New Approaches to Model Pyrotechnic Reactions

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Abstract: *In most cases pyrotechnic mixtures are constituted from granular components. A theoretical study of such a granular system describes the temperature and concentration evolution in the energetic material by using hot spots as source terms for temperature and particles. The progress of the reaction is mainly influenced by particle properties which are size, melting and evaporation, gasification and surface reactions. In a first step the influence of the particle size ratio between fuel and oxidizer particles is investigated.*

Keywords: *hot-spot model, combustion, ignition, pyrotechnics, Green's method*

Introduction

The work presented in this paper is part of some ongoing efforts to model combustion and ignition processes of propellants and pyrotechnics.[2–7] The aim of this work is not a perfect simulation of a certain process but to investigate single effects and their consequences on a system and the method applied is to make parameter studies resulting in a better understanding of the principal combustion mechanism. For a parameter study it is necessary to perform a greater number of calculations. Therefore models and codes are needed which are fast enough to do this in a reasonable time. As a consequence the models have a reduced complexity but high performance. This paper concentrates on a model, which is called Hot-Spot Model.

Model Description

From a physical point of view combustion processes are mainly dealing with heat transfer: it means heat is generated and consumed by different processes at different locations. Pyrotechnics are usually solid materials. Therefore the model description starts with the partial differential equation of heat transfer in a solid, where convective effects can be neglected (equation 1, below).

$$\frac{\partial T[\vec{x},t]}{\partial t} - \frac{\lambda}{\rho c_p} \cdot \Delta T[\vec{x},t] = \frac{\dot{Q}[\vec{x},t]}{\rho c_p} \quad (1)$$

There are several analytical and numerical methods to solve the differential equation. Here Green's method[1] is chosen because, if the appropriate Green's function for the homogeneous problem is known, it only has to be integrated with the source term of the differential (equation 2, below).

$$T[\vec{x},t] = \int G_U[\vec{x}-\vec{x}',t-t'] \cdot \frac{\dot{Q}[\vec{x},t]}{\rho c_p} \cdot d\vec{x}' \cdot dt'$$

The Green's function for the above differential equation in three dimensions is a Gaussian-like function (equation 3, below).

$$G_U[\vec{x}-\vec{x}',t-t'] = \left(\frac{\rho c_p}{4\pi\lambda(t-t')} \right)^{3/2} \cdot e^{-\frac{\rho c_p (\vec{x}-\vec{x}')^2}{4\lambda(t-t')}}$$

The great advantage of this method is that numerical integration is a much faster and a much more stable process than differentiation.

The next step is to choose the source terms. Two types of heat sources may be considered. One is the combustion enthalpy of the chemical reaction of the material. The simplest reaction is of 0th order described by an Arrhenius term.

$$\dot{Q}_{reac} = q_{reac} Z \cdot e^{-\frac{E}{RT}} \quad (4)$$

The other one is the ignition energy which is introduced in the system at a certain moment to start a reaction. This is the hot spot and it can be described by a Gaussian function or a Dirac delta function (equation 5, overleaf).

If there are only hot spots, integration can be done analytically. But this is not possible with the Arrhenius term for the chemical reaction. Therefore numerical integration is needed. The algorithm used for this purpose mainly consists of three steps. The first step is to generate an initial temperature profile resulting from the initially

$$\dot{Q}_{hs}[\vec{x},t] = \frac{Q_0}{(2\pi)^{3/2}\,\sigma_x\sigma_y\sigma_z} \cdot e^{-\left(\frac{(x-x_0)^2}{2\sigma_x^2}+\frac{(y-y_0)^2}{2\sigma_y^2}+\frac{(z-z_0)^2}{2\sigma_z^2}\right)} \cdot \delta[t-t_0] \qquad (5)$$

$$T_1[\vec{x},t] = \sum_{i=1}^{n}\left(\frac{Q_0}{\rho c_p (2\pi)^{3/2}\,\sigma_x\sigma_y\sigma_z} \cdot e^{-\left(\frac{(x'-x_i)^2}{2\sigma_x^2}+\frac{(y'-y_i)^2}{2\sigma_y^2}+\frac{(z'-z_i)^2}{2\sigma_z^2}\right)}\right)\cdot\delta[t'-t] \qquad (6)$$

