

Simple Finite Element modelling applied to the problems in Energetic Materials Characterisation: Design of Pyrotechnic Devices and Explosives Calorimetric Studies

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Abstract

Many thermal studies involving energetic materials are carried out in fixed geometry and these processes are usually governed by an energy balance between heat liberated from reaction and that dissipated by conduction away from the reaction zone. Many combustion and thermal explosion problems applications are defined by similar mathematical equations, albeit with different initial and boundary conditions.

Flexible finite element software employing a high level language input and with adaptive meshing refinement is now readily available. This coupled with modern PC's have made simulations of thermal reaction processes both straightforward and requiring little time or testing unlike the more challenging large finite element codes of the last 20 years usually requiring main-frame computers and individual pre-and post-processors.

This paper will cover two disparate applications –

(i) Pyrotechnic delays.

Pyrotechnic delays can loosely be categorised into those in which the effects of gas flow can be ignored and those in which gas flow influences the delay time. Heat loss takes place primarily by radiation and convection from the container walls and by the release of hot gas in open systems. Metallic confinement acts as a heat sink but also as a conduit for improved thermal conduction to the unreacted pyrotechnic.

This study involves comprehensive models to simulate both types of pyrotechnic

and will illustrate sensitivities to different design parameters.

(ii) Calorimetric Studies.

A simulation of an Accelerating Rate Calorimetry (ARC) is described as part of a study of onset reactions in ammonium nitrate decomposition. The ARC involves comparatively small samples (few grams) and has a phi factor in excess of 2: near adiabaticity is obtained via temperature measurement and heaters governed by electronic feedback. The determination of the onset of exothermic reaction in ammonium nitrate presents a challenge to the thermal analyst.

Ammonium nitrate chemistry involves a reversible endothermic reaction, several irreversible dissociations and phase changes. The results from the experimental study were simulated using physical and chemical property data from the open literature.

These two applications illustrate the use of this type of software in both teaching, research and design applications involving thermal processes in energetic materials.

Introduction

This paper is concerned with the simulation of reactions in solid-state media in which, with the exception of the perimeter of the device, energy transfer is largely governed by heat conduction. The specific simulations reported here involve a deflagration in a pyrotechnic delay column and thermal explosion in reactive media. These two systems involve the time dependent solution of energy and mass

conservation relations with chemical reaction.

A number of approaches have been used to simulate thermal explosion and deflagration ranging from analytic mathematical descriptions [1], large finite element codes [2] and bespoke software [3, 4]. The advent of fast personal computers and mathematical software [5] utilizing high level languages offers an alternative more flexible modelling tool for both teaching and engineering design.

Mathematical Models

The time dependent studies illustrated here have been carried out in cylindrical coordinates for exemplification purposes. The equations solved consist of:

- (i) energy conservation
- (ii) mass conservation
and, where required,
- (iii) momentum conservation
- (iv) equation of state (ideal gas)
- (v) thermal feedback (ARC)

subject to initial and boundary conditions discussed in each study. Variables include local temperatures, pressures, extent of reaction and gas velocities. Details of the equations are given later for each application.

Simulation Software

Ideally, these applications require software that is flexible and easy to use. It should be available for common operating systems platforms with graphical output and compatibility to other graphics packages. The solutions of the comparatively simple models here often have to be extended to complex geometries and mixed boundary conditions. Solvers employ finite element or difference procedures, which require the setting up of a mesh. Use of adaptive mesh rezoning in problems whose reaction zone is small compared with the total geometry is preferred as this enables more accurate

simulations in a finite computer memory. Ideally the software should employ a high level programming language enabling the description of a simulation in conventional mathematical notation.

FlexPDE [5] (PDE Solutions Inc) offers all the above features in a standalone computer program and has been used in all the simulations described in this paper. The software has been previously used by the present authors in a number of applications related to this paper and for which analytic solutions were available [1]: agreement has always been good.

Applications to Pyrotechnic Delays

A cylindrical delay element in an aluminium casing has been simulated. Longitudinal and axial conduction are included as well as radiative and convective heat losses on the outer surface of the casing. The initiation of the pyrotechnic was introduced by means of a heat pulse. A similar system has been comprehensively studied elsewhere [3].

