Erroneous use of balance equations in combustion theory of energetic materials

Ошибки использования балансовых соотношений в теории горения энергетических материалов

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Presentation outline

Introduction

1. Justification of correct use of ignition criterion

1.1 Mathematical model of transient EM combustion

1.2 Simulation of model EM ignition

2. Recalculation of burn rate dependencies on initial temperature and radiant flux

Conclusions

Introduction

It can be shown that in several cases balance equations are used in combustion theory without proper theoretical substantiation, in particular, when employing ignition criterion in the form of failure of heat balance in reaction zone and recalculating burn rate dependencies on initial temperature and radiant flux. One has to remember that experimental data ***in principle*** could not be used for justification of theoretical statements and it is necessary to conduct theoretical research to derive proper generalization of experimental information.

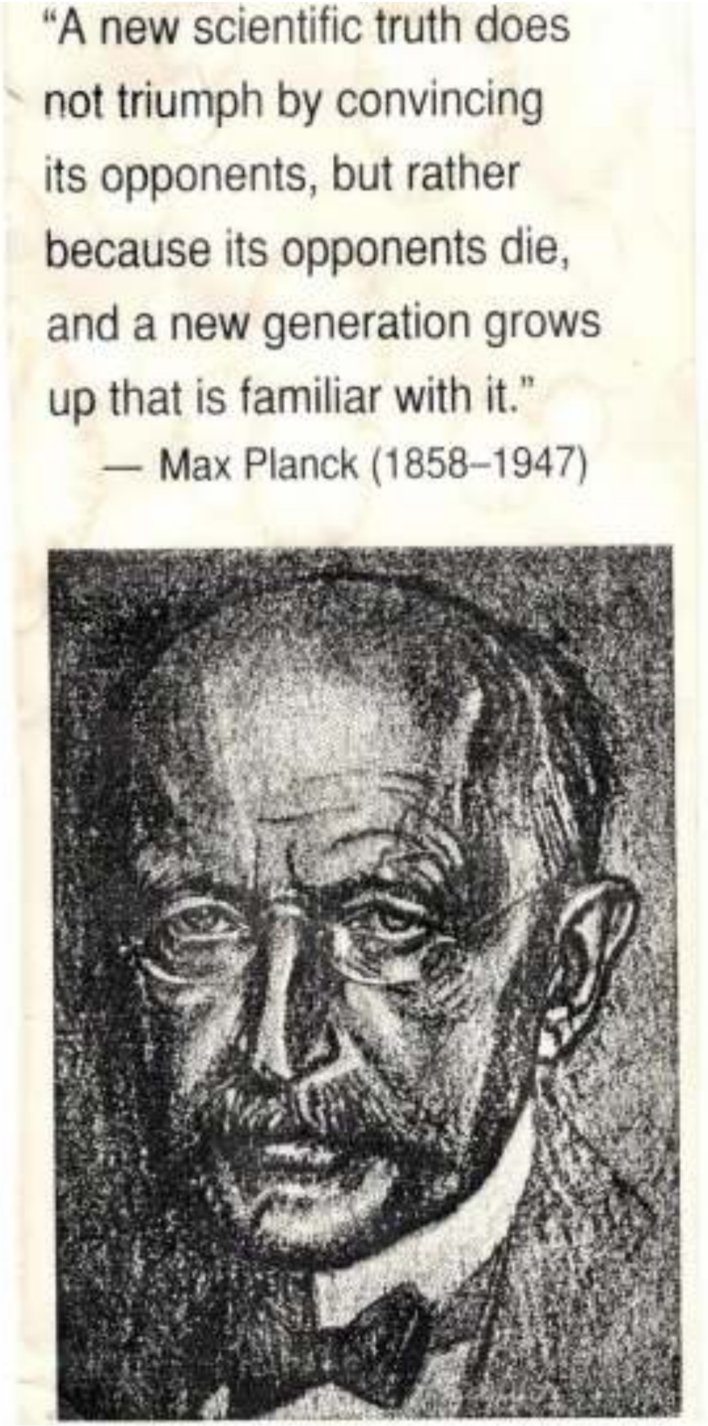
The paper reports on erroneous use of balance equations in combustion theory and gives recommendations on the ways to solve such problems.

"NO EXISTE CANTIDAD DE EXPERIMENTACIÓN QUE PUEDA DEMOSTRAR QUE TENGO RAZÓN, PERO BASTA UN SOLO EXPERIMENTO PARA DEMOSTRAR QUE ESTOY EQUIVOCADO"

"NO HI HA QUANTITAT D'EXPERIMENTACIÓ QUE PUGA DEMOSTRAR QUE TINC RAÓ, PERO AMB UN SOL EXPERIMENT N'HI HA POGUT PER A DEMOSTRAR QUE ESTIC EQUIVOCAT"

"NO AMOUNT OF EXPERIMENTATION CAN EVER PROVE ME RIGHT; A SINGLE EXPERIMENT CAN PROVEME WRONG"

Город искусств и наук, Валенсия



"A new scientific truth does not triumph by convincing its opponents, but rather because its opponents die, and a new generation grows up that is familiar with it."

