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ANALYSIS OF IGNITION OF A POROUS ENERGETIC MATERIAL

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Abstract

A theory of ignition is presented to analyze the effect of porosity on the time to ignition of a semi-infinite porous energetic solid subjected to a constant energy flux. An asymptotic perturbation analysis, based on the smallness of the gas-to-solid density ratio and the largeness of the activation energy, is utilized to describe the inert and transition stages leading to thermal runaway. As in the classical study of a nonporous solid, the transition stage consists of three spatial regions in the limit of large activation energy: a thin reactive-diffusive layer adjacent to the exposed surface of the material where chemical effects are first felt, a somewhat thicker transient-diffusive zone, and finally an inert region where the temperature field is still governed solely by conductive heat transfer. Solutions in each region are constructed at each order with respect to the density-ratio parameter and matched to one another using asymptotic matching principles. It is found that the effects of porosity provide a leading-order reduction in the time to ignition relative to that for the nonporous problem, arising from the reduced amount of solid material that must be heated and the difference in thermal conductivities of the solid and gaseous phases. A positive correction to the leading-order ignition-delay time, however, is provided by the convective flow of gas out of the solid, which stems from the effects of thermal expansion and removes energy from the system. The latter phenomenon is absent from the corresponding calculation for the nonporous problem and produces a number of modifications at the next order in the analysis arising from the relative transport effects associated with the gas flow.

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1. Introduction

The theory of ignition of combustible mixtures and materials from a nonreacted state has long been a fundamental topic in the field of combustion. For many problems of interest, it is characterized by a gradual increase in temperature due to external heating, followed by a rapid temperature increase over a very short time, often referred to as a thermal explosion, as exothermic reactions begin to occur. The time it takes for the latter to occur once such external heating has commenced is generally referred to as the ignition-delay time, or simply the time to ignition, and is clearly a function of the specifics of the problem at hand (*cf.* Williams, 1985). The case of spatially homogeneous ignition, for example, was originally studied by Frank-Kamenetskii and others under various assumptions (*cf.* Zel'dovich et al., 1985), while the analysis of spatially inhomogeneous problems in which heating occurs at a surface, such as the one to be considered in the present study, has a somewhat more recent history.

In ignition problems, the ignition time is inherently tied to the Arrhenius nature of the reaction-rate expressions, and thus it is necessary to retain this feature of the problem in the analysis. Not surprisingly, therefore, activation-energy asymptotics provides a main framework for obtaining approximate analytical estimates of the ignition-delay time and other aspects of the ignition process. Indeed, one of the first examples of such an analysis was the calculation of the time to ignition of a reactive solid subjected to a constant energy flux (Liñán and Williams, 1971). Related results have since been obtained for the case of ignition of a gaseous premixture, and, in fact, the analysis has been extended, under certain approximations, to describe the complete development of a propagating combustion wave (*cf.* Kapila, 1981; Kassoy and Poland, 1980, 1981). Summaries of other related analyses have been described elsewhere (*cf.* Buckmaster and Ludford, 1982; Williams, 1985), but are otherwise not immediately applicable to the present study.

The problem of interest here is the generalization of the Liñán/Williams analysis (Liñán and Williams, 1971), hereafter denoted by LW, to the problem of ignition of a *porous* reactive solid. Such a problem arises from safety and/or surety concerns regarding aged or damaged energetic materials that, as a consequence of either long-term storage or exposure to abnormal thermal environments, may have undergone some degree of decomposition and hence developed significant porosities with respect to their original pristine state. Thus, for simplicity, the physical geometry is as depicted in Figure 1, which indicates a one-dimensional, semi-infinite, porous energetic solid subjected to a uniform heat flux commencing at time zero. The task is then to calculate the time to ignition, accounting for the effects of two-phase flow within the material. It will be shown that there are important modifications, compared to the nonporous case, that arise from the relative

transport effects associated with the two-phase nature of the problem.

2. Formulation

The problem, as illustrated in Figure 1, is governed by a system of partial differential equations for the two-phase flow with respect to time and the spatial coordinate normal to the surface that is being heated. We thus seek to determine the temporal history of the spatially varying solution up to the point of thermal explosion, or runaway, at some spatial location, signaling the onset of ignition. Based on the analysis in LW, we anticipate the following sequence of events, appropriately modified by two-phase-flow effects for the present case of a porous solid. Initially, the temperature is too low for chemical reaction to occur, and thus the first portion of the ignition process is characterized by an inert stage in which the solid is in a purely conductive state, though influenced by interphase heat transfer with the gaseous phase, which, because of its thermal expansion, has a relative motion with respect to the solid. The external heat flux eventually causes the temperature near the surface to reach a level at which exothermic chemical reactions can start to occur. Termed the transition stage, it was shown in LW that this temporal region is characterized by a thin surface region in which there is a reactive-diffusive balance, followed by a somewhat thicker transient-diffusive region in which solutions match with both the inner solutions in the reactive-diffusive zone and the inert solution in the outermost region, where chemical effects are not yet felt (Figure 2). Thermal runaway then occurs in the inner region, marking the end of the transition stage and defining the time to ignition. Since the transition stage occurs on a much shorter time scale relative to the inert stage of the heating, the leading-order time to ignition is essentially defined as the duration of the latter.

The mathematical formulation of the problem is based on the two-phase-flow formulation presented in several recent studies (Margolis and Williams, 1995a,b, 1996). Although these analyses allowed for melting of the solid, as frequently occurs in the deflagration of nitramine propellants such as HMX, we simplify the problem by assuming a single-step exothermic reaction $R(c) \rightarrow P(g)$ in which the condensed (solid) material is converted directly to gaseous products, where the latter are assumed to constitute the gas-phase component of the porous solid. Dimensional quantities are denoted with a tilde, and nondimensional quantities are defined as