Data on the pyrotechnic were taken from an Sb/KMnO₄ study [6] and key parameters are included in Table 1. This system has been modelled as a solid phase reaction, though allowance for air in the porous pyrotechnic has been included in a constant gas density process with no gas flow. The delay element comprised an open cylinder 22mm long and of internal and external diameters 3.4 and 6.4mm respectively. The pyrotechnic was assumed to be at 80% of its maximum density.

Reaction was assumed to take place at temperatures in excess of a defined ignition temperature. For the purposes of this study, physical properties were assumed temperature invariant

TABLE I : Pyrotechnic Properties

Heat of reaction	9.10 ⁶ J/kg
Reaction order	2/3
Activation energy	20700 J/mol
Arrhenius factor	9.25 s ⁻¹
Ignition temperature	506 K
Heat capacity	540 /kg ⁻¹ K ⁻¹
Thermal conductivity	0.3 Wm ⁻¹ K ⁻¹
Reactant Density	2300 kgm ⁻³
Product density	2070 kgm ⁻³

FlexPDE (v3.01e, PDESolutions Inc) [5] was used to solve the following equations

$$\nabla^2(kT) - q \frac{d\lambda}{dt} = [(\rho - \lambda(\rho_s - \rho_p))C_{p_p} + ((1-\eta)\rho_g - \lambda(\rho_s - \rho_p))C_{p_g}] \frac{dT}{dt} \quad (1)$$

where $k, \lambda, T, C_p, \rho, \eta,$ and Q denote thermal conductivity, fraction of pyrotechnic unreacted, specific heat (gas or pyrotechnic), density, temperature, solid fraction and heat of reaction respectively: subscripts s, g and p refer to reactant pyrotechnic, reaction products and air.

$$\frac{d\lambda}{dt} = k\lambda^n e^{(-E/RT)} \quad (2)$$

where n, a and E denote reaction order, Arrhenius factor and activation energy: no reaction is allowed below a preset ignition temperature. Equation (1) is simplified for the unreactive aluminium casing as Equation (2) is not required.

The initial conditions are ambient temperature and no reaction with a heat pulse into the front end of the pyrotechnic starting at zero time given by a heat flux term of the form $\beta_1 e^{-\beta_2 t}$ where β_1 and β_2 are set at 10⁶ and 10 respectively. The boundary conditions for the whole assembly consist of standard radiative/ natural convective heat

loss terms for aluminium in cylindrical geometry. An example program listing is included in Appendix 1.

Deflagration velocities were determined by tracking the location of the maximum temperature history in the central core of the pyrotechnic. These data were fitted to a cubic in distance to allow for an accelerating wave due to preheating of unreacted pyrotechnic. A typical result is given in Figure 1 for the case of a reduced (50%) reaction rate. Some slight acceleration is observed as a departure from a linear distance-time plot.

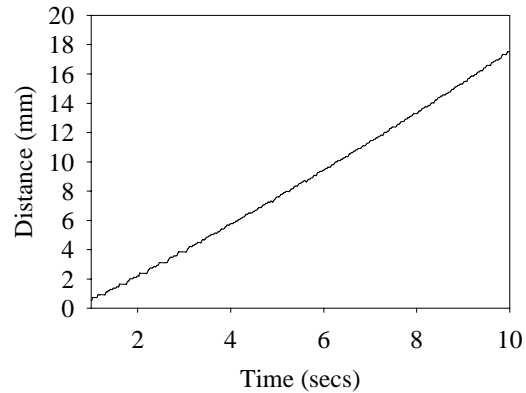
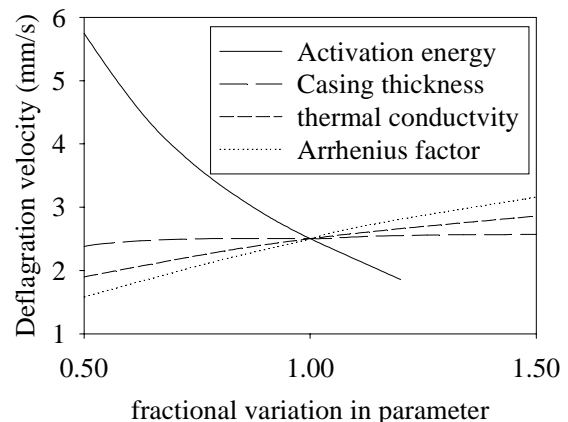
**Figure 1 Maximum axial temperature history**

Figure 2 illustrates the sensitivities of the burn rate to fractional changes in activation energy, casing thickness, pyrotechnic conductivity and Arrhenius factor.

