THERMAL THEORY OF FLAME PROPAGATION IN A CONDENSED MEDIUM

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The asymptotic methods described permit calculation of the burning rate and the temperature and concentration fields in a condensed medium.

§1. The known mechanisms of propagation of a first-order exothermic reaction front in the condensed phase (combustion of gasless compositions, progressive polymerization, combustion of nonvolatile condensed substances, linear pyrolysis) lead to the steady-state problem of determining the concentration and temperature fields and the burning rate from the equations

$$k\frac{d^2T}{dx^2}-u\rho c\frac{dT}{dx}+h\Phi(a,\ T)=0,$$
$$u\rho\frac{da}{dx}+\Phi(a,\ T)=0 \qquad (1)$$

with the conditions

$$x=-\infty,\ T=T_0,\ a=1;$$
$$x=0,\ T=T_n,\ k\frac{dT}{dx}=-q_n\geqslant 0, \qquad (2)$$

where k, ρ, and c are constants and $\Phi(a, \mathrm{T}) = a\rho \times \mathrm{B}\exp[-\mathrm{E/RT}]$ at $\mathrm{T}_1 < \mathrm{T} \le \mathrm{T}_n$, and $\Phi(a, \mathrm{T}) \equiv 0$ at $\mathrm{T}_0 \le \mathrm{T} \le \mathrm{T}_1$. The heat flow q_n to the condensed medium may be derived from external sources or from exothermic reactions in the gas or smoke-gas (fizz zone) phase in the presence of dispersion. However, cases are also possible in which there is no flow of heat from the gasification products to the condensed phase, i.e., $q_n = 0$.

Assuming that $h > 0$ as a result of the exothermicity of the processes involved, we can easily demonstrate the monotonically increasing character of the function $\mathrm{T}(x, u)$, i.e., $dT/dx > 0$ at $-\infty < x < 0$. Integrating system (1) from $-\infty$ to 0, and using condition (2), we obtain

$$T_n=T_0+\frac{q_c}{u\rho c}+\frac{h}{c}\left[1-a(0,\ u)\right],\ q_0=-q_n\geqslant 0,$$

whence, by virtue of the condition $0 \le a(0, u) < 1$, we have $T_n > T_0$.

In [1] it was shown that there exists a unique solution of problem (1), (2), while in [2] an approximate solution based on averaging the temperature gradient in the reaction zone was obtained. A similar approximate method, involving the approximation of the source $\Phi(a, T)$ in the reaction zone, was proposed in [3]. Special cases of the problem were investigated in [4, 5], where approximations in which the convective term is disregarded were obtained for various types of chemical reactions. In all these studies of the thermal theory of combustion, it is assumed that the activation energy is much greater than the thermal energy of the molecules ($E/RT_n \gg 1$).

Retaining this assumption, we wish to propose an approximate but, in our view, simpler and more rigorous method of solving problem (1), (2).

First, we reduce problem (1), (2) to dimensionless form, setting

$$z=\frac{T_n-T}{T_n-T_0},\quad y=\frac{dT/dx}{T_n-T_0}\sqrt{\frac{k\exp\varkappa}{\rho cB}},$$
$$m=u\sqrt{\frac{c\rho\exp\varkappa}{Bk}},$$
$$\varkappa=\frac{E}{RT_n},\ \lambda=1-\frac{T_0}{T_n},$$
$$\beta=\frac{h}{c(T_n-T_0)},\quad \delta=\frac{T_n-T_1}{T_n-T_0},$$
$$d=\frac{q_0\exp\frac{\varkappa}{2}}{(T_n-T_0)\sqrt{k\rho cB}},$$
$$\varphi(z)=\exp\left(-\frac{\varkappa\lambda z}{1-\lambda z}\right)\ \text{at}\ 0\leqslant z<\delta,$$
$$\varphi(z)\equiv 0\ \text{at}\ \delta\leqslant z\leqslant 1\ (0<\delta<1). \qquad (3)$$

Clearly, for determining the functions $a(z, m)$, $y(z, m)$ and the parameter m on the interval $0 \le z \le \delta$, we have the problem

$$\left.\begin{aligned} y\frac{dy}{dz}+my-\beta a\varphi(z)&=0,\\ my\frac{da}{dz}-a\varphi(z)&=0,\end{aligned}\right\} \qquad (4)$$
$$z=0,\ y=d, \qquad (4')$$
$$z=\delta,\ y=m(1-\delta),\ a=1. \qquad (4'')$$

