Remarks on Self-Propagating Reactions in Finite Pellets

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It is well established that the method of self-propagating high-temperature synthesis (SHS) can be utilized to produce a wide variety of advanced materials such as borides, carbides, nitrides, silicides, intermetallics and composites (cf. Munir and Anselmi-Tamburini, 1989; Merzhanov, 1990). The process is based on the concept that once initiated, a highly exothermic reaction can become self-sustaining and will propagate through the mixture of initial reactants in the form of a combustion wave. In addition to many experimental studies that have appeared in the literature, significant effort has also been directed toward modeling and theoretical analysis of the process. However, previous analyses have invariably treated infinitely long systems, which lead to analytical expressions of the velocity of the combustion front as a function of the various system parameters, such as heat capacity, adiabatic temperature and activation energy, but independent of position within the pellet (cf. Novozhilov, 1961; Margolis, 1983; Puszynski et al., 1987).

It has recently been shown that for pellets of finite length, the reaction front movement is influenced by boundary conditions at the ends, and therefore the propagation rate of the combustion front is, in fact, a function of position: a constant-pattern behavior cannot exist for a finite system (Varma et al., 1990). It was also shown that, when increasing the pellet length, the system may exhibit periods of time where *almost* constant-pattern behavior occurs: the location of the conversion front appears almost to be a linear function of time.

This observation prompted us to investigate further how constant-pattern behavior arises for infinitely long systems, where the influence of end boundary conditions is absent, and this issue is addressed in the present communication. A comparison is made with theoretical relationships that provide the propagation velocity of the combustion front for infinitely long systems. Since previous theoretical works were confined primarily to the study of adiabatic systems, we also consider only adiabatic conditions in the present communication.

Basic Equations

If all heat losses are neglected, the dimensionless mass and heat balances for a cylindrical pellet of finite length, reacting according to a first-order reaction, reduce to the following system of partial differential equations (cf. Varma et al., 1990):

$$\frac{\partial \eta}{\partial \tau} = (1-\eta)\exp\left[\gamma\left(1-\frac{1}{\theta}\right)\right] \tag{1}$$

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial x^2} + \beta(1-\eta)\exp\left[\gamma\left(1-\frac{1}{\theta}\right)\right] \tag{2}$$

with initial (IC's) and boundary conditions (BC's):

$$\theta = \theta_0, \eta = 0; \qquad \tau = 0, \qquad 0 < x < L \tag{3}$$

$$\theta = \theta_h; \qquad \tau > 0, \qquad x = 0 \tag{4}$$

or

$$-\frac{\partial \theta}{\partial x} = \phi; \qquad 0 < \tau < \tau_\phi, \qquad x = 0 \tag{5a}$$

$$\frac{\partial \theta}{\partial x} = 0; \qquad \tau > \tau_\phi, \qquad x = 0 \tag{5b}$$

$$\frac{\partial \theta}{\partial x} = 0; \qquad \tau > 0, \qquad x = L \tag{6}$$

where η and θ are the conversion and dimensionless temperature, respectively, and all the other quantities are defined in the Notation section.

If a constant-pattern exists, that is, the combustion front propagates at a constant velocity (w), a system of coordinates attached to it can be defined as follows:

$$\xi = x - w\tau. \tag{7}$$

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Starting from the system of Eqs. 1-4 and 6, and repeating the procedure followed by previous workers (cf. Novozhilov, 1961; Puszynski et al., 1987), it can be seen that the following eigenvalue problem is obtained:

$$w^2 \frac{d\eta}{d\theta} = \frac{(1-\eta)\exp[\gamma(1-1/\theta)]}{(\theta-\theta_0)-\beta\eta} \equiv \delta \tag{8}$$

$$\eta = 0; \qquad \theta = \theta_0 + \epsilon_1 \tag{9a}$$

$$\eta = 1; \qquad \theta = \theta_h - \epsilon_2 = \theta_0 + \beta - \epsilon_2 \tag{9b}$$

whose numerical solution provides the value of the velocity, w of the constant-pattern propagation front. It is worth noting that the equivalence $\theta_h = \theta_0 + \beta$ can be obtained easily by following the above-mentioned procedure, in particular when the reference temperature T^* is taken as the adiabatic temperature T_{ad}, it follows that $\theta_h = 1$. In the sequel, without any loss of generality, we limit the analysis to the case $\theta_h = 1$, i.e., $\theta_0 + \beta = 1$. In Eqs. 9a and 9b, ϵ_1 and ϵ_2 are small quantities, typically 10^{-4}, and are introduced to prevent the singularity at $\eta = 0$ and the form 0/0 at $\eta = 1$ when solving the above eigenvalue problem numerically.

