentally obtained values of u of 9-10 ms^{-1}, while for macrogranulometry in the range 16-18 mesh the corresponding values of u are in the range 15.5-17.3 ms^{-1}, depending on the quality of the tested black powder.
Under these configurations, the application of the one dimensional model confirmed the hypothesis of a pure deflagration phenomenon determined by a convective heat transfer mechanism.
On the contrary, the results obtained in connection with a macrogranulometry of 8 mesh, with measured velocities in the range 178-222 $m \cdot s^{-1}$, put in evidence the determining role of different and more complicated energy transport mechanism, causing a transition to a slow detonation regime.

4. CONCLUSIONS

The present study of the transition fire-deflagration of black powder-based fireworks shows that the burning rate is sensitive to the macrogranulometry and degree of compactness.
It is experimentally confirmed the deflagration and slow detonation transition in systems individually non explosive. The reaction front speed increased with decreasing the granulometry of blackpowder. An approximate conductive and filtration convective modeling approach is developed, showing a fairly good agreement for the model mixture in the region of fire and deflagration, so as to foresee the evolving accident scenarios.

5. REFERENCES

Basco, A., Cammarota, F., Salzano, E., (2010), The risk of storage plant of pyrotechnics, Chemical Engineering, Transactions, 19, 231-236.

Boddington, T., Laye, P.G., Tipping, J., Whalley, D., (1986), Kinetic analysis of temperature profiles of pyrotechnic systems, Combustion and flame, 63, 359-368.

Carson, P., Mumford, C., (2003), Pyrotechnics and loss prevention, Loss Prevention Bulletin, 173, 3-15.

Carslaw, H.S., Jaeger, J.C., 1959, Conduction of heat in solids, Oxford University Press, U.K.

Conkling, J.A. 1985, Chemistry of pyrotechnics. Basic principles and theory, Marcel Dekker, inc., NY-Basel.

Goodfield, J., Rees, G.J., (1985), Metal/oxidant combustion reactions: variation of propagation rate with consolidation pressure, Fuel, 64, 1627-1630.

Frolov, Y.V., Korostelev, V.G., (1989), Combustion of gas-permeable porous systems, Propellants, Explosives, Pyrotechincs, 14, 140-149.

Perry, R.H., Green, D.W., 1998, Perry's Chemical Engineers Handbook, 7th ed., McGraw-Hill, Australia.

Petralia, S. , 2000, Compendio di esplosivistica, Mariperman, La Spezia.

Russel, M.S., 2000, The Chemistry of Fireworks, RSC Paperbacks, Royal Society of Chemistry publ., U.K.