NUMERICAL MODELING NON-STATIONARY COMBUSTION OF

EVAPORATED ENERGETIC MATERIALS¹

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ABSTRACT

Energetic materials (EM) that melt and evaporate in the combustion wave are widely used in various applications. Theoretical description of such EM combustion is not elaborated in sufficient manner. This especially regards transient combustion regimes. The present work formulates transient combustion problem for melted and evaporated EM in terms of global chemistry and investigates the effect of physicochemical parameters variation on the combustion behavior and stability limits of EM steady-state combustion. Analysis shows that the limits of steady-state combustion depend on the magnitude of the melting latent heat and on the difference between the burning surface and melting temperatures. Transient combustion behavior upon ignition of melted and evaporated EM has been studied in dependence of chemical kinetics of reactions in the condensed and gas phase. Intrinsic instability of stationary combustion regimes for EM with high heat release in the condensed phase is discussed. The effect of the melting parameters on the pressure driven burning rate response function has been investigated.

INTRODUCTION

Study of transient combustion regimes of energetic materials (EM) has important meaning for practical applications. At the same time, it may serve as a source of useful information on chemical kinetics in the reaction zones. Combustion modeling the evaporated EM takes consideration of specific coupling between physical and chemical processes on the burning surface. Energetic materials that melt and evaporate in the combustion wave are widely used in various applications. These are classical explosives (RDX, HMX) and recently synthesized high energy compounds HNF, ADN, and CL-20.

¹ Proc. of Int. Conf. on Combustion and Detonation. Zel'dovich Memorial II (Moscow, 2004).

The combustion mechanism for such materials is characterised by melting of the material at a temperature below the burning surface temperature and simultaneously occurring processes of thermal decomposition and vaporisation in the surface layer. In early studies of combustion of melted explosives it was assumed that, since the activation energies of thermaldecomposition reactions exceed by several times the latent heat of vaporisation (for example, according to [1] they can differ by a factor of 2 or 3), such materials burn without appreciable heat release in the condensed phase and endothermal vaporisation dominates on the surface. Consequently, the combustion of melted materials has been mostly interpreted in terms of a gas-phase burning rate control mechanism. Some later, new experimental data were obtained on the kinetics of thermal decomposition and vaporisation of energetic materials and inconsistency with classical concepts was revealed [2]. A steady-state combustion model of evaporated EM has been firstly proposed by A.F. Belyaev and Ya.B. Zeldovich for secondary explosives for which the reactions occurring in the condensed phase can be neglected [3,4]. The up-to-date models developed for nitramines take into account the global reactions in the liquid phase, the detailed reaction kinetics in the gas phase, and non-equilibrium evaporation at the surface [5-7].

Actually, the conditions of evaporation for the burning EM can be reasonably well described in equilibrium manner because deviation of the partial pressure of vapor from its equilibrium value is of the order of the square of the Mach number for the combustion products, with the magnitude of this number being much less than unity. Note that for precise calculation of nonequilibrium vapor pressure one needs to know the values of sticking coefficients for vapor molecules colliding with the liquid-gas interface, which are not reliably known. The use of detailed gas phase reaction kinetics in the combustion model is not fully justified because due to the lack of reliable data the reaction kinetics in the condensed phase is still described in terms of the global reactions. Below we discuss some simplified formulation of the global chemistry combustion model, which was applied for exploring basic phenomena observed in the combustion of melted and evaporated EM. The goal of this research was to investigate the effects of the melting and evaporation parameters on the combustion behavior of melted and evaporated EM. Detailed comparison with experimental data for particular EM is beyond the scope of the present paper.

PROBLEM FORMULATION

In the condensed phase, a model describes heat propagation in the solid and liquid states (heat capacity and density are taken equal for both of the states while thermal conductivity coefficients for solid λ_c and for liquid λ_l are assumed to be different); melting at temperature T_m with endothermic effect Q_m ; global exothermic reaction in the liquid phase of a 1st order with thermal effect Q_c ; thermal sources spatially distributed in the bulk of condensed phase according to the Beer law $q_r \alpha \exp(-\alpha x)$.