$$\begin{aligned} t &= \frac{\tilde{q}^2 \tilde{t}}{\tilde{\lambda}_s \tilde{\rho}_s \tilde{c}_s \tilde{T}_0^2}, \quad \zeta = \frac{\tilde{q} \tilde{\zeta}}{\tilde{\lambda}_s \tilde{T}_0}, \quad T = \frac{\tilde{T}}{\tilde{T}_0}, \quad \rho_g = \frac{\tilde{\rho}_g}{\tilde{\rho}_g^0}, \quad u_g = \frac{\tilde{\rho}_s \tilde{c}_s \tilde{T}_0 \tilde{u}_g}{\tilde{q}}, \quad Q = \frac{\tilde{Q}}{\tilde{c}_s \tilde{T}_0}, \\ E &= \frac{\tilde{E}}{\tilde{R}^0 \tilde{T}_0}, \quad A = \frac{\tilde{\lambda}_s \tilde{\rho}_s \tilde{c}_s \tilde{T}_0^2 \tilde{A}}{\tilde{q}^2}, \quad \hat{A} = AQ, \quad \hat{r} = \frac{\tilde{\rho}_g^0}{\tilde{\rho}_s}, \quad \hat{b} = \frac{\tilde{c}_g}{\tilde{c}_s}, \quad \hat{l} = \frac{\tilde{\lambda}_g}{\tilde{\lambda}_s}, \end{aligned} \quad (1)$$

where $\tilde{t}$ and $\tilde{\zeta}$ are the time and space variables, and $\tilde{T}$ is the temperature. The initial temperature is denoted by $\tilde{T}_0$, $\tilde{q}$ is the external heat flux, $\tilde{\rho}$ and $\tilde{u}$ denote density and velocity, and $\tilde{\lambda}$, $\tilde{c}$ and $\tilde{Q}$,

assumed constant, stand for thermal conductivity, heat capacity (at constant pressure) and heat release, respectively, where subscripts s and g refer to the solid and gaseous phases, and a subscript or superscript 0 denotes evaluation at initial conditions. The kinetic parameters $\tilde{E}$ and $\tilde{A}$ are the activation energy and pre-exponential rate constant, respectively, and $\tilde{R}^\circ$ is the gas constant. The ratios $\hat{r}$, $\hat{b}$ and $\hat{l}$ represent gas-to-solid ratios of density, heat capacity and thermal conductivity, respectively, where the initial gas-phase density $\bar{\rho}_g^0$ is used in the definition of $\hat{r}$, and the solid density is assumed constant. Finally, we note that the nondimensional coordinate ζ ranges from 0 at the heated surface of the solid to $+\infty$.

The conservation equations for two-phase reactive flow (Margolis and Williams, 1995a,b, 1996) are presented here in the single-temperature limit of large interphase heat-transfer coefficients and in the limit of constant pressure. The latter is justified by the fact that gas can escape out the surface at $\zeta = 0$ (see below) and the reasonable expectation that gas velocities are small compared with the speed of sound. As a consequence, the model collapses to a set of equations describing conservation of mass and energy and the gas-phase equation of state. In particular, condensed-phase continuity is given by

$$\frac{\partial \alpha}{\partial t} = (\hat{A}/Q)(1 - \alpha)e^{-E/T}, \quad (2)$$

where α is the gas-phase volume fraction, or porosity, of the material, and overall continuity, obtained by combining the gas-phase continuity equation with condensed-phase continuity, Eq. (2), is expressed as

$$\frac{\partial}{\partial t}(\alpha \rho_g) + \frac{\partial}{\partial \zeta} \left[\alpha \rho_g (u_g - \frac{\partial x_s}{\partial t}) \right] = (1/\hat{r}) \frac{\partial \alpha}{\partial t}. \quad (3)$$

Here, x_s denotes the location of the solid surface as a function of time in a laboratory-fixed reference frame (the coordinate ζ is actually a moving coordinate defined such that the solid surface is always at $\zeta = 0$). Since it turns out that reactant consumption, and hence surface regression, can be neglected in the present analysis, it will be found that $\partial x_s / \partial t$ can be set to zero, although it is retained here for completeness. We note that the solid velocity, u_s , is taken to be zero, so that only the gas velocity u_g appears in Eq. (3). Finally, in the single-temperature limit described above, overall energy conservation is given by

$$\frac{\partial}{\partial t} \left[(1 - \alpha)T + \hat{r}\hat{b}\alpha u_g \right] + \hat{r}\hat{b} \frac{\partial}{\partial \zeta} \left[\alpha (u_g - \frac{\partial x_s}{\partial t}) \right] = \frac{\partial}{\partial \zeta} \left[(1 - \alpha + \hat{l}\alpha) \frac{\partial T}{\partial \zeta} \right] + \hat{A}(1 - \alpha)e^{-E/T}, \quad (4)$$

and the gas-phase equation of state, for constant pressure, is determined by the ideal gas law as

$$\rho_g T = 1, \quad (5)$$

which may be used to eliminate ρ_g from Eqs. (2) – (4). We note the explicit appearance of the gas-to-solid parameter ratios $\hat{r}$, $\hat{b}$ and $\hat{l}$ in Eqs. (2) and (3), where the characteristic smallness of the first of these will be exploited to obtain a perturbation expansion of the solution.

To complete the specification of the problem, we apply initial and boundary conditions as follows. First, for $t \geq 0$, the surface condition is

$$(1 - \alpha + \hat{l}\alpha) \frac{\partial T}{\partial \zeta} \Big|_{\zeta=0} = -1, \quad (6)$$

corresponding to a constant heat flux at the surface of the porous solid. The remaining initial and boundary conditions are given by

$$T(\zeta \rightarrow \infty, t) = T(\zeta, t = 0) = 1 \quad (7)$$

and

$$u_g(\zeta \rightarrow \infty, t) = u_g(\zeta, t = 0) = 0, \quad (8)$$

where u_g is allowed to be nonzero at $\zeta = 0$, corresponding to a flow of gas out of the solid arising from thermal expansion.

