Modeling Transitional Burning Modes of Aluminum Particles

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Aluminum particle burn-rates are known to be a strong function of particle size because the mode of combustion transitions from diffusion to kinetics controlled. To better understand the rate dependent diffusion and kinetic processes, a mixture fraction based particle burn model is developed. In this approach, the vapor phase equations are first recast in terms of mixture fraction space. The appeal of this formulation is it allows for computationally efficient solutions of the flame eigenvalue problem. Several cases are explored using the newly developed model for the burning of Al particles in air, carbon-dioxide and water-vapor environments. Predictions of burn-rates vs. particle size, reveal significant deviations from a diffusion control limited - highlighting the importance of accounting for finite-rate chemistry in modeling the burning of sub-micron Al particles. Lastly, estimates of flame speed are compared to experimental data for aluminum particle dust in air revealing a maximum in flame speed with decreasing particle size.

1 Introduction

The use of aluminum particles continues to be of interest as an additive for propellants [1] and aviation fuels [2, 3] to increase energy density and specific impulse. Recent studies have focused on the transition of diffusion to kinetically controlled burning with decreasing particle size [4–6]. One of the primary motivations for developing a better understanding of this transition is the desire to use sub-micron to nano-scale sized particles in fuels to shorten ignition times [7] and accelerate flame speeds [5].

The transition of diffusion to kinetically controlled combustion was studied by Bazyn \textit{et al.} as a function of both particle size and pressure using a reflected shock-tube facility for $O_2$ and $CO_2$ environments [4]. For a pressure of $8.5 \text{ atm}$, the limit of a diffusion flame was observed to occur for a particle sizes less than $\sim 20$ microns as reactions migrate closer to the droplet surface.

Aluminum particle combustion in the $2 - 20$ micron range was studied by Dreizin \textit{et al.} using an electro-static aerosol generator and ignited with a $CO_2$ laser [8]. Using $AlO$ emission measurements to determine burn-times and average temperatures, Dreizin \textit{et al.} estimated the transition from diffusion to kinetically controlled combustion occurred at $\sim 10$ microns in air.

Washburn \textit{et al.} conducted detailed numerical simulations of aluminum particles in oxygen, carbon dioxide and steam environments [6, 9]. Cases were conducted using $3 - 11$ micron sized particles
and compared to burn-time data from Bazyn et al. [4]. Overall agreement was reasonable with some discrepancies observed for pressures below $\sim 10$ atm in CO$_2$ and H$_2$O environments. Differences were attributed to the distribution of particles in the experiments which tends to skew burn-time measurements at lower pressures.

Huang et al. conducted a study of flame speed of aluminum particle dust in air [5]. Model predictions of flame speed are compared to data using phenomenologically derived burn rate models. For larger micron-sized particles, ignition temperature is correlated with data and overall mixture burn rate use particle burn-time correlations developed by Beckstead [10]. For smaller nano-sized particles, the burn rates are assumed to follow that of a molecular limit using the chemical kinetics mechanism developed by Catoire et al. [11]. Flame speed predictions are shown to increase with decreasing particle diameter as $\sim d^{-0.92}$ - consistent with $D^2$ theory (see discussion regarding estimates of $S_L$ in results section). For particles less than $\sim 10$ microns, however, further reduction in particle diameter results in a more gradual increase in flame speed, scaling as $\sim d^{-0.52}$, as the rate of burning becomes more kinetically controlled. Huang et al. estimate a maximum flame speed of 5.82 m/s as the particle diameter reaches a molecular asymptotic limit.

The transition from diffusion to kinetically controlled combustion is a recurring theme in the aforementioned studies and plays a crucial role in burning modes for decreasing pressures and particle sizes. In particular, particles that are $\sim 10$ microns and smaller exhibit a clear dependance on the rate limiting chemical kinetics. To date there have not been theoretical estimates of this transition as a function of particle size where burn-times increase with decreasing pressure. To better understand the rate dependent diffusion and kinetic processes, a mixture fraction based particle burn model is developed in this study. In this approach, the vapor phase equations are first recast in terms of mixture fraction space. Since the conditions at the liquid-vapor boundary interface are part of the solution, the resulting system of flamelet equations differ from those typically solved for single-phase flows (e.g., an opposed-jet configuration) [12]. The appeal of this formulation is the ability to efficiently solve for the flame structure in the solution of the particle eigenvalue problem.

The rest of the study is as follows. First the model formulation is presented with a brief summary of the solution method. Model predictions are presented with comparison to the burn-time measurements from Bazyn et al. [4] and numerical simulations of Washburn et al. [6]. Burn-time predictions are couched in terms of a modified $D^2$ - law where the burn rate “constant” ($K$) becomes a function of particle diameter and pressure to account for the effects of finite rate chemistry. This simplified model is used to compute flame speed calculations of Al-air dust and compared to theory and data. Finally, the conclusions from this study are summarized.