$$T_2[\vec{x},t] = T_1[\vec{x},t] + \frac{q_{reac}\cdot Z}{\rho c_p}\cdot e^{-\frac{E}{R\left(T_1[\vec{x},t]+T_0\right)}}\cdot\Delta t \qquad (7)$$

$$T_3[\vec{x},t] = \int\left(\frac{\rho c_p}{4\pi\lambda\Delta t}\right)^{3/2}\cdot e^{-\frac{\rho c_p(\vec{x}-\vec{x}')^2}{4\lambda\Delta t}}\cdot T_2[\vec{x},t]\cdot dx'\,dy'\,dz' \qquad (8)$$

given hot spots (equation 6).

In the second step the progress of the chemical reaction for a small time step Δt is calculated (equation 7). The third step is to calculate the heat diffusion for the same time step Δt by integrating the convolution of the temperature profile and the Green's function (equation 8).

Steps 2 and 3 are repeated for every time step. Step 1 can be included as often as new hot spots occur.

From the above description the following features can be mentioned: the model is a transient one and it describes the heat generation by a chemical
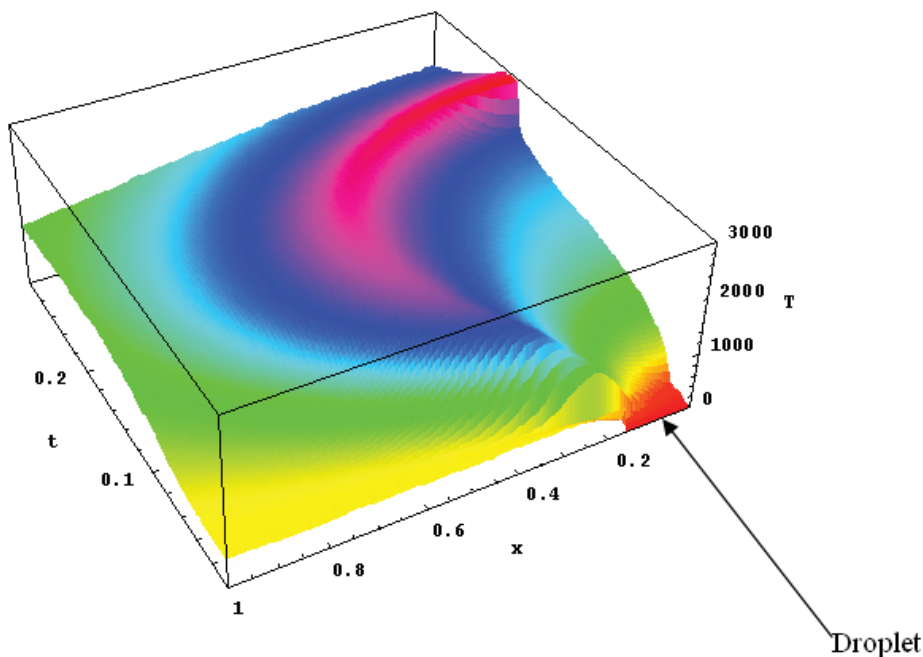

Figure 1 *Temperature profile for a burning particle at the right corner.*

reaction and the heat transport by conduction.

Fuel and oxidizer particles as sources of matter can also be described as hot spots. Including diffusion they can react as soon as gaseous fuel and oxidizer come into contact. The model does not include any convection or radiation. Implementing the model into computer code, we developed several versions of the model for different purposes. One version includes phase transition.

To run the program three types of parameters are necessary:

- Different spatial and temporal distributions of hot spots: energy, size and number of hot spots
- Material parameters: density, heat capacity, heat conductivity, diffusion coefficient
- Reaction parameters: maximum temperature, Arrhenius-parameters (frequency factor and activation energy)

The calculations result in two-dimensional temperature and concentration profiles for every time step, and in heat output, pressure and chemical rate over time.