The problem defined by Eqs. (2) – (8) can be further simplified by considering the realistic regime of small gas-to solid density ratio ($\hat{r} \ll 1$) and large heat release ($Q \gg 1$). As a result, the restriction that the last term in Eq. (4), which is equal to $Q(\partial\alpha/\partial t)$, be at most $O(1)$, so as not to exceed the magnitude of the other terms in that equation, allows one to conclude from Eq. (2) that $\partial\alpha/\partial t$ is small, implying that reactant consumption can be neglected during the inert and transition stages of interest here. Consequently, we deduce from Eq. (2) that, to a good approximation, α is equal to α_s , the initial porosity of the solid, which eliminates Eq. (2) and removes α as a variable. Furthermore, the right-hand side of Eq. (3), which may be expressed as $(\hat{r}Q)^{-1} \hat{A}(1-\alpha) e^{-E/T}$, may also be neglected to a first approximation in the limit $Q \gg \hat{r}$. Although the latter is less likely to be satisfied in practice, this term is still negligible everywhere in Figure 2 (due to the smallness of the Arrhenius factor), except possibly in the thin reactive/diffusive layer in the transition region. Accordingly, in order to simplify the problem further, we shall assume that this term is $o(1)$, which allows its neglect to the order of approximation required here. With these assumptions, the actual problem to be analyzed is thus reduced to

$$\frac{\partial}{\partial t} (\alpha_s \rho_g) + \frac{\partial}{\partial \zeta} (\alpha_s \rho_g u_g) = 0, \quad (9)$$

$$\frac{\partial}{\partial t} [(1 - \alpha_s)T + \hat{r}\hat{b}\alpha_s u_g] + \hat{r}\hat{b} \frac{\partial}{\partial \zeta} (\alpha_s u_g) = \frac{\partial}{\partial \zeta} \left[(1 - \alpha_s + \hat{l}\alpha_s) \frac{\partial T}{\partial \zeta} \right] + \hat{A}(1 - \alpha_s) e^{-E/T}, \quad (10)$$

subject to

$$(1 - \alpha_s + \hat{l}\alpha_s) \frac{\partial T}{\partial \zeta} \Big|_{\zeta=0} = \begin{cases} 0, & t < 0 \\ -1, & t \geq 0, \end{cases} \quad (11)$$

$$T(\zeta \rightarrow \infty, t) = T(\zeta, t = 0) = 1, \quad (12)$$

$$u_g(\zeta \rightarrow \infty, t) \rightarrow 0. \quad (13)$$

This problem reduces to the classical LW problem in the nonporous limit $\alpha_s = 0$. In what follows, we make use of the fact that $\hat{r} \ll 1$ and seek perturbation solutions of the problem defined by Eqs. (9) – (13) in the form

$$T \sim T^{(0)} + \hat{r}T^{(1)} + \dots, \quad u_g \sim u_g^{(0)} + \hat{r}u_g^{(1)} + \dots, \quad \rho_g \sim \rho_g^{(0)} + \hat{r}\rho_g^{(1)} + \dots, \quad (14)$$

with a corresponding expansion for the ignition time t_c given by

$$t_c \sim t_c^{(0)} + \hat{r}t_c^{(1)} + \dots \quad (15)$$

Our ultimate goal in the analysis that follows is the calculation of the first two terms in the expansion for t_c , where the second term will specifically account for the leading-order effects of two-phase flow on the time to ignition.

3. Leading-Order Solutions

Substituting the expansions (14) into the problem defined by Eqs. (9) – (13) and collecting terms of like powers of $\hat{r}$, we obtain a sequence of problems for the recursive determination of the coefficients in these expansions. In particular, the leading-order problem is given by

$$\frac{\partial \rho_g^{(0)}}{\partial t} + \frac{\partial}{\partial \zeta} \left[\rho_g^{(0)} u_g^{(0)} \right] = 0, \quad (16)$$

$$(1 - \alpha_s) \frac{\partial T^{(0)}}{\partial t} = (1 - \alpha_s + \hat{l}\alpha_s) \frac{\partial^2 T^{(0)}}{\partial \zeta^2} + \hat{A}(1 - \alpha_s) e^{-E/T^{(0)}}, \quad (17)$$

subject to the initial/boundary conditions (11) – (13) with T and u_g replaced by their leading-order approximations $T^{(0)}$ and $u_g^{(0)}$, respectively. The leading-order equation for $T^{(0)}$ is decoupled from $u_g^{(0)}$, and thus Eqs. (17) and (16) may be solved sequentially. In fact, the problem for $T^{(0)}$ is, except for the factors $a = 1 - \alpha_s$ and $b = 1 - \alpha_s + \hat{l}\alpha_s$, the same as that analyzed by LW. Indeed, the problem can be made identical to that of LW by introducing new variables t' and ζ' and rescaling $\hat{A}$ according to

$$t' = \frac{t}{ab}, \quad \zeta' = \frac{\zeta}{b}, \quad \hat{A}' = ab\hat{A}, \quad a \equiv 1 - \alpha_s, \quad b \equiv 1 - \alpha_s + \hat{l}\alpha_s. \quad (18)$$

In terms of these quantities the problem is thus reduced to a problem identical in form to Eq. (17), subject to Eqs. (11) and (12), but with each of the factors $(1 - \alpha_s)$ and $(1 - \alpha_s + \hat{l}\alpha_s)$ replaced by unity. In the inert region, where the reaction-rate term in Eq. (17) is exponentially small, the problem thus collapses to a pure heat-conduction problem whose solution is given by

$$T^{(0)}(\zeta', t') = T_I^{(0)} = 1 + 2\sqrt{\frac{t'}{\pi}} e^{-\zeta'^2/4t'} - \zeta' \operatorname{erfc}(\zeta'/2\sqrt{t'}). \quad (19)$$

Clearly, this inert solution, which is monotonically increasing in time, cannot be valid indefinitely since, for sufficiently large values of temperature, chemical reaction will begin to occur (at $\zeta' = 0$, since $T^{(0)}$ is maximal there). Consequently, we formally introduce a critical temperature T_c , assumed to be a property of the solid energetic material (and hence *not* expanded in powers of $\hat{r}$) such that when $T_I(0, t'_c) \approx T_c$, the inert solution (19) is no longer valid. This quantity, along with the coefficients in the expansion of the corresponding ignition time t'_c given by Eq. (15), is to be determined by the analysis that follows. From Eq. (19), however, we immediately determine that the leading-order relationship between T_c and $t_c = abt'_c$ is given by

$$T_c = 1 + 2\sqrt{\frac{t_c^{(0)}}{\pi ab}}, \quad (20)$$

so that, in terms of T_c , the leading-order ignition time is given by

$$t_c^{(0)} = \frac{1}{4}\pi ab(T_c - 1)^2. \quad (21)$$

However, for future reference, we emphasize that Eqs. (20) and (21) constitute a relationship between T_c and the *leading-order* ignition time $t_c^{(0)}$ only, since Eq. (19) is itself only the leading-order approximation in the expansion (14) for the inert solution T_I , and t_c , in turn, has the expansion (15).