The model neglects the change in the liquid layer density due to reactions. This assumption is of minor importance in case of liquid decomposition products. In the presence of gaseous products it implies an effective removal of gas from the liquid layer. For example, this removal may occur via molecular diffusion of dissolved gas from a very thin subsurface reaction zone.

In the present model we consider the simplest case of constant density over the liquid layer. This corresponds to the case of gases dissolved in liquid without formation of bubbles or the case of instantaneous removal of gas out of the liquid layer. It should be mentioned that for very thin layers diffusion is also able to provide fast removal of gas from liquid. To estimate, let us assume that gaseous products start to evolve in the bulk of EM at the distance from the surface equal to the length of reaction zone, $l_{ch} \approx 0.1$ ($\lambda / C\rho$)_{liq}/r_b. If the residence time for liquid in the reaction zone, l_{ch}/r_b , is greater than the diffusion time $(l_{ch})^2/D$, where D is the diffusion coefficient, the bubbles will not form. The above condition is formulated as $D(T_s) > r_b l_{ch} = 0.1 \ (\lambda / C\rho)_{liq}$. A simple estimate shows that the condition is approximately hold for typical melted EM with $D \ge 10^{-4} \text{ cm}^2/\text{s}$ and $(\lambda / C\rho)_{liq} = 0.001 \text{ cm}^2/\text{s}$.

On the burning surface, the phase equilibrium is assumed according to the Clausius-Clapeyron condition. In the gas phase, a model describes heat propagation and diffusion of gas species along with chemical transformations via two global reactions of arbitrary order. The calculation domain is shown in Fig.1. The coordinate $x = x_m$ corresponds to the interface between liquid phase and solid phase domains with the temperature of phase transition being equal to T_m .



Fig.1. Sketch of the calculation domain

Let us choose movable coordinate system (x,t) attached to the burning surface to derive the system of equations describing heat propagation in the condensed phase:

a) solid state ($x_m(t) \le x \le x_R$)

$$C_{c}\rho_{c}\left(\frac{\partial T_{c}}{\partial t} - V_{m}\frac{\partial T_{c}}{\partial x}\right) = \lambda_{c}\frac{\partial^{2}T_{c}}{\partial x^{2}} + q(t)\alpha\exp(-\alpha x)$$

$$(1)$$

 $T_c(x,0) = T_0$, $T_c(x_m,t) = T_m$, $\left(\frac{\partial T_c}{\partial x}\right)_{x=R} = 0$, $V_m = \frac{ux_m}{dt}$,

b) liquid state ($0 \leq x \leq x_{_{\rm m}}$)

$$C_{1}\rho_{c}\left(\frac{\partial T_{c}}{\partial t} - (V_{c} + \frac{x}{x_{m}}(V_{m} - V_{c}))\frac{\partial T_{c}}{\partial x}\right) = \lambda_{1}\frac{\partial^{2}T_{c}}{\partial x^{2}} + \Phi_{c} + q(t)\alpha\exp(-\alpha x)$$
(2)

$$\rho_{c} \left(\frac{\partial y_{c}}{\partial t} - (V_{c} + \frac{x}{x_{m}} (V_{m} - V_{c})) \frac{\partial y_{c}}{\partial x} \right) = -\omega_{c}$$
(3)

$$\Phi_{c} = Q_{c}\omega_{c}, \quad \omega_{c} = A_{c}\rho_{c}y_{c}\exp(-E_{c}/RT_{c})$$
(4)

$$y_{c}(x_{m},t) = 1$$
, $T_{c}(x,0) = T_{0}$, $T_{c}(x_{m},t) = T_{m}$, $-\lambda (\frac{\partial T_{c}}{\partial x})_{x=x_{m}+0} + L_{m}V_{m}\rho_{c}$

It is assumed that the condensed phase reaction produces intermediate product and in the gas phase there exist 3 components: vapor, intermediate product, and final combustion product. Decomposition of vapor as well as chemical conversion of intermediate product proceeds via reactions of arbitrary order. The scheme of chemical transformations is shown in Fig. 2, where index 1 corresponds to vapor, index 2 to intermediate product, and index 3 to final combustion product, respectively.



