EFFECTS OF INITIAL REACTANT TEMPERATURE ON FLAME SPEEDS IN ALUMINUM DUST SUSPENSIONS

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Abstract

It has been proposed that metals could be used as an energy carrier and alternative fuel source to hydrocarbons and fossil fuels due to their abundance and comparable energy densities, making them applicable to large scale industrial power generation cycles (e.g. boilers and large heat engines). The knowledge of the dependence of flame speed on the initial temperature of the unburned mixture is important for the understanding of the role of radiation heat transfer and stabilization mechanisms of flames in metal particle suspensions. A newly constructed flat-flame counter-flow metal dust burner allows for measurement of burning velocities in aluminum-air suspensions preheated to temperatures up to 524 K using Particle Image Velocimetry (PIV). The experimental method was verified by measuring burning velocities in preheated methane-air mixtures at different fuel-oxygen equivalence ratios, compared with known experimental data and theoretical predictions. Whereas flame speeds in methane-air mixtures increase by 2.75 times with increase in temperature to about 524 K, flames speeds in aluminum-air mixtures increase by less than 2 times over the same temperature interval. Nearly constant adiabatic flame temperatures for preheated aluminum-air flames suggest practically constant reaction rates for both kinetic and diffusive regimes of particle combustion. Continuous theory can explain the observed flame speed sensitivity to preheat through an increase in heat diffusivity and a lowering of the heat required for reaction onset at lower ignition temperatures. However, discrete theory may also be suitable for physically explaining the preheat effect due to partially discrete heat sources in aluminum-air flames, resulting in a stronger dependence on heat diffusivity than in continuous theory. Theoretical agreement with experimental results could suggest that either continuous or discrete theory are applicable, although it is evident that further studies of ignition phenomena in dust flames, as well as further studies using the discrete model, are needed to fully resolve the problem of metal dust flame stabilization.

Abrégé

Les métaux peuvent être utilisés comme vecteurs énergétiques et sources de combustibles de substitution aux hydrocarbures et aux combustibles fossiles en raison de leur abondance et de leur densité énergétique comparable, ce qui les rend applicables aux cycles de production industrielle d'électricité à grande échelle. La connaissance de la dépendance de la vitesse de la flamme par rapport à la température initiale du mélange est importante pour la compréhension du rôle du transfert de chaleur par radiation et des mécanismes de stabilisation des flammes. Un nouveau brûleur de poudre métallique à contre-courant permet de mesurer la vitesse de flamme dans des suspensions d'aluminium à des températures allant jusqu'à 524 K, en utilisant la vélocimétrie par image de particules. La méthode expérimentale a été vérifiée en mesurant les vitesses de flamme dans des mélanges de méthane-air, par rapport aux données expérimentales connues et aux prévisions théoriques. Alors que les vitesses de flamme dans les mélanges méthane-air augmentent de 2,75 fois avec l'augmentation de la température à environ 524 K, les vitesses de flamme dans les mélanges aluminium-air augmentent de moins de 2 fois pour le même intervalle de température. Des températures de flamme adiabatique presque constantes pour les flammes préchauffées suggèrent des taux de réaction pratiquement constants peu importe le régime de combustion des particules. La théorie continue prévoit que la sensibilité de la vitesse de la flamme provient d'une augmentation de la diffusivité de chaleur et d'une diminution de la chaleur requise pour le début de la réaction. Cependant, la théorie discrète peut aussi expliquer physiquement l'effet de préchauffage dû à des sources de chaleur partiellement discrètes dans les flammes d'aluminium-air, ce qui entraîne une plus grande dépendance de la diffusivité de la chaleur. L'accord théorique avec les résultats expérimentaux pourrait suggérer que la théorie continue ou discrète est applicable, bien qu'il soit évident que d'autres études sont nécessaires pour résoudre entièrement le problème de la stabilisation des flammes métalliques.

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Contents

	Abst	tract .		ii		
	Abre	égé		iii		
	Ack	cknowledgements				
	List	List of Figures				
	List	of Sym	bols	х		
1	Intr	oducti	ion	1		
	1.1	Overv	iew	1		
	1.2	Radia	tion Effects in Heterogeneous Flames	3		
	1.3	Effects	s of Initial Temperature: Gaseous Flames	8		
	1.4	Qualit	ative dust flame models	11		
		1.4.1	Regimes of particle combustion	11		
		1.4.2	Discrete theory	15		
2	Exp	erime	ntal Methods	17		
	2.1 Description of Preheat Apparatus			17		
		2.1.1	Overall description	17		
		2.1.2	Dispersion system	18		
		2.1.3	Length of heating tube	20		
		2.1.4	Preheat temperature measurements	21		
	2.2	2 Diagnostics				

	2.3	Validation of experimental se	tup	25
		2.3.1 PIV validation: cold	low	25
		2.3.2 PIV validation: prehe	ated methane-air flame speeds	25
	2.4	Flame speed measurements i	n aluminum-air mixtures	29
		2.4.1 Experimental procedu	re for aluminum-air flames	31
3	Res	ılts		33
	3.1	Methane-air validation result	s	33
	3.2	Aluminum-air flame speed re	sults	35
	3.3	Uncertainty in aluminum-air	flame speed measurement	38
4	Dise	ussion		40
	4.1	Sensitivity of $T_{\rm ad}$ to preheat		40
4.2 Preheat effects: continuous flame theory		ame theory	43	
		4.2.1 Preheat effects: kinet	ic-regime	43
		4.2.2 Preheat effects: diffus	ive-regime	45
		4.2.3 Comparison of contin	ous flame theory with experimental results	47
	4.3	Preheat effects: discrete flam	e theory	50
5	Con	clusion		53
	5.1	Future Work		54
Bi	Bibliography 5			