— Max Planck (1858–1947)

J. H. van't Hoff. Etudes de dynamics chimique, *Amsterdam:**1884***

"ignition temperature is the temperature at which the (initial) heat loss conditioned by thermal conductivity equals the heat generated over the same time by a (chemical) transformation."

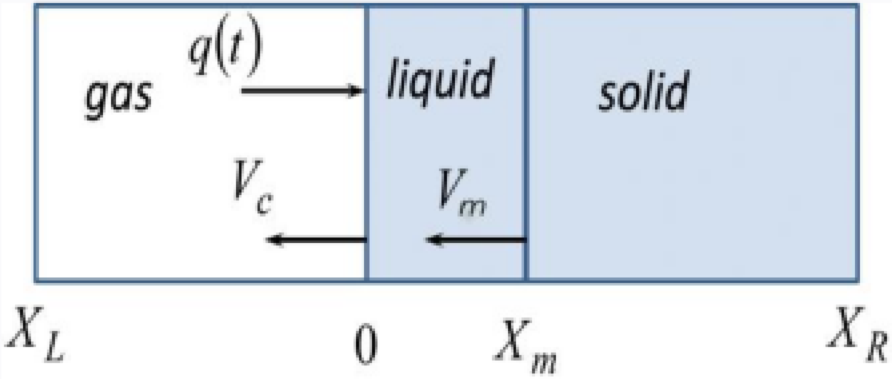
A. G. Merzhanov. Thermal explosion and ignition as a method for formal kinetic studies of exothermic reactions in the condensed phase. *Combustion and Flame 11(3)* ***(1967)*** *201-211.*

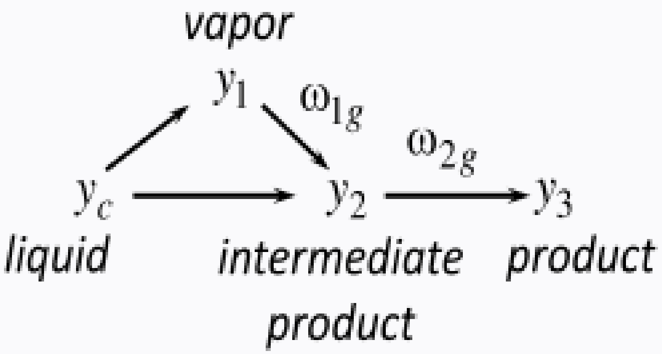
$$\boldsymbol{q_{chem} = q_{therm}}$$

$$q_{chem} = Q\rho_c x_{ch} k_0 exp(-E/RT_s);\quad q_{therm} = q_s = \lambda_c(\partial T/\partial x)_{x=0} \quad x_{ch} \cong \frac{\Delta T_{ch}}{(\frac{\partial T}{\partial x})_{x=0}}$$

$$\boldsymbol{q_s^2 = \Psi \lambda Q \rho k_0 \left(RT_s^2/E\right) exp(-E/RT_s)}$$

Numerical solution





Solid phase energy equation ($x_m \le x \le x_R$)

Liquid phase energy equation ($0 \le x \le x_m$)

Gas phase energy equation ($\mathrm{x}_\mathrm{L} \le \mathrm{x} \le 0$)

$$y_1 = \frac{M_1}{M}\exp\left[-\frac{LM_1}{R}\left(\frac{1}{T_s}-\frac{1}{T_b}\right)\right]$$