Fig.2: Scheme of chemical transformations upon burning evaporated EM.

The values in the brackets stand for the order of reaction. The temperature of the components is uniform at the given point of space. The system of equations describing heat propagation and chemical transformations in the gas phase is as follows ($x_L < x < 0$):

$$C_{p}\rho\left(\frac{\partial T}{\partial t} - (V - V_{c} - \sum_{i=1}^{3}\frac{C_{pi}}{C_{p}}D_{i}\frac{\partial y_{i}}{\partial x})\frac{\partial T}{\partial x}\right) = \frac{\partial}{\partial x}(\lambda - \frac{\partial}{\partial x}T) + \Phi_{1} + \Phi_{2} + W$$
(5)

$$\rho \left(\frac{\partial y_1}{\partial t} + (V - V_c) \frac{\partial y_1}{\partial x} \right) = \frac{\partial}{\partial x} \left(\rho D_1 \frac{\partial y_1}{\partial x} \right) - \omega_1$$
(6)

$$\rho \left(\frac{\partial y_2}{\partial t} + (V - V_c) \frac{\partial y_2}{\partial x} \right) = \frac{\partial}{\partial x} (\rho D_2 \frac{\partial y_2}{\partial x}) - \omega_2 + \omega_1$$
(7)

$$\frac{\partial \rho}{\partial t} - V_c \frac{\partial \rho}{\partial x} + \frac{\partial (\rho V)}{\partial x} = 0$$
(8)

$$\mathbf{p} = \mathbf{R}\boldsymbol{\rho}\mathbf{T}/\mathbf{M} \tag{9}$$

$$\frac{1}{M} = \left(\frac{y_1}{M_1} + \frac{y_2}{M_2} + \frac{y_3}{M_3}\right), \quad \Phi_1 = Q_1 \omega_1, \quad \Phi_2 = Q_2 \omega_2$$

$$\omega_1 = A_1 (\rho \ y_1)^{N_1} \exp(-E_1/RT), \qquad \omega_2 = A_2 (\rho \ y_2)^{N_2} \exp(-E_2/RT),$$

$$W = \text{const} = \text{qz at } x_L \le x \le 0, \quad \text{tz}_1 \le \text{t} \le \text{tz}_2,$$

$$W = 0 \quad \text{at other eases}$$

$$w = 0$$
 at other cases,

$$T(x,0) = T_0$$
, $y_1(x,0) = y_2(x,0) = 0$, $\frac{\partial T}{\partial x} = \frac{\partial y_1}{\partial x} = \frac{\partial y_2}{\partial x} = 0$ at $x = x_1$

The term W in Eq. 5 depicts the action of externally imposed heating in the gas phase in order to trigger ignition of gases above the EM surface. The gas heater acts during period of time (tz_1, tz_2) in spatial domain (x_l, x_r) .

Mass fraction of the combustion products and their effective diffusion coefficient are determined on the basis of mass conservation equation and condition of individual diffusion fluxes zero total sum:

$$y_1 + y_2 + y_3 = 1$$

$$D_1 \frac{\partial y_1}{\partial x} + D_2 \frac{\partial y_2}{\partial x} + D_3 \frac{\partial y_3}{\partial x} = 0$$