Results

Single particle combustion

First implementation is a one-dimensional version of the model. It describes a single particle in a reactive atmosphere. As spherical symmetry is assumed one spatial dimension is enough to describe evaporation or gasification of the particle and succeeding combustion. The phase transition at the particle surface is implemented as an artificial high concentration. No heat transfer to the interior of the particle is included. Although these are very strong simplifications there are some interesting results.

Figure 1 gives the temperature profiles in a 3 D plot. The front edge is the spatial axis and the left side is the time axis. The evaporating particle is placed at the lower right corner. As no heat transfer into the particle is included its temperature is set to zero. The surrounding gaseous oxidizer has a temperature of 500 K that is enough to evaporate a small portion of the particle and to start the reaction. In this Figure the evaporation ends when temperature reaches the time axis on the right side. The flame is marked by the region of the highest
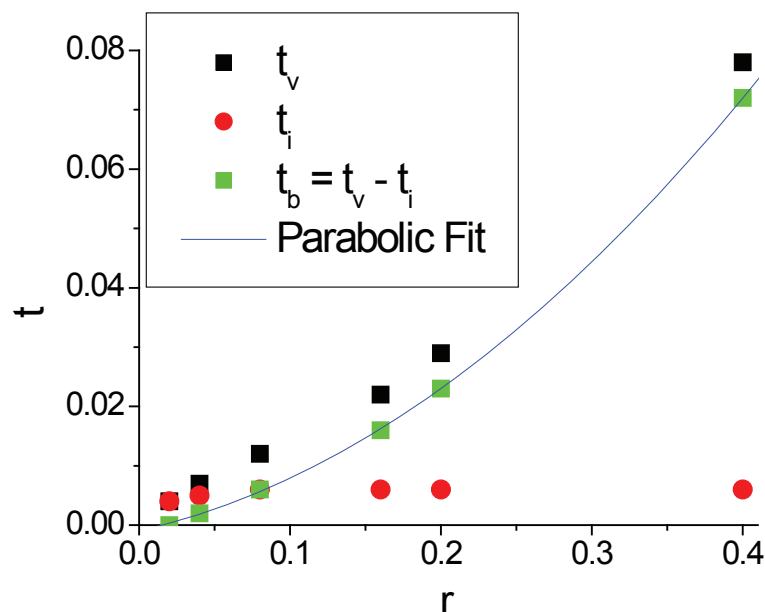

Figure 2 *Burning time $t_b = t_v - t_i$ vs. initial radius and parabolic fit.*
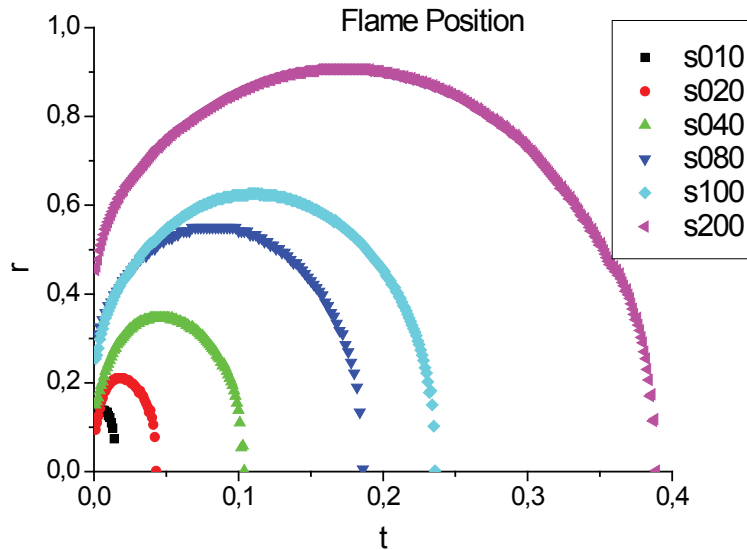
Figure 3 *Flame position as location of the highest temperature vs. time.*

temperature.

