The Inability of Heterogeneously Reacting Particles to Ignite Below a Critical Size

Michael Soo[1], Samuel Goroshin[1], James Lightstone[2], David L. Frost[1], and Jeffrey M. Bergthorson[1]
[1]McGill University, Montreal, QC
[2]Naval Surface Warfare Center, Indian Head EOD Technology Division

1 Introduction

The word *ignition* is often used colloquially to describe the initiation of a reaction leading to self-sustained combustion in an energetic material or condensed-phase fuel system. In the context of the combustion of particles in gaseous suspensions, however, *ignition* has a precise definition that is often misconstrued as a general term for the initiation of reaction. Ignition for a particle is classically defined as the critical transition from a regime where the reaction rate is controlled mainly by kinetics to a regime controlled mainly by diffusion [1].

For many solid fuel particles, ignition behavior is, arguably, heterogeneous in nature. Refractory materials such as carbon, boron, and some metals have relatively high volatilization temperatures, and the reactions of metal gases with several oxidizers are nearly unactivated [2]. As a result, vapors from metals even with relatively low boiling points cannot premix significantly with oxidizer and will burn either heterogeneously at the particle surface or in a diffusion micro-flame eveloping the particle. Accordingly, the basic behaviors of metal particle ignition can be understood from the classic theory of heterogeneous ignition [3]. The simplicity of the model makes it a valuable tool for developing an intuition of the expected changes in the ignition and combustion behavior as a function of the various physical and chemical properties of the fuel and oxidizing gas.

Heterogeneous ignition theory is an extension of non-adiabatic Semenov thermal explosion theory [4], and was first applied by Vulis [3] and Frank-Kamenetskii [1] to study coal char particle combustion. The primary appeal of the theory is the possibility of understanding the critical transitions, between the kinetic and diffusion combustion regimes, by examining the heat generation and heat loss functions, without examining the transient processes.

One particularly useful variation on the heterogeneous ignition analysis, outlined by Vulis [3], is the determination of steady-state particle temperature as a function of the initial temperature of the gas. This *thermal regimes* analysis is of practical value because realistic fuel systems of dispersed particles may experience a range of gas temperatures. Using the steady thermal regimes analysis, it can be clearly shown that, as the initial particle size approaches a critical value, the phenomenon of ignition will degenerate. Below this critical size, the notion of characteristic measurable quantities like ignition temperature and ignition delay for individual particles are ill-defined since there is no clear critical transition from kinetic to diffusion regimes

Correspondence to: michael.soo@mail.mcgill.ca

that classically indicate *ignition*. The purpose of this paper is to show the utility of the steady thermal regimes analysis to understand this phenomenon and to find an expression for the critical particle size where ignition becomes impossible.

2 Thermal Limits of Reaction

Following the approach to heterogeneous ignition first outlined by Vulis [3] and Frank-Kamenetskii [1], the overall reaction rate of a heterogeneously burning single particle in an oxidizing gas is governed by the interplay between oxidizer transport to the particle surface and the kinetic reaction rate at the particle surface. For simplicity, the following assumptions are made: (i) the particle is spherical, (ii) the Biot number is small, (iii) the contributions of Stefan flow are negligible, and (iv) the quasi-steady-state approximation is used to determine the heterogeneous reaction rate and accounts for the rate of chemical reaction at the particle surface and the rate of oxidizer transport. This approximation is useful since the concentration of oxidizer at the particle surface does not need to be explicitly determined. In the case where the surface reaction rate follows single-step, first-order Arrhenius kinetics, the effective reaction rate can be expressed in terms of the combined diffusion and kinetic terms as

$$\dot{\omega}_{\text{eff}} = \frac{k\beta}{k+\beta} C_0 \tag{1}$$

where $\dot{\omega}_{\text{eff}}$ is the mass of particle reacting per unit surface area per unit time, and C_0 is the concentration of oxidizer in the bulk gas far from the particle surface. The kinetic term k is given by the Arrhenius expression shown in Eq. 2, and β is the mass transfer coefficient between the particle and the gas. In the absence of Stefan flow, the mass transfer coefficient takes the simple form shown in Eq. 3.

$$k = \kappa_0 \exp(-E_{\text{a}}/R_{\text{u}}T_{\text{s}}) \tag{2}$$

$$\beta = \text{Sh}\mathcal{D}/2\text{r}_0 \tag{3}$$

In Eq. 2, κ_0 is the pre-exponential factor, E_{a} is the activation energy, R_{u} is the universal gas constant, and T_{s} is the particle temperature. In Eq. 3, $\mathcal{D}$ denotes the oxidizer diffusivity at the particle-gas interface, and r_0 is the particle radius. For a spherical particle that is stationary relative to the gas, the exact solution to the steady-state spherical diffusion equation yields a Sherwood number (Sh) equal to 2.