The numerical method described by Varma et al. (1990) was used to solve the governing balance, Eqs. 1-2, and the details are not reported here for brevity. It is worth noting that owing to larger values adopted for the pellet length, higher numbers of interior grid points (typically 200) were used.

Results and Discussion

As noted earlier, the primary goal of this work is to demonstrate how constant-pattern behavior could arise for infinitely long systems. The range of the dimensionless parameters used for the computations were typical for SHS processes (Varma et al., 1990) and were selected to satisfy all of the various stability criteria proposed by previous workers (cf. Shkadinskii et al., 1971; Matkowsky and Sivashinsky, 1978; Dimitriou et al., 1989).

The case where the $x = 0$ end is suddenly elevated and maintained at temperature θ_h: the BC of Eq. 4, which has been treated most commonly by previous workers, was investigated first. Figure 1a shows that if the pellet is sufficiently long, the position where the 50% conversion point is located, which indicates the location of the reaction front, appears to be a *linear* function of the dimensionless time, that is, a constant-pattern behavior exists *except* for end effects. As has been discussed before (Varma et al., 1990), because of the insulating BC at $x = L$, a rapid temperature rise occurs as the reaction front approaches $x = L$, accompanied by a sharp acceleration in the conversion. In addition, it is apparent that the front propagation velocity, which can be easily computed as the slope of the straight line obtained for each pellet length sufficiently far from the ends, is actually the *same* for each value of L. The same conclusion can also be drawn from Figure 1b, which considers the case where ignition is caused by a constant heat flux ϕ for a relatively short period of time τ_ϕ, that is, the BC of Eqs. 5a and 5b. By computing the slope of the straight line, one can find the same propagation velocity as that obtained for the case reported in Figure 1a. Thus, it can be concluded that the velocity of the constant-pattern propagating front is

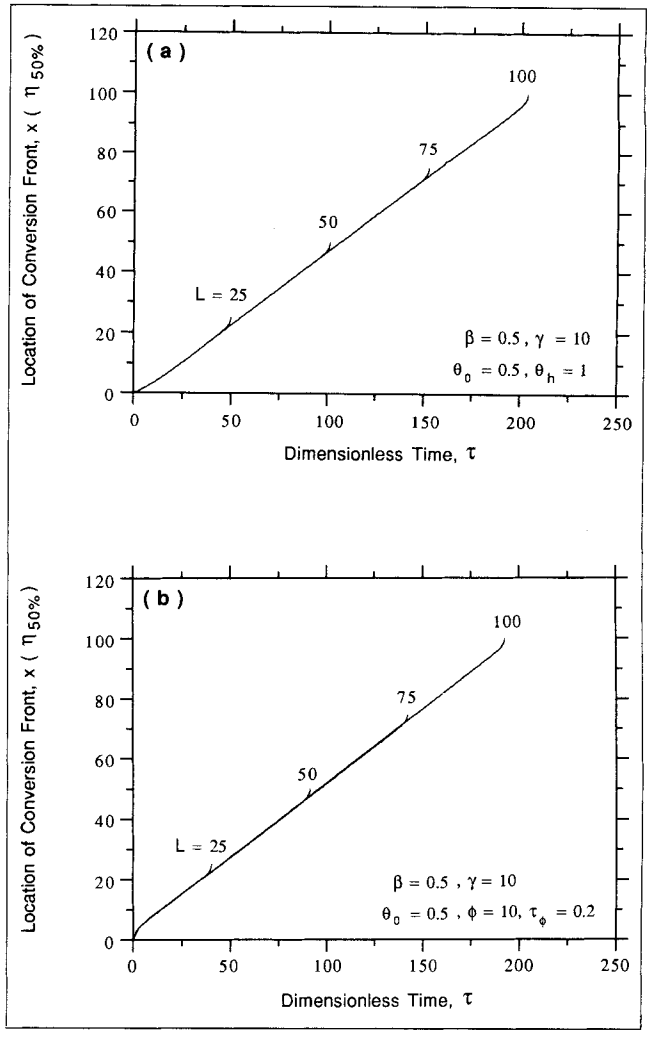

Figure 1. Location of 50% conversion front as a function of time for different pellet lengths.

a. Boundary condition of Eq. 4.
b. Boundary condition of Eq. 5.

independent of the ignition procedure and is determined solely by the system parameter values.