Since system (4) has a first integral, under conditions (4") we obtain

$$y(z,\ m)=m\left[1-z-\beta+\beta a(z,\ m)\right], \qquad (5)$$

where at $0 < z \le \delta$ $y(z, m) > 0$ and by virtue of (4'), the surface concentration $a(0, m) = \alpha(m)$ is

$$\alpha(m)=\frac{1}{\beta}\left[\frac{d}{m}-1+\beta\right],\quad 0\leqslant\alpha(m)<1. \qquad (6)$$

Using expressions (5) and (6) and making the change of variables

$$dv = \varphi(z)\,dz, \quad v = \int_0^z \varphi(s)\,ds, \tag{7}$$

we obtain the problem, equivalent to problem (4)–(4"),

$$\frac{dv}{da} = \varepsilon\,\frac{1 - z(v) - \beta + \beta a}{a}, \quad \varepsilon = m^2, \tag{8}$$

$$a = \alpha(\varepsilon), \quad v = 0, \tag{8'}$$

$$a = 1, \qquad v = \int_0^\delta \varphi(s)\,ds. \tag{8"}$$

For the cases of most practical interest, $\varkappa \gg 1$, and $\lambda = 0.5$–0.9. Hence, the chemical reaction takes place mainly in the region of temperatures close to the surface temperature T_n, i.e., in the region of small z and v. Then expanding the function z(v) in series in a neighborhood of v = 0 and discarding small terms of the second or higher order, in accordance with transformation (7), we have

$$z(v) \approx v. \tag{9}$$

Substituting (9) into (8) and integrating with observance of condition (8'), we obtain

$$v(a, \varepsilon) = \left(1 - \beta\right)\left[1 - \left(\frac{\alpha(\varepsilon)}{a}\right)^{\varepsilon}\right] + \\ + \beta\,\frac{\varepsilon}{1+\varepsilon}\,a\left[1 - \left(\frac{\alpha(\varepsilon)}{a}\right)^{1+\varepsilon}\right]. \tag{10}$$

Now, using condition (8") and noting that $\varkappa\lambda \gg 1$

$$\int_0^\delta \varphi(s)\,ds \approx \int_0^1 \varphi(s)\,ds,$$

we have a transcendental equation for the parameter ε:

$$Y(\varepsilon) \equiv \int_0^1 \varphi(s)\,ds + (\beta - 1)\left[1 - (\alpha(\varepsilon))^{\varepsilon}\right] - \\ - \beta\,\frac{\varepsilon}{1+\varepsilon}\left[1 - (\alpha(\varepsilon))^{1+\varepsilon}\right] = 0. \tag{11}$$

We now show that Eq. (11) has a unique solution at any value of $\beta > 0$. Since

$$Y(d^2) = \int_0^1 \varphi(s)\,ds, \quad 0 < \int_0^1 \varphi(s)\,ds < 1,$$

at $\beta \geq 1$, $d \geq 0$ Y(ε) changes sign from plus to minus on the interval $d^2 < \varepsilon < \infty$, while at $0 < \beta < 1$, $d > 0$, an analogous change in the sign of the function Y(ε) on the interval $d^2 < \varepsilon < d^2/(1-\beta)^2$ occurs if the following condition is satisfied:

$$\int_0^1 \varphi(s)\,ds < 1 - \frac{\beta(1-\beta)^2}{(1-\beta)^2 + d^2}.$$

Thus, the existence of a solution of Eq. (11) has been proved. For this solution to be unique, it is necessary that the functions Y(ε) decrease monotonically on the corresponding intervals, i.e., $Y'_\varepsilon < 0$. Since

$$\frac{dY}{d\varepsilon} = \frac{\beta\,\alpha^{1+\varepsilon}}{(1+\varepsilon)^2}\left[\varepsilon(1+\varepsilon)^2\,\frac{\alpha'_\varepsilon}{\alpha^2}\,\frac{d}{\beta\sqrt{\varepsilon}} + 1 - \right. \\ \left. - \frac{d - (\beta-1)\sqrt{\varepsilon}}{d + (\beta-1)\sqrt{\varepsilon}}\ln\left(\frac{1}{\alpha}\right)^{1+\varepsilon} - \left(\frac{1}{\alpha}\right)^{1+\varepsilon}\right] \tag{12}$$

and, in accordance with (6), $\alpha'_\varepsilon \leq 0$ at $d \geq 0$, as a result of the fact that $1 + \ln x < x$ at $x > 1$, the derivative of the function Y(ε) is negative at $\beta > 1$, $d \geq 0$; $\beta \leq 1$, $d > 0$.