The resulting expression for the heat release rate, assuming a stoichiometric mass coefficient of unity for the particle fuel and oxidizer, is shown in Eq. 4. For simplicity, molecular conductivity is assumed to be the dominant mechanism of heat loss from the particle, and the heat loss rate is described by the expression in Eq. 5.

$$\dot{Q}_{\text{R}} = qA\dot{\omega}_{\text{eff}} = qA\frac{k\beta}{k+\beta}C_0 \tag{4}$$

$$\dot{Q}_{\text{L}} = hA(T_s - T_g) \tag{5}$$

In Eq. 4, q is the heat of reaction and A is the particle surface area. In Eq. 5, T_{g} is the bulk gas temperature, and the heat transfer coefficient for a spherical particle is $h = \text{Nu}\lambda/2r_0$ where λ is the interfacial thermal conductivity and the Nusselt number (Nu) is equal to 2 for conditions of a spherical particle stationary relative to the gas.

In order to determine steady states, the heat generation rate $\dot{Q}_{\text{R}}$ in Eq. 4 is set equal to the heat loss rate $\dot{Q}_{\text{L}}$ in Eq. 5.The resulting expression can be rearranged to find the difference between the particle temperature and the gas temperature as

$$T_\mathrm{s} - T_\mathrm{g} = \frac{D}{\alpha}\left(\frac{k(T_\mathrm{s})}{k(T_\mathrm{s}) + \beta(r)}\right)\frac{qC_0}{c_\mathrm{g}\rho_\mathrm{g}} \tag{6}$$

expressed in terms of the thermal diffusivity of the gas $\alpha = \lambda/\rho_\mathrm{g}c_\mathrm{g}$ where ρ_g and c_g are the density and the heat capacity of the gas respectively. For simplicity of the analysis, the Lewis number Le=α/D is assumed to be unity.

Written in this way, it is clear that the relative values of the particle-temperature-dependent k term and particle-size-dependent β term will alter the steady state temperature of the particle compared to the gas temperature. The competition between these two terms admits two asymptotic temperature states. As diffusive rates become fast compared to kinetic rates ($\beta \gg k$), the temperature separation of the particle and gas approaches zero and the particle and gas will assume the same temperature $T_\mathrm{s} = T_\mathrm{g}$. In this limit, the reaction rate is considered to be at the *kinetic limit*.

When kinetic rates are fast compared to diffusive rates ($k \gg \beta$), the particle temperature is

$$T_\mathrm{s} = T_\mathrm{g} + \frac{qC_0}{c_\mathrm{g}\rho_\mathrm{g}} = T_\mathrm{stoich} \tag{7}$$

This maximum particle temperature, assuming a Lewis number of unity, is equivalent to the flame temperature of the stoichiometric mixture of particles and gas T_stoich, assuming a negligible contribution of the reaction products to the overall heat capacity of the mixture [1]. In this temperature, the reaction is considered to be at the *diffusion limit*.

3 Thermal Regime S-Curve Analysis

In practice, the asymptotic kinetic and diffusion limits of particle combustion are never fully realized, and the particle will reach some intermediate temperature state. This is illustrated by solving Eq. 6 to map the steady-state particle temperature as a function of the initial gas temperature. This is of practical value for understanding systems where dispersed particles may experience an externally imposed gas temperature such as in a flame or shock tube [5, 6].

The qualitative solutions to Eq. 6 for several different initial particle sizes are shown in Fig. 1. The temperatures are normalized to the stoichiometric, adiabatic temperature in Eq. 7. The kinetic and diffusion rate resistances produce S-curve forms which are also observed in the analysis of well-stirred reactors [7]. The upper branch of the S-curve, close to the diffusion limit on Fig. 1, is termed the *diffusion regime*. The lower branch, close to the kinetic limit, is termed the *kinetic regime*. The S-curve analysis shows that at some critical gas temperature, labeled point *I* on curve 2 in Fig. 1, the stable temperature state of the particle shifts discontinuously from the kinetic regime up to a stable point in the diffusion regime, and is what is classically defined as particle ignition. This is marked by a large increase in particle temperature compared to the gas. The critical gas temperature at which ignition can occur is termed the *ignition temperature*.

The extinction point, labeled point *E* on curve 2 in Fig. 1, is the critical point at which the reverse transition from the diffusion to the kinetic regime occurs. It is noted that the extinction temperature will always be lower than the ignition temperature, which implies that, after particle ignition, the burning rate is somewhat resistant to changes in the temperature of the surrounding medium.

