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by Moshe Matalon

of Engineering Sciences and Applied Mathematics
The Technological Institute
Northwestern University
Evanston, Illinois 60201

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COMBUSTION OF A SOLID PARTICLE

Moshe Matalon

Engineering Sciences and Applied Mathematics
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Northwestern University
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Abstract

We consider the quasi-steady burning of a carbon particle which undergoes gasification at its surface by chemical reactions, followed by a homogeneous reaction in the gas phase. The burning rate $M$ is found as a function of the gas phase Damköhler number $D_g$ for the whole range $0 < D_g < \infty$. The monotonic $M(D_g)$ curve, obtained for relatively very hot or very cold particles, describes the gradual transition from frozen flow to equilibrium. For moderate particle temperatures the transition is abrupt and the $M(D_g)$ curve is either S-shaped or Z-shaped. In the former the burning is enhanced at ignition while in the latter it is slowed down; this depends on the relative importance of the two competitive surface reactions. At extinction, the reverse is true: burning is slowed down in the case of an S curve and is enhanced in the case of a Z curve.

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INTRODUCTION

The current theory of combustion of solid particles is based on the quasi-steady approximation. Accordingly, one assumes a slow rate of change in the particle size and considers a steady burning for a given particle diameter. For definiteness, we consider here the problem of a carbon particle in a quiescent oxidant atmosphere as representing heterogeneous combustion between solid and gas followed by homogeneous burning in the gas-phase.

Two basic models have been proposed [1]: Nusselt [2] assumes that the only oxidation of carbon (C+O_2) occurs at the surface of the particle and Burke and Schumann [3] assumes that carbon is consumed by CO_2 at the surface while the CO thus formed reacts with O_2 at a flame sheet to form CO_2. They have been called the single and double film models respectively. Indeed, they correspond to the limits in which the homogeneous reaction is either frozen (D_g \to 0) or is very fast and equilibrium prevails in the gas phase (D_g \to \infty); here D_g is the Damköhler number. Recently, Matalon [4,5] studied the departure from these limiting cases in order to determine the behavior of the system over a wider range of D_g. Other works on the subject have been cited in the referred papers. The present study gives a complete picture of the process spanning the whole range of parameter values. Starting with the conservation equations of mass and energy governing the combustion process, we look for solutions over the whole range 0 \leq D_g \leq \infty (D_g represents either the particle size or the ambient pressure). Furthermore, the whole parameter plane T_s (surface temperature) - T_\infty (ambient temperature) will be considered and the response of the burning rate M versus D_g will be determined in each case. There
are two different types of response curves (see Fig. 4): the monotonic curve characterized by a unique solution for each $D_g$ (regions II, III) and $S$ or $Z$ curves characterized by multiple solutions for a certain range of $D_g$ (regions I). The monotonic curve describes the gradual transition from a frozen gas phase through partial burning to equilibrium. The $S$ or $Z$ curves, indicate that the transition from weak to strong burning or vice versa, is abrupt (assuming that the middle branch is unstable) so that the system exhibits ignition and extinction phenomena. The various states followed along the curves have been delineated as well as the mode of the combustion along each branch.

Since there are two competitive reactions taking place at the surface of the particle, the ratio of their rates $\gamma$, which is a function of $T_s$ alone, plays a significant role. It determines whether the burning rate for equilibrium flow exceeds that for frozen behavior and as a consequence whether the response curve is $S$ or $Z$ shaped. In the former case the burning rate is enhanced at ignition whereas in the latter it is slowed down (the reverse is true at extinction). It should be emphasized that in the present context ignition/extinction refer only to the homogeneous reaction $\text{CO} + \text{O}_2$; the heterogeneous reactions at the particle surface are continuously active as long as $T_s$ is high enough to make their rate significant.
FORMULATION

We consider a particle which undergoes gasification by surface chemical reactions followed by an exothermic homogeneous reaction in the surrounding gas phase. For a spherical particle and under suitable conditions, the governing equations in the gas phase in a dimensionless form are

\[ L(Y_i) = \beta_i \Omega, \quad i=1,N \]

\[ L(T) = \Omega \]

\[ \sum_{i=1}^{N} Y_i = 1 \]

where \( Y_i \) is the mass fraction of species \( i \) and \( T \) is the temperature. Equation (1) is a mass balance for species \( i \) (\( N \) species are in the mixture), (2) an energy balance and (3) an overall mass conservation. The spherically symmetric operator

\[ L = \frac{M-2r}{r^2} \frac{d}{dr} - \frac{d^2}{dr^2} \]

is convective-diffusive where \( M \) is the burning rate and \( r \) the radial coordinate \( (1 \leq r < \infty) \). The coefficients \( \beta_i \) depend in general on the stochiometric numbers of the specific chemical reactions involved in the process and \( \Omega \) is the rate of the homogeneous reaction. The boundary conditions associated with (1-3) are the given ambient conditions, namely as \( r \to \infty \)

\[ T = T_\infty, \quad Y_i = Y_{i_\infty} \quad \text{for} \quad i=1,N \]

and mass and energy balances at \( r=1 \), which depend of course, on the specific surface chemical reactions.

For definiteness, we treat the case of a carbon sphere in an oxidizing atmosphere which outlines the way other solid fuels could be analyzed.

