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Technical Notes

Simplified Theory for Ignition Times of Hypergolic Gelled Propellants

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Introduction

ALONG with current studies of the combustion of gelled fuels [1–3] is interest in hypergolic propellant combinations [4,5]. Complementary to detailed numerical computations of flow and combustion-chamber processes [5–8] are simplified models that can be used for making quick and inexpensive estimates of ignition times subsequent to the injection of cold hypergolic propellants. Since short ignition times can produce unacceptably high pressure peaks in the combustion chamber [8], considerations of adjustment of parameters appearing in ignition-time formulas derived from simplified models may suggest approaches to the achievement of acceptable performance. The objective of the present contribution is to provide one such formula from basic theory, identifying relevant parameters that deserve further study.

Simplified Model

Consider two adjacent half-spaces, one occupied by fuel and the other by oxidizer. The constant thermal conductivity, heat capacity, and density of each may differ, so that the thermal diffusivities α_F and α_O, where the subscripts F and O identify fuel and oxidizer, respectively, need not be the same. If x denotes the spatial coordinate normal to the planar interface and t time, then the heat equation obeyed by the temperature T of each propellant is

$$\alpha_i \partial T/\partial t = \partial^2 T/\partial x^2, \qquad i = F, O \tag{1}$$

Let λ_i denote the thermal conductivity of propellant i, and presume a hypergolic exothermic Arrhenius reaction at the interface with overall activation energy E and constant prefactor Q, energy released per unit area per unit time. This can be related to the product of the heat of combustion per unit mass of reactants consumed and the mass rate of consumption of reactants per unit volume by multiplying by a characteristic thickness of the interface. The statement of energy conservation across the interface, having temperature T_I, conveniently placed at $x = 0$, can then be written as

$$\lambda_F \partial T_F/\partial x + \lambda_O \partial T_O/\partial x = -Qe^{-E/RT_I} \quad \text{at } x = 0 \tag{2}$$

where R is the universal gas constant and, for convenience, x is defined to be positive in each propellant.

The problem addressed is one in which the fuel at temperature T_{F_o} and oxidizer at temperature T_{O_o} are brought together instantaneously at time $t = 0$, as may happen, for example, in an impinging-stream combustor at the moment of propellant injection. The initial and boundary conditions that complete the specification of a well-posed problem are then

$$\begin{aligned} T_F &= T_{F_o} \quad \text{at } t = 0 (0 < x < \infty) \quad \text{and} \quad \text{at } x = \infty (0 < t < \infty) \\ T_O &= T_{O_o} \quad \text{at } t = 0 (0 < x < \infty) \quad \text{and} \quad \text{at } x = \infty (0 < t < \infty) \end{aligned} \tag{3}$$

Equation (1) is to be solved in the region $0 < t < \infty$ and $0 < x < \infty$, subject to the boundary condition at $x = 0$ in Eq. (2) for $0 < t < \infty$ and to the initial and boundary conditions in Eq. (3).

Derivation of the Integral Equation

The first task is to determine the interface temperature T_I at $t = 0$: namely, T_{I_o}. This is straightforward because the finite rate exothermic reaction has not yet begun. From the well-known error-function solution

$$T_i = T_I + (T_{i_o} - T_I)\text{erf}[x/(2\sqrt{\alpha_i t})], \qquad i = F, O \tag{4}$$

resulting in

$$\lambda_i (\partial T_i/\partial x)_{x=0} = \lambda_i (T_{i_o} - T_I)/\sqrt{\pi \alpha_i t}, \qquad i = F, O \tag{5}$$

it is seen by application of Eq. (2) with zero on the right-hand side that

$$T_{I_o} = (r_F T_{F_o} + r_O T_{O_o})/(r_F + r_O) \tag{6}$$

where $r_i = \lambda_i/\sqrt{\alpha_i}$ could be called the thermal responsivity of propellant i. Given this initial interface temperature, the principal interest then is to find how T_I varies with time.

Since the temperature differences $T_i - T_{I_o}$ have null initial and boundary conditions, the Laplace transforms

$$\bar{T}_i = \int_0^\infty (T_i - T_{i_o}) e^{-st} \mathrm{d}t, \qquad i = F, O \tag{7}$$

which are found from Eq. (1) to obey second-order linear ordinary differential equations in x, must have the bounded solutions

$$\bar{T}_i = \bar{F}_i e^{-x\sqrt{s/\alpha_i}}, \qquad i = F, O \tag{8}$$

where the functions $\bar{F}_i(s)$ are to be determined by the boundary conditions at $x = 0$. Continuity of temperature at $x = 0$ implies that

$$\bar{F}_F - \bar{F}_O = (T_{O_o} - T_{F_o})/s \tag{9}$$

and the Laplace transform of Eq. (2) is, in view of Eq. (8),

$$\sqrt{s}(r_F \bar{F}_F + r_O \bar{F}_O) = Q \int_0^\infty e^{-E/RT_I} e^{-st} \mathrm{d}t \tag{10}$$