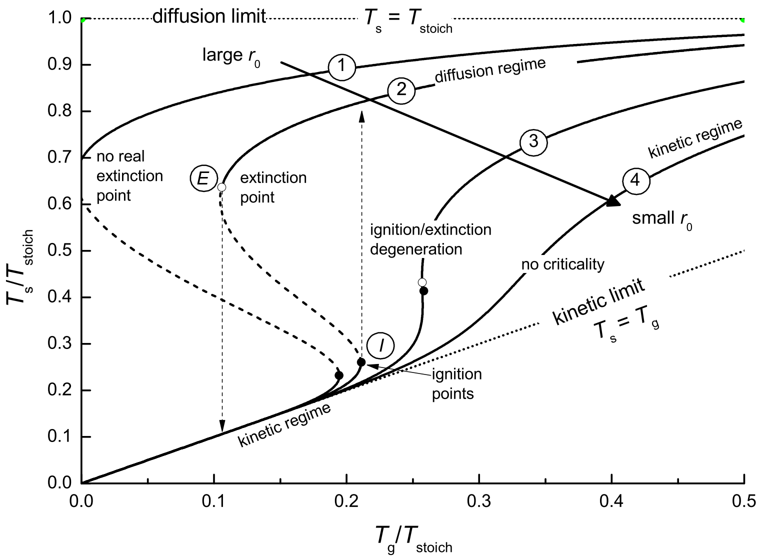

Figure 1: S-curves for a range of particle sizes. At a critical size, ignition degenerates, and the particle reaction is limited to the kinetic regime. Dashed portions of the S-curves represent unstable solutions.

The underlying assumption in many experimental studies that focus on the combustion of single particles is that, after ignition, the gas temperature of the medium has little effect on the reaction rates of the particles. The degree to which this assumption is true is a function of the various physical and chemical properties of the particle and oxidizing gas mixture. In particular, it is of interest to determine how particle size affects this assumption, as it is an adjustable parameter in practical fuel systems.

For larger particles shown on curve 1 of Fig. 1, the gas temperature at which ignition occurs is lower than for smaller particles, the maximum temperature is closer to the diffusive limit, and the extinction points may not be physical[1]. This implies that, for a large enough particle, a significant portion of the combustion occurs near the diffusion limit, and it is more likely that the particle will not be able to reach the extinction point, until very close to burnout [8]. After ignition, a large particle burning near asymptotic diffusion limit has a reaction rate essentially independent of any changes to surrounding gas temperature.

As initial particle sizes decreases, as shown for curve 2 on Fig. 1, the ignition and extinction temperature points begin to move closer together. This suggests that, after ignition, a changing gas temperature can possibly alter the burning state during combustion, shifting the particle from the diffusion regime back to the kinetic regime. It is also important to note that even after ignition and transition to the diffusion regime, the particle temperature departs significantly from the diffusion limit. Particles in this size range will burn transiently in *mixed* diffusion and kinetic regimes of combustion as demonstrated in previous studies [8].

For some critical particle size shown for curve 3 on Fig. 1, the ignition and extinction points coincide, leading to the degeneration of the ignition phenomenon. At this critical size, the criticalities of ignition and extinction, leading to discontinuous stable-state transitions, will disappear, and the particle temperature will be a continuous function of the gas temperature. In this case, the boundaries between the diffusion and

---

[1] A non-physical solution would occur when the absolute extinction temperature is negative.

kinetic regimes becomes ill-defined.

After the degeneration of ignition, the particle will no longer be able to burn as a micro-diffusion reactor with a reaction rate isolated from changes in the gas temperature. This behavior is, overall, more consistent with the description of the kinetic regime than the diffusion regime. Therefore, after ignition degeneration occurs, the entire stretched S-curve is considered to be in the kinetic regime as shown for curves 3 and 4 on Fig. 1.

Even in this redefined kinetic regime, it is important to note that the temperature of the particle can still overshoot the gas temperature by some degree. However, this temperature separation will be a continuous function of the gas temperature, and no critical gas temperature exists.

4 Critical Particle Size for Ignition Degeneration

The critcal particle size at which ignition degenerates can be determined from classic heterogeneous ignition theory. As shown by Vulis [3] and Yarin and Hestroni [9], the solution for the particle temperature that satisfies the Semenov particle ignition criteria ($\dot{Q}_\mathrm{R} = \dot{Q}_\mathrm{L}$ and $\mathrm{d\dot{Q}_R/dT_s = d\dot{Q}_L/dT_s}$) is a quadratic formula which generally admits the two solutions of ignition and extinction. However, it is clear that in order for ignition and extinction to exist, the discriminant must have a positive, real value.