In order to solve numerically the problem (1-9) a spatial domain $x_L < x < x_R$ has to be chosen on the basis of physical considerations or numerical experiment. If one assumes that the pressure and/or the radiation flux vary in time the problem (1-9) allows studying the burning rate behavior during combustion transients and evaluating the response of burning rate to oscillating pressure or the heat flux. Boundary conditions on the burning surface are as follows:

$$\lambda \frac{\partial T}{\partial x}\Big|_{x=-0} = \lambda_c \frac{\partial T_c}{\partial x}\Big|_{x=+0} + q_r - y_c \rho_c v_c L$$
(10)

$$-\rho (\mathbf{v} - \mathbf{v}_{c}) \mathbf{y}_{1} + \mathbf{D}_{1} \rho \frac{\partial \mathbf{y}_{1}}{\partial \mathbf{x}} = \mathbf{y}_{c} \rho_{c} \mathbf{v}_{c}$$
(11)

$$-\rho (\mathbf{v} - \mathbf{v}_{c}) \mathbf{y}_{2} + \mathbf{D}_{2} \rho \frac{\partial \mathbf{y}_{2}}{\partial \mathbf{x}} = (1 - \mathbf{y}_{c}) \rho_{c} \mathbf{v}_{c}$$
(12)

$$\rho(\mathbf{v} - \mathbf{v}_{c}) = \rho_{c} \mathbf{v}_{c} \tag{19}$$

$$y_1 = \frac{M_1}{M} \exp\left(-\frac{LM_1}{R} \left(\frac{1}{T_s} - \frac{1}{T_b}\right)\right)$$
(20)

Numerical method

To solve thermal conductivity equation with convective term an original quasi-monotonous difference scheme of second order was elaborated that has been shown to be effective for real computational grids. An example of scheme application is shown below. Let us consider a model equation of thermal conductivity,

$$\frac{\partial \mathbf{T}}{\partial t} + \mathbf{u}\frac{\partial \mathbf{T}}{\partial \mathbf{x}} = \kappa \frac{\partial^2 \mathbf{T}}{\partial \mathbf{x}^2} + \alpha \mathbf{T}$$
(21)

where T is the temperature, u is the velocity of medium, κ is the thermal diffusivity and α is the heat exchange coefficient. Owing the presence in Eq. (21) of the convective term $u\partial T/\partial x$ the classical central difference schemes usually give oscillations of numerical solution near the points of its sharp change (in combustion problem this corresponds to the combustion wave front which is characterized by high temperature gradients). In order to avoid this difficulty we used difference scheme based on "hyperbolic" approximation. To this end the left right side of Eq. (21) is written along the direction (characteristic line) dx/dt = u and the finite difference scheme becomes as follows.

$$\frac{\mathbf{T}_{i}^{n+1} - \mathbf{T}_{i}^{n}}{\tau} = \delta \kappa_{i}^{n+1} \left(\frac{\partial^{2} \mathbf{T}}{\partial \mathbf{x}^{2}} \right)_{i}^{n+1} + (1 - \delta) \kappa_{*}^{n} \left(\frac{\partial^{2} \mathbf{T}}{\partial \mathbf{x}^{2}} \right)_{*}^{n} + \delta \alpha_{i}^{n+1} \mathbf{T}_{i}^{n+1} + (1 - \delta) \alpha_{*}^{n} \mathbf{T}_{*}^{n}$$
(22)

Here τ , h are the temporal and spatial steps, correspondingly, with $t = n * \tau$, x = i * h and n = 0,...,M, i = 0,...,N. The values with index * in Eq. (21) are calculated in the intersection points of characteristic line originated in the point (n+1, i) with the lines belonging the grid (horizontal line, if $h/\tau > u$ and vertical one, if $h/\tau < u$). Using the value $\delta = 1/2$ provides second order of accuracy for the difference scheme.

CALCULATION RESULTS AND DISCUSSION

Below the results of calculations via use of the problem formulation (1-9) are presented. The effects of the magnitude of the melting point as well as melting and evaporation latent heat on stability of self-sustaining combustion and transient combustion behavior are discussed.