Clapeyron-Clausius equation

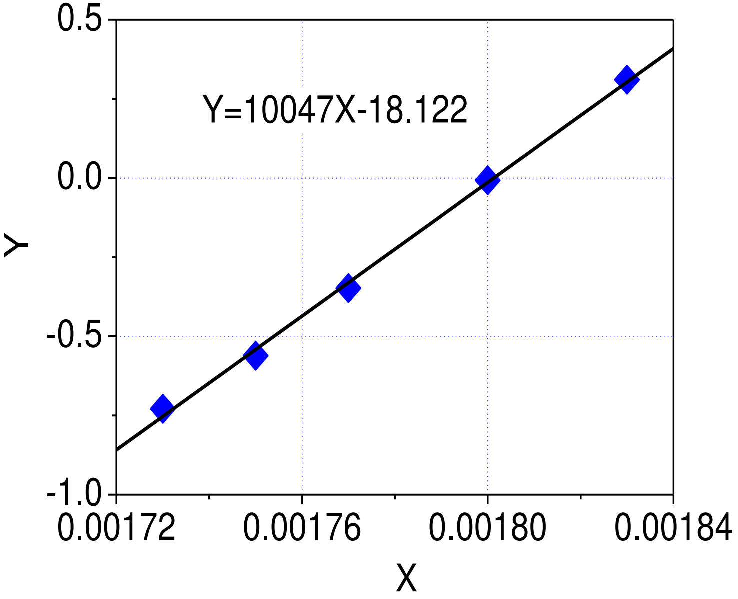
Model EM characteristics

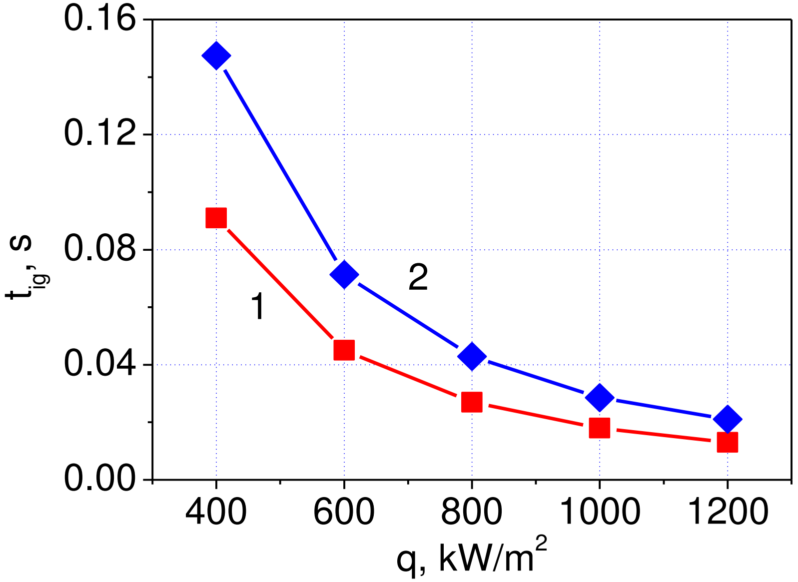
Parameter	Value
Density ρ [kg/m^3]	1 720
Condensed phase reaction heat Q [kJ/ kg]	1 700
Thermal conductivity coefficient λ [kW/(m·K)]	$2.3 \cdot 10^{-4}$
Specific heat capacity c [kJ/(kg·K)]	1.256
Melting temperature T_m [K]	480
Melting heat L_m [kJ/kg]	0
Boiling temperature T_b [K]	575
Evaporation heat L [kJ/kg]	1000
Pre-exponential factor k_0 [s^{-1}]	10^{19}

$$q_s^2 = \Psi\lambda Q\rho k_0\left(RT_s^2/E\right)exp\left(-E/RT_s\right) \quad (*)$$

$$ln\frac{T_s}{q} = \frac{1}{2}ln\frac{E}{\lambda Q\rho k_0 R} + \frac{E}{2R}\cdot\frac{1}{T_s} \qquad T_s = T_0 + \frac{2q}{\sqrt{\pi\lambda c\rho}}\sqrt{t_{ig}}$$

$E/2R$; $lnE/\lambda Qk_0\rho R$





Rectification of “experimental” data. Y=$ln(T_3/q_0)$; X=$(1/T_3)$.
L_m=0, E = 200 kJ/mole

1 – analytical calculations by (*),
2 – numerical calculations.
Ψ=61; E* = 167 kJ/mole