It is clear from Figures 1a and 1b, as it would be expected on physical grounds, that end effects play a relatively more important role for smaller values of the pellet length L. Thus, the period during which constant pattern behavior exists for smaller L is a relatively smaller fraction of the total reaction time, as compared to cases when L is larger.

Table 1. Numerical vs. Theoretical Values for the Reaction Front Propagation Velocity

θ_0	β	γ	w_θ	w_ϕ	w_E	w_M	w_N	w_t
0.8	0.2	40	0.394	0.393	0.390	0.385	0.353	0.349
0.67	0.33	20	0.431	0.427	0.428	0.422	0.389	0.380
0.5	0.5	15	0.388	0.386	0.384	0.382	0.365	0.354
0.5	0.5	12	0.437	0.437	0.436	0.432	0.408	0.393
0.5	0.5	10	0.489	0.489	0.487	0.479	0.447	0.428
0.375	0.625	10	0.417	0.417	0.416	0.413	0.400	0.383
0.3	0.7	10	0.391	0.386	0.386	0.385	0.378	0.362

The values of the front velocity for $L=100$ in Table 1, computed for various sets of parameter values, are denoted by w_θ and w_ϕ depending on the ignition procedure selected: the BC of Eq. 4 and the BC of Eqs. 5a and 5b, respectively. Table 1 also lists the values of the combustion velocity w_E computed by solving the eigenvalue problem described above. As expected, the agreement among w_θ, w_ϕ, and w_E is quite good (the largest difference is less than 1.1%), the value of w_E being somewhat more accurate since it follows from the solution of a single ordinary-differential equation. A comparison with theoretical relationships that provide the propagation rate of the combustion front for infinitely long systems is also shown in Table 1. Apparently, the expression derived by Novozhilov (1961) which can be written as:

$$w_N^2 = 1/\beta\gamma \tag{10}$$

leads to relatively large (less than about 9%) errors with respect to the eigenvalue solution w_E. This expression, derived subsequently also by many other workers (cf. Merzhanov and Khaikin, 1988), involves two approximations. The first is the so-called *thin-zone* assumption, under which the reaction is confined to a relatively narrow zone near the propagating front, while the second is the well-known Frank-Kamenetskii (F-K) approximation. Both of these approximations become more valid as the product $\beta\gamma \to \infty$ (Margolis, 1983).

It is possible to obtain relationships between the true propagation velocity (w or w_E), and the velocities obtained by either the thin-zone approximation alone (w_t) *or* by both the thin zone and the F-K approximations (i.e., w_N). This can be achieved by examining Eqs. 8-9. For the case of the thin-zone approximation, $\theta = 1$ in the denominator of δ, so that δ is replaced by:

$$\delta_t = \exp[\gamma(1-1/\theta)]/\beta < \delta. \tag{11}$$

Since the BC's given by Eq. 9 remain unchanged, it follows by integrating Eq. 8 that

$$w_E^2 \int_0^1 d\eta = w_E^2 = \int_{\theta_0}^1 \delta d\theta, \tag{12a}$$

while similarly

$$w_t^2 = \int_{\theta_0}^1 \delta_t d\theta. \tag{12b}$$

From Eq. 11, we can then conclude that

$$w_t < w_E. \tag{13}$$

The F-K approximation, introduced subsequent to the thin-zone approximation, means that δ is now replaced by:

$$\delta_N = \exp[\gamma(\theta-1)]/\beta > \delta_t, \tag{14}$$

where the inequality above arises because $\theta < 1$. Following the same procedure used to obtain Eq. 12, we have

$$w_N^2 \int_0^1 d\eta = w_N^2 = \int_{\theta_0}^1 \delta_N d\theta, \tag{15}$$

and using Eqs. 12b and 14,

$$w_t < w_N. \tag{16}$$

Although we are not able to prove analytically that $w_N < w_E$, the numerical results shown in Table 1 support this conclusion, so that the relationship appears to be:

$$w_t < w_N < w_E. \tag{17}$$

Since the rigorous lower bound on the front propagation velocity is w_t, it is worthwhile to obtain an analytical expression for it. Introducing the variable $y = 1/\theta$, from Eq. 12b,

$$w_t^2 = \frac{\exp(\gamma)}{\beta} \int_1^{1/(1-\beta)} \frac{\exp(-\gamma y)}{y^2}\, dy. \tag{18}$$