## 2 Model Formulation

A spherically symmetric particle is assumed for formulating the gas phase flow. Assuming Fick’s law with equal diffusivities among all species the governing equations for species and enthalpy transport are given as the following set of equations,
\[
\frac{1}{r^2} \frac{d}{dr} \left( \frac{m_T}{4\pi} Y_i - \rho Dr^2 \frac{dY_i}{dr} \right) = \dot{m}_i'' \\
\frac{1}{r^2} \frac{d}{dr} \left( \frac{m_T}{4\pi} h - \rho Dr^2 \frac{dh}{dr} \right) = 0
\]

where \( \dot{m}_T (\equiv \dot{m}_{Al} - \dot{S}_{max}) \) is the total mass flow rate. In the derivation of Eq.(1b) a unity Lewis number assumption is employed and the effects of thermal radiation ignored. The boundary conditions at the liquid aluminum-gas interface are shown below as,

\[
\text{Total Mass:} \quad \dot{m}_T = \dot{m}_{Al} - \dot{S}_{max} \\
\text{Aluminum:} \quad \dot{\dot{m}}_{Al,l} = \dot{m}_TY_{Al,l} - 4\pi r^2 \rho D \frac{dY_{Al}}{dr} \bigg|_{s} \\
\text{Aluminum Oxide:} \quad -\dot{\dot{S}}_{max,l} = \dot{m}_TY_{max,s} - 4\pi r^2 \rho D \frac{dY_{max}}{dr} \bigg|_{s} \\
\text{Product Species:} \quad \dot{\dot{m}}_{prodi,l} = \dot{m}_TY_{prodi,s} - 4\pi r^2 \rho D \frac{dY_{prodi}}{dr} \bigg|_{s} \\
\text{Oxidizer Species:} \quad \dot{\dot{m}}_{ox,l} = \dot{m}_TY_{ox,s} - 4\pi r^2 \rho D \frac{dY_{ox}}{dr} \bigg|_{s} \\
\text{Inert Species:} \quad \dot{\dot{m}}_{I,l} = \dot{m}_TY_{I,s} - 4\pi r^2 \rho D \frac{dY_{I}}{dr} \bigg|_{s} \\
\text{Energy:} \quad \dot{Q}_l + \dot{m}_{Al,l}h_{Al} - \dot{S}_{max}h_{max} = \dot{m}_Th_s - 4\pi r^2 \rho D \frac{dh}{dr} \bigg|_{s}
\]

where \( \dot{S}_{max} \) is the rate of metal oxide deposition to the particle surface as condensed aluminum oxide, \( Al_2O_3 \). The quantity \( \dot{Q}_l \equiv \dot{q}'4\pi r^2 \) is the total heating rate of the molten aluminum. Equations (1) and (2) comprise a system of \( N+1 \) second order, non-linear, ordinary differential equations to solve for the eigenvalue \( \dot{m}_T \) and the thermodynamic state at the vapor surface. The total number of unknowns includes the composition and enthalpy at the surface (\( N+1 \)), the mass flow rates of inert and oxidizer in the liquid along with the metal oxidize deposition rates (\( N+1 \)) and the heating of liquid for a total of \( 2(N+1) \) unknowns. Given that the far-field conditions are known, then \( N+1 \) constraints are required to close the system which are defined by either the flow rate of mass or energy into the liquid phase, or specifying values at the surface. Assuming steady-state burning and insolubility of the oxidizer, inert species and product subspecies into the molten aluminum then \( \dot{Q}_l = \dot{m}_{ox,l} = \dot{m}_{I,l} = \dot{m}_{prodi,l} = 0 \). Assuming the deposition of aluminum oxide is sufficiently fast then the mass fraction of the species is zero at the surface. This assumption provides an upper limit on the amount of metal oxide that can be deposited to the surface - similar to previous studies. For the limiting case of infinitely fast chemistry, these equations can be reduced to a system of non-linear algebraic equations and solved via coupling functions [13].