Ψ → 10^8 with L_m=100 kJ/kg; E*→100 kJ/mole

$\Psi = \Psi(q, E, \lambda, etc.)$

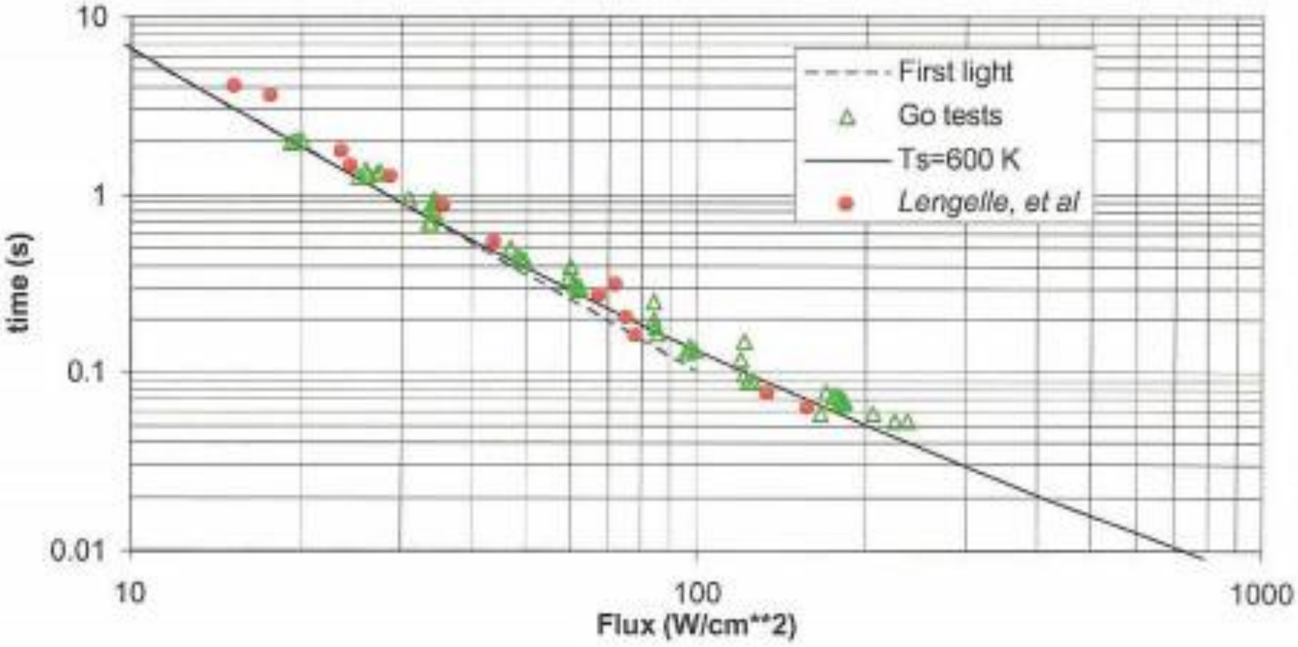
Symposium on Propulsion Physics Versailles-Paris, France, 6-9 July 2009

EUCASS ADVANCES in AEROSPACE SCIENCES Vol. 2 - Propulsion

RADIATIVE IGNITION OF SOLID PROPELLANTS

Franck Cauty, Yves Fabignon, and Charles Eradès

ONERA, France



“If we consider that the exothermal reaction of degradation adds a flux which accelerates the temperature increase, the ignition could occur when this flux becomes equal to the incident flux. The temperature at ignition becomes:”

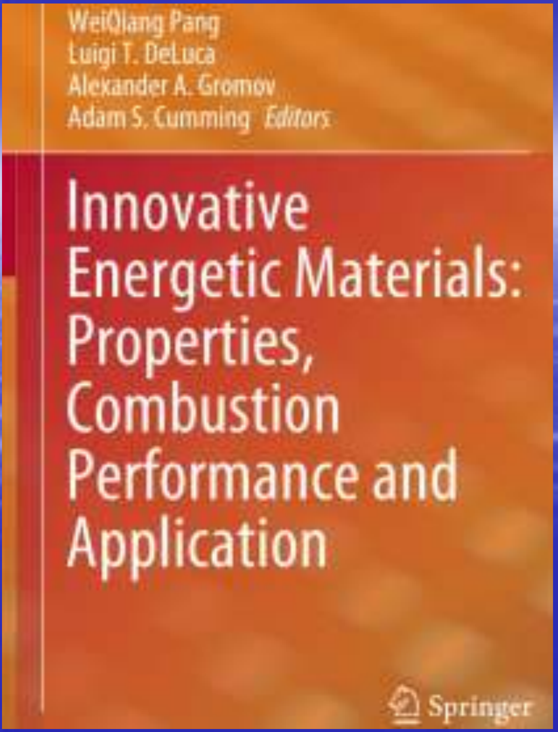
$$\boxed{T_{s.ign} = -\frac{E_p}{R\,\ln\left(\dfrac{\varepsilon\Phi_0}{\rho_p\,\beta\,A_p\,Q_s}\right)} \qquad (6)}$$

$$V_c = A_p\,\beta\exp\left(-\frac{E_p}{R\,T_s}\right) \qquad (1)$$

$$T(x,t) = T_0 + \frac{\phi_p}{\lambda}\left[2\sqrt{\frac{k\,t}{\pi}}\,e^{-\alpha} - x\,\mathrm{erfc}\left(\frac{x}{2\sqrt{k\,t}}\right)\right] \qquad (2)$$

$$\phi_p = \varepsilon\left(\Phi_0 - \sigma T_s^4\right) \approx \varepsilon\Phi_0 \qquad (3) \qquad \text{and } \alpha = \frac{x^2}{4\,k\,t},\; k = \frac{\lambda}{\rho\,Cp}$$

What is the form of the Ignition Criterion based on Eq.6 !? $\Phi_p \rightarrow q_s$



WeiQiang Pang
Luigi T. DeLuca
Alexander A. Gromov
Adam S. Cumming *Editors*

Innovative Energetic Materials: Properties, Combustion Performance and Application

Springer

Zarko V.E., Knyazeva A.G. (2020)
Current Problems in Energetic Materials Ignition Studies.
In: Innovative Energetic Materials: Properties, Combustion Performance and Application. Springer, Singapore.
pp. 67-108.