Calculations with different initial radii leads to corresponding evaporation times t_v for the particles. If ignition time t_i is defined as the time to reach the flame temperature then the burning time $t_b = t_v - t_i$ can be fitted by a parabolic function (Figure 2). This is well known as the r^2-law from theory[8] as expressed in equation 9, overleaf.

Figure 4 *Series of temperature profiles for ignition with hot particles.*

$$t_b = \frac{\rho_l \cdot c_{pg} \cdot r^2}{2 \cdot \lambda_g \cdot \ln(B+1)} \tag{9}$$

On the other hand if the flame position as the location of the highest temperature is taken from the same calculations Figure 3 results. As can be seen the flame moves with time. There is no constant distance to the particle surface and the flame exists much longer than the particle. Simple expressions to describe these findings like the r^2-law can not be found in theory, but measurements on burning droplets show a similar behavior.[9]

Ignition with hot particles

For the investigation of ignition processes with hot particles a full three-dimensional version was developed. A reactive material is hit by hot particles which are used as heat sources to start the chemical reaction of the reactive material. Figure 4 displays a short series of temperature profiles. From left to right it shows the initial state when the particles hit the reactive material. Then the heat spread and chemical reaction of the material produces additional heat. Finally a closed reaction front is formed.

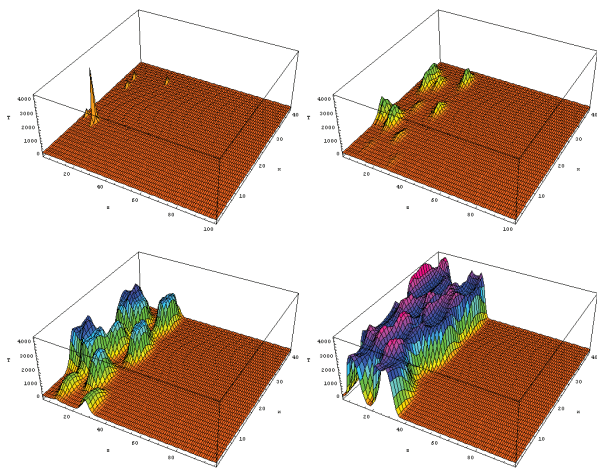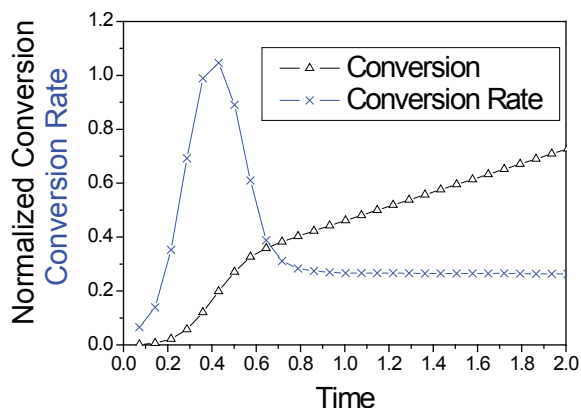The amount of heat produced and the resulting temperature can be used as a measure for the

Figure 5 *Normalized conversion and conversion rate during ignition with hot particles.*

progress of the reaction. In Figure 5 it is called normalized conversion. The time derivation of this quantity is the conversion rate. The peak at the beginning of the curve of the conversion rate results from the fact that at the beginning every particle has its own reactive sphere. Later these spheres overlap and the total reactive area reduces (see Figure 4). Then the reaction of the material goes to a steady state burning.