The surface reactions associated with carbon are the direct oxidation \( 2C + O_2 \to 2CO \) and the indirect reaction \( C + CO_2 \to 2CO \). The carbon
monoxide thus formed may react in the gas phase surrounding the particle according to \( \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \). Therefore, in the present \( N = 4 \) and the subscripts \( i = 1, 4 \) stand for \( \text{CO} \), \( \text{O}_2 \), \( \text{CO}_2 \) and inert respectively. Then the stochiometric coefficients \([4]\) are: \( \beta_1 = - (1 - \alpha) \), \( \beta_2 = - \alpha \), \( \beta_3 = 1 \) and \( \beta_4 = 0 \) where \( \alpha \) is half the molecular weights ratio of \( \text{O}_2 \) to \( \text{CO}_2 \) (\( \alpha = 0.3636 \)). The reaction rate \( \Omega \) becomes

\[
\Omega = D_g \rho^2 Y_1 Y_2^{1/2} \exp (-\theta/T)
\]

where \( D_g \) is the gas phase Damköhler number, \( \rho \) is the mixture density given by \( \rho = 1/T \) and \( \theta \) is the activation energy. For more details on the various assumptions made in this formalism as well as on the dimensionless analysis, reference [4] should be consulted.

The boundary conditions for the \( Y_i \)'s at \( r = 1 \) state that the net mass flux equals the rate of consumption/production per unit area by the surface reactions. Thus

\[
\begin{align*}
MY_1 - Y_1' &= [(1 - \alpha)/\alpha] [D_s Y_2 + 2\alpha D_s Y_3] \\
MY_2 - Y_2' &= -D_s Y_2 \\
MY_3 - Y_3' &= -D_s Y_3 \\
MY_4 - Y_4' &= 0
\end{align*}
\]

where prime ('') denotes differentiation with respect to \( r \), and \( D_s, D_s \) are the surface Damköhler numbers corresponding to the direct and indirect reactions respectively. We assume that the surface temperature of the particle is given, namely

\[
T = T_s \text{ at } r = 1,
\]

rather than writing an energy balance similar to (6). This simplification, made mainly for analytic convenience, can be justified for large
activation energies of the surface reactions which indeed is a realistic assumption in the present case.

There are several parameters involved in the problem: the Damköhler numbers $D_g, D_s$ and $\overline{D}_s$ and the burning rate $M$. Whereas $D_g$ is proportional to $(ap_o)^2$ where $a$ is the radius of the particle and $p_o$ the uniform ambient pressure, $D_s$ and $\overline{D}_s$ are proportional to $ap_o$ but depend on $T_s$ as well. Thus, for a specific set of chemical reactions and for a given $T_s$, all the Damköhler numbers are related. In particular, the ratio $\gamma = D_g / D_s$, is a function of $T_s$ alone. By varying $D_g$ from $0$ to $\infty$, the product $ap_o$ will continuously increase and we may say that $D_g$ controls either the particle size or the ambient pressure. On the other hand, variations in $\gamma$, which measures the relative importance of the surface reactions, are determined explicitly by the surface temperature $T_s$. Our main goal is to determine the burning rate $M$ and its dependence on $D_g$ and $\gamma$.

For the general problem of a solid fuel, the right hand sides of the boundary conditions (6) will be modified to include the relevant surface reactions whereas $\Omega$ will be determined by the rate of the homogeneous reaction. As a consequence there may be several Damköhler numbers, but only two independent parameters: one associated with $ap_o$ and the other with $T_s$. We see that qualitatively the specific case considered contains the essence of the general problem although they may differ in details.

(1) The surface Damköhler number has the form $D_g = k_s \exp(-\theta_s/T)$ where $k_s$ is the pre-exponential factor and $\theta_s$ the surface activation energy. Writing $k_s = \exp(\theta_s/T_s)$ we see that, in the limit $\theta_s \to \infty$, $D_g$ is $O(1)$ when $T = T_s + O(\theta_s)$. Similarly, $\overline{D}_s$ can be treated.
This would not be true for example, if only one surface reaction was considered.
THE PROBLEM

The governing equation (1,2) sum to five second order equations for the five unknowns \( Y_i \) and \( T \). Associated with them are ten boundary conditions (4,6,7). The additional equation (3) serves to determine \( M \). Solutions for the \( Y_i \)'s (i=1,3) and \( T \) involve nonlinear two point boundary value problems coupled among themselves through \( \Omega \). However, not all the equations have to be considered because the system can be simplified as follows.

We start by writing the solution for the inert species

\[
(7) \quad Y_4 = Y_4^\infty \exp(-M/r)
\]

Then, we observe that the source terms can be eliminated from both the equations and the boundary conditions at \( r=1 \), if a proper combination of the mass fractions is chosen. The resulting linear problem, yields

\[
(8) \quad \alpha [Y_1 - Y_1^\infty \exp(-M/r)] + (1-\alpha)[Y_2 - Y_2^\infty \exp(-M/r)] + 2\alpha(1-\alpha)[Y_3 - Y_3^\infty \exp(-M/r) = 0
\]

Using (3) and (7) we obtain a second relation

\[
(9) \quad Y_2 + \alpha Y_3 = \nu^{-1} \exp(M^\infty - M/r)
\]

where \( \nu=(1-2\alpha)/\alpha \) and \( M^\infty = \ln[1+\nu(Y_2^\infty + \alpha Y_3^\infty)] \) have been introduced for convenience. (The notation \( M^\infty \) is based on the results indicating that this value corresponds to the burning rate \( M \) when all Damköhler numbers tend to infinity). Now only one mass fraction equation remains to be solved; the others result from (8) and (9).