V.E. Zarko, A.G. Knyazeva. Determination of kinetic parameters of exothermic condensed phase reaction using the energetic material ignition delay data // Combustion and Flame (2020)221,453-461.
https://doi.org/10.1016/j.combustflame.2020.08.022

Konev E. V. Influence of Light Radiation on the Burning Rate of N Powder. ***Combustion, Explosion, and Shock Waves*** (1965). 1(2). 53-56.

"equivalence principle" - equivalence between heat absorbed and increase in initial propellant temperature; $(p,T_0,q)=m(p,T_0+q/mc,0)$

Huggett C., Bartley C. E., and **Mills M.M.** *Solid Propellant Rockets,* Princeton University Press, Princeton, New Jersey, 1960.

Ibiricu, M. M., Williams, F. A. Influence of Externally Applied Thermal Radiation on the Burning Rates of Homogeneous Solid Propellants. ***Comb. Flame,* (1975)**24, 185.

S.F. Son, M.Q. Brewster. Radiation-augmented combustion of homogeneous solids, ***Comb Sci Tech***, (1995) 107:1-3, 127-154.

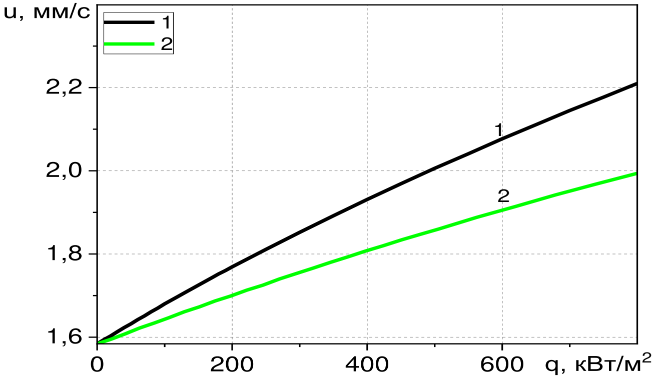
$$\boldsymbol{cm(T_s - T_0) = q_g + q} \qquad q_g = idem$$

$$cm(T_s - T^*_0) = q_g;\ \ T^*_0 = T_0 + q/cm;\ \ \Delta T_0 = q/cm$$

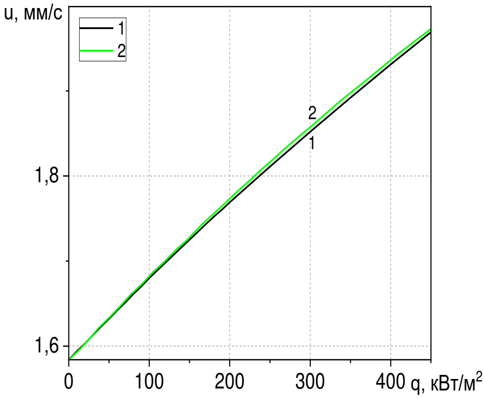
$$\boldsymbol{cm(T_s - T_0) = \Phi_m\delta + q_g + q}$$

$$\boldsymbol{T^*_0 = T_0 + (q/cm)\xi_1(T_0)}$$

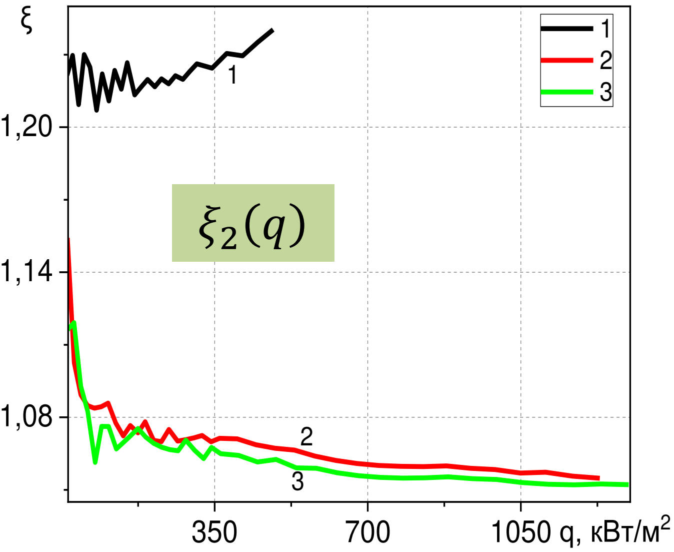
$$\boldsymbol{q^* = cm(T^*_0 - T_0)/\xi_2(q)}$$



