Effect of Radiation on the Combustion Rate in a Condensed Phase

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Although combustion reactions of the solid-solid type are not as well-known as gas-solid or gas-gas reactions, they nevertheless are of technical importance. Industrial processes operated in the Soviet Union produce TiC and $MoSi_2$ by condensed-phase combustion. This method of synthesis, referred to as SHS, is actively researched in the U.S. These reactions are characterized by a large amount of heat of reaction, a necessary condition for the self-propagation of the front and high activation energy. The latter requirement ensures that the reaction is limited to a thin sheet, similar to a flame front in gaseous combustion.

Different models of condensed-phase combustion have been used by Novozhilov (1961), Sivashinsky (1981), and Puszynski et al. (1986). The only difference of these models is the way that the reaction term is approximated. For example, Sivashinsky proposed a delta-function approximation, which limits the reaction zone to an infinitesimally thin sheet. Introducing this discontinuity in the model led to a jump in the flux of energy across the front. Puszynski et al. expressed the reaction to be the same as in conventional chemical reactor modeling. Although the high activation energy acts as a switch that turns the reaction off when the temperature is only slightly below the (maximum) reaction temperature, this model does not limit the reaction to a certain part of the domain. Consequently it makes any analysis of the problem difficult. Novozhilov considered the reaction zone to be thin, but of finite thickness. He neglected convection and assumed that the temperature is constant (adiabatic value) in the flame zone and derived expressions for the speed of propagation for different kinetics. In all these models, conduction and convection were considered as the only mechanisms of heat transfer.

The preheating rate determines the front propagation rate. An increase in the conductivity of the reactants is expected to lead to an increase in the flame speed. Rao et al. (1987) imbedded a thin copper rod in a cylindrical sample of a slow-burning pyrotechnic composition to improve burning rate, enhance the reliability of ignition transfer, and prevent flame quenching. Heat losses become more pronounced when the samples are small. Nonadiabatic models (Firsov and Shkadinskii, 1987), which include heat losses at the surface of the reacting sample, showed that their front speed decreased much more than the adiabatic case, and if the cooling was too much, extinction occurred. A limiting situation exists when the sample has substantially high conductivity. The integrity of the flame front will no longer be preserved, and simultaneous heat-up of the whole sample will lead to a thermal explosion.

A shortcoming of these models is the omission of radiation. Typical combustion temperatures are between 1,800°C and 3,000°C, at which radiation plays a role. Varma et al. (1990), by including radiation at the surface of the sample as an additional mechanism of heat loss, found that radiative heat losses play a major role in SHS reactions. In this work, radiation was included as an additional mechanism for preheating. For the special case of an adiabatic pellet, the radiation effect on the propagation speed was determined.

Model

In SHS systems, the samples consist of fine opaque particles packed closely together, representing systems of high optical densities. Vortmeyer (1980), however, showed that the two-term radiation model of Viskanta (cf. Viskanta and Menguc, 1990) reduces to Eq. 1 under optically dense conditions:

$$\frac{\partial}{\partial x'}\left[(k+4\phi\sigma_B dT^3)\,\frac{\partial T}{\partial x'}\right] - U\rho Cp\,\frac{\partial T}{\partial x'} + (-\Delta H)k_0 C e^{-\frac{E}{R_g T}} = \rho Cp\,\frac{\partial T}{\partial t} \qquad (1)$$

In dimensionless form, the concentration and energy balances can be written as:

$$\frac{\partial C}{\partial \tau} + \frac{\partial C}{\partial x} = -\Lambda C e^{\gamma\left(\frac{\beta\theta+\sigma-1}{\beta\theta+\sigma}\right)} \qquad (2)$$

$$\frac{\partial \theta}{\partial \tau} + \frac{\partial \theta}{\partial x} = \frac{\partial}{\partial x}\left[(1+\epsilon_1\theta^3+\epsilon_2\theta^2)\,\frac{\partial \theta}{\partial x}\right] + \Lambda C e^{\gamma\left(\frac{\beta\theta+\sigma-1}{\beta\theta+\sigma}\right)} \qquad (3)$$