If the boundary conditions (6) are now introduced in (9), the relation

\[
(10) \quad D_s Y_2^s + \alpha D_s Y_3^s = \nu^{-1} M
\]
can be derived, where the subscript \( s \) in \( Y_2 \) and \( Y_3 \) denotes the surface values. (at \( r=1 \)), as yet unspecified. It is interesting to note that for the special case \( \gamma=1 \), (9) and (10) yields the transcendental equation

\[
(11) \quad M - \tilde{D}_s \left[ \exp(M_{oo} - M) - 1 \right] = 0
\]

for \( M \). This relation, which has been derived directly from the governing equations, does not involve any approximation; the complete solution however, which will be discussed next for general \( \gamma \), will be based on an asymptotic limit. We will delay the discussion on (11) to a later stage.

To summarize, we address the problem

\[
-\alpha^{-1} L(Y_2) = L(T) = 0
\]

(12) \( M Y_2 - Y_2' = -D_s Y_2 \), \( T = T_s \) at \( r=1 \)

\( Y_2 = Y_2, T = T_\infty \) as \( r \to \infty \),

after which \( Y_3 \) is determined from (9), \( Y_1 \) from (8) and \( M \) from (10).

Considering the limit \( \theta \to \infty \), a realistic approach for many combustion problems [6], we write

\[
(13) \quad \frac{D_g}{D_g} = \tilde{D}_g \exp(\theta/T_c)
\]

and in doing so, define a characteristic temperature \( T_c \), \( \tilde{D}_g \), which is at most algebraically large in \( \theta \), represents the small \( O(\theta^{-1}) \) variations\(^{(2)}\) from \( T_c \) and will be determined in the analysis.

\(^{(2)}\)This can be easily seen if (13) is rewritten in the form

\[
D_g = \exp[\theta/(T_c + \theta^{-1} T_c^2 \ln \tilde{D}_g)]
\].
WEAK BURNING

The limit \( D_\theta \to 0 \) corresponding to a frozen gas phase has been previously analysed [5]. Since \( \Omega \) is negligibly small for all \( r \geq 1 \), the problem (12) reduces to a linear one, and

\[
\phi_i = \phi_i^{\infty} + (\phi_i^{1,3} - \phi_i^{\infty}) \frac{[1-\exp(-M/r)]/[1-\exp(-M)]}{1+(1+D_s/M)(\exp M-1)}
\]

where \( \phi \) stands for either \( T \) or \( Y_i \), \( i=1,3 \). The values \( Y_i \) can be evaluated by applying the boundary conditions; then we obtain the transcendental equation

\[
M - D_s [\exp(M_\infty-M) - 1] + \nu(D_s-D_\infty) \left\{ \frac{Y_i^{1,3}}{1+(1+D_s/M)(\exp M-1)} \right\} = 0
\]

for \( M \). Note that when \( \gamma=1 \), (15) reduces to (11). The dependence of \( M \) on \( D_s \) is shown in Fig. 1 for various values of \( \gamma \). For small \( D_s \), i.e. low surface temperature \( T_s \), the surface reactions are very weak and \( M \to 0 \). The burning rate \( M \) increases with \( D_s \) and tends asymptotically to \( M_\infty \).

According to (13) and in the limit \( \theta \to \infty \) the frozen limit is obtained even for small \( D_\theta \) (not necessarily \( \to 0 \)) provided \( T_c > T \); the reason being that the factor \( \exp(\theta/T_c - \theta/T) \) is then exponentially small everywhere in the flow field. However, when \( T_c \approx \max[T_s,T_\infty] \), or more precisely when \( T_c \) is close to the larger between \( T_s \) or \( T_\infty \) to within \( O(\theta^{-1}) \), there exists a boundary layer either adjacent to the particle or at infinity, where \( \Omega \) cannot be neglected; i.e. a weak reaction develops.

For the case \( T_s > T_\infty \), the solution (14) is valid for \( r > 1 \) and breaks down as the particle surface is reached. Stretching the coordinate near the surface, \( r = 1 + \varepsilon A \cdot \xi \) where \( A = M(T_s - T_\infty)/(\exp M-1) \) and \( \varepsilon = T_s^2 \theta^{-1} \), then writing
\[
T = T_\infty + \xi t + \ldots \quad , \quad Y_i + Y_i - \xi Y_i + \ldots \quad i=1,4 ,
\]
we obtain diffusive-reactive balances in the boundary layer. In particular, the equation for the temperature is

\[
\begin{aligned}
\left\{
\frac{d^2 T}{d\xi^2} + \frac{1}{2} \Lambda \exp(t) &= 0 \\
t(0) &= 0 , \quad dt/d\xi = -1 \quad \text{as} \quad \xi \to -\infty
\end{aligned}
\]

where \( \Lambda = 2Y_1 Y_2 \Delta^{-2} \theta^{-1} \exp(-\theta/T_s) \). Similar equations can be written for the \( \bar{\eta}_i \)'s. As shown in [5] the structure of the reaction zone which can be solved analytically, leads to the equation

\[
(17) \quad M - \frac{Y_2}{Y_1} \left[ \exp(M - M) - 1 \right] + \frac{V(D_s - D_s)}{1 + (1 + D_s/M) \exp(M - M)} = 0
\]

for the burning rate \( M \). We see that two solutions exist for \( \Lambda < 1 \) and none for \( \Lambda > 1 \). In the limit \( \Lambda \to 0 \), one of the solutions reduces to that for a frozen flow (i.e. to equation (15)) while the other tends to a different limit the premixed flame, discussed later. As \( \Lambda \to 1 \), the two distinct solutions coincide and \( \Lambda = 1 \) gives the maximum value of the Damköhler number, namely \( \bar{D}_s \sim \exp(\theta/T_s) \), for which a weak gas phase burning is possible. It is appropriate to mention at this point that \( Y_1 \) and \( Y_2 \), appearing in \( \Lambda \) are defined when writing the complete solution in the boundary layer. Note again that for \( \gamma = 1 \), (17) reduces to (11) as it should. Furthermore, the two values for \( M \) are both higher or both lower than the corresponding value for frozen flow, depending on whether \( \gamma > 1 \) or \( \gamma < 1 \) respectively (see Fig. 2).