In terms of the transform

$$\bar{F} = (r_F \bar{F}_F + r_O \bar{F}_O)/(r_F + r_O) \tag{11}$$

Eq. (9) implies that

$$\begin{aligned} \bar{F}_F &= \bar{F} + r_O (T_{O_o} - T_{F_o})/[(r_F + r_O)s] \\ \bar{F}_O &= \bar{F} + r_F (T_{F_o} - T_{O_o})/[(r_F + r_O)s] \end{aligned} \tag{12}$$

and Eq. (10) is

$$\sqrt{s}(r_F + r_O)\bar{F} = Q \int_0^\infty e^{-E/RT_I} e^{-st} \mathrm{d}t \tag{13}$$

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The function $\bar{F}(s)$ may be seen from Eqs. (5) and (12) to be the Laplace transforms of $T_I - T_{I_O}$, so that its inverse transform is

$$F = T_I - T_{I_O} \tag{14}$$

the measure of the interface temperature of interest. Application of the convolution theorem to the product $s\bar{F}$ and $1/\sqrt{s}$ in Eq. (13) yields, after taking the inverse transform, the integral equation:

$$(r_F + r_O)\int_0^t \left\{ \frac{\mathrm{d}F(t')}{\mathrm{d}t'} \Big/ \sqrt{\pi(t-t')} \right\} \mathrm{d}t' = Qe^{-E/RT_I} \tag{15}$$

To view the problem as that of determining the time t as a function of the temperature increase F, Eq. (15) is written explicitly as

$$\int_0^F \frac{r_F + r_O}{\sqrt{t(F) - t(F')}}\,\mathrm{d}F' = \sqrt{\pi}Qe^{-E/R(T_{I_O}+F)} \tag{16}$$

The method of activation-energy asymptotics is readily applicable to this last integral equation, which is seen to be nonlinear in $t(F)$ and of the Volterra type, of the first kind.

Application of Activation-Energy Asymptotics

The small parameter of expansion in activation-energy asymptotics is

$$\varepsilon = RT_{I_O}/E \tag{17}$$

Representative numerical values of ε are 0.1 or less. The appropriate independent variable to measure the temperature is

$$\theta = F/(T_{I_O}\varepsilon) = (T_I - T_{I_O})/(T_{I_O}\varepsilon) \tag{18}$$

Introduction of this variable into Eq. (16) indicates that the associated nondimensional time is best defined as

$$\tau = \left[\frac{\pi Q^2 e^{-2E/RT_{I_O}}}{(r_F + r_O)^2\varepsilon^2}\right]t \tag{19}$$

Equation (16) then becomes

$$\int_0^\theta \frac{\mathrm{d}\theta'}{\sqrt{\tau - \tau'}} = e^{\theta/(1+\varepsilon\theta)} \tag{20}$$

where $\tau = \tau(\theta)$ and $\tau' = \tau(\theta')$.

Equation (20) is not singular. It possesses solutions for all time, with θ becoming proportional to $\sqrt{\tau}e^{1/\varepsilon}$ as τ approaches infinity. But $e^{1/\varepsilon}$ is very large for small ε, and the original model becomes meaningless for such large times. Reactant depletion, for example, will occur to reduce the heat-release rate. The model is useful only during the initial ignition period. An expansion for small ε can address that period. To leading order, when ε is small Eq. (20) becomes

$$\int_0^\theta \frac{\mathrm{d}\theta'}{\sqrt{\tau - \tau'}} = e^{\theta} \tag{21}$$

This integral equation, however, is singular because of the continuing growth of e^θ with increasing θ. The equation is singular in the sense that θ approaches infinity at a finite value of τ; that is, solutions do not exist for all time. Stated differently, in Eq. (21) τ approaches a finite value as θ approaches infinity. This finite value can be considered to be a reasonable estimate of the nondimensional ignition time. A value of τ (say, $\tau = c$) of order unity, is thus determined by Eq. (21) by letting θ go to infinity. This is a thermal-runaway approximation for the ignition time, and since Eq. (21) is parameter-free, the number c is a universal constant. According to Eqs. (17) and (19), in terms of this universal constant the ignition time is

$$t_{\mathrm{ign}} = \frac{c}{\pi}\left[\frac{(\lambda_F/\sqrt{\alpha_F} + \lambda_O/\sqrt{\alpha_O})RT_{I_O}}{EQe^{-E/RT_{I_O}}}\right]^2 \tag{22}$$

This ignition time increases with the thermal responsivity of the propellants and decreases with increasing initial temperature and heat of reaction, reaction rate, and activation energy of the hyperbolic reaction.