The cubic form of the dimensional radiation term produces a third-order polynomial in θ. Due to the small contribution of the two lower-order terms, only second- and third-order terms are retained. The sample is assumed to be of infinite length. Under steady-state conditions, the front propagates with velocity U that is constant, and the equations are presented for a coordinate system that is attached to the steady-state front. Boundary conditions ahead of $(x \to -\infty)$ and behind the front $(x \to +\infty)$ are:

$$x = z + U \times \tau \tag{4}$$

$$\theta = 0, \quad x \to -\infty \tag{5}$$

$$C = 1 \tag{6}$$

and for $x \geq 0$,

$$\theta = 1 \tag{7}$$

$$C = 0. \tag{8}$$

Flame Speed with Radiation

The steady-state solutions of Eqs. 2 and 3 outside the flame sheet are:

$$C = 1, x < 0$$
$$C = 0, x > 0 \tag{9}$$

$$\ln\theta + \frac{\epsilon_1}{3}\theta^3 + \frac{\epsilon_2}{2}\theta^2 - \left[\frac{\epsilon_1}{3} + \frac{\epsilon_2}{2}\right] = x, x < 0$$
$$\theta = 1, x > 0. \tag{10}$$

For the sake of conciseness, define:

$$\epsilon = \epsilon_1 + \epsilon_2$$
$$\epsilon_C = 3\epsilon_1 + 2\epsilon_2.$$

Since γ is considered as a large value, it is used as an expansion parameter to stretch the length scale within the front, and θ and C are sought as perturbation series solutions. The stretched variable is defined as:

$$\xi = \gamma \times x. \tag{11}$$

$$\theta = \theta_o + \frac{1}{\gamma}\theta_1 + \ldots \tag{12}$$

$$C = C_o + \frac{1}{\gamma}C_1 + \ldots \tag{13}$$

$$\Lambda = \gamma\lambda_o + \lambda_1 + \ldots \tag{14}$$

The 0(1) solution is $\theta_o = 1$, and the $0(1/\gamma)$ equations are:

$$(1+\epsilon)\frac{d^2\theta_1}{d\xi^2} + \lambda_o C_o e^{\beta\theta_1} = 0 \tag{15}$$

$$\frac{dC^o}{d\xi} = -\lambda_o C_o e^{\beta\theta_1}. \tag{16}$$

Substituting the reaction term in Eq. 15 from Eq. 16 and integrating ξ to $\xi \to +\infty$, one obtains:

$$(1+\epsilon)\frac{d\theta_1}{d\xi} = C_o. \tag{17}$$

Replacing this relation for C_o into Eq. 15 and integrating ξ to $\xi \to +\infty$ gives:

$$\frac{d\theta_1}{d\xi} = \frac{\lambda_o}{\beta}(1 - e^{\beta\theta_1}). \tag{18}$$

The outer solution at $x < 0$ can be expressed in terms of the inner variable ξ, and matching $d\theta_1/d\xi$ with the inner solution gives:

$$\lambda_o = \frac{\beta}{1+\epsilon}. \tag{19}$$

This result can be compared with the expression for flame speed derived by Novozhilov (U_N). Including radiation in the model makes the flame speed faster:

$$\frac{U}{U_N} = [1+\epsilon]^{0.5}. \tag{20}$$

Of course, heat losses to the surrounding medium will decrease the flame speed. Experimental confirmation of the theory will be complicated by the opposite effects of internal radiation and radiative heat losses at the surface of the sample.

The equations of $0(1/\gamma^2)$ are:

$$(1+\epsilon)\frac{d^2\theta_2}{d\xi^2} + (\epsilon_C)\frac{d}{d\xi}\left(\theta_1\frac{d\theta_1}{d\xi}\right) - \frac{d\theta_1}{d\xi} =$$
$$-[\lambda_o(C_o\beta\theta_2 - \beta^2\theta_1^2 + C_1) + \lambda_1 C_o]e^{\beta\theta_1} \tag{21}$$

$$\frac{dC_1}{d\xi} = -[\lambda_o(C_o\beta\theta_2 - \beta^2\theta_1^2 + C_1) + \lambda_1 C_o]e^{\beta\theta_1}. \tag{22}$$