**Figure 2 Sensitivities of Deflagration velocity**

As would be anticipated, the deflagration rate is dependent on activation energy and to a lesser extent on Arrhenius pre-exponential factor and pyrotechnic conductivity. As the activation energy is increased the reaction slows down and ultimately there is insufficient stimulus to initiate combustion from the fixed energy pulse used in these studies.

The pyrotechnic deflagration study was extended to examine the effects of gas flow, both radial and axial, assuming Darcy's law e.g.

$$u = -\xi \frac{\partial P}{\partial z} \text{ and } w = -\xi \frac{\partial P}{\partial y} \quad (3)$$

where P, ξ, r and z denote pressure, Darcy constant, radial and axial coordinates respectively.

In addition to Equations (1) and (2) the following three relations are required to describe gas flow with pyrotechnic burning:

$$\rho u = -\frac{\xi}{2RT} \frac{\partial P^2}{\partial z} \quad (4)$$

$$\rho w = -\frac{\xi}{2RT} \frac{\partial P^2}{\partial r} \quad (5)$$

$$T \nabla^2 (P^2) - \frac{\partial y}{\partial r} \frac{\partial P^2}{\partial r} - \frac{\partial y}{\partial z} \frac{\partial P^2}{\partial z} - \frac{2RT^2 V}{\xi} \frac{\partial \rho}{\partial t} = 0 \quad (6)$$

The initial and boundary conditions used were similar to the study with the gas stationary prior to reaction. The cylinder was taken as open at the initiation end and closed at the far end for the duration of the simulation.

Increased convective heating from internal gas flow increases the deflagration velocity: the motion of the wave is illustrated in Figure 3, by monitoring the progress of the maximum temperature during the pyrotechnic combustion. The velocities, taken from a cubic fit to the plots in Figure 3, are 2.58 and 2.89 mm/s without and with gas flow.

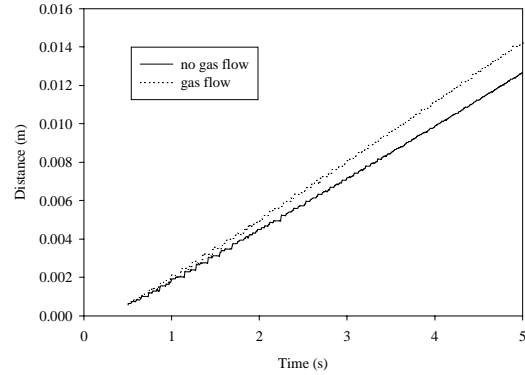


Figure 3 – Effect of gas flow on deflagration wave

The resultant pressure profile in the pyrotechnic delay after 5 seconds is illustrated in Figure 4. The radial pressure gradient is small with the pressure a maximum at the reaction front with gas vented through the initiation end of the delay.

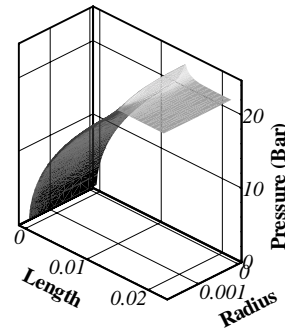


Figure 4 3_D pressure profile in pyrotechnic after 5 seconds

Applications in Calorimetric Studies - Onset Temperatures for pure Ammonium Nitrate – Modelling Study

A joint experimental/ modelling study was undertaken to assess the thermal stability of Ammonium Nitrate (AN). The aim of the modelling study was to interpret the different thermal tests, Accelerating Rate Calorimetry (ARC) and Adiabatic Dewar Calorimetry in order to be able to predict the

effects of scale and boundary conditions on observable onset of exothermic reaction. For the purposes of this paper, exemplifying the use of modelling software, the case of pure AN in an ARC will be discussed only.

Pure AN is a strong oxidizer with a complex set of decomposition and chemical dissociation pathways [7]. AN overheating can result in a thermal explosion or an explosive deflagration (when at high pressure). In extreme circumstances a detonation can ensue.