Reacting particles

In most cases pyrotechnic mixtures are constituted from granular components, *i.e.* fuel and oxidizer are reactive particles. In the framework of this model they can be described as sources of material which then react and produce heat. In addition to the temperature concentration profiles are
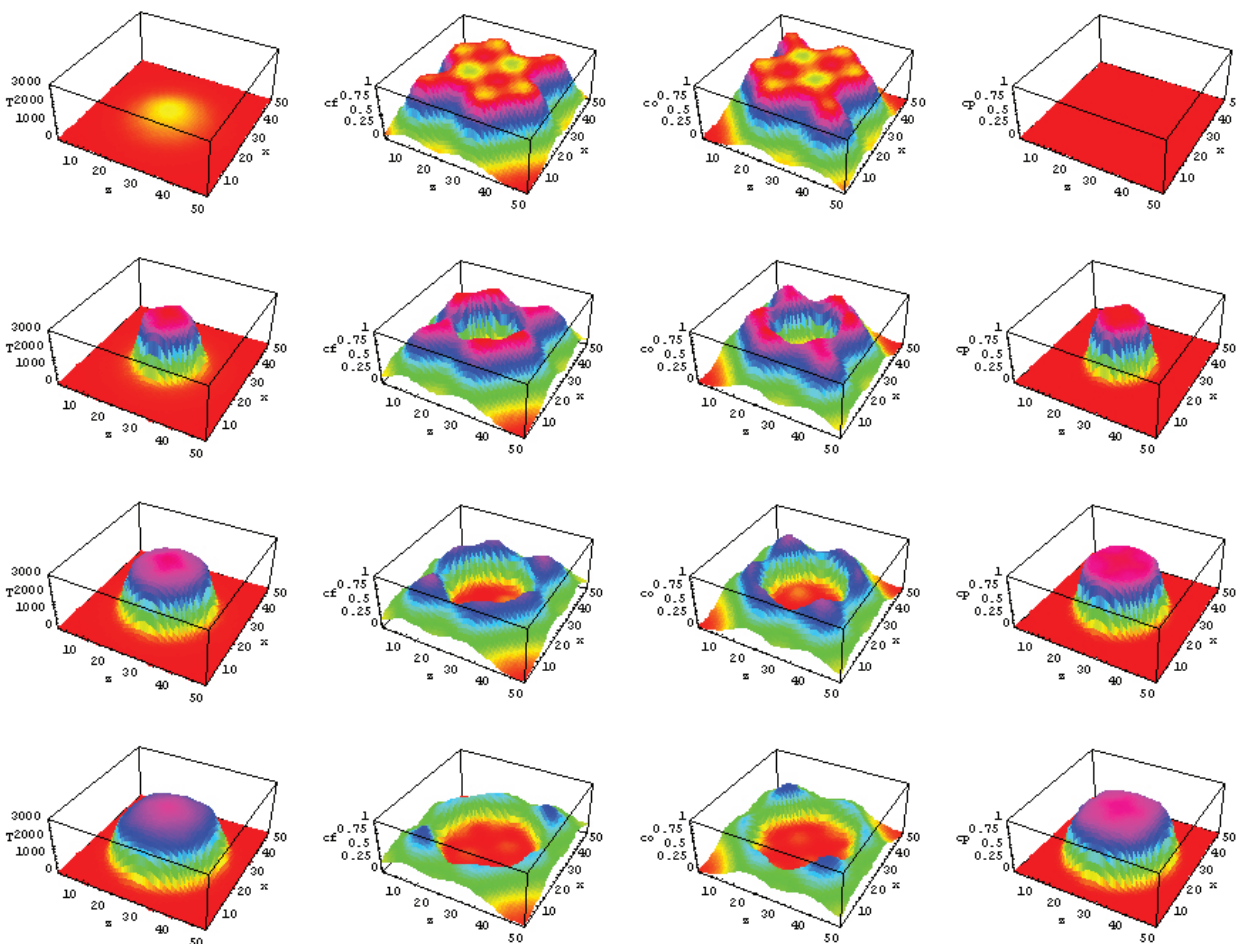