Including detailed chemistry requires numerical solution which can be efficiency solved by recasting Eqs.(1) and (2) in terms of a mixture fraction coordinate, \( Z = Y_{Al} + \sum v_{mox,i} Y_{Al,O_{mox}} \) where
\( \nu_{mox,i} \equiv nMW_{Al}/MW_{Al,O_{i}} \) is the mass ratio of aluminum to total mass of the oxide and sub-species. Noting that the value of the mixture fraction can fluctuate at the surface of the particle it is necessary to guess an initial value of \( Z_{s} \) and solve the resulting flamelet equations associated with the mass fractions mapped in the new \( Z \)–space. A pseudo time step method is employed to solve the system of stiff ODEs that emerge from the inclusion of finite rate chemistry. The solution returns the gradients of the aluminum and aluminum oxide species at the surface and are used to determine the ratio of deposition to evaporation and the total mass flow rate. Recognizing that mixture fraction and enthalpy are both conserved scalars with the same functional form in radial coordinates provides the necessary link to solve for the eigenvalue \( \dot{m}_{T} \). Setting the two resultant equations equal to one another allows enthalpy to be expressed in terms of mixture fraction or vice versa. An updated value of \( Z_{s} \) is attained and iterated upon until the guessed value of \( Z_{s} \) is returned from the equation of \( Z \) in terms of enthalpy. The chemical mechanisms employed are the same as those used by Washburn et al. [6, 16].

The mass flux of aluminum from the surface and the deposition of the aluminum oxide can be determined when the eigenvalue solver is converged. Particle burn-times can be calculated from an integration over the initial mass of the particle with a variable mass loss rate of aluminum, \( t_{b} = \int^{m_{0}}_{0} \frac{1}{\dot{m}_{Al}} dm \). It has been confirmed from the data such burn-times are in fact equivalent to a \( D^{2} \) law and the error between the mass integration and the \( D^{2} \) law is shown in Fig. 1, where the error decreases as the particle size increases. A geometrical consideration of cap formation was considered by assuming the alumina cap and liquid aluminum intersected as two spheres. However, when calculating burn-times with a mass integration considering variable solid angle, evaporation and deposition rates, burn-times were found to increase by \( \sim 15\% \) compared with burn-times without a shape factor considered. To reduce the computational cost of integrating from initial particle size to burnout, the burn-times can be sufficiently calculated by using the \( D^{2} \) law, where the burn constants are defined as: \( K = 4\dot{m}_{Al}/(\pi \rho_{Al} D_{p}) \).

3 Results and Discussion

Burn-times for aluminum in oxygen versus pressure and oxygen content are compared with experimental data of Bazyn et al. [4] and detailed numerical simulations (DNS) of Washburn et al. [6, 16]. Figure 2 shows comparisons of burn-times with increasing pressure. The burn-times increase with decreasing pressure as the mode of burning transitions from diffusion to kinetically controlled. Good agreement can be seen between the model results and experimental data and DNS with the 3 and 11 micron cases bounding data for particles with a 10 micron average diameter. Reasonable agreement is also seen between data and model results for sensitivity to far-field oxygen in Fig. 3. With increasing \( O_{2} \), burn-time decreases due to an increase in the flame temperature and hence increase in heating and evaporation rates. Aluminum combustion in \( O_{2} \) is fairly well understood and documented as a primary oxidizer. However, aluminum can also oxidize in carbon-dioxide and steam environments. This is of particular interest when aluminum is mixed within a binder where combustion products of the binder result in the production of \( CO_{2} \) and \( H_{2}O \). Burn-times were calculated for different pressures and different mole fractions of \( CO_{2} \) in Figs. 4 and 5, respectively. Experimental data shows an increase in burn-time with pressure over the entire range of pressures. However, if only considering burn-times from the data for atmospheric pressures ranging from 12 to 30 atm the burn-times tend to decrease with increasing pressure, consistent
with the values obtained by the model. Burn-times for the steam environments are depicted in Figs. 6 and 7 versus pressure and steam content. To best match conditions of the experiments [14], the model environment is set to 50% H₂O and 50% argon for a variety of pressures. Burn-times for different mole fractions of steam are also shown in Fig. 7 showing a decrease in burn-times with increasing water mole fraction.

One objective of this study was to explore modification of standard $D^2$ – law theory to account for the effects of finite-rate chemistry for use in simplified models of particle burning. In the limit of large particles and high pressures, the burn rate “constant” ($K$) is a truly a constant because the particle burns in a diffusion controlled mode - consistent with $D^2$ theory. At lower pressure and smaller particles, however, this is no longer the case and $K = K(D_p, P, Ox)$. Figures 8, 9 and 10 show $K/K_{max}$ as a function of pressure and different particle sizes for $O_2$, $CO_2$ and $H_2O$ oxidizers, respectively. $K_{max}$ corresponds to the large particle/pressure limit when $K$ is a constant. A decrease in $K/K_{max}$ from unity indicates the transition of particle burning from diffusion to a kinetically controlled limit. These $K/K_{max}$ curves can be used in simplified analysis where burn-time information is required. For instance, Huang et al. conducted detailed numerical simulations of flame propagation in Al-air dusty gas [5]. A similar analysis is conducted here where a simplified flame propagation theory is used starting with the definition of flame speed from 1D theory: $S_L = \left[ -2\alpha (\nu + 1) \frac{\dot{m}_F}{\rho_u} \right]^{1/2}$, where $\alpha$ is the thermal diffusivity, $\nu$ is the mass based stoichiometric fuel to air ratio, $\dot{m}_F$ is the mass consumption rate of the fuel in the mixture and $\rho_u$ is the density of the un-burnt mixture. Substituting in for $\dot{m}_F$ in terms of the burn rate and droplet number density and using the definition of the mixture equivalence ratio ($\Phi$) then the following relation can be derived for the flame speed,