For the case \( T_\infty > T_s \) the boundary layer is at \( r = \infty \) so that, in the outer region \( r < \infty \), the solution (14) is valid only to leading order. In particular, when applying the boundary conditions at \( r = 1 \),
we obtain (15) for $M$. The correction to the burning rate comes from
the first order term of the outer solution after matching with the structure of the reaction zone. Stretching the coordinate by $r = \varepsilon^{-1/2} \Delta \cdot R$ where
$$\Delta = M(T_m - T_s)/(1 - \exp(-M))$$
and $\varepsilon = T_m^2 \theta^{-1}$, then writing
$$T = T_\infty + \varepsilon t + \ldots, \quad Y_i = Y_{i,\infty} + \varepsilon \eta_i + \ldots, \quad i=1,4$$
we obtain for the temperature
\[
\begin{cases}
\frac{d^2 t}{dt^2} + \frac{2}{R} \frac{dt}{dR} + \Lambda \exp(t) = 0 \\
\lim_{R \to \infty} t(R) = 0, \quad R^2 \frac{dt}{dR} = 1 \text{ at } R = 0
\end{cases}
\]
where $\Lambda = \left[ T_\infty^4 Y_{1,\infty} Y_{2,\infty} \frac{1}{2} \Delta^2 / \theta^3 \right] D_g \exp(-\theta/T_\infty)$. The condition as $R \to \infty$ reflects the original boundary conditions (4) whereas matching with (14) leads to the condition at $R = 0$. Similar equations to (18) can be written for the $\eta_i$'s; in particular they lead to
\[
\eta_2/\alpha + t = -\left[ 1 + (Y_{2,\infty} - Y_{2, s}) / \alpha(T_\infty - T_s) \right] R^{-1}
\]
and other relations for $\eta_1$ and $\eta_3$.

Now, let us include the first order $O(\varepsilon)$ terms of the outer solution; writing $Y_i + \tilde{\varepsilon}Y_i + \ldots$, $T + \varepsilon T + \ldots$, $M + \varepsilon m + \ldots$, then substituting into (12), we obtain
\[
\begin{cases}
L(\tilde{Y}_2) = m r^{-2} (dY_2/dr) \\
(M + D_s) \tilde{Y}_2' - \tilde{Y}_2 = -mY_2 \text{ at } r = 1 \\
\tilde{Y}_2 = -\alpha c \quad \text{as } r \to \infty
\end{cases}
\]
where the constant $c$ is determined from matching. The solution of the linear problem (20) can be readily written and the value $\tilde{Y}_{2,s}$ obtained in terms of $c$. Then, the correction to the burning rate is given implicitly by
We see that all is needed for the determination of \(m\) is the constant \(c\) which, in the absence of an analytical solution to (18), has to be found numerically. Using the transformation \(\zeta = 1/R\), the equation takes the form \(\zeta'' + \Lambda e^\zeta = 0\) with the conditions \(t(0) = 0\) and \(t = -\zeta + c\) as \(\zeta \to \infty\). We start by prescribing a value to \(c\) and then integrate from large \(\zeta\) down to see whether \(t(0) = 0\). The correct value of \(c\) is determined when both boundary conditions are satisfied. The results indicate that two distinct values for \(c\) exist when \(\Lambda < \Lambda_o\) and none when \(\Lambda > \Lambda_o\); the solution is unique for \(\Lambda = \Lambda_o\) and this critical value is determined numerically. In the limit \(\Lambda \to 0\), one of the solutions is \(t = -1/R\) with \(c = 0\); this corresponds of course, to the frozen limit. The other solution tends to the partial burning flame discussed later.

We find again that \(M(D)\) is double valued for \(D < D^{I}_g\) and the maximum Damköhler number \(D^{I}_g\) depends among others on the numerical constant \(\Lambda_o\); in particular \(D^{I}_g \sim \exp(\Theta/T_\infty)\).
COMPLETE BURNING

The limit $D_s \to \infty$ corresponds to an equilibrium state in which both reactants $CO$ and $O_2$ are completely consumed at a flame sheet standing at a well defined distance from the particle. In [4] it has been shown that for $\overline{D}_s > \overline{D}_s^O$ where $\overline{D}_s^O = M_s/[\exp(M_s-M_s)-1]$ and $M_s = \ln(1+\sqrt{Y_2})/2$ the flame is standing away from the particle at a distance $r_+ = M/M_s$ and the burning rate is given by the same equation as (11). The flame temperature is then

$$T_e = T_s + \left(\frac{Y_2}{\alpha + T_e} - T_e\right)\left(\exp(M-M_s)-1\right)/\left(\exp M - 1\right)$$

where $M$ is the solution of (11). When $\overline{D}_s \to \overline{D}_s^O$, the flame reaches the particle ($r_+ \to 1$), the burning rate $M = M_s$ and $T_e = T_s$. For lower values then $\overline{D}_s^O$, the flame is sitting at the surface, its temperature remains $T_s$ and $M$ is given by

$$M = \overline{D}_s\left(\exp(M_s-M_s)-1\right) + 2(\overline{D}_s - \overline{D}_s^O)(\exp(M_s-M_s)-1) = 0.$$ 