Figure 6 *Temperature and concentration profiles for eight fuel and eight oxidiser particles of same size. A thermal hot spot at the center ignites the material. From left to right: temperature, fuel concentration, oxidiser concentration, product concentration.*
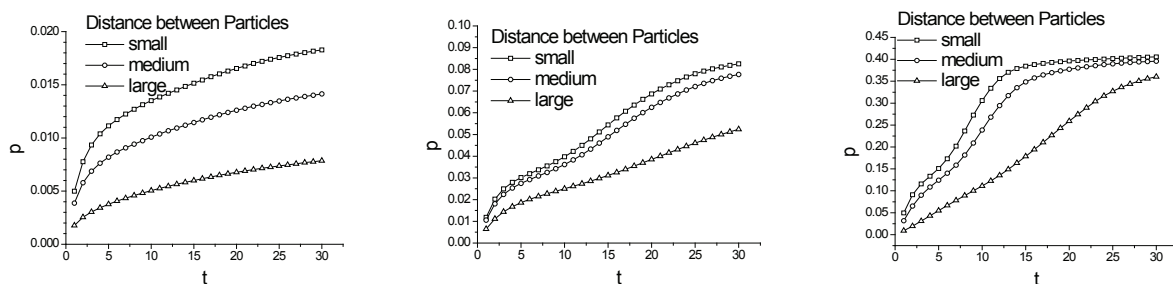
Figure 7 *Conversion for 1, 2 and 8 particles of fuel and oxidizer of same size (from left to right) and different distances between the particles.*

calculated. Figure 6 gives a short series of profiles for temperature, fuel concentration, oxidizer concentration and product concen-tration. The reaction of the particles is started by a thermal hot spot in the center.

For the results displayed in Figure 7 the number

of particles and the distance between the particles were varied. The size was the same for all particles. As expected the best burn out is achieved for the smallest distance between the particles. For more than one particle there is a step in the curve.

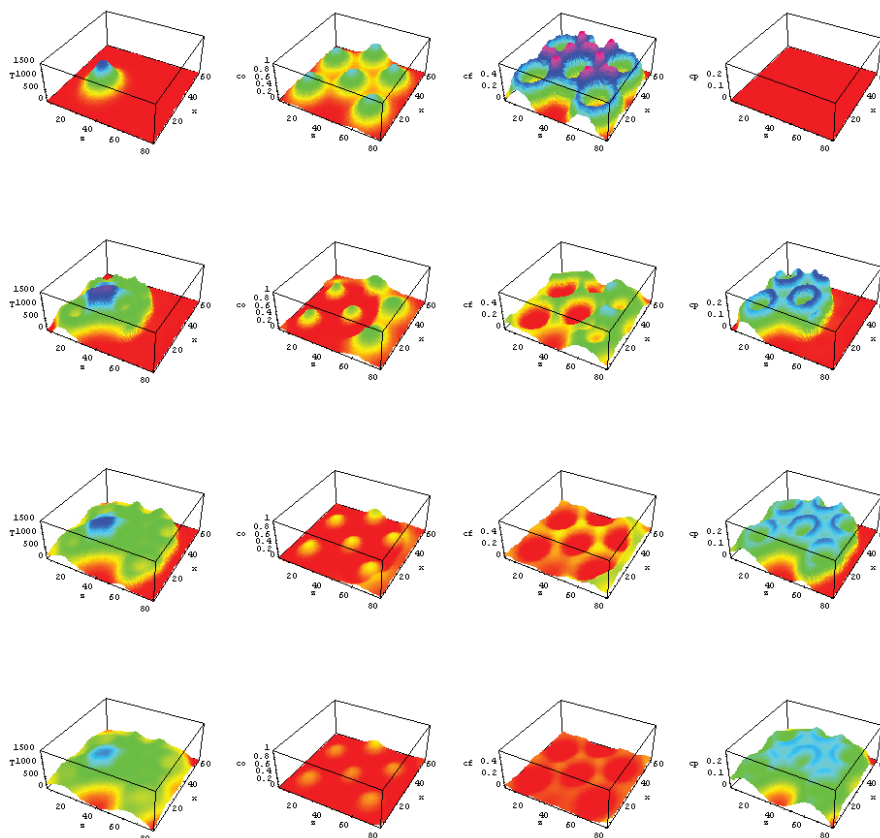Usually the particles of the oxidizer and the fuel are