The case $\beta = 1$, $d = 0$ does not require additional investigation, since when the condensed medium is completely burned up in the absence of external sources, $\alpha = 0$ and from Eq. (11) there follows

$$\varepsilon = \frac{\int_0^1 \varphi(s)\,ds}{1 - \int_0^1 \varphi(s)\,ds}, \tag{13}$$

and the functions $a(z, \varepsilon)$, $y(z, \varepsilon)$ have the form

$$a(z, \varepsilon) \approx \frac{\int_0^z \varphi(s)\,ds}{\int_0^1 \varphi(s)\,ds}, \quad y(z, \varepsilon) \approx \sqrt{\varepsilon}\,[a(z, \varepsilon) - z]. \tag{14}$$

We note that when $\beta = 1$, $d = 0$, as when $\beta > 1$, $d = 0$ (incomplete combustion of the material in the condensed phase and burnup in the autoignition regime outside the condensed medium in the absence of external sources), the results of [4, 5] give values of the burning rate lower than those given by Eq. (11). In the general case the propagation velocity ε of the flame front depends on the two parameters β and d, i.e., on the temperature and the heat flux at the surface of the condensed medium. The latter may be given in each specific case by certain additional relations.

Thus, having found ε from Eq. (11), on applying relations (7) and (10) we approximately compute the function $a(z, \varepsilon)$ given implicitly by

$$\int_0^z \varphi(s)\,ds \approx (1 - \beta)\left[1 - \left(\frac{\alpha(\varepsilon)}{a}\right)^{\varepsilon}\right] + \\ + \beta\,\frac{\varepsilon}{1+\varepsilon}\,a\left[1 - \left(\frac{\alpha(\varepsilon)}{a}\right)^{1+\varepsilon}\right]. \tag{15}$$

Then, in accordance with (5), we find y(z, ε) and the function $z = z(x, \varepsilon)$

$$x = -\sqrt{\frac{k\exp\varkappa}{c\rho B\varepsilon}}\int_0^z \frac{ds}{1 - s - \beta + \beta a(s, \varepsilon)}, \tag{16}$$

and, hence, the temperature and concentration fields $T = T_n\,[1 - \lambda z(x, \varepsilon)]$ and $a(x, \varepsilon)$. According to (5), the burning rate

$$u = \sqrt{\frac{Bk\varepsilon}{c\rho}}\exp\left(-\frac{\varkappa}{2}\right). \tag{17}$$

§2. We now consider the burning of a powder from the standpoint of the processes taking place in the condensed phase in the case of a zero-order reaction and assume that the dispersion of the condensed material is not accompanied by a heating effect. Then the starting steady-state system of equations which describe the combustion process have the form [6]

$$k\frac{d^2T}{dx^2}-u\rho c\frac{dT}{dx}+h\Phi(T)=0,$$

$$u=u_p+u_d,\quad u_p=\int_{-\infty}^{0}B\exp\left(-\frac{E}{RT(x,u)}\right)dx,$$

$$\Phi(T)=B\rho\exp\left(-\frac{E}{RT}\right)\quad\text{at}\quad T_1<T\leqslant T_n,$$

$$\Phi(T)\equiv 0\quad\text{at}\quad T_0\leqslant T\leqslant T_1. \tag{18}$$

To determine the temperature field T(x, u) and the burning rate u, we impose on system (18) the boundary conditions

$$x=-\infty,\ T=T_0;\ x=0,\ T=T_n. \tag{19}$$

Introducing the degree of dispersion $\eta_d = u_d/u$ and carrying out transformation (3), we have on the interval $0 \le z \le \delta$ the problem for determining the parameter m and the function y(z, m):

$$y\frac{dy}{dz}+my-\beta\varphi(z)=0,$$

$$z=0,\ y=m[1-(1-\eta_d)\beta],$$

$$z=\delta,\ y=m(1-\delta),\ 0<\delta<1. \tag{20}$$

As distinct from Merzhanov and Dubovitskii [7], we apply the Zel'dovich procedure [8] to problem (20) and determine the burning rate

$$m\approx\frac{1}{1-\eta_d}\sqrt{\frac{2}{\beta}\int_0^1\varphi(s)\,ds}\,. \tag{21}$$