In order to proceed farther, it is necessary to consider the chemical reaction term appearing in Eq. (10). Thus, seeking approximate solutions in the limit of large activation energy E , we introduce the small parameter $\epsilon = T_c^2/E$ such that $\epsilon \ll \hat{r}$. Following LW and Kapila (1981), we then introduce the departure from the inert solution $\Phi = T - T_I \sim \Phi^{(0)} + \hat{r}\Phi^{(1)} + \dots$, where, consistent with Eqs. (14) and (19), $\Phi^{(0)} = T^{(0)} - T_I^{(0)}$. We also scale $\hat{A}$ in the temperature regime of interest by defining $\bar{A} = \hat{A}e^{-E/T_c}$, and thus the Arrhenius factor in the leading-order (with respect to $\hat{r}$) version of Eq. (10) may be written as

$$\begin{aligned} \hat{A}e^{-E/T} &= \bar{A}e^{(E/T_c)(T-T_c)/T} \\ &= \bar{A}e^{(E/T_c)[\Phi + (T_I - T_c)]/(\Phi + (T_I - T_c) + T_c)} \\ &\sim \bar{A}e^{(1/\epsilon)\{\Phi^{(0)} + (T_I^{(0)} - T_c) + O[\Phi^{(0)2}, \Phi^{(0)}(T_I^{(0)} - T_c), (T_I^{(0)} - T_c)^2]\}} \end{aligned} \quad (22)$$

where the last step follows from the assumed smallness, with respect to ϵ , of the coefficients in the $\hat{r}$ -expansions for Φ and $T_I - T_c$ in the transition region where chemical activity is no longer exponentially negligible. In terms of $\Phi^{(0)}$ and the primed variables introduced above, Eq. (17) becomes

$$\frac{\partial \Phi^{(0)}}{\partial t'} = \frac{\partial^2 \Phi^{(0)}}{\partial \zeta'^2} + \bar{A}' e^{(1/\epsilon)\{\Phi^{(0)} + (T_I^{(0)} - T_c) + O[\Phi^{(0)2}, \Phi^{(0)}(T_I^{(0)} - T_c), (T_I^{(0)} - T_c)^2]\}}, \quad (23)$$

where $\bar{A}' = ab\bar{A}$, subject to homogeneous initial and boundary conditions

$$(\partial \Phi^{(0)} / \partial \zeta')|_{(\zeta'=0, t')} = \Phi^{(0)}(\zeta \rightarrow \infty, t') = \Phi^{(0)}(\zeta', t' = 0) = 0. \quad (24)$$

In the inert region just described, $T_I^{(0)} - T_c$ is $O(1)$ with respect to ϵ , the reaction rate term is exponentially small, and the solution to the reactionless version of Eqs. (23) – (24) is the inert solution $\Phi^{(0)} = 0$. It is readily anticipated, based on the behavior of the inert solution (19), that $\Phi^{(0)}$ first becomes appreciable near $\zeta' = 0$ when $T_I^{(0)}$ approaches T_c , which, from Eq. (21), occurs when t' approaches $t_c'^{(0)}$. In this range, Eq. (19) may be expanded as

$$T_I^{(0)} - T_c \sim -\zeta' + \frac{t' - t_c'^{(0)}}{\sqrt{\pi t_c'^{(0)}}} + O[\zeta'^2, (t' - t_c'^{(0)})^2, \zeta'(t' - t_c'^{(0)})], \quad (25)$$

which suggests the introduction of stretched variables

$$\tau = \frac{t' - t_c'^{(0)}}{\epsilon}, \quad \xi = \frac{\zeta'}{\epsilon}, \quad (26)$$

and an expansion for $\Phi^{(0)}$ in the form

$$\Phi^{(0)} \sim \epsilon \phi_0 + \epsilon^{3/2} \phi_1 + \epsilon^2 \phi_2 + \dots, \quad (27)$$

where the expansion in half powers of ϵ is anticipated by the introduction below of a second stretched spatial variable. Indeed, the solution in this temporal zone, which LW termed the transition region, turns out to involve three spatial regimes, as briefly described earlier and depicted in Figure 2. We summarize the construction of the solution in each region as follows.

In the innermost region defined by Eqs. (26), substitution of the expansions (25) and (27) into Eq. (23) and collection of coefficients of like powers of ϵ gives, at leading order,

$$\frac{\partial^2 \phi_0}{\partial \xi^2} = 0, \quad (28)$$

subject to the boundary/matching conditions $\partial \phi_0 / \partial \xi = 0$ at $\xi = 0$, $\phi_0 \rightarrow 0$ as $\tau \rightarrow -\infty$ and, ideally, $\phi_0 \rightarrow 0$ as $\xi \rightarrow \infty$. The latter two conditions denote a matching with the inert solution for sufficiently early times and distances sufficiently far from the surface, but it can be seen that only the trivial solution can satisfy Eq. (28) and all these conditions. Accordingly, the matching condition as $\xi \rightarrow \infty$ is dropped, which implies the need to construct solutions in an intermediate (outer) region in order to match the inner solution to the inert solution in the (far outer) interior region of the porous solid. Consequently, the solution for ϕ_0 is $\phi_0 = f_0(\tau)$, with $f_0(\tau)$ still to be determined subject to $f \rightarrow 0$ as $\tau \rightarrow -\infty$. The next-order inner problem is then given by

$$\frac{\partial^2 \phi_1}{\partial \xi^2} = A_0 e^{f_0(\tau) - \xi + \tau / \sqrt{\pi t_c'^{(0)}}}, \quad (29)$$

where $\bar{A}' = \epsilon^{-1/2} A_0$ is the appropriate algebraic scaling for $\bar{A}'$ that allows for a reactive-diffusive balance at this order. Subject to the same homogeneous boundary conditions at $\xi = 0$ and the

same matching condition as $\tau \rightarrow -\infty$ as the leading-order problem for ϕ_0 , the solution of Eq. (29) is given by

$$\phi_1 = -A_0 e^{f_0(\tau) + \tau/\sqrt{\pi t'_c(0)}} (e^{-\xi} + \xi) + f_1(\tau), \quad (30)$$

where $f_1 \rightarrow 0$ as $\tau \rightarrow -\infty$, but is otherwise still to be determined.