Figure 8 *Temperature and concentration profiles for fuel and oxidizer particles of different size. A thermal hot spot ignites the particles. From left to right: temperature, oxidizer concentration, fuel concentration, product concentration.*
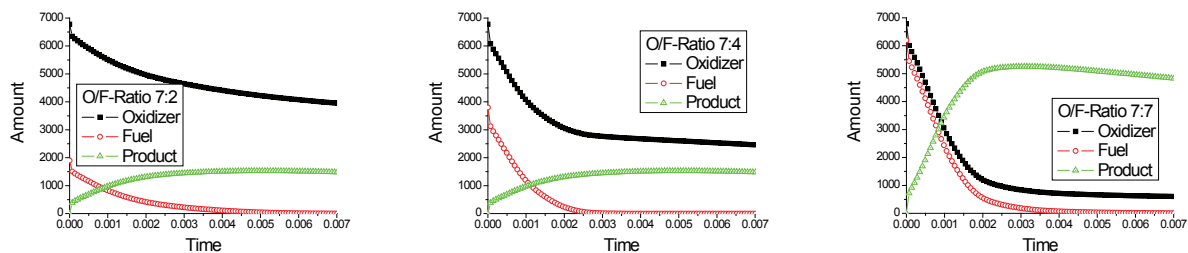
Figure 9 *Amount of oxidizer, fuel and product for different O/F-ratios vs. time (from left to right: 7:2, 7:4. 7:7)*

of different size. Figure 8 shows an example with a series of temperature and concentration profiles where large oxidizer particles are surrounded by smaller fuel particles.

Varying the initial amount of fuel leads to different oxidizer-fuel ratios. Figure 9 gives the curves of the total amount of oxidizer, fuel and product *vs.* time for three different O/F ratios. The best O/F ratio depends on the type of the chemical reaction.

In Figure 10 the heat output of the reaction is given dependent on the energy of the initial thermal hot spot. As can be seen the influence of this parameter is less important if the energy is high enough to start the reaction.

Conclusion

As the examples show the hot-spot model is a useful tool to make parameter studies. Parameters that can be varied are number, size and distribution of particles and some material properties (c_p, λ, ρ, D). Simple chemistry is included. The computer code runs fast and is very stable because there is no need to calculate derivations numerically. Further steps will be to include phase change also in the 3 D version and more complex chemistry. After validation a lot of calculations have to be done studying the influence of the different parameters.

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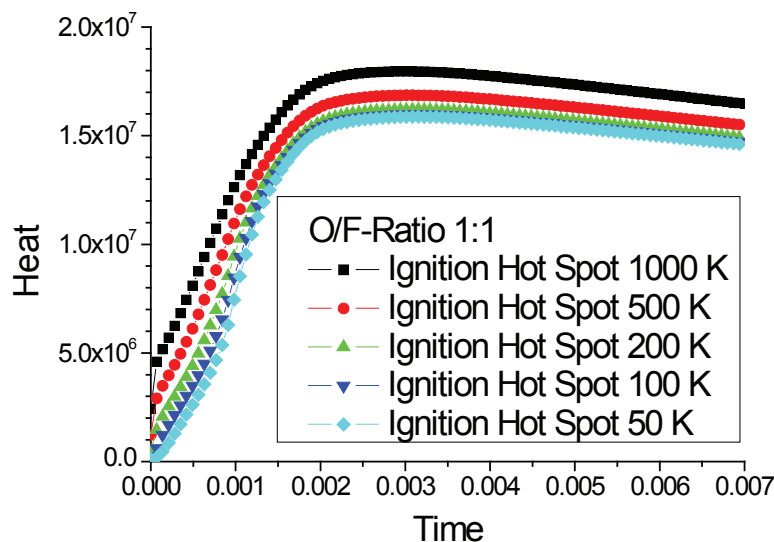
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Figure 10 *Heat output for varying ignition energy.*

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Errata

The following errors in previous editions of the Journal of Pyrotechnics have been communicated to us. We apologise for any inconvenience or confusion caused.

Issue and Page	Incorrect text	Corrected text
Issue 22 - Sponsors details - PyroShows	email and web address	email: info@pyroshowsusa.com web: www.pyroshowsusa.com
Issue 22 - Page 40, right column, 2nd paragraph 4th line	Mis-spelling of "hydrrogen"	Correct spelling to "hydrogen"