For flameless combustion, when the process depends only on the heat released in the condensed phase $T_n = T_0 + (h/c)(1 - \eta_d)$ and

$$m\approx\sqrt{2\beta\int_0^1\varphi(s)\,ds.} \tag{22}$$

In the absence of dispersion, $\eta_d = 0$ and

$$m\approx\sqrt{\frac{2}{\beta}\int_0^1\varphi(s)\,ds.} \tag{23}$$

Equations (21) and (23) determine the parameter m with a rather high degree of accuracy, exceeding that of the method proposed in [6, 7]. To determine the function y(z, m) and, hence, T(x, u) at m < 1, we can use an asymptotic approximation having the form

$$y(z,\ m)\sim\sum_{k=0}^{N}m^k y_k(z), \tag{24}$$

where $y_k(z)$ (k = 0, 1, 2, . . . , N) are found from the recurrence differential equations obtained by substituting (24) into (20) and equating terms with like powers of m.

Example. Let $\varkappa\lambda = 17$, $\eta_d = 0$, $\beta = 0.912$, $\varphi(z) = \exp(-\varkappa\lambda z)$. From (23), m = 0.359 (numerical integration of system (20) gives m = 0.362; the formula in [7] gives m = 0.329). Confining ourselves to two terms of series (24), we have

$$y(z,\ m)\approx\sqrt{\frac{2\beta}{\varkappa\lambda}\left(1-\varphi(z)\right)}-m\times$$

$$\times\left[\frac{\frac{2}{\varkappa\lambda}\left(\ln\left[1+\sqrt{1-\varphi(z)}\right]-\sqrt{1-\varphi(z)}\right)+z}{\sqrt{1-\varphi(z)}}-\right.$$

$$\left.-(1-\beta)\right]. \tag{25}$$

Since, from (25), m can be calculated correct to 3% (m = 0.374), the determination of the function y(z, m) is sufficiently accurate.

§3. With certain simplifying assumptions, the investigation of the particular class of liquid and fusible homogeneous nonvolatile condensed substances whose combustion mechanism was examined in [9] reduces to system (1), where $\Phi(a, T) \equiv 0$ at $T_0 \le T \le T_1$, h > 0 and

$$\Phi(a,\ T)=B\rho a\left[1+(1-a)\times\right.$$

$$\left.\times\left(\rho\frac{RT}{p\mu}-1\right)\right]^{-1}\exp\left(-\frac{E}{RT}\right)\quad\text{at}\quad T>T_1. \tag{26}$$

To determine the functions T(x, u), *a*(x, u) and the burning rate u, we impose on system (1) the conditions

$$x=-\infty,\ T=T_0,\ a=1;\ x=\infty,\ a=0,\ \frac{dT}{dx}=0. \tag{27}$$

As in §1, we note that dT/dx > 0 on the interval $(-\infty < x < \infty)$ and $T_n = T_0 + h/c$. Setting

$$\pi=\frac{p\mu}{RT_n\rho},\quad\varepsilon=\frac{m^2}{\pi} \tag{28}$$

and using expressions (3) and (7) to transform the starting system, we obtain

$$y(z,\ m)=m(a-z), \tag{29}$$

where the concentration *a*(z, ε) and the parameter ε are found from the problem

$$\frac{dv}{da}=\varepsilon F(v,\ a),\quad F(v,\ a)=$$

$$=\frac{a-z(v)}{a}\left[\pi+(1-a)\left(1-\pi-\lambda z(v)\right)\right], \tag{30}$$

$$a=0,\ v=0;\ a=1,\ v=\int_0^\delta\varphi(s)\,ds,\ 0<\delta<1. \tag{31}$$

If we assume that $1 - \pi - \lambda > 0$, which is always satisfied in practice, we can easily prove the existence of a unique solution of problem (30), (31) and show that, for sufficiently large values of $\varkappa\lambda$,

$$\frac{2}{1+\pi}\int_0^1\varphi(s)\,ds<\varepsilon<0{,}5. \tag{32}$$

Using (32) we find the solution of Eq. (30) in the form of an asymptotic series:

$$v(a,\ \varepsilon)=\varepsilon v_1(a)+\varepsilon^2 v_2(a)+\varepsilon^3 v_3(a)+\ldots \tag{33}$$