$\xi_2 = 0.75$



$\xi_2 = 1.25$



$\xi_2(q)$

1 – E= 1.5·10⁵; 2 – E= 1.71·10⁵;
3 - E= 1.88·10⁵ J/mole

***E* = 1.5·10⁵ J/mole (36.1 kcal/mole)**

$\xi_1(T_0)$ ~ 1.25 (q = 10 kW/m^2); 1.44 (q = 900 kW/m^2)

$\xi_2(q)$ ~ 1.23÷1.25 (q = 10 – 500 kW/m^2)

***E* = 1.88·10⁵ J/mole (45.2 kcal/mole)**

ξ_1 = 1.12 (q = 10 kW/m^2; 1.05 (q = 1250 kW/m^2)

ξ_2 = 1.09 (q = 10 kW/m^2); 1.05 (q = 1250 kW/m^2)

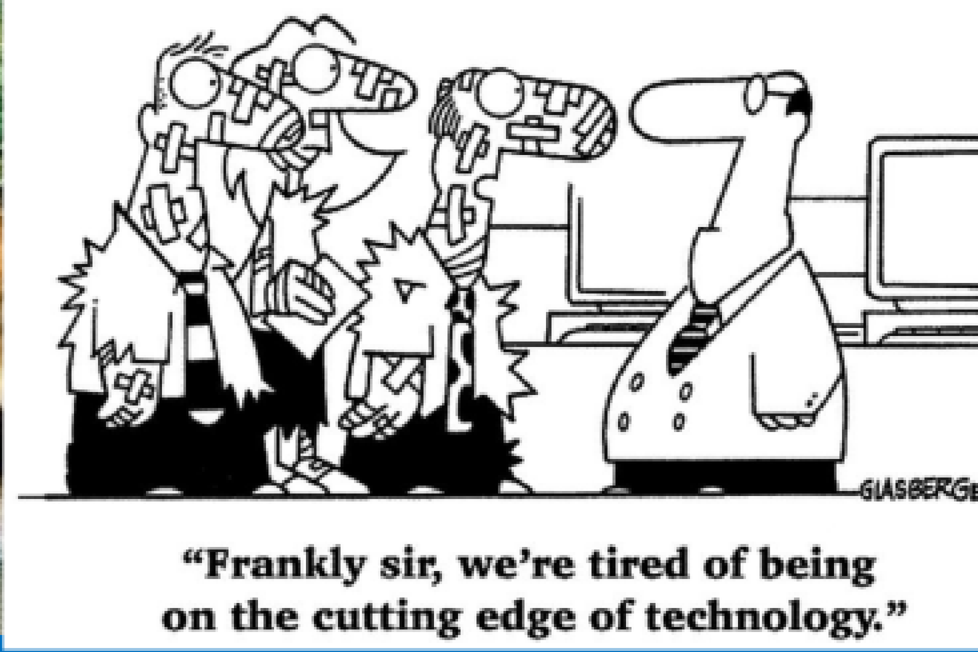
Conclusions

1. The known in combustion theory balance equations do not have detailed theoretical justification. Their verification can be made by mathematical simulation.
2. Simple application of Merzhanov's ignition criterion does not allow obtaining reliable data on the kinetics of condensed phase exothermic reaction. In particular, derived by rectification of virtual ignition "experimental" data values of activation energy are lower of the original value by 1.2-2 times and product Qk_o is lower by 60-800 times. Consequently, the ignition delays calculated on the basis of "derived" kinetics turned out shorter by 1.6-2 times.

Conclusions (contd)

3. Principle of equivalence between absorbed radiation heat and increase in initial EM temperature is based on oversimplified heat balance equation. The fitting coefficients may change in the limit of 15-40% and their magnitude becomes lower at higher energy activation.
4. There exists an urgent need for developing theoretically justified approaches to determine true kinetics of global condensed-phase reactions via using an EM ignition database. The approach must use adequate physiochemical mechanisms of EM behavior under high temperature and fast heating rate, which are specific of different EMs. Same problems should be solved when recalculating dependencies of burn rate on initial temperature and radiant flux.

What did you finally get?!



"Frankly sir, we're tired of being on the cutting edge of technology."

Before I came here I was confused about this subject. Having listened to your lecture I am still confused. But on a higher level.

Enrico Fermi

Thanks for your attention!