Note the continuous transition in $M$ as $\overline{D}_s$ approaches $\overline{D}_s^O$. The $M(\overline{D}_s)$ curve is identical to the one shown in Fig. 1 for $Y = 1$. For $Y \neq 1$, $M$ depends on $Y$ only for $\overline{D}_s < \overline{D}_s^O$ (see Fig. 5 in [4]) whereas for larger values of $\overline{D}_s$ it follows the same curve as for $Y = 1$ and tends asymptotically to $M_s$.

It is easy to verify that in the limit $\theta \to \infty$ the equilibrium behavior is obtained for large $D_s$ provided $T_c < T_e$; the reason being that the factor $\exp(\theta/T_c - \theta/T_e)$ is then exponentially large and as a consequence $\Omega$ is finite only if $Y_1 Y_2 = 0$ (i.e. both reactants do not coexist in the outer regions). Whether the flame is adjacent to the particle surface or is in the interior of the gas phase, its thickness is exponentially small in $\theta$ and therefore, the product $Y_1 Y_2 = 0$ to all
orders in $\theta^{-1}$. However, when $T_c = T_e + O(\theta^{-1})$, the flame thickness in $O(\theta^{-1})$ and the last conclusion is no longer true; in particular when $r_* \neq 1$, $Y_2 = 0$ for $r < r_*$ only to leading order. The first order term $\epsilon Y_2$, where $\epsilon = T_e^2 \theta^{-1}$, should satisfy the following problem:

\[
(24) \quad L(\tilde{Y}_2) = 0, \quad (M+D_s)\tilde{Y}_2 - \tilde{Y}_2' = 0 \text{ at } r=1, \quad \tilde{Y}_2 = \text{const. at } r=r_*^-,
\]

where the constant at $r=r_*^-$ is determined numerically from the details of the flame structure [4]. In particular, the solution for $\tilde{Y}_2$ leads to the corrected burning rate

\[
(25) \quad M - \epsilon \{\nu(D_s - D_g) \tilde{Y}_2 \left[1 + D_g \exp(M_g - M)\right]^{-1}\}.
\]

When $r_* = 1$, equation (25) is still valid; $\epsilon = T_s^2 \theta^{-1}$ and $\tilde{Y}_2$ is obtained directly from the flame structure problem. In both cases, the evaluation of $\tilde{Y}_2$ indicates that for $D_g > D_g^E$ the solution is double valued and does not exist otherwise. An explicit equation was given in [4] for $D_g^E \sim \exp{(\theta/T_e})$. Thus, the $M(D_g)$ curve has a turning point at $D_g^E$ as in Figure 3. When $D_g \rightarrow \infty$, one of the solutions reduces to the equilibrium limit while the other tends to a partial burning, a case which will be discussed next. The dependence on $\gamma$ is also indicated in Figure 3; the burning rate branches above its equilibrium value when $\gamma > 1$ and below it when $\gamma < 1$. The analysis in [4] was restricted to flame temperatures $T_e$ being the maximum in the flow field. Thus, for a hot particle in a relatively cold ambient, i.e. $T_s > T_\infty$, the requirement $T_s - T_\infty < Y_2/\alpha$ was imposed whereas for a cold particle in a relatively hot ambient, i.e. $T_s < T_\infty$, the requirement is $T_\infty - T_s \leq f(T_s)$. Here, $f(T_s) - 2(\nu \alpha)^{-1} [1 - \exp(M_g - X)]$ and $X(T_s)$ satisfies $X = D_g \left[\exp(M_g - X) - 1\right]$ (the dependence of $X$ on $T_s$ results from $D_g^*$). The solution is therefore restricted to region I of the parameter plane $T_s - T_\infty$ (see Figure 4).
Complete burning will also occur when the particle is extremely hot or cold (regions II & III in Fig. 4), but with a flame temperature $T_\neq T_e$ being an intermediate value in the field. The flame structure in this case is slightly different and the results will be discussed later.
PARTIAL BURNING

Under certain conditions, the flame surrounding the particle consumes only a fraction of the reactant CO and O₂. In this case, the flame temperature T* is not necessarily Tₑ. According to (13), if T* is the maximum in the field then, in the limit θ → ∞, T* = Tₑ and Ω is exponentially small on both sides of the flame. We see in this case that T* is determined explicitly by the Damköhler number D. If the location of the flame is denoted by r* to be specified, then the temperature and mass fraction profiles are given by

\[ \phi = \begin{cases} \phi_s + (\phi_s - \phi_o)(\exp(M/M) - 1)/(\exp(M/M) - 1), & \text{for } r < r_* \\ \phi_o + (\phi_o - \phi_m)(\exp(-M/M) - 1)/(\exp(-M/M) - 1), & \text{for } r > r_* \end{cases} \]

where \( \phi \) stands for either \( Y_i \), i=1,3 or \( T \).