$$S_L = \left[ \frac{3\alpha (\nu + 1) \rho_{air} \Phi}{\rho_u (\nu + \Phi)} K(D) \right]^{1/2} \frac{1}{D}. \quad (3)$$

For constant values of $K$, Eq. (3) shows that $S_L$ is inversely proportional to diameter - consistent with the findings of Huang et al. where a $D^{-0.92}$ power law was determined in the limit of large particles [5]. Decreasing particles size therefore results in an increase in flame speed from the associated increase in surface area. For small particles that are kinetically controlled, $K$ decreases, resulting in a maximum in flame speed as a function of diameter. Figure 11 shows this behavior with comparisons of predictions using Eq. (3) to data [5, 17–21] and the limiting cases of kinetically and diffusion controlled where $S_L$ scales as $D^{-0.52}$ and $D^{-1}$, respectively. Based on experimental burn-time data, Huang et al. derived a $D^{-0.13}$ dependence which is also included in Fig. 11. Reasonable agreement is shown between model predictions, data and scaling theories.

4 Conclusion

A mixture fraction formulation first used to described combustion in turbulent conditions was applied to the particle domain in spherical coordinates to study the transition of diffusion to kinetics controlled combustion. Predictions using this model compare favorably to experimental data [4, 15] and detailed simulations [6, 16] over a range of pressure and oxidizer environments. A modified $D^2$ theory is developed to correct burn-rate constants to account for finite-rate chemistry and used to prediction flame speeds of Al-air dusty gases. Predictions using a simplified theory
of flame speed compared to data and scaling theories. This further validates the conclusion of the importance of chemical kinetic effects on burn-times and flame speeds as particle sizes decrease below $\sim 10$ microns. Further research includes the study of decreasing particle radii to the sub-micron range while including chemical kinetics to gain a better understanding of aluminum particle additives in different oxidizing environments.

**Figures**

![Figure 1: Comparison of mass integration and $D^2$ approach to calculating burn-times at various pressures.](image)

Figure 1: Comparison of mass integration and $D^2$ approach to calculating burn-times at various pressures.
Figure 2: Burn-times vs. pressure compared to DNS [6, 16] and experimental data [4, 15] for atmospheric conditions $T = 2650 \, K$, 40\% $O_2$ and 60\% $Ar$.

Figure 3: Burn-times vs. mole fraction of $O_2$ to DNS [6, 16] and experimental data [4, 15] for atmospheric conditions $P = 8.5 \, atm$, $T = 2650 \, K$. 


Figure 4: Burn-times vs. pressure compared to DNS [6, 16] and experimental data [4, 15] for atmospheric conditions $T = 2650\, K$, 40% $CO_2$ and 60% Ar.

Figure 5: Burn-times vs. mole fraction of $CO_2$ for atmospheric conditions $P = 17\, atm$, $T = 2650\, K$. 
Figure 6: Burn-times vs. pressure compared to DNS [6, 16] and experimental data [4, 15] for atmospheric conditions $T = 2650 \, \text{K}$, 50% $H_2O$ and 50% Ar

Figure 7: Burn-times vs. mole fraction of $H_2O$ for atmospheric conditions $P = 17 \, \text{atm}$, $T = 2650 \, \text{K}$
Figure 8: Normalized $K$ as a function of particle diameter up to 11 microns for atmospheric conditions $T = 2650\, \text{K}$ and 40\% $O_2$ at various pressures.

Figure 9: Normalized $K$ vs. particle Diameter up to 11 microns for atmospheric conditions $T = 2650\, \text{K}$ and 50\% $H_2O$ at various pressures.
Figure 10: Normalized K vs. particle Diameter up to 11 microns for atmospheric conditions $T = 2650 \, K$ and 40% $CO_2$ at various pressures.

Figure 11: Flame speed for Al particles in air with $\Phi = 0.85$, $T_\infty = 300 \, K$ compared to shock tube experimental data. Experimental data from Risha et al. [5], Boichuk et al. [17], Goroshin et al. [18, 19], Ballal [20] and Cassel [21].
References