Processing data on radiative ignition

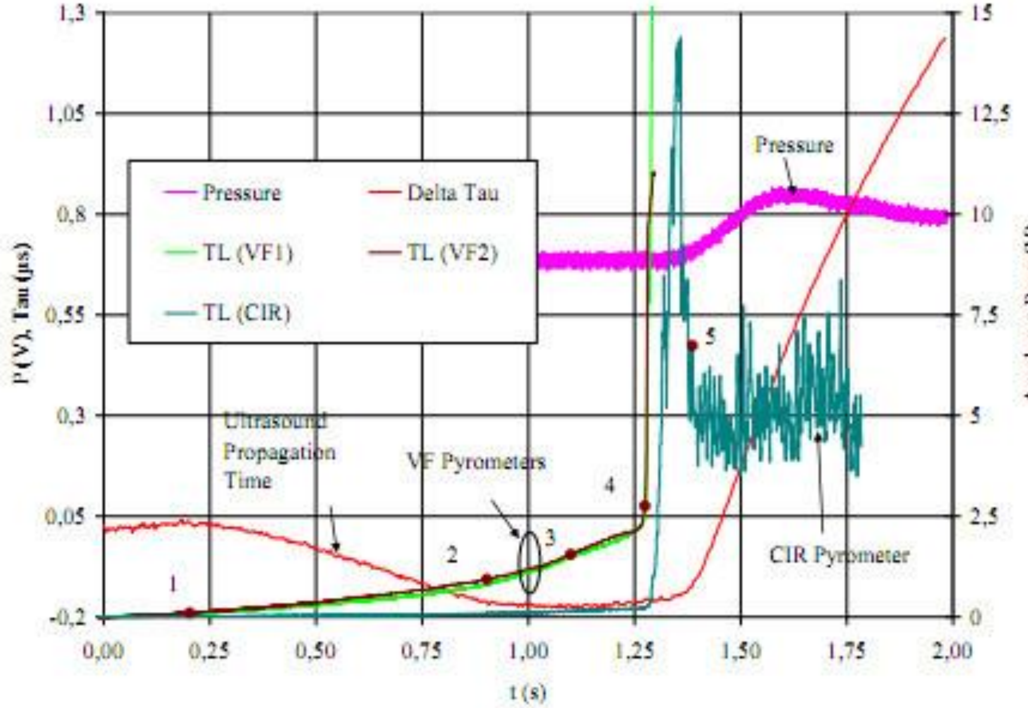


Fig. 6 – Example of results for a test performed under 0.38 MW/m^2 at 0.15 MPa.

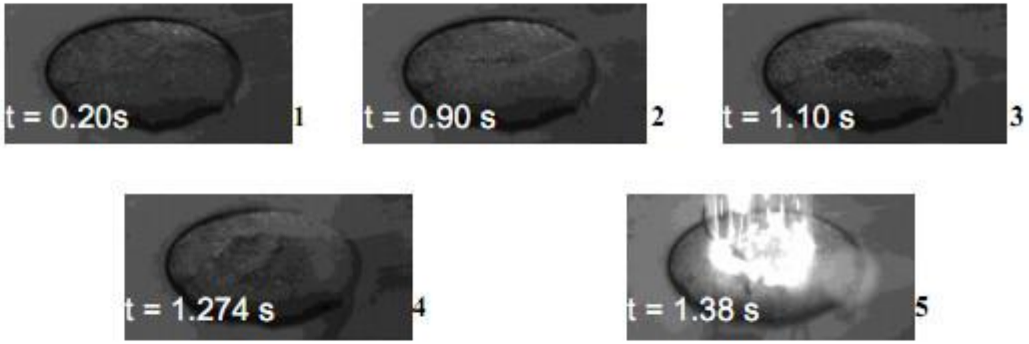


Fig. 7 – Images of the sample during the test under 0.38 MW/m^2 at 0.15 MPa.

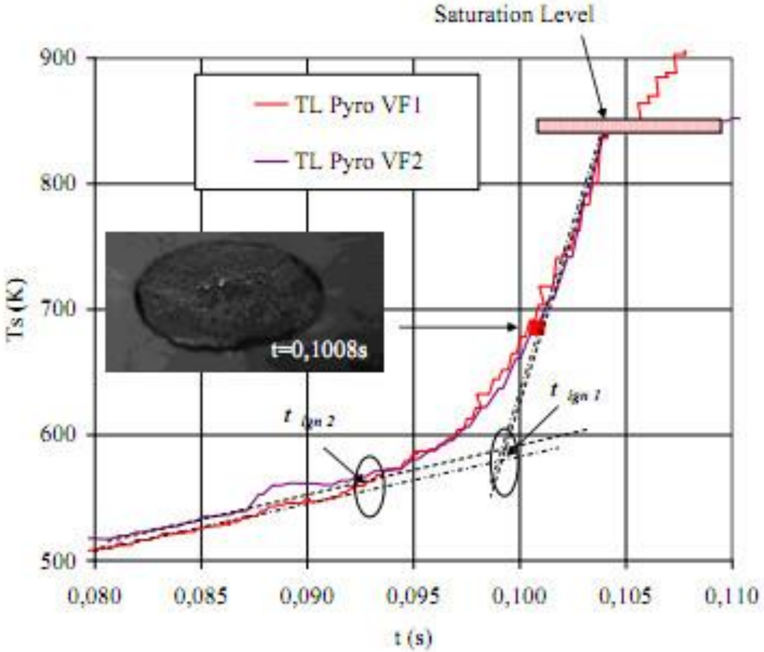
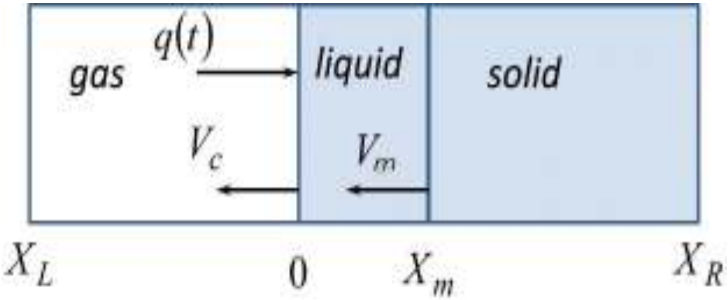
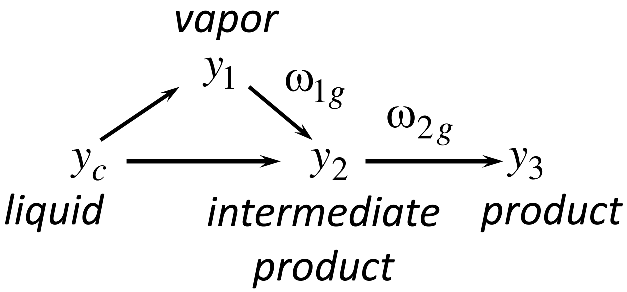