Onset temperatures for pure AN will be dependent on a number of factors, many of which will depend on the instrument and method used:

- (i) local pressure
- (ii) boundary conditions at wall – dissipative terms
- (iii) phi factor (total thermal mass/sample thermal mass)
- (iv) artefacts – phase changes, cold zones, unrepresentative samples

Description of Model

A number of studies [8-10] have been undertaken to simulate exothermic chemical reactions in calorimeters. These have incorporated a variety of chemical reaction types in a computer model using a high-level language. Some published work [9,10] has included the effect of sample vessel walls. However, no models in the open literature have been found to date that include complex geometry, different boundary conditions and phase changes.

The mathematical model is similar to that used to discussed earlier for the porous pyrotechnic with the exceptions of no gas voidage, different geometries and boundary conditions. The ARC simulation was carried out in an axi-symmetric geometry. A thermal feedback was introduced to simulate the oven control, following the measured sample temperature. The equations used for the ARC simulation are included below.

$$\text{div}(k_c \text{grad}T) + \frac{da}{dt} Q - \rho C_p \frac{dT}{dt} = 0 \quad (7)$$

$$\frac{da}{dt} = -k_r a e^{-E_{act}/RT} \quad (8)$$

$$\frac{dT_c}{dt} = C(T_{ref} - T_c) \quad (9)$$

where $k_c, T, \rho, C_p, k_r, a, E_{act}$ are defined as thermal conductivity, temperature, density, specific heat, reaction rate constant, extent of reaction and activation energy respectively. The thermal feedback for the oven control is approximately described by a derivative control between the oven temperature, T_c , and a reference temperature, T_{ref} . As with the pyrotechnic study standard radiative and convective loss terms were included at the boundary.

(i) Accelerating Rate Calorimetry.

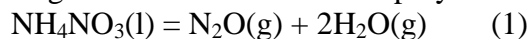
A number of authors have discussed this technique in detail [e.g. 11]. In essence, the test is designed to look at a few grams of sample, under pseudo-adiabatic conditions. This is achieved by controlling the temperature of an external “oven” using thermocouples and heaters such that the external temperature always matches that of the spherical sample bomb. It has the convenience of a relatively small sample size but drawbacks include the comparatively small sample size/ large phi factor and the large capital cost of the equipment

The ARC works on the basis that the surrounding oven temperature will follow the temperature recorded by the thermocouple attached to the bomb vessel. Inevitably there will be a small lag between detection and oven response. The actual instrument uses a proportional-integral-differential control algorithm to ensure that the oven temperature tracks the sample temperature, at heating rates as high as $10^\circ\text{C min}^{-1}$. The exact algorithm is of a

proprietary nature. However, for the purposes of the present study, only the initial stages of reaction are of importance, where heating rates are below $0.1^{\circ}\text{C min}^{-1}$. As a result, a much simpler feedback algorithm has been used.

(ii) Model Chemistry

As described in the introduction, a single-reaction model was employed:



The chemistry of AN decomposition is complex and a full simulation, including all potential chemical reactions and phase transitions would be well beyond the scope of this study. Instead, it was hoped that by using a single reaction of the appropriate nature, it would be possible to elucidate the main effects of the experimental techniques on the measured onset temperatures.

Parameters for AN have been taken from the literature [8] and are included in Table 2. Gas phase reactions and catalysis (by change in pH for instance) have been ignored.

Table 2 Physical and Chemical Property Data

Material	Ammonium Nitrate (l)
Heat capacity/ $\text{J K}^{-1} \text{kg}$	2352
Density/ kg m^{-3}	1420
Thermal Conductivity/ $\text{W m}^{-1} \text{K}^{-1}$	0.24
Reaction Rate s^{-1}	$10^{11} e^{(-18000/T)}$ T (K)
Heat of Reaction J kg^{-1}	$0.7076 \cdot 10^6$

(iii) Simulation Results

Figure 5 gives an example of a simulation of an ARC experiment with 3 g of AN.

Temperature rise vs. time is plotted for an initial temperature of 200°C . The different curves in Figure 6 refer to different parts of the ARC bomb.