Stability of steady-state combustion regimes

As a rule, upon studying an intrinsic stability of the EM self-sustaining combustion on the basis of the Zeldovich-Novozhilov (Z-N) approach the phase transition in the combustion wave has been neglected. However, the problem can be easily formulated to take account of the phase transition within the framework of phenomenological approach [8]. Calculations show that the stability limits depend on classical parameters k and r as well as on additional parameters \overline{Q}_m , $\overline{\lambda}$ and ϑ_m , which are defined as follows:

$$\mathbf{k} = (\mathbf{T}_{s} - \mathbf{T}_{o}) (\partial \ln r_{b} / \partial T_{o})_{p}; \qquad \mathbf{r} = (\partial T_{s} / \partial T_{o})_{p};$$

$$Q_m = Q_m/c(T_s - T_o);$$
 $\overline{\lambda} = \lambda_c/\lambda_l;$ $\vartheta_m = (T_m - T_o)/(T_s - T_o)$

Figure 3 shows the stability limits at $\overline{\lambda}=1$, $\overline{Q}_m = 0.3$ for different values of ϑ_m . Stability domain is located above the solid line. The calculated stability boundary is shifted from curve

A in direction to curve B with decrease in ϑ_m -value. The origin of the curve A : $r = (k^*-1)^2/(k^*+1)$, where $k^*=(T_s - T_o + Q_m/c) \partial \ln r_b/\partial T_o = k(1+\overline{Q}_m)$, is determined by the value of \overline{Q}_m . When this result is compared with that of "classical" approach [8] stating the stability limit at $r = (k-1)^2/(k+1)$, it becomes obvious that the melting decreases stability of combustion.



Fig. 3. Combustion stability limit at $\overline{\lambda}=1$, $\overline{Q}_m = 0.3$ for different values of ϑ_m . Curve A: $\mathbf{r} = (\mathbf{k}^*-1)^2/(\mathbf{k}^*+1)$; Curve B: $\mathbf{r} = (\mathbf{k}-1)^2/(\mathbf{k}+1)$

The result obtained for relatively small values of k and r is non-trivial one. It shows the possibility of combustion instability for melted EM at k<1. Note that according to classical Z-N approach the combustion without melting is unambiguously stable at k<1.

Figure 4 shows the stability limit at $\overline{\lambda} = 1$, $\vartheta_m = 0.7$ for various \overline{Q}_m values. It is seen that when \overline{Q}_m increases, the stability boundary shifts to the left of the basic line ($\overline{Q}_m = 0$) that

means that a domain of stable combustion becomes smaller in size. A general character of the dependence of the stability limit position on the parameters of ϑ_m and \overline{Q}_m is shown in Fig. 5 in coordinates k* and r.



Fig. 4. Combustion stability limit at $\overline{\lambda} = 1$, $\Im m = 0.7$ for various values of \overline{Q}_m .

With this coordinate transformation all curves originate from the point (1, 0). It is seen that the smaller the ϑ_m value on the line examined, the larger the distance between the origin of coordinates and branching from the basic line $r=(k^*-1)^2/(k^*+1)$. The magnitude of curve $r(k^*)$ deviation from the basic line has a positive dependence on \overline{Q}_m .

The observed behavior of curves has a simple physical meaning. Note that the temperature profile in the bulk of condensed phase displays peculiarity due to phase transition only starting from the distance x_m from the burning surface. When $0 < x < x_m$, the Mikhelson profile is realized in the steady-state regime, which coincides with that for EM without phase transitions but with reduced initial temperature $T_o^* = T_o - Q_m/c$.

It is easy to calculate that $x_m = [\lambda_{liq}/(r_b \ c_{liq}\rho_{liq})]ln[(1+Q_m)/(\vartheta_m + Q_m)]$. Note also that the harmonic thermal perturbations propagating with a frequency f_0 in the bulk of EM practically decay at a distance $x_{tf} \propto (f_0)^{0.5}$.