Retaining the same transition-zone temporal scaling given by the first of Eqs. (26), the outer spatial region is defined by the variable η as

$$\eta = \epsilon^{-1/2} \zeta' = \epsilon^{1/2} \xi, \quad (31)$$

where the solution for $\Phi^{(0)}$ is sought in the form

$$\Phi^{(0)} \sim \epsilon \psi_0 + \epsilon^{3/2} \psi_1 + \epsilon^2 \psi_2 + \dots \quad (32)$$

With these scalings, the reaction-rate term is again exponentially small, and the leading-order problem becomes

$$\frac{\partial \psi_0}{\partial \tau} = \frac{\partial^2 \psi_0}{\partial \eta^2}, \quad (33)$$

subject to a set of matching conditions given by

$$\psi_0 \rightarrow f_0(\tau), \quad \frac{\partial \psi_0}{\partial \eta} \rightarrow -A_0 e^{f_0(\tau) + \tau/\sqrt{\pi t'_c(0)}} \text{ as } \eta \rightarrow 0, \quad (34)$$

$$\psi_0 \rightarrow 0 \text{ as } \eta \rightarrow \infty, \quad (35)$$

$$\psi_0 \rightarrow 0 \text{ as } \tau \rightarrow -\infty, \quad (36)$$

where Eqs. (34) are derived from a (1,2) matching with the inner solution above. If we now make one final transformation,

$$\hat{\tau} = \frac{\tau}{\sqrt{\pi t'_c(0)}} + \ln [A_0 (\pi t'_c(0))^{1/4}], \quad \hat{\eta} = \frac{\eta}{(\pi t'_c(0))^{1/4}}, \quad (37)$$

the problem expressed by Eqs. (33) – (36) becomes

$$\frac{\partial \psi_0}{\partial \hat{\tau}} = \frac{\partial^2 \psi_0}{\partial \hat{\eta}^2}, \quad (38)$$

$$\left. \frac{\partial \psi_0}{\partial \hat{\eta}} \right|_{\hat{\eta}=0} = -e^{\psi_0(0, \hat{\tau}) + \hat{\tau}}; \quad \psi_0 \rightarrow 0 \text{ as } \hat{\eta} \rightarrow \infty, \hat{\tau} \rightarrow -\infty, \quad (39)$$

In this form, the problem for ψ_0 is parameter-free and identical to the problem given by Eqs. (28) in LW. It can be converted to an integral equation by using Laplace transforms, but the problem is implicit and ultimately requires a numerical integration. The primary result of interest is that the solution for ψ_0 becomes infinite at $\hat{\eta} = 0$ as $\hat{\tau}$ approaches a finite value c_0 given by $c_0 \doteq -0.431$.

At this point, recognizing that there always exists some degree of arbitrariness in the physical definition of ignition temperature, we adopt and extend the mathematical approach of LW by defining it as the value that corresponds to the singularity in $\psi_0(0, \tau)$ occurring at $\tau = \tau_c = -\sqrt{\pi t_c^{(0)}} \ln(ab)$. This value is the unique choice that collapses to the LW convention $\tau_c = 0$ in the limit of zero porosity (*i.e.*, $a = b = 1$) and insures that T_c , which is regarded as a material property of the solid, has no explicit dependence on porosity when the latter is nonzero [see Eqs. (20) and (41) below]. We note, however, that since τ is a stretched variable according to the definition (26), variations in this chosen value would produce at most an $O(\epsilon)$ difference in the subsequent value of the $O(1)$ ignition time $t_c^{(0)}$. Thus, from the first of Eqs. (37) and the various definitions associated with the reaction-rate coefficient, we obtain

$$ab e^{c_0} / (\pi t_c^{(0)})^{1/4} = A_0 = \epsilon^{1/2} \bar{A}' = (T_c^2/E)^{1/2} ab \bar{A} = (T_c/\sqrt{E}) ab \hat{A} e^{-E/T_c}, \quad (40)$$

or, from Eq. (20) and the definitions (18),

$$\hat{A} = \frac{\sqrt{E} e^{c_0}}{(\pi t_c^{(0)}/ab)^{1/4} [1 + 2(t_c^{(0)}/\pi ab)^{1/2}]} e^{E/[1 + 2(t_c^{(0)}/\pi ab)^{1/2}]}, \quad (41)$$

where $ab = (1 - \alpha_s)(1 - \alpha_s + \hat{l}\alpha_s)$. Comparing this result with Eq. (29) of LW, we see that they are identical in the limit $ab = 1$, *e.g.*, in the nonporous limit $\alpha_s = 0$. Equation (41) is discussed in detail in LW, where it is further compared to an empirical formula obtained by Bradley (1970) based on numerical calculations of the original system of equations. Here, we simply conclude from Eq. (40) that there exists a correspondence between the porous and nonporous problems for the leading-order ignition time $t_c^{(0)}$ given by

$$t_c^{(0)(nonporous)} \longleftrightarrow \frac{t_c^{(0)(porous)}}{(1 - \alpha_s)(1 - \alpha_s + \hat{l}\alpha_s)}. \quad (42)$$

That is, to a first approximation, the ignition time for the porous problem is simply shortened by the factor $(1 - \alpha_s)(1 - \alpha_s + \hat{l}\alpha_s)$ relative to the ignition time for the nonporous problem. This, however, is only the leading-order result, corresponding to the first term $t_c^{(0)}$ in the expansion (15) for the ignition time, and does not reflect the perturbative effects of convective gas-phase transport, which we now consider. Such effects will be represented in the calculation of the next-order coefficient $t_c^{(1)}$, which we anticipate will give a positive correction to the leading-order ignition-delay time determined by Eq. (41).