Again a linear relation between C_1 and θ_2 is found by substituting for the reaction term:

$$C_1 = (1+\epsilon)\frac{d\theta_2}{d\xi} + \epsilon_C\theta_1\frac{d\theta_1}{d\xi} - \theta_1. \tag{23}$$

This result is substituted in Eq. 21 to obtain a single equation in θ_2. Following Margolis (1983), the independent variable ξ is exchanged for θ_1, this is permissible because θ_1 is monotone on the interval $\xi \epsilon [-\infty, 0]$. Applying the chain rule and using the following results,

$$\frac{d\theta_1}{d\xi} = \frac{1 - e^{\beta\theta_1}}{1+\epsilon} \tag{24}$$

$$C_o = (1 - e^{\beta\theta_1}) \tag{25}$$

Eq. 21 can be written as:

$$(1+\epsilon)\frac{d}{d\theta_1}\left[\frac{d\theta_2}{d\theta_1}\frac{(1-e^{\beta\theta_1})}{(1+\epsilon)}+\lambda_o\theta_2 e^{\beta\theta_1}\right]-\frac{\beta\epsilon_C\theta_1}{1+\epsilon}e^{\beta\theta_1}$$
$$+\frac{\epsilon_C(1-e^{\beta\theta_1})}{1+\epsilon}-1-\lambda_o\beta^2\theta_1^2(1+\epsilon)e^{\beta\theta_1}+\epsilon_C\theta_1\lambda_o e^{\beta\theta_1}$$
$$-(1+\epsilon)\lambda_o\theta_1\frac{e^{\beta\theta_1}}{(1-e^{\beta\theta_1})}+\lambda_1(1+\epsilon)e^{\beta\theta_1}=0 \quad (26)$$

Integrating Eq. 26 from $-\infty$ to $\theta_1=0$, one gets:

$$\lambda_1=\frac{2\beta}{1+\epsilon}-\frac{\pi^2}{6(1+\epsilon)}+\frac{\epsilon_C}{(1+\epsilon)^2}. \quad (27)$$

Note that integrating Eq. 26, a term of the following form results:

$$\int_{-\infty}^{o}\frac{ye^y dy}{1-e^y}=-\frac{\pi^2}{6},$$

which was obtained by Margolis (1983). Radiation will change the flame speed as follows:

$$U^2=\frac{1+\epsilon}{\beta\gamma+2\beta-\frac{\pi^2}{6}+\frac{\epsilon_C}{1+\epsilon}}\kappa k_o e^{-\frac{E}{R_g T_a}} \quad (28)$$

Setting ϵ to zero, the result of Margolis is recovered. Radiation will increase the flame speed if $\beta\gamma \gg 1$, and increasing the particle size will enhance this effect. It also becomes more important with an increase in the adiabatic temperature rise. Although solid-gas systems were not addressed in this work, the $Ta-N_2$ system, with typically large Ta particles and high adiabatic temperature rise, is an example of a system where radiation plays an important role.

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Notation

C = concentration of reactant
Cp = specific heat
d = particle diameter
E = activation energy
$(-\Delta H)$ = heat of reaction
k = thermal conductivity
k_o = frequency factor
p = emissivity of particles
R_g = universal gas constant
T = temperature
t = time
U = speed of propagation
x = dimensionless distance $x'U/\kappa$

Greek letters

β = $C_o(-\Delta H)/(\rho CpT_a)$
ϵ_1 = $4\phi\sigma_B d(T_a-T_o)^3/k$
ϵ_2 = $12\phi\sigma_B d(T_a-T_o)^2 T_o/k$
ϕ = radiation transfer factor $2/[(2/p-0.264)]$
γ = $E/R_g T_a$
κ = $k/\rho Cp$
θ = $(T-T_o)/(T_a-T_o)$
Λ = $\kappa k_o e^{-E/R_g T}/U^2$
ρ = density of mixture
σ = T_o/T_a
σ_B = Stefan-Boltzmann constant
τ = tU^2/κ

Subscripts

o = initial condition
a = adiabatic value

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