The critical gas $T_\text{g,degen}$ and particle temperature $T_\text{s,degen}$ at the point of degeneration can then be determined from the zero-valued discriminant condition of the quadratic solution. Discarding the non-physical, negative values of temperature, the critical temperatures are found to be

$$T_\text{g, degen} = \frac{E_\mathrm{a}}{R_\mathrm{u}} \frac{\sqrt{\Omega(\Omega+\mathrm{Le})} - \Omega}{2\mathrm{Le}} \quad (8) \qquad T_\text{s, degen} = \frac{E_\mathrm{a}}{R_\mathrm{u}} \frac{\sqrt{\Omega(\Omega+\mathrm{Le})}}{2\Omega + 2\mathrm{Le}} \quad (9)$$

where the term $\Omega = qC_0R_\mathrm{u}/c_\mathrm{g}\rho_\mathrm{g}E_\mathrm{a}$ is a non-dimensional number relating the potential heat release to the activation energy and Le is the Lewis number. Notably, these critical temperatures are characteristics of the fuel and oxidizer mixture and independent of particle size.

By inserting the value from Eqs. 8 and 9 into the first Semenov condition ($\dot{Q}_\mathrm{R} = \dot{Q}_\mathrm{L}$), a solution for the minimum particle size where the critical conditions can be satisfied at a real initial gas temperature for $\mathrm{Le} = 1$ is found to be

$$r_\text{0,cr} = r_n \left(2\Omega - 2\sqrt{\Omega(\Omega+1)} + 1\right) \exp\left(2\sqrt{\tfrac{\Omega+1}{\Omega}}\right) \quad (10)$$

where $r_\mathrm{n} = \mathcal{D}/\kappa_0$ is a chracteristic length scale of the problem related to the interplay between reaction and diffusion processes. This expression permits the calculation, from first principles, of the critical particle size where the ignition phenomenon degenerates and the particle burns strictly in the kinetic regime. Particle sizes within the range of this critical size would be expected to have a burning behavior that depends non-trivially on the kinetics, and the assumption of burning in the *diffusion limit* can no longer be justified. Within this size range, ignition may still occur, but subsequent extinction or transition back to the kinetic regime may control the burning behavoir significantly [8]. This is important for the interpretation of experimental data and to assess the range of validity for combustion models that suppose asymptotic regimes of combustion. The critical size may be large for small values of Ω, where the activation energy is large compared to the heat release.

5 Conclusion

Historically, the majority of research on heterogeneous combustion has focused on experimental and theoretical studies of ignition and combustion of relatively large, isolated particles in the range of tens to hundreds of microns. While the reaction of large particles is typically transport controlled, smaller particles may shift to a radically different reaction regime controlled by kinetics. The thermal regimes analysis presented in this paper demonstrates that ignition of isolated, small particles that burn in the kinetic regime is not possible due to the degeneration of the ignition phenomenon at a critical particle size. An extension of classic heterogeneous particle ignition theory reveals that the critical size is a function of the fuel kinetic parameters, the oxidizer diffusivity and concentration, the gas density and heat capacity, and the specific heat release of the fuel-oxidizer reaction.

References

[1] Frank-Kamenetskii, DA. (1969). Diffusion and Heat Transfer in Chemical Kinetics. Plenum Press, New York. ISBN 9780306303494.

[2] Fontijn, A, Felder, W, Houghton, JJ. (1977). HTFFR kinetics studies. Temperature dependence of Al/O_2 and AlO/O_2 kinetics from 300 to 1700/1400 K. Symp. (Int.) Combust. 16(1): 871.

[3] Vulis, LA. (1961). Thermal Regimes of Combustion. McGraw-Hill, New York.

[4] Semenov, NN. (1935). Chemical Kinetics and Chain Reactions. Clarendon Press, Oxford.

[5] Friedman, R, Maček, A. (1962). Ignition and combustion of aluminium particles in hot ambient gases. Combust. Flame 6: 9.

[6] Servaites, J, Krier, H, Melcher, JC, Burton, RL. (2001). Ignition and combustion of aluminum particles in shocked $H_2O/O_2/Ar$ and $CO_2/O_2/Ar$ mixtures. Combust. Flame 125(1-2): 1040.

[7] Law, CK. (2006). Combustion Physics. Cambridge University Press. ISBN 978-0521870528.

[8] Soo, M, Goroshin, S, Bergthorson, JM, Frost, DL. (2015). Reaction of a particle suspension in a rapidly-heated oxidizing gas. Propellants, Explos. Pyrotech. 40(4): 604.

[9] Yarin, LP, Hetsroni, G. (2004). Combustion of Two-Phase Reactive Media. Springer. ISBN 9783540403395.