The structure of the flame at \( r_* \) is analysed by first stretching the coordinates according to \( r = r_* + (2/H)\xi \), where \( \xi = T_*^2\theta^{-1} \) and \( H = -[(dT/dr)_{r_*^+} - (dT/dr)_{r_*^-}] \); thus |H| is the magnitude of the jump in the temperature gradients across the flame. Then, perturbing all variables about their values at the flame, namely

\[ T = T_* + \xi(t + \beta_\xi) + \ldots, \quad Y_i = Y_i^* + \xi \eta_i + \ldots, \quad i=1,3, \]

where \( \beta = [(dT/dr)_{r_*^+} - (dT/dr)_{r_*^-}] / H \), the resulting equation is a balance between diffusion and chemical reaction. The reaction term differs significantly whether \( Y_2^* = 0 \) or not; in the former case it will take the form \( -\Lambda \eta_2^{\frac{1}{2}} \exp(t + \beta \xi) \) whereas in the latter \( \eta_2(\xi) \) will be replaced by the constant \( Y_2^* \neq 0 \). When, both \( Y_1^* = Y_2^* = 0 \) the complete burning structure is recovered.
We consider first the case for which $Y_2^* = 0$. This condition implies that $Y_2 = 0$ for $r < r_\star$, and provides a formula for $r_\star$ given by

$$r_\star = M/\ln\left\{ (T_\infty Y_2^* / \alpha - T_s) / [T_\star - T_s + (T_\infty Y_2^* / \alpha - T_\star) \exp(-M)] \right\}.$$  

Now $Y_1^*$ and $Y_3^*$ can be readily obtained from (8), (9) and (27). Indeed $Y_2^* = 0$ and from (9), $Y_3^* = \exp(M_\infty - M)/(1 - 2\alpha)$, which gives once more the equation (11) for $M$. In writing the governing equation of the structure problem, we note that both $t$ and $\eta_2/\alpha$ satisfy identical equations and, in particular, $t + \eta_2/\alpha = \xi$ is obtained after matching with the outer solutions. Then

$$\begin{align*}
\frac{d^2 t}{d\xi^2} &= -\Lambda(\xi-t)^{3/2}\exp(t+\beta \xi) \\
\frac{dt}{d\xi} &= \pm 1 & &\text{as } \xi \to \pm \infty
\end{align*}$$

where $\Lambda = (4\alpha Y_1^* T_\infty H^{-3/2})^{3/2}$. An analytical solution to (28) is not available so that a numerical integration is necessary. Using a shooting technique we start with $t = \xi + \text{const.}$ at large negative $\xi$ and integrate out to large positive $\xi$ to see whether $dt/d\xi = -1$ as required. The constant, determined when both boundary conditions are satisfied, equals

$$\alpha^{-1} \lim_{\xi \to -\infty} \eta_2(\xi);$$

a value needed for matching as will be discussed next.

In order to find the $O(\xi)$ correction to $M$, we consider the first order terms of the outer solution. In particular, the $O_2$ mass fraction for $r < r_\star$ takes the form $\psi Y_2$. The function $\tilde{Y}_2$ should satisfy the same equation as (24) except that now the constant at $r_\star$ is $\lim_{\xi \to -\infty} \eta_2(\xi)$ obtained numerically from (28). After evaluating $\tilde{Y}_2$ the corrected burning rate follows from (25). Before discussing the numerical results, we note that after multiplying (23) by $dt/d\xi + \beta$ and integrating from $\xi = -\infty$.
to $\xi = +\infty$ while making use of the boundary conditions, we obtain the restriction: $\beta > 0$. This requirement is equivalent to $T_\ast > T_\infty + Y_2 \alpha / 2 \alpha$.

Another requirement comes from the assumption $Y_1^* \neq 0$ which translates to $T_\ast < T_e$. Thus, the solution is restricted to $T_\ast$ satisfying $T_\infty + Y_2 \alpha / 2 \alpha < T_\ast < T_e$, or equivalently for a corresponding range of $D_s$. For such values equation (28) has been integrated as indicated above and a unique solution was found for each $D_s$; then the curve $M(D_s)$ has a unique branch in this range.

The next case under consideration is when both $Y_1^*$ and $Y_2^*$ are $O(1)$. As indicated previously, $T_2 \frac{1}{2}$ in the reaction term is now replaced by the constant $(Y_2^*) \frac{1}{2}$ and as a consequence $\tilde{\Lambda} = (Y_2^* \alpha / T_\ast^2)^{\frac{1}{2}}$ replaces $\Lambda$; then a first integration of the governing equation leads to $\beta = o(3)$. This condition states that $(dT/dr)_{r=+}^r$ and $(dT/dr)_{r=-}^r$ have the same magnitude but opposite signs. When applied, this condition provides a formula for $r_\ast$, namely

$$
(29) \quad r_\ast = M/\ln\left(\frac{T_\ast - T_\infty}{(T_\ast - T_\infty) + (T_e - T_\ast)\exp(-M)}\right),
$$

after which $Y_i^*$, $i=1,3$ can be easily evaluated. The boundary conditions at $r=1$ determine the $Y_i$'s and $M$ is obtained from

$$
(30) \quad M - D_s \left[ \exp(M_\infty - M) - 1 \right] + \nu(D_s - D_s) \left\{ \frac{Y_2 \alpha - 2 \alpha (T_\ast - T_\infty)}{1 + (1 + D_s / M) \exp(M - 1)} \right\} = 0.
$$

Although one can proceed in calculating the first order correction to $M$ with no conceptual difficulties, there is no immediate need for such an improvement presently because, unlike previous cases, the leading order of $M$ given by (30) establishes the dependence of $M$ on $D_s$, $D_s$ as well

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(3) An analytical solution for the structure problem can be written in this case (e.g. see [7]) but such details will not be discussed in the present.
as on $D_g$ (through $T_\infty$). Note that the only condition we have required in deriving (30) is that both reactants do not vanish at the flame which can also be written as $T_\infty < T_\infty + Y_2/2$. Therefore, the $M(D_g)$ curve thus obtained is restricted to a certain range of $D_g$ corresponding to $\max[T_s, T_\infty] < T_\infty < T_\infty + Y_2/2$.