The integral on the righthand side can be written first in terms of the exponential integral and then related to the incomplete gamma function (Abramowitz and Stegun, 1965), leading to:

$$w_t = \frac{1}{(\beta\gamma)^{1/2}} \left[\gamma^2 \exp(\gamma) \left\{ \Gamma(-1,\gamma) - \Gamma\left(-1, \frac{\gamma}{1-\beta}\right) \right\} \right]^{1/2}. \tag{19}$$

For large γ, the asymptotic expansion of the gamma function (Abramowitz and Stegun, 1965), keeping only up to the $1/\gamma^2$ term, leads to:

$$w_t = \frac{1}{(\beta\gamma)^{1/2}} \left[1 - \frac{1}{\gamma} + \frac{5}{2\gamma^2} + O\left(\frac{1}{\gamma^3}\right) \right], \tag{20}$$

which can be compared with the expression

$$w_t = \frac{1}{(\beta\gamma)^{1/2}} \left[1 - \frac{1}{\gamma} + \frac{2}{\gamma^2} \right] \tag{21}$$

obtained numerically by Puszynski et al. (1987). The values of w_t calculated by using Eq. 19 are also shown in Table 1 for comparison, where the inequality given by Eq. 16 may be confirmed.

In Table 1, the values of the propagation velocity, calculated by the procedure of Margolis (1983)

$$w_M^2 = 1/[\beta\gamma + \{2\beta - (\pi^2/6)\} + O(1/\beta\gamma)] \tag{22}$$

are also shown. This expression, obtained by a perturbation expansion using $1/\beta\gamma$ as the small parameter, includes, as the leading term, the expression of Novozhilov given by Eq. 10. Since Eq. 22 is asymptotically correct up to the first-order term, it provides values closer to the true propagation velocity w_E, when compared to those given by Eq. 10.

As shown above (cf. Figure 1), except for end effects, a constant pattern behavior exists for sufficiently long pellets, and moreover the velocity of the propagating front approaches the corresponding value for an infinite system. This, however,

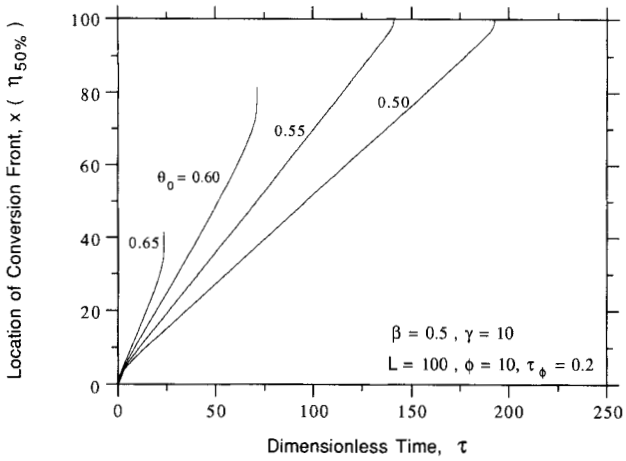

Figure 2. Location of 50% conversion front as a function of time for different initial temperature values.

is true only when the reaction occurs in the form of a thin reaction zone propagating through the reacting mixture, and this requires that the initial temperature θ_0 be sufficiently small. The results of a specific case for various values of the initial temperature are shown in Figure 2. For $\theta_0 = 0.50$ and 0.55, the reaction does occur only in the form of a thin propagating reaction zone. However, for $\theta_0 \geq 0.60$, as may be seen in Figure 3, there is significant reaction also occurring downstream of the sharp front. In fact, for sufficiently large θ_0, the entire pellet volume reacts homogeneously, and so the process approaches the *reactive sintering* regime, as has been discussed previously (cf. Bose et al., 1988; Varma et al., 1990).