Fig. 8 – Ignition delay determination.

Simulation of transient combustion of melted EMs





Solid phase energy equation, $x_m \le x \le x_R$

$$C_c\rho_c\left(\frac{\partial T_c}{\partial t} - v_m\frac{\partial T_c}{\partial x}\right) = \lambda_c\frac{\partial^2 T_c}{\partial x^2} + q(0,t)\alpha_c\exp(-\alpha_c x)$$

Liquid phase energy equation, $0 \le x \le x_m$

$$C_l\rho_c\left(\frac{\partial T_c}{\partial t} - \left(V_c + \frac{x}{x_m}(V_m - V_c)\right)\frac{\partial T_c}{\partial x}\right) = \lambda_l\frac{\partial^2 T_c}{\partial x^2} + \Phi_{c1} + \Phi_{c2} + q(0,t)\alpha_c\exp(-\alpha_c x)$$

$$\rho_c\left(\frac{\partial y_c}{\partial t} - \left(V_c + \frac{x}{x_m}(V_m - V_c)\right)\frac{\partial y_c}{\partial x}\right) = -\omega_{c1} - \omega_{c2}$$

$$\Phi_{ci} = Q_{ci}\omega_{ci}, \quad \omega_{ci} = A_{ci}\rho_c y_c \exp(-E_{ci}/RT_c), \quad i = 1, 2$$

Gas phase energy equation, $x_L \le x \le 0$

$$C_p\rho\left(\frac{\partial T}{\partial t} - (V - V_c - \sum_{i=1}^{3}\frac{C_{pi}}{C_p}D_i\frac{\partial y_i}{\partial x})\frac{\partial T}{\partial x}\right) = \frac{\partial}{\partial x}(\lambda\frac{\partial T}{\partial x}) + \Phi_1 + \Phi_2 +$$

$$+ q_0\rho y_1\alpha_g\exp(-\alpha_g\int_{x_L}^{x}\rho y_1 d\,x)$$

$$\frac{1}{\mathrm{M}} = \left(\frac{\mathrm{y}_1}{\mathrm{M}_1} + \frac{\mathrm{y}_2}{\mathrm{M}_2} + \frac{\mathrm{y}_3}{\mathrm{M}_3}\right), \quad \Phi_1 = \mathrm{Q}_1\omega_1, \quad \Phi_2 = \mathrm{Q}_2\omega_2$$

$$\omega_1 = \mathrm{A}_1(\rho\ \mathrm{y}_1)^{\mathrm{N}_1}\exp(-\mathrm{E}_1/\mathrm{RT}), \qquad \omega_2 = \mathrm{A}_2(\rho\ \mathrm{y}_2)^{\mathrm{N}_2}\exp(-\mathrm{E}_2/\mathrm{RT}),$$

$$\lambda\left(\frac{\partial T}{\partial x}\right)_{x=-0} = \lambda_c\left(\frac{\partial T_c}{\partial x}\right)_{x=+0} + q(t) - y_c\rho_c V_c L$$

$$-\rho(\mathrm{V} - \mathrm{V}_c) = -\rho_c\mathrm{V}_c, \quad \mathrm{y}_1 = \frac{\mathrm{M}_1}{\mathrm{M}}\exp\left[-\frac{\mathrm{LM}_1}{\mathrm{R}}(\frac{1}{\mathrm{T}_s} - \frac{1}{\mathrm{T}_b})\right]$$