Determination of the Universal Constant

For small values of θ, e^θ is nearly unity, and the solution to Eq. (21) for t approaches $\tau = (\pi\theta/2)^2$, as may be seen from the substitution $y = \theta'/\theta$, since

$$\int_0^1 \frac{\mathrm{d}y}{\sqrt{1-y^2}} = \frac{\pi}{2}$$

For large vales of θ, the solution to the associated hypothetical half-space heat-conduction problem with surface heating approaches similarity with a similarity variable $x/\sqrt{c-\tau'}$, applicable in an ever-narrower surface layer as the heating rate grows exponentially to infinity. From this similarity behavior, it may be inferred that for large θ,

$$\tau = c - \frac{\pi^2}{4}e^{-2\theta} + f(\theta) \tag{23}$$

where $f(\theta)$ is small compared with $e^{-2\theta}$ for large θ. The coefficient of $e^{-2\theta}$ in Eq. (23) is determined by neglecting $f(\theta)$ and extending the upper limit of integration to infinity in the variable $y = e^{2(\theta-\theta')} - 1$, since

$$\int_0^\infty \frac{\mathrm{d}y}{\sqrt{y}(y+1)} = \pi$$

In the transition from the small-θ form to the large-θ form there is an inflection point of the function $\tau(\theta)$ at a value of θ of order unity. The value of c depends on the shape of the function $\tau(\theta)$ over the entire range $0 < \theta < \infty$ and thus must be determined numerically.

One numerical approach can be based on the finite difference approximation to Eq. (21),

$$\sum_{k=0}^{m-1}(t_m - \tau_k)^{-1/2} = \frac{e^{m\Delta\theta}}{\Delta\theta}, \qquad m = 1, 2, \ldots \tag{24}$$

which may be solved sequentially in m, with $\tau_0 = 0$, by employing a systematic trial-and-error search procedure to find τ_m, corresponding to $\theta_m = m\Delta\theta$, at each step. This method, however, encounters difficulties, especially as τ approaches c, because the differences that have to be computed in the denominator on the left-hand side during the Newton-like iteration become very small. To achieve convergence, the tolerances must be large, resulting in a systematic overestimate of τ_m at each step. The accumulation of this error for computations with somewhat large step sizes have produced values of c greater that 10, whereas the true value is less than 2. This difficulty motivates investigating different numerical procedures.

The artificial problem for $f(\tau, \xi)$, in the region $\tau > 0$, $\xi > 0$, defined by

$$\partial f/\partial\tau = \partial^2 f/\partial\xi^2, \qquad \partial f/\partial\xi = -e^f/\sqrt{\pi} \quad \text{at } \xi = 0$$
$$f = 0 \quad \text{at } \tau = 0 \quad \text{and} \quad \text{at } \tau = \infty \tag{25}$$

has $f(\tau, 0) = \theta(\tau)$ for the function $\theta(\tau)$ defined by Eq. (21). It becomes convenient to introduce the transformed coordinates

$$\sigma = \tau/c, \qquad \eta = \xi/(2\sqrt{c-\tau}) \tag{26}$$

so that the region of interest is $0 < \sigma < 1$, $\eta > 0$. In these coordinates, the differential equation in Eq. (25) reduces to

$$4(1-\sigma)\partial f/\partial\sigma + 2\eta\partial f/\partial\eta = \partial^2 f/\partial\eta^2 \tag{27}$$

Besides the initial and boundary conditions that $f(\sigma, \eta) = 0$ at $\sigma = 0$ and $f(\sigma, \eta)$ approaches 0 as η approaches infinity, the boundary condition for the derivative at $\xi = 0$ becomes

$$\partial f/\partial \eta = -2\sqrt{c/\pi}\sqrt{1-\sigma}e^{f} \quad \text{at } \eta = 0 \tag{28}$$

In the solutions to this problem, the derivative $\partial f/\partial \eta$ at $\eta = 0$ is zero at $\sigma = 1$ if c is too small but approaches infinity before $\sigma = 1$ because of the exponential forcing factor if c is too large. The correct value of c then is the value that causes this derivative to be nonzero but finite at $\sigma = 1$ and that the value of the derivative, in fact, can be shown from the large-θ solution to be -1. The strong sensitivity of the solution to the value of c in the vicinity of the correct value thus, in principle, enables c to be determined very accurately. The divergence that occurs if c is too large, however, causes finite difference numerical methods to generate divergences in the solutions at values of c that are less than the correct value. Initial computations with somewhat large step sizes found divergences at values of c less than 0.2, whereas the true value is greater than 1.

For these two approaches, then, the first gives a value of c that is too large, and the second gives a value that is too small. Refining step sizes in each method could provide bounds on the value of c. A reasonable estimate of the correct value may be obtained from the small-θ and large-θ expansions for $\tau(\theta)$ given previously. Requiring that these expansions agree in both value and slope at some intermediate value of θ (found to be between 0.4 and 0.5) gives $c = 1.5$. This result is approximately correct, and the exact value of c is not particularly important for the problem, because all of the significant functional dependences are independent of the value.

Conclusions

With a one-step Arrhenius interface reaction of zero order and high activation energy, the ignition times of hypergolic gelled propellants increase with increasing thermal conductivities of each propellant and decrease with increasing thermal diffusivities, initial temperature, heat of reaction, reaction rate, and overall activation energy. A thermal responsivity is defined that combines the effects of thermal conductivities and thermal diffusivities. A simple ignition-time formula is available, involving a universal constant, the value of which is approximately 1.5. The formula, which may be useful for correlating data then estimating ignition times, may help in investigating transient ignition pressure peaks. Future work should address more complex ignition chemistry and reactant-diffusion effects, since only the simplest chemistry and transport models underlie the results.

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