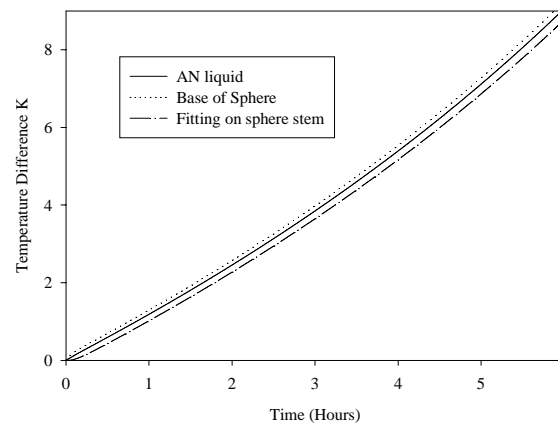


Figure 5 Temperature increase vs. time. 3 g AN. Initial temperature 200°C .

Figure 5 illustrates a number of interesting points:

(i) Firstly, the initial rate of increase of the sample thermocouple temperature is approximately $0.02^{\circ}\text{C min}^{-1}$. The experimentally measured onset temperature for AN in the ARC, defined by a rate of self-heating of $0.02^{\circ}\text{C min}^{-1}$, is close to 200°C [12]. The measured and simulated initial heating rates are thus very close, using the literature rate constants.

(ii) Temperature gradients are small and thermocouple attached to the base of the spherical bomb is reliably determine the temperature in the bomb.

The values of external heat transfer and thermal feedback coefficients were varied, in order to assess the effect of these model variables on the results. It was found that varying heat transfer coefficient by a factor of 100 from 0.1 to 10 changed the initial rate of self-heating by only 10 %, demonstrating that the actual value of the heat transfer coefficient is not very important, at least during the initial stages of the reaction.

An effective phi-factor was estimated by setting the heat capacity of stainless steel

and temperature gradients at the surface of the bomb to zero. Equating the phi-factor to the ratio of initial self-heating rates gives $\phi = 2.9$. A simple calculation of the phi-factor based on the masses of the bomb, thermocouple clip and Swagelok fitting gives $\phi = 3.25$, so the simulation suggests that the Swagelok fitting does not fully contribute to the dynamic phi-factor.

Repeating the simulation with 1 g of AN, with and without heat losses to the ARC bomb gave $\phi = 6.4$. If the phi-factor scaled simply with mass, a value of $\phi = 8.7$ would be expected. This result demonstrates that the effective phi-factor for ARC experiments can be a complex function of the masses of both the sample and the bomb.

Conclusions

Using a flexible Windows based partial differential equation solver it has been possible to simulate a variety of condensed phase combustion and explosion problems in a very short time. The models can be readily extended to 3_D geometries. The approach has immediate applications to both teaching and condensed phase combustion research.

Acknowledgement

The authors would like to thank Orica Explosives for permission to use the AN results and data. In addition the paper draws heavily on references 3 and 4 from Manchester University for both checks and comparisons.

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Appendix 1

TITLE

"Axisymmetric Pyrotechnic"

COORDINATES

ycylinder('R','Z')

SELECT

thermal_colors on

VARIABLES

temp(range=300,2500)

{aa is fraction unreacted}

aa(range=0,1)