Partial burning will also occur when the particle is extremely hot or cold (regions II & III in Fig. 4), but the flame temperature in this case is at an intermediate value between $T_s$ and $T_\infty$. The resulting response will be discussed later.
RESPONSE CURVES

In constructing the response of \( M \) versus \( D_g \), we consider first region Ia in the parameter plane \( T_s - T_m \) (see Fig. 4). Starting with small values of \( D_g \), the gas phase is completely frozen and \( M \) increases with \( D_g \) according to (15). Indeed, the burning rate is controlled only by the surface reactions. By slightly increasing \( D_g \), a weak reaction \( \text{CO} + \text{O}_2 \) develops in a boundary layer adjacent to the particle surface (because \( T_s > T_m \)). Now \( M \) is given by one of the solutions of (17) corresponding to the minus sign in front of the square root. The burning rate exceeds its frozen value or is below it, depending on whether \( \gamma \) is greater or less than one, respectively. This behavior persists until the values \( D_g^I \) is reached (or \( \Lambda \) in (17) becomes 1). The response then follows the second solution of (17) while \( D_g \) decreases below \( D_g^I \). Therefore, \( D_g^I \) marks a turning point of the response curve. This second branch tends eventually to a partial burning flame obtained when \( \Lambda \to 0 \) in (17) or, on the other hand, when \( T_* = T_s \) in (30). The flame in this limit is adjacent to the particle as suggested by (29). The Damköhler number \( D_g \) can be further decreased as \( T_* \) increases from \( T_s \) to \( T_e \). The flame, which first consumes only a small portion of the reactants \( \text{CO} \) and \( \text{O}_2 \), moves away from the particle according to (29), uses more of the reactants and its temperature \( T_* \) increases, simultaneously. The burning rate is now given by (30). When the intermediate value \( T_* = T_m + Y_2/2 \alpha \) is reached all the oxygen is consumed at the flame (\( Y_2^* = 0 \)) and (30) for \( M \) reduces to (11)\(^4\).

\(^4\)Although the correction to the burning rate has to be added to \( M \) obtained from (11) as described earlier, the leading term in this case is only slightly perturbed and therefore determines the main behavior of the curve. This is not so when complete burning occurs.
Although all the oxygen is depleted at the flame, only a fraction of CO is burnt and $Y_1^* \neq 0$. This behavior persists while decreasing $D_g$ until $T_\ast \approx T_e$; in this limit a complete burning of reactants take place. Now, the flame is at $r_\ast = M/M_s$ and the corrected burning rate given by (25) is double valued for all $D_g < D^E_g$. Thus, we first follow one of the branches down to $D^E_g$ which marks a turning point in the response curve. Then increasing $D_g$ again, the other solution of (25) takes over; now the Damköhler number can be increased indefinitely and the burning rate tends asymptotically to $M_\infty$. Along the branches resulting from complete burning, the flame temperature remains at most within $O(\theta^{-1})$ from $T_e$ and the flames moves $O(\theta^{-1})$ distances from $r_\ast = M/M_s$. Note that for $\gamma > 1$, $M$ approaches the equilibrium limit from below whereas for $\gamma < 1$ it approaches this limit from above.

In region Ib, the construction of the response curve follows the same outlines indicated previously. However, the physical states followed along the curve are slightly different. Since her $T_\infty > T_s$, the reaction $CO + O_2$ starts being active at large distances from the particle until $D^I_g$ is reached, then by decreasing $D_g$, the weak burning tends to partial burning and a flame thus formed moves towards the particle. The flame temperature $T_\ast$ increases from $T_\infty$ up to $T_e$ along this branch and when complete burning is achieved the flame is located at $r_\ast = M/M_s$. Reaching the point $D^E_g$, the Damköhler number can be only increased again and now indefinitely, so that in the limit $D_g \to \infty$, the burning rate tends to $M_\infty$.

The response curves in region I are characterized by having multiple solutions for $D^E_g < D_g < D^I_g$, because

$$D^E_g \sim \exp(\theta/T_e), \quad D^I_g \sim \begin{cases} \exp(\theta/T_s), & \text{for } T_s > T_\infty \\ \exp(\theta/T_\infty), & \text{for } T_\infty > T_s \end{cases}$$
and therefore $D_g^I$ always exceeds $D_g^E$ in this region. It is generally believed that the middle branch is unstable and therefore the corresponding states cannot be realized physically. Some evidence are found in [8] and [9] for example. Indeed the concepts of ignition and extinction depend on these facts. For, if $D_g$ is slowly increased the weak burning solution is followed up to $D_g^I$ where the response jumps to the complete burning solution and it follows that as $D_g$ is increased further. Thus, $D_g^I$ marks the gas-phase ignition. Similarly, $D_g^E$ is the extinction value since the response jumps from a complete burning to a nearly frozen flow.