4. Solution for the Leading-Order Gas Velocity

The solution for the leading-order gas velocity $u_g^{(0)}$ in the inert region follows from Eq. (16), where, from Eq. (5), $\rho_g^{(0)} = 1/T_g^{(0)}$, subject to the initial and boundary conditions (8). In terms

of the primed coordinates (18), the problem for $u_g^{(0)}$ is thus given by

$$\frac{1}{a} \frac{\partial \rho_g^{(0)}}{\partial t'} + \frac{\partial}{\partial \zeta'} [\rho_g^{(0)} u_g^{(0)}] = 0, \quad (43)$$

subject to

$$u_g^{(0)}(\zeta' \rightarrow \infty, t') = u_g^{(0)}(\zeta', t' = 0) = 0. \quad (44)$$

Performing an integration with respect to ζ' , we obtain

$$\begin{aligned} u_g^{(0)}(\zeta', t') &= \frac{1}{a \rho_g^{(0)}(\zeta', t')} \int_{\zeta'}^{\infty} \frac{\partial \rho_g^{(0)}(\zeta^*, t')}{\partial t'} d\zeta^* \\ &= -a^{-1} T^{(0)}(\zeta', t') \int_{\zeta'}^{\infty} [T^{(0)}(\zeta^*, t')]^{-2} \frac{\partial T^{(0)}(\zeta^*, t')}{\partial t'} d\zeta^*. \end{aligned} \quad (45)$$

Hence, using the result (19) for $T^{(0)} = T_I^{(0)}$, we obtain a closed-form expression for the leading-order inert gas velocity $u_g^{(0)}(\zeta', t') = u_{g,I}^{(0)}$ as

$$u_{g,I}^{(0)} = \frac{1}{a\sqrt{\pi t'}} \left[1 + 2\sqrt{\frac{t'}{\pi}} e^{-\zeta'^2/4t'} - \zeta' \operatorname{erfc}\left(\frac{\zeta'}{2\sqrt{t'}}\right) \right] \int_{\infty}^{\zeta'} \frac{e^{-\zeta^{*2}/4t'} d\zeta^*}{\left[1 + 2\sqrt{\frac{t'}{\pi}} e^{-\zeta^{*2}/4t'} - \zeta^* \operatorname{erfc}\left(\frac{\zeta^*}{2\sqrt{t'}}\right) \right]^2}. \quad (46)$$

Plots of $u_g^{(0)}$ as a function of the original spatial variable ζ , for several values of t and α_s , are exhibited in Figures 3a,b. It is readily seen that this quantity is negative, reflecting the motion of gas out the heated end of the sample, where it achieves its largest magnitude. As ζ increases, $u_g^{(0)}$ decreases in magnitude, approaching zero in the far interior of the sample so as to satisfy the boundary condition (44). At any spatial location, the rate of gas flow increases with time because of continued thermal expansion as the temperature increases throughout the sample. It is also seen that $u_g^{(0)}(\zeta, t)$ increases as the porosity increases, due to the more rapid heating of the porous solid, as described above, and the corresponding increased rate of thermal expansion of the gas.

5. Calculation of the Correction to the Ignition-Delay Time

In order to determine the correction, produced by the effects of porosity and two-phase flow flow, on the time to ignition, it is necessary to calculate the next-order coefficient $T^{(1)}$ in the temperature expansion given by the first expression in Eq. (14). Thus, from Eqs. (10) – (12) and (14), the problem for $T^{(1)}$ is determined as

$$\begin{aligned} \frac{\partial}{\partial t} \left[(1 - \alpha_s) T^{(1)} + \hat{b} \alpha_s u_g^{(0)} \right] + \hat{b} \frac{\partial}{\partial \zeta} \left[\alpha_s u_g^{(0)} \right] = \\ \frac{\partial}{\partial \zeta} \left[(1 - \alpha_s + \hat{l} \alpha_s) \frac{\partial T^{(1)}}{\partial \zeta} \right] + \hat{A} E (1 - \alpha_s) \frac{T^{(1)}}{T^{(0)2}} e^{-E/T^{(0)}}, \end{aligned} \quad (47)$$

where the source term in the equation is obtained by expanding the Arrhenius factor $e^{-E/T}$ when the expansion (14) is substituted for T , and the initial/boundary conditions are given by

$$\left. \frac{\partial T^{(1)}}{\partial \zeta} \right|_{\zeta=0} = 0, \quad T^{(1)}(\zeta \rightarrow \infty, t) = T^{(1)}(\zeta, t=0) = 0. \quad (48)$$

We again exploit the limit of large activation energy to determine $T^{(1)}$, which preserves the same zone structure (Figure 2) as before.

In the inert region, the source term is again exponentially small, and, in terms of the variables ζ' and t' introduced in Eqs. (18), Eq. (47) for the inert solution $T^{(1)}(\zeta', t') = T_I^{(1)}$ simplifies to

$$\frac{\partial T_I^{(1)}}{\partial t'} - \frac{\partial^2 T_I^{(1)}}{\partial \zeta'^2} = -\hat{b}\alpha_s \left[\frac{1}{a} \frac{\partial u_{g,I}^{(0)}}{\partial t'} + \frac{\partial u_{g,I}^{(0)}}{\partial \zeta'} \right], \quad (49)$$

subject to the boundary conditions (48) written in terms of ζ' and t' . This constitutes a nonhomogeneous heat-conduction problem, where the nonhomogeneous terms in Eq. (49) are known from the solution (46) for $u_g^{(0)}$. Denoting the right-hand side of Eq. (49) by $g(\zeta', t')$, we can express the solution as

$$T_I^{(1)}(\zeta', t') = \int_0^{t'} \int_0^\infty G(\zeta', t'|x, \sigma) g(x, \sigma) dx d\sigma, \quad (50)$$

where the appropriate Green's function $G(\zeta', t'|x, \sigma)$ for Eqs. (48) – (49) is given by

$$G(\zeta', t'|x, \sigma) = \frac{1}{\sqrt{4\pi(t' - \sigma)}} \left[e^{-(\zeta' - x)^2/4(t' - \sigma)} + e^{-(\zeta' + x)^2/4(t' - \sigma)} \right]. \quad (51)$$

It can be demonstrated that the correction $\hat{r}T_I^{(1)}$ to the leading-order inert solution $T_I^{(0)}$ is usually negative, reflecting the fact that the effect of gas flow out of the solid removes energy from the system, thereby lowering the rate of temperature rise caused by the external heating. However, for sufficiently large times, and at locations sufficiently close to the heated surface, this correction may become positive as points further within the interior of the solid are heated and contribute to gas-phase thermal expansion, thereby producing a convective flux of warmer gas towards the surface. The above solution has been evaluated numerically, and its profile is plotted in Figures 4a,b for several different values of time and porosity ($\alpha_s = 0.05$ and 0.4 , respectively), where, as in the previous figures, Eq. (18) has been used to convert back to the physical (ζ, t) variables. These results indicate that the magnitude of $T_I^{(1)}$ increases as the porosity increases, as illustrated more clearly in Figure 5, where $T_I^{(1)}$ is plotted against the porosity α_s for a fixed position ζ at two different values of the time t .