Fig. 5. Combustion stability limits in modified coordinates. Curve A: $r = (k^{*}-1)^{2}/(k^{*}+1)$

Obviously, with $x_{tf} < x_m$ the model is "insensitive" to phase transitions. For EM without phase transitions the results of Ref. 8 are hold. Therefore, with $x_{tf} < x_m$ the stability limit coincides with Curve A. As the melting temperature decreases, the thickness of the melted layer x_m increases. To preserve the equality $x_m = x_{tf}$, the branching point must be shifted along the basic line towards the lower frequencies (i.e. far from the origin of coordinates).

Consider now the case of fairly low perturbation frequencies when the characteristic distance of thermal wave decay x_{tf} becomes larger than the thickness of melted layer x_m . It means that the perturbations reach the surface of phase transition. According to the Le Chatelier principle

this must strengthen the decay of perturbations that occurs the stronger, the larger is the heat of the phase transition. As a result, it leads to increase of stability domain at $\vartheta_m = \text{const}$ in coordinates r and $k^* = k(1 + Q_m)$. This result reflects a dual nature of the effect of melting heat on the combustion stability. First of all, the finite value melting heat leads, at arbitrary melting temperature, to decrease of stability domain caused by effective decrease of initial temperature. One may recognize this effect in Figs. 3 and 4, when analyzing the position of the beginning (r=0) of curves A. At the same time, with the given value of melting temperature, when the temperature profile oscillations reach the liquid-solid interface, the melting heat acts as a damper and plays positive role in increasing combustion stability in plane r - k* (see Fig. 3). However, this does not change overall conclusion about total negative effect of melting heat on the combustion stability because of predominant influence of the first factor. Note that the treatment of the results of calculations at r $\longrightarrow 0$ (the region of high frequencies, Figs. 3-5) requires special analysis since it is necessary to take into account finite transition times in the gas phase and in the condensed phase reaction zone [9].

Multistage ignition regimes

The assignment of heat release sources with different kinetics of chemical transformations determines a multistage ignition process under particular conditions of heating. Figure 6 illustrates a three-stage ignition of melting EM upon the action of radiant flux with amplitude decreasing with time. The figure presents the ignited EM parameters versus time (6a) and their distribution in space in particular instants of time (6 b,c,d). The initial stage starts under the action of a relatively high heat flux that exceeds almost two-fold that on the burning surface in the self-sustaining combustion regime. For relatively slow reaction kinetics in the gas phase the flame cannot appear near the surface due to the short residence time of EM gasification products in this zone. A decrease in the radiant flux intensity leads to decrease in

the gasification products flow velocity that favors the course of reaction in gas due to increase of residence time. However, since the exothermic vapor decomposition occurs relatively far from the surface, the heat feedback from gas is not large (Fig. 6b) and it is necessary to further reduce an external heat supply to facilitate reaction in gas near the EM surface. Figures 6c and 6d show that the flame arises at the finite distance from the surface and propagates towards the propellant surface.



A decrease in the burning rate at the end of the second stage of ignition is determined by nonlinear interaction of nonstationary temperature and concentration fields in the gas and condensed phases. Finally, the gas temperature reaches its maximum and flame provides sufficient heat feedback to the condensed phase (Fig. 6d).

It is interesting to note that very similar phenomena were experimentally observed in the early 1950s in the Institute of Chemical Physics (Moscow) upon radiative ignition of double base propellants. It was revealed that the flame originates first at some finite distance from the propellant surface and then is established at small height. Our experiments on nitramines have revealed similar behavior of the gas flame reactions [10]. In particular, if heated in nitrogen at atmospheric pressure by radiant flux of 8-10 cal/cm²s, the pressed RDX samples react first in the flameless regime. However, after short action of external small hot gas jet the sample starts to burn with developed flame. Such combustion behavior of RDX is readily simulated with presented here combustion model for melted and evaporated EM if the calculations are performed with inclusion of short action of intense heating source in the gas phase near the surface.