The parameter $\gamma$, representing the relative importance of the two competitive surface reactions, is a function of $T_s$ alone. Thus, assuming $\gamma > 1$ for large $T_s$ (suggested by various experimental data reported in the literature), the parameter plane $T_s - T_\infty$ is divided as in Fig. 4. When $\gamma < 1$ (see Fig. 1), $M$ for frozen flow is lower than $M$ for equilibrium and the response curve is S-shaped. As $\gamma$ approaches one from below, the middle branch of the S curve coalesce to a single monotonic curve which represents both the frozen and equilibrium limits. Although the three distinct solutions in the range $D_g^E < D_g < D_g^I$ have the same value for $M$, they still differ in details. They have a different flame temperature, consume different portion of reactants and the flame is located at different positions. As $\gamma$ increases slightly above one, $M$ takes again different values for each of the three solutions but now the upper and lower branches change their roles. The response curve is now z-shaped. Thus depending on whether $\gamma$ is less or greater than one, the jump at ignition occurs from a lower to a higher $M$ and vice versa, respectively. The reverse is true at extinction.
When \( \gamma = 1 \), the burning rate varies continuously along the curve but a jump in the flame temperature, from \( T_s \) (or \( T_e \)) to \( T_e \) occurs at ignition while the flame suddenly appears at \( r_* = M/M_s \). The reverse situation occurs at extinction.

Finally, we will discuss the extreme cases of a very hot (region II in Fig. 4) particle. When \( T_s > T_\infty + Y_2 \omega / \alpha \), the weak burning solution is no longer double valued because one of the solutions of (17) (namely that with the + sign) gives rise to \( Y_2 < 0 \) and is not physically acceptable. Furthermore, its structure differs slightly at an intermediate value of \( \Lambda < 1 \) as \( Y_2 \) vanishes and remains so as \( \Lambda \) increases towards 1. The only change in (17) is the replacement of the last \( O(1) \) term on the right hand side by an \( O(T_s^{-2}g^{-1}) \) term. Here \( D_g \) can be increased beyond \( D_g \) and the resulting partial burning flame with complete oxygen depletion (\( Y_2^* = 0 \)), moves away from the particle and its temperature \( T_* \) is lowered (5) below \( T_s \). While increasing \( D_g \) further, a point is reached where \( Y_1^* = 0 \), i.e. now the CO is also completely depleted at the flame. Both the partial and the complete burning flames obtained in this case differ slightly from those discussed previously. No leakage of \( O_2 \) is allowed through the flame and \( Y_2 \equiv 0 \) for \( r < r_* \) to all orders. As a consequence the burning rate \( M \) is given by (11) to all orders in \( g^{-1} \). Furthermore, the structure of the complete burning flame is unique (6) leading to a single branch of the response.

(5) Although \( T_* \) is no longer the maximum temperature in the field, \( G \) is still negligibly small on both sides of the flame because \( T > T_* \) either \( Y_1 \) or \( Y_2 \) vanish identically to all orders, whereas for \( T < T_* \) the previous argument holds.

(6) In [4] the structure was discussed only for \(|g| < 1 \) and the solution was double valued. For \(|g| > 1 \), a unique solution exists for all \( \Lambda \).
The $M(D_g)$ curve obtained now is a monotonic curve which tends asymptotically to $M_\infty$.

In region III, the response is again monotonic but now, the partial burning flame originating at infinity is of a different type. CO is totally consumed at the flame ($Y_1^* = 0$) but oxygen is not. As $D_g$ increases and the flame approaches the particle, the flame temperature $T_*$ is lowered below $T_\infty$ until a point is reached where $Y_2^*$ also vanishes. The complete burning thus obtained does not allow any CO leakage, but $O_2$ can leak through and as a consequence $M$ is given by (11) to leading order. The $O(\epsilon^{-1})$ correction is unique, leading to a single branch of the response curve. The $M(D_g)$ curve is again a monotonic curve.

In summary, two distinct response curves are found. The monotonic curve obtained in regions II and III, show the gradual transition from a frozen gas phase through partial burning to equilibrium, as $D_g$ increases (by increasing the particle size for example). The reason for such a smooth behavior is due to the excess of heat provided either by the particle or by the ambient. For moderate values of $T_g$ and $T_\infty$ the process is described by the $S$ or $Z$ responses (region I), which exhibit the phenomenon of ignition and extinction. A flame is suddenly ignited as $D_g$ increases slightly above $D_g^I$ and is extinguished as $D_g$ decreases slightly below $D_g^E$. The transition from frozen gas phase to equilibrium is abrupt in this case.
References


The solution of equation (11) for various values of $\gamma$; calculated for representative values of the ambient conditions:

$$Y_1 = 0.05, \quad Y_2 = 0.3, \quad Y_3 = 0.2$$

The weak burning solution: (a) for $Y > 1$, (b) for $Y < 1$; calculated for $T_s > T_\infty$ and for representative values of the other parameters.

Here $\tilde{D}_g = D_0 \exp(-\beta/T_s)$.

The complete burning solution: (a) for $Y > 1$, (b) for $Y < 1$; calculated for some representative values.

The response curves in the different regions of the parameter plane $T_s - T_\infty$. The broken lines with the $F, E$ notation represent the frozen and equilibrium limits, respectively. $D^{I}_g$ and $D^{E}_g$ are the ignition and extinction Damköhler numbers respectively.