As in the case of the leading-order temperature solution $T^{(0)}$, the above solution for $T^{(1)}$ in the inert stage ceases to be valid in the vicinity of the ignition time t'_c . The leading-order approximation for $t'_c = t_c/ab$, namely $t'_c{}^{(0)}$, was determined implicitly by Eq. (41), and it is now

desired to calculate the next-order correction $t_c'^{(1)}$ according to the expansion (15). Since the breakdown of $T_I^{(1)}$ will occur in the vicinity of $\zeta' = 0$ and $t' = t_c'^{(0)}$, in what follows it will be useful to write the Taylor expansion for $T_I^{(1)}$ in this neighborhood explicitly as

$$T_I^{(1)} \sim c_1 + c_2(t' - t_c'^{(0)}) + c_3\zeta' + \dots, \quad (52)$$

where the coefficients c_1 , c_2 and $c_3 = 0$ are obtained from Eqs. (50) and (51) in the form of integrals over the dummy variables x and σ .

Thus, we again consider the transition stage, and the solution for the next-order coefficient $\Phi^{(1)} = T^{(1)} - T_I^{(1)}$ in the $\hat{r}$ -expansion for the departure Φ from the inert solution. In the inner reactive-diffusive zone of the transition region, we again introduce the stretched variables τ and ξ defined by Eqs. (26) and, consequently, Eq. (47), expressed in terms of $\Phi^{(1)}$, is written in this zone as

$$\frac{\partial \Phi^{(1)}}{\partial \tau} + \hat{b}\alpha_s \left[\frac{1}{a} \frac{\partial v_g^{(0)}}{\partial \tau} + \frac{\partial v_g^{(0)}}{\partial \xi} \right] = \frac{1}{\epsilon} \frac{\partial^2 \Phi^{(1)}}{\partial \xi^2} + \frac{1}{\epsilon} \bar{A}' [c_1 + O(\epsilon)] e^{(1/\epsilon)[\Phi^{(0)} + (T_I^{(0)} - T_c) + \dots]}, \quad (53)$$

subject to the homogeneous conditions (48) [with $T^{(1)}$ replaced by $\Phi^{(1)}$]. Here, $v_g^{(0)} = u_g^{(0)} - u_{g,I}^{(0)}$ denotes the departure of the leading-order gas velocity from its inert value given by Eq. (46), $\bar{A}'$ is the same scaled rate coefficient that appears in Eq. (23) for $\Phi^{(0)}$, and $T_I^{(0)} - T_c$ is given in the present region of interest by Eq. (25). Since, as noted below Eq. (29), $\bar{A}' = \epsilon^{-1/2} A_0$ is $O(\epsilon^{1/2})$ and $v_g^{(0)} \sim O(\epsilon)$, it is clear that the appropriate expansion for $\Phi^{(1)}$ in this region is given by

$$\Phi^{(1)} \sim \epsilon^{1/2} \hat{\phi}_0 + \epsilon \hat{\phi}_1 + \epsilon^{3/2} \hat{\phi}_2 + \dots. \quad (54)$$

Substituting this expansion into the equation for $\Phi^{(1)}$ above, we obtain the leading-order problem for $\hat{\phi}_0$ as

$$\frac{\partial^2 \hat{\phi}_0}{\partial \xi^2} = -c_1 A_0 e^{[\phi_0 - \xi + \tau / \sqrt{\pi t_c'^{(0)}}]}, \quad (55)$$

where $\phi_0 = f_0(\tau)$ is the leading-order term in the expansion (27) for $\Phi^{(0)}$, subject to $\partial \hat{\phi}_0 / \partial \xi = 0$ at $\xi = 0$ and $\hat{\phi}_0 \rightarrow 0$ as $\tau \rightarrow -\infty$, along with a matching with the corresponding solution in the transient-diffusive zone as before. These results, as it turns out, are sufficient to determine $t_c'^{(1)}$, and thus it is not necessary to proceed any further with the transition-stage analysis. In particular, since we have already determined that $\phi_0 \rightarrow \infty$ as $\tau \rightarrow -\sqrt{\pi t_c'^{(0)}} \ln(ab)$, it is clear from Eq. (55) that $\hat{\phi}_0$ will also become infinite at this same critical value of τ . Consequently, the relationship (40) between T_c and $t_c'^{(0)}$, namely

$$\hat{A} = \frac{\sqrt{E} e^{c_0}}{(\pi t_c'^{(0)})^{1/4} T_c} e^{E/T_c}, \quad (56)$$

remains valid, reflecting the physical fact that the ignition temperature T_c is a material property in the sense that it is unaffected by higher-order effects associated with gas flow within the porous solid. Substituting the result (20) from the leading-order inert solution $T_I^{(0)}$ evaluated at $\zeta' = 0$ and $t' = t_c^{(0)}$, we thus recover Eq. (41) for the ignition time $t_c^{(0)}$ alone. That is, Eqs. (20) and (56) are two equations for the two unknowns $t_c^{(0)}$ and T_c , the solution of which gives Eq. (41).

To obtain the correction to the leading-order result (41) for t_c' , we retain Eq. (56), which remains valid through all orders, but in place of Eq. (20), we have the more accurate result

$$T_c \approx T_I^{(0)}(0, t_c') + \hat{r} T_I^{(1)}(0, t_c'), \quad (57)$$

where $T_I^{(0)}(0, t_c') = h_0(t_c') = 1 + 2\sqrt{t_c'/\pi}$ from Eq. (19), and $T_I^{(1)}(0, t_c') = h_1(t_c')$ is obtainable from Eq. (50). Substituting the expansion (15) for t_c' into Eq. (57), we calculate

$$\begin{aligned} T_c &\approx h_0(t_c^{(0)} + \hat{r} t_c^{(1)} + \dots) + \hat{r} h_1(t_c^{(0)} + \hat{r} t_c^{(1)} + \dots) \\ &\sim h_0(t_c^{(0)}) + \hat{r} \left[h_1(t_c^{(0)}) + t_c^{(1)} dh_0/dt_c' \big|_{t_c'=t_c^{(0)}} \right]. \end{aligned} \quad (58)$$

Thus, at leading order we have $T_c = h_0(t_c^{(0)})$, which, in conjunction with Eq. (56) determines $t_c^{(0)}$ according to Eq. (41) as before. At the next order, the term proportional to $\hat{r}$ in the last line of Eq. (58) must vanish, which determines the correction coefficient $t_c^{(1)}$ as

$$t_c^{(1)} = - \frac{h_1(t_c^{(0)})}{dh_0/dt_c' \big|_{t_c'=t_c^{(0)}}}. \quad (59)$$