Instability of combustion induced by high heat release in the condensed phase

A particular feature of the mathematical problem under discussion is the formulation of conditions for EM vaporization on reacting surface in the form of the Clausius-Clapeyron law (Eq. 20) The ratio between the values of the latent vaporization heat and activation energy of decomposition in liquid EM determines the relative contributions of vaporization and decomposition to the total consumption of the condensed phase. The existence of heat sink on EM surface due to vaporization of liquid EM restricts an increase in the surface temperature upon heating by external source.

Numerical modeling revealed an intrinsic instability of steady-state regimes of combustion of EM with relatively strong heat release in the condensed phase and relatively weak heat feedback from the gas phase. In this case the maximum of temperature is formed in the bulk of condensed phase. This results in a local thermal explosion in subsurface layer. An example of temporal behavior of burning rate in course of ignition transients and appropriate spatial distributions of temperature and reacting components are shown in Fig.7.



Fig.7. Temporal (a) and spatial (b) distribution of parameters in ignited EM with relatively high condensed phase heat release.

Analytical study of the combustion stability in the case of existence of temperature maximum in the bulk of EM revealed that steady-state combustion may occur only in restricted domain of determining parameters. With high enough Q_c and relatively weak heat feedback from the flame the steady-state solution of energy equation with temperature maximum in subsurface layer becomes unstable to small perturbations. With further increase in Q_c it becomes totally impossible to obtain steady-state solution because of thermal explosion which develops in a subsurface layer. However, if for given propellant there is a coupling between burning rate and heat flux to the surface according to which a random increase of burning rate (velocity of gases issued from the surface) leads to decrease of heat feedback into condensed phase, there is a relatively small range of intermediate values of Q_c when steady-state solution may exist.

Burning rate response to the pressure oscillations

It is important from a practical point of view to predict the EM combustion behavior under periodical pressure variations in order to estimate the possible growth of acoustic oscillations in the combustion chamber. The burning rate responses have been calculated for the reference parameters selected according to published data and with provision of coincidence with experimental data on RDX burning rate over the pressure range 1-90 atm. The reference parameters are listed in Table below.

Table. Reference Parameters for EM Physicochemical Properties.

thermal conductivity, $\lambda_c = \lambda_l = 0.00055 \text{ cal/} (\text{cm s K})$, specific heat of condensed phase, $C_c = C_l = 0.3 \text{ cal/ g K}$, density of condensed phase, $\rho_c = \rho_l = 1.72 \text{ g/cm}^3$, latent heat of evaporation, L=112 cal/g, latent melting heat, $Q_m = 38 \text{ (or 60) cal/g}$, melting temperature, $T_m = 480 \text{ (or 580) K}$, boiling temperature at atmospheric pressure, $T_b = 613 \text{ K}$, initial temperature, $T_0 = 300 \text{ K}$, condensed phase Arrhenius activation energy, $E_c = 47100 \text{ cal/mol}$, condensed phase reaction heat, $Q_c = 613 \text{ cal/g}$, gas phase Arrhenius activation energy, $E_1 = 15500 \text{ cal/mol}$ and $E_2=50000 \text{ cal/mol}$, gas phase reaction heat, $Q_1 = 725 \text{ cal/g}$ and $Q_2 = 235 \text{ cal/g}$, gas reaction order, $N_1 = N_2 = 1.6$, pre-exponential factor, $A_c = 10^{18.3} \text{ l/s}$, $A_1=10^{10.2} \text{ g/(cm^3 \text{ s atm}^{N_1})}$, $A_2 = 10^{10.2} \text{ g/(cm^3 \text{ s atm}^{N_2})}$, molecular mass of vapor, $M_1 = 222 \text{ g/mol}$, molecular mass of decomposition products, $M_2 = 35 \text{ g/mol}$, molecular mass of combustion products, $M_3 = 30 \text{ g/mol}$,