The temperature and conversion profiles shown in Figure 3 also explain why in Figure 2, for $\theta_0 = 0.60$ and 0.65, the location of the 50% conversion front ends abruptly at a position less than the full pellet length, $L = 100$. Owing to the aforementioned homogeneous reaction, after a certain time, the conversion exceeds 50% throughout the pellet. Beyond this value of time, the pellet reacts relatively quickly to consume all of the remaining reactant mixture.

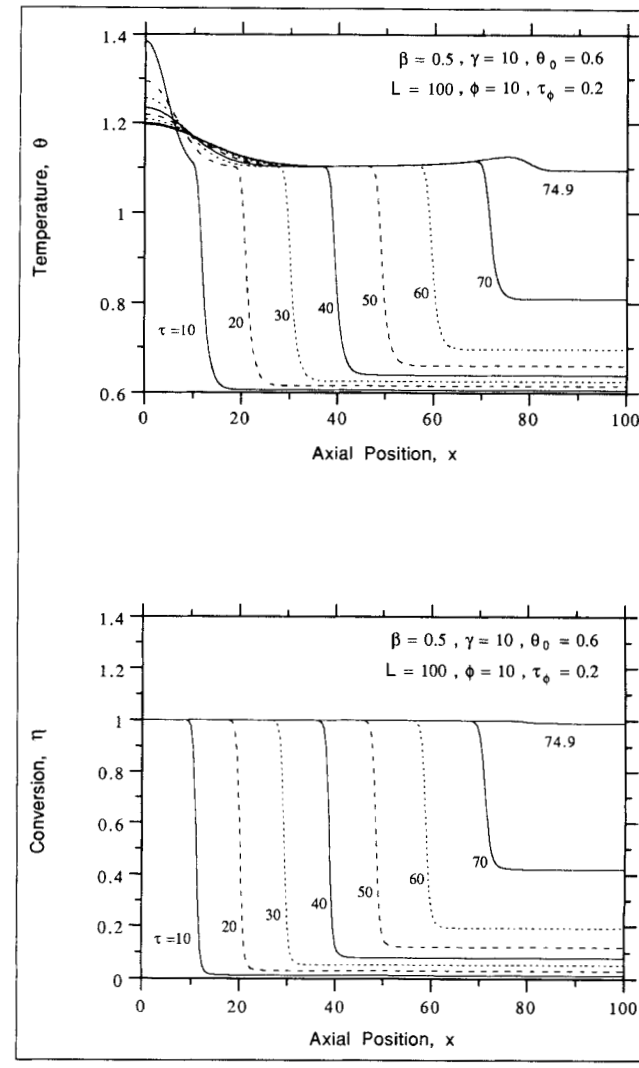

Figure 3. Time-space temperature and conversion profiles for a relatively high value of initial temperature.

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Notation

c_s = reactant concentration
c_p = heat capacity
E = activation energy
k_0 = frequency factor
l = pellet length
L = dimensionless pellet length $[l/z^*]$
R = universal gas constant
q = heat flux
t = time
t^* = reference time $[\exp(\gamma)/k_0]$
T = temperature
T^* = reference temperature
v = constant-pattern propagating velocity
w = dimensionless constant-pattern propagating velocity $[vt^*/z^*]$
x = dimensionless distance $[z/z^*]$
z = distance
z^* = reference distance $[(t^*\lambda/\rho c_p)^{1/2}]$

Greek letters

β = dimensionless heat of reaction parameter $[(-\Delta H)C_{s0}/\rho c_p T^*]$
γ = dimensionless activation energy $[E/RT^*]$
δ = function defined by Eq. 8
η = conversion $[1 - C_s/C_{s0}]$
θ = dimensionless temperature $[T/T^*]$
ξ = coordinate attached to the wave front $[x - w\tau]$
λ = thermal conductivity
ρ = pellet density
τ = dimensionless time $[t/t^*]$
ϕ = dimensionless flux $[qz^*/\lambda T^*]$

Subscripts

E = value obtained by solving the eigenvalue problem of Eqs. 8-9
h = value at $x = 0$
M = value obtained from Eq. 22
N = value obtained from Eq. 10
o = initial value
t = value related to the thin-zone approximation
θ = value obtained with the BC of Eq. 4
ϕ = value obtained with the BC of Eq. 5

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