Evaluating this expression using the above definitions of h_0 and h_1 , we obtain the final expression for $t_c^{(1)}$ as

$$t_c^{(1)} = \sqrt{t_c^{(0)}} \int_0^{t_c^{(0)}} \int_0^\infty \frac{e^{-x^2/4(t_c^{(0)}-\sigma)}}{\sqrt{t_c^{(0)}-\sigma}} g(x, \sigma) dx d\sigma. \quad (60)$$

The integral (60) was evaluated numerically, where the value of $t_c^{(0)}$ was calculated from Eq. (41) using representative values of physical parameters for HMX given in Li *et al.* (1990) and Bradley (1970). The results are displayed in Figure 6, which shows the physical correction coefficient $t_c^{(1)}$ in the ignition-time expansion plotted against the porosity α_s for two different values of the gas-to-solid thermal conductivity ratio $\hat{l}$. It is seen that $t_c^{(1)}$ is a positive and increasing function of α_s , implying that there is a delay with respect to the leading-order ignition time. This result is therefore consistent with the physical expectation that there should be a delay relative to the leading-order result in which the effects of a nonzero gas velocity are absent, since the flow of gas out of the porous solid removes energy from the system and hence slows down the rate at which the temperature would otherwise increase within the solid. However, the dominant effect of porosity is given by the leading-order result (42), which shows an ignition time shortened by the factor $(1 - \alpha_s)(1 - \alpha_s + \hat{l}\alpha_s)$ relative to the nonporous case. Thus, the appearance of the gas-to-solid thermal conductivity ratio $\hat{l}$ at leading order indicates that diffusive gas-phase transport is

more significant than the convective transport effects just described in determining the ignition-delay time. In terms of the critical temperature T_c , Eqs. (15), (18), (21) and (60) yield the final approximation for the ignition time t_c as

$$t_c \approx \frac{1}{4} \pi (1 - \alpha_s) (1 - \alpha_s + \hat{l} \alpha_s) (T_c - 1)^2 \times \left[1 + \frac{2\hat{r}}{\sqrt{\pi} (T_c - 1)} \int_0^{\pi(T_c-1)^2/4} \int_0^\infty \frac{2e^{-x^2/[(\pi(T_c-1)^2-4\sigma]}}{\sqrt{\pi(T_c-1)^2-4\sigma}} g(x, \sigma) dx d\sigma \right]. \quad (61)$$

It may be remarked that the above approximation applies in the realistic limit of small gas-to-solid density ratios. If, however, this quantity becomes $O(1)$, as occurs at very high pressures, then the validity of the result (61) will naturally diminish both for this reason as well as the inaccuracy of the ideal-gas law (5) in such a regime.

6. Conclusion

The focus of this work has been the extension of the classical analysis (Liñán and Williams, 1971) of radiant ignition of an energetic solid to a porous energetic material, taking into account the effects of the two-phase nature of the medium. A perturbation analysis based on the smallness of the gas-to-solid density ratio and the largeness of the activation energy was used to obtain the leading-order ignition-delay time and the next-order correction arising from the effects of two-phase flow. The former result was shown to be reduced by the factor $(1 - \alpha_s)(1 - \alpha_s + \hat{l} \alpha_s)$ relative to the nonporous case, where α_s is the porosity and $\hat{l}$ is the gas-to-solid ratio of thermal conductivities. Thus, the leading-order ignition time is reduced by one factor reflecting the diminished amount of solid material subjected to the same energy flux, and a second factor proportional to the average rate of diffusive heat transport in the two-phase medium relative to that in the pure solid. Although the second of these factors theoretically could lengthen the ignition time with respect to that of the nonporous material if the gas had a thermal conductivity sufficiently higher than that of the solid, gas conductivities generally are smaller in practice and thus $\hat{l}$ is typically less than unity. The correction to this leading-order result, on the other hand, was shown to provide a small increase in the ignition-delay time resulting from the fact that gas flow out of the porous solid, induced by thermal expansion, removes energy from the system and slows the rate at which the solid is otherwise heated. Both effects were shown to become more significant as the porosity increases. This overall reduction in the ignition time of a porous material relative to its nonporous counterpart at leading order raises safety concerns with respect to degraded energetic materials.

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Figure Captions

Figure 1. Physical description of the problem. A constant energy flux is applied to one surface of a semi-infinite porous energetic solid, leading to thermal runaway (ignition) in finite time.

Figure 2. Schematic illustration of the spatial and temporal regions of interest.

Figure 3. Leading-order gas velocity profile $u_g^{(0)}$ as a function of the spatial coordinate ζ , for several values of time; (a) $\alpha_s = 0.05$, $\hat{l} = 0.9$; (b) $\alpha_s = 0.2$, $\hat{l} = 0.9$.

Figure 4. Correction coefficient $T_I^{(1)}$ in the inert region as a function of ζ for several values of time; (a) $\alpha_s = 0.05$, $\hat{b} = 1.0$; (b) $\alpha_s = 0.4$, $\hat{b} = 1.0$.

Figure 5. Correction coefficient $T_I^{(1)}$ as a function of porosity α_s for two different values of time ($\zeta = 1.0$, $\hat{b} = 1.0$).

Figure 6. Correction coefficient $t_c^{(1)}$ as a function of the porosity α_s , for two values of the gas-to-solid thermal conductivity ratio $\hat{l}$ ($\hat{b} = 1.0$, $Q = 8.0$, $E = 77.5$ and $\hat{A} = 4.72 \times 10^{16}$, where the latter two quantities were calculated from Eq. (1) using the dimensional values $\tilde{E} = 46,200$ cal/mole, $\tilde{T}_0 = 298$ °K, $\tilde{A} = 5 \times 10^{15}$ /sec, $\tilde{\lambda}_s = 5 \times 10^{-4}$ cal/cm/sec/°K, $\tilde{\rho}_s = 1.9$ g/cm³, $\tilde{c}_s = 0.35$ cal/g/°K and $\tilde{q} = 5.0$ cal/cm²/sec).

Figure 1

Figure 2

Figure 3a

Figure 3b

Figure 4a

Figure 4b

Figure 5

Figure 6

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