Substituting (33) into (30) and expanding the function F(v, a) in powers of ε,

$$
\begin{aligned}
F(v,\ a) &= F(0,\ a) + \varepsilon F_V(0,\ a)\,v_1 + \\
&+ \frac{\varepsilon^2}{2}\,[F_{V^2}(0,\ a)\,v_1^2 + 2F_V(0,\ a)\,v_2] + \ldots,
\end{aligned}
$$

after equating terms with like powers of ε, we obtain the following differential recurrence relations for determining the coefficients of series (33):

$$
\frac{dv_1}{da} = F(0,\ a),\quad \frac{dv_2}{da} = F_V(0,\ a)\,v_1(a),
$$

$$
\frac{dv_3}{da} = \frac{1}{2}\,F_{V^2}(0,\ a)\,v_1^2(a) + F_V(0,\ a)\,v_2(a) \quad \text{etc.} \tag{34}
$$

Bearing in mind that z = z(v) is given by relation (7) and attaching to system (34) the conditions $v_i(0) = 0$ (i = 1, 2, ...), which follow from (31) with a = 0, we obtain, on confining ourselves to three terms of series (33),

$$
\begin{aligned}
v_1(a) &= a\left[1 - \frac{1-\pi}{2}\,a\right],\\
v_2(a) &= -a + \left[\frac{3}{2}(1-\pi) - \lambda\right]\frac{a^2}{2} + \\
&+ \left[\frac{\lambda}{2}(3-\pi) - \frac{(1-\pi)^2}{2}\right]\frac{a^3}{3} - \frac{\lambda}{8}(1-\pi)\,a^4,\\
v_3(a) &= a - \frac{a^2}{2}\left[\frac{\lambda}{2}(\varkappa-2) + \frac{7}{4}(1-\pi) - \frac{3}{2}\lambda\right] + \\
&+ \frac{a^3}{6}\Bigl[\lambda\,(2\,(1-\pi)\,(\varkappa-1) - 2 - \varkappa\lambda) + \\
&+ (1-\lambda-\pi)\times \\
&\times\left(\frac{3}{2}(1-\pi) - \lambda\right) - \frac{\lambda}{3}(3-\pi) + \frac{(1-\pi)^2}{3}\Bigr] + \\
&+ \frac{a^4}{4}\Bigl[\varkappa\lambda + (1-\pi)\,(\varkappa\lambda + 2 - \varkappa\,(1-\pi)) - \\
&- \frac{\varkappa-2}{4}(1-\pi)^2 + \frac{\lambda}{8}(1-\pi) + \\
&+ \frac{1-\lambda-\pi}{6}\left(\lambda\,(3-\pi) - (1-\pi)^2\right) + \\
&+ \frac{\lambda}{2}\left(\frac{3}{2}(1-\pi) - \lambda\right)\Bigr] + \\
&+ \frac{a^5}{5}\Bigl[\frac{\lambda}{6}\left(\lambda\,(3-\pi) - (1-\pi)^2\right) - \\
&- \frac{\lambda}{8}(1-\pi)\,(1-\lambda-\pi) - \\
&- \varkappa\lambda\,(1-\pi) - \frac{(1-\pi)^2}{4}\bigl(\varkappa\lambda + 2 - \\
&- \varkappa\,(1-\pi)\bigr)\Bigr] + \frac{a^6}{24}\,\lambda\,(1-\pi)\left[\varkappa\,(1-\pi) - \frac{\lambda}{2}\right].
\end{aligned} \tag{35}
$$

We can now use condition (31) with a = 1 and obtain a cubic equation for the approximate determination of the parameter

$$
v_3(1)\,\varepsilon^3 + v_2(1)\,\varepsilon^2 + v_1(1)\,\varepsilon - \int_0^1 \varphi(s)\,ds = 0. \tag{36}
$$

Having computed the root of this equation satisfying condition (32), we find $m^2 = \varepsilon\pi$ and, in accordance with (3), the burning rate u. Using representation (7), we can approximately find the function $a(z, \varepsilon)$ from expression (33) and then, in accordance with (29), we find y(z, m). The temperature and concentration in the condensed medium are calculated as in §1, using a single quadrature. Calculations based on Eqs. (35) and (36) gave very good agreement when compared with the results of numerical integration [9].

NOTATION

T is the temperature of the condensed medium; T_0 is the temperature of the starting substance remote from the combustion zone; T_n is the temperature at the surface of the burning substance (or the maximum temperature, if there is no surface); x is the linear coordinate; a is the concentration of the condensed substance; c is the specific heat; k is the thermal conductivity; ρ is the density; h is the energy release of the processes in the condensed phase; u is the burning rate; E is the activation energy; R is the gas constant; u_p is the linear decomposition rate; B is the preexponential; u_d is the linear dispersion rate; p is the pressure; μ is the mean molecular weight of the gaseous products; δ is the "cutoff" parameter of the function φ(z).

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