DEFINITIONS

length = 0.022 {length, m}

radCase = 0.0032 {Outside radius, m}

radPyro = 0.0017 {Pyro. core radius, m}

Ts = 300 {Ambient temperature, K}

SB = 5.67e-8 {Stefan-Boltzmann constant, W m⁻² K⁴}

rho {density, kg m⁻³}

k {thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$ }
 cp {heat capacity, $\text{J kg}^{-1} \text{K}^{-1}$ }
 λ {used to differentiate between pyro and case}
 β {used to turn reaction on/off based on temp vs T_{Ign} }
{Case}
 $\rho_{\text{Case}} = 2707$ {density - Al, kg m^{-3} }
 $k_{\text{Case}} = 204$ {thermal conductivity - Al, $\text{W m}^{-1} \text{K}^{-1}$ }
 $cp_{\text{Case}} = 896$ {heat capacity - Al, $\text{J kg}^{-1} \text{K}^{-1}$ }
 $em_{\text{Case}} = 0.15$ {emissivity of Al}
{Pyrotechnic Composition}
 $k_{\text{PSR}} = 0.300$ {thermal conductivity - porous solid, $\text{W m}^{-1} \text{K}^{-1}$ }
 $cp_{\text{PSR}} = 540$ {heat capacity - porous solid, $\text{J kg}^{-1} \text{K}^{-1}$ }
 $\rho_{\text{PSR}} = 2300$ {density - porous solid, kg m^{-3} }
 $\rho_{\text{PSP}} = 2070$ {density - products, kg m^{-3} }
 $cp_{\text{G}} = 950$ {heat capacity - Gas/Air, $\text{J kg}^{-1} \text{K}^{-1}$ }
 $\rho_{\text{G}} = 1.28$ {density - Air, kg m^{-3} }
 $\eta = 0.8$ {volume fraction of solid}
 $Q = 9e6 * (\rho_{\text{PSR}} - \rho_{\text{PSP}})$ {exothermicity, J m^{-3} }
 $A_{\text{react}} = 9.25 * \rho_{\text{PSR}} / (\rho_{\text{PSR}} - \rho_{\text{PSP}})$
{pre-exponential coefficient}
 $E_{\text{react}} = 19000 / 8.31441$ {Activation energy/R, K}
 $Order = 2/3$ {Order of reaction}
 $T_{\text{Ign}} = 506$ {Ignition temperature, K}
 $h = 2.095$ {heat transfer coefficient, $\text{W m}^{-1} \text{K}^{-1}$ }
{Ignition flux constants}
 $t1 = 0.3$
 $fluxDur = 10$ {controls duration}
 $fluxAmp = 1e6$ {controls amplitude}
INITIAL VALUE
 $temp = T_s$
 $aa = 1$
EQUATIONS
 $div(k * grad(temp)) + A_{\text{react}} * \beta * \min(1, \max(0, aa))^{Order} * \exp(-$

$E_{\text{react}} / temp) * \lambda * Q = ((\rho - \lambda * ((1 - \min(1, \max(0, aa))) * (\rho_{\text{PSR}} - \rho_{\text{PSP}}))) * cp + \beta * ((1 - \min(1, \max(0, aa))) * (\rho_{\text{PSR}} - \rho_{\text{PSP}}) + (1 - \eta) * \rho_{\text{G}}) * cp_{\text{G}}) * dt(temp)$
 $dt(aa) = -\beta * A_{\text{react}} * \min(1, \max(0, aa))^{Order} * \exp(-E_{\text{react}} / temp)$
BOUNDARIES
region 1 {Outer Cylinder - Steel}
 $k = k_{\text{Case}}$
 $cp = cp_{\text{Case}}$
 $\rho = \rho_{\text{Case}}$
 $\lambda = 0$
 $\beta = 0$
 $natural(temp) = fluxAmp * (\exp(-fluxDur * t))$
 $natural(aa) = 0$
 $start(0, 0)$
 $line\ to\ (radPyro, 0)$
 $natural(temp) = -em_{\text{Case}} * sb * ((temp^4) - T_s^4) - h * (temp - T_s + 1)^{1.25}$
 $line\ to\ (radCase, 0)$
 $line\ to\ (radCase, length)\ to\ (0, length)$
 $natural(temp) = 0$
 $line\ to\ finish$
region 2 {Pyrotechnic}
 $k = k_{\text{PSR}}$
 $cp = cp_{\text{PSR}}$
 $\rho = \rho_{\text{PSR}}$
 $\lambda = 1$
 $\beta = \text{if } temp \geq T_{\text{Ign}} \text{ then } 1 \text{ else } 0$
 $start(0, 0)$
 $line\ to\ (0, length)\ to\ (radPyro, length)\ to\ (radPyro, 0)\ to\ finish$
TIME 0 to 8.5 by 0.5
PLOTS
For $t=0$ by 1 to 8
Surface (temp)
Contour (temp) as "Device temperature"
Report GlobalMax(temp)
Surface($\min(1, \max(aa, 0))$)
Contour ($\min(1, \max(aa, 0))$) as "Mass remaining"
Elevation(temp) from (0,0) to (0,length)
range (300,2300) as "Temperature - Central axis"


```
history(temp) at (0,0) (0,length*.1)
(0,length*.2) (0,length*.3) (0,length*.4)
(0,length*.5)
(0,length*.6) (0,length*.7) (0,length*.8)
(0,length*.9) (0,length) range (300,2300) as
"Core temperature History"
For t = 0 by 0.1 to 8
table(globalmax_y(temp))
history(globalmax_y(temp))
END
```