The calculated results for $R_p = (\Delta r_b / r_b) / (\Delta p/p)$ at pressure 70 atm are presented in Fig 8. It is seen that the magnitude of maximum of the pressure driven burning rate response function decreases with increase of melting temperature and corresponding decrease of the melted layer width. Qualitative explanation of such behavior can be done in a following way. According to the Le Chatelier principle a phase transition (melting) diminishes an amplitude of oscillations of thermal profile but it works only at frequencies not exceeding certain limiting value. The lower the melting temperature, the wider melted layer and the lower limiting frequency



Fig. 8. Response function R_p vs frequency of pressure oscillations (p = 70 atm, $\Delta p/p = 0.02$). 1 -- T_m =580 K, Q_m = 38 cal/g; 2 -- T_m =480 K, Q_m = 38 cal/g; 3 -- T_m =480 K, Q_m = 60 cal/g.

The reason why the curve 1 in Fig 8 has relatively small maximum is that the melted layer is very narrow at $T_m = 580$ K. Comparison of curves 2 and 3 indicates that increase in the

melting heat leads to the loss of combustion stability that is in agreement with the results of analysis of intrinsic combustion stability.

When analyzing Fig. 8, one may recognize that behavior of the burning rate response function at high frequencies does not follow classical pattern with diminishing the response function magnitude to infinitely small value. Instead, it is seen that response function reaches at high frequencies some finite magnitude. Similar result was reported earlier [8] for the common case when one does not use an assumption of existence of unambiguous correlation between surface temperature and burning rate. Simple qualitative explanation of the result discussed follows from the theory of heat propagation that states that the amplitude of oscillations of surface temperature diminishes to zero at high frequencies of oscillating heat feedback to the solid. In the case when the relationship $r_b = r_b(T_s)$ is hold, this leads to diminishing the amplitude of oscillations of burning rate. However, in common case when such correlation does not exist the finite amplitude oscillations of r_b at high frequencies are possible.

SUMMARY AND CONCLUDING REMARKS

In this work the effects of the EM melting and evaporation on the combustion stability and transient combustion behavior have been examined. Despite relatively small value of the melting heat its accounting in theoretical analysis leads to decrease in the combustion stability domain for self-sustaining combustion regime. It is found that the larger the difference between the melting point and the burning surface temperature, the narrower the combustion stability domain.

It has been shown that depending on the EM kinetic parameters and temporal behavior of a radiant flux an ignition of evaporated EM with exothermic condensed and two gas phase reactions may occur in three stages. Obviously, the number of stages depends on the number of global reactions under consideration and their particular kinetics.

The combustion of EM with remarkable heat release in the condensed phase and weak heat feedback from the gas flame has been shown to be intrinsically unstable. The reason for that is the existence of the heat sink at the interface between condensed and gas phase, which restricts the magnitude of the burning surface temperature and leads to development of thermal explosion in subsurface layer.

It has to be noted that theoretical study of evaporated EM combustion behavior needs further experimental justification. In particular, there are not detailed data on the structure of the condensed phase subsurface layer during real combustion process. Such data have to provide evidences in favor of the true mechanism of the decomposition products removal from the reaction zone in the condensed phase.

Preliminary calculations showed that the radiation driven combustion of evaporated EM may occur in gasification regime, i.e. with negligible heat feedback from the gas phase. The reason for such behavior is rather simple: in the case of sufficiently high velocity of gases issued from the surface a characteristic reaction time in decomposition products is larger than the hydrodynamic time that prevents development of exothermic reactions in close vicinity of the regressing surface. When realized in experiment, the steady-state radiation driven gasification (flameless) regime may serve as a source of important information on global kinetics of reactions in the condensed phase.

Valuable information can be obtained in experiments with measurement of the combustion response to time-dependent external radiant flux action. Theoretical study of such response can be made for the cases of periodical variations and step-wise temporal history of radiant flux. Proper experimental data, if available, may give background for choosing the global kinetic mechanism for particular EM in specified and well characterized conditions of combustion. Obviously, this will take development of advanced experimental methods for recording the combustion wave parameters in steady-state and transient conditions.

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