List of Figures

1.1	Experimental flame speeds of methane, propane, and ethylene mixtures	
	at varying initial temperatures [26]	9
1.2	Depiction of kinetic and diffusion limits of particle combustion, showing	
	profiles of both temperature and oxidizer concentration [45]	11
1.3	Flame structure of dust flame in continuous regime with constant heat	
	release rate.	13
2.1	Depiction of experimental apparatus: (left) image of burner and sup-	
	porting structure; (middle) schematic of counterflow preheat burner;	
	(right) schematic of stabilized flat flame	18
2.2	Metal powder dispersion system: (left) picture of dispersion system	
	including stepper motor assembly, piston cylinder, and "airknife" as-	
	sembly; (right) schematic of dispersion system assembly	19
2.3	Particle size distribution and SEM image of Valimet H2 Aluminum	
	powder. Particle sizing results obtained using Horiba LA-920	20
2.4	Radial temperature profiles of aluminum suspension at varying tube-	
	wall temperatures.	22
2.5	Schematic of laser diagnostic systems, including PIV and dust concen-	
	tration monitoring.	23

2.6	Concentration calibration results showing the line of best fit, 95% con-	
	fidence interval (shaded), and prediction bands at two standard devi-	
	ations (dotted).	24
2.7	Averaged experimental cold stagnation flow profile compared with an-	
	alytical model [45]	26
2.8	Averaged experimental counterflow methane-air flame profile ($\phi = 1.0$,	
	no preheat) compared with simulation results obtained using the GRI	
	3.0 kinetic mechanism.	27
2.9	Averaged experimental counterflow methane-air flame profiles at ϕ =	
	1.0 and $T_{\rm u} = 300$ K for stretch rates of $K = 342$ 1/s (red), 365 1/s	
	(blue), and 402 1/s (black), compared with GRI 3.0 stagnation flame	
	simulations at the same stretch rates (solid lines).	28
2.10	Averaged experimental counterflow methane-air flame profiles at ϕ =	
	1.0 and $K\approx$ 410 1/s for initial temperatures of $T_{\rm u}$ = 293 K (black),	
	353 K (blue), and 438 K (red), compared with GRI 3.0 stagnation	
	flame simulations at the same initial temperatures (solid lines)	29
2.11	Extrapolation of stretched methane-air burning velocities to zero-	
	stretch for $\phi = 0.9, 1.0,$ and 1.2 and $T_{\rm u} = 293$ K (\blacksquare), 353 K (\square), and	
	438 K (\blacksquare). Simulated flames are represented by triangles	29
2.12	Comparison of aluminum-air and methane-air flame speed measure-	
	ments. (a.i/b.i) Flat aluminum/methane flames. (a.ii/b.ii) Left: PIV	
	image showing illuminated aluminum/alumina particles; Right: Pro-	
	cessed velocity vector field of counterflow aluminum/methane flame.	
	(a.iii/b.iii) Representative velocity profile of flat aluminum/methane	
	flame	30
3.1	Validation results of preheated methane-air flames at $\phi = 0.9, 1.0,$	
	and 1.2, compared to GRI 3.0 kinetic mechanism predictions	34

3.2	Experimental preheated methane-air flame speeds compared to free-	
	flame GRI 3.0 simulations at multiple equivalence ratios. Error bars	
	represent one standard deviation of the zero-stretch flame speeds. $\ . \ .$	34
3.3	Flame speeds of aluminum-air suspensions at different initial temper-	
	atures of the unburned mxiture	35
3.4	Flame speeds of aluminum-air suspensions at different fuel-rich con-	
	centrations of aluminum.	36
3.5	Measured aluminum-air flame stretch rates for various initial temper-	
	atures. Red dotted line represents estimated strain rate	37
4.1	Calculated adiabatic flame temperatures for methane-air and	
	aluminum-air stoichiometric mixtures at different temperatures of	
	the unburned mixture	42
4.2	Comparison of sensitivity of experimental aluminum-air dust flame	
	speed on initial mixture temperature with results for methane-air flame	
	and theoretical predictions considering a) kinetically reacting particles,	
	b) particles burning in the diffusion regime	48
4.3	Comparison of sensitivity of experimental aluminum-air dust flame	
	speed on initial mixture temperature assuming discrete and continuous	
	flame propagation and $T_{ig} = 2000$ K	50
4.4	Comparison of sensitivity of experimental aluminum-air dust flame	
	speed on initial mixture temperature for different discreteness param-	
	eters	52

List of Symbols

- α thermal diffusivity
- $\dot{\omega}$ reaction rate
- \dot{m} mass flow rate
- Γ extinction coefficient
- γ preheat power law exponent
- λ thermal conductivity
- \mathcal{D} mass diffusivity
- \mathcal{K} pre-exponential factor
- Le Lewis number
- R universal gas constant
- Ze Zeldovich number
- ϕ equivalence ratio
- $\rho_{\rm g}$ gas density
- σ optical thickness
- au characteristic heating time

- $\tau_{\rm c}$ discreteness parameter
- θ non-dimensional heat required for ignition
- A cross-sectional area
- B dust concentration
- $C_{\rm g}$ oxidizer concentration
- $c_{\rm p,g}$ gas specific heat
- $c_{\rm p}$ gas specific heat
- $c_{\rm s}$ metal specific heat
- $d_{\rm n}$ distance from nozzle to flame
- $E_{\rm A}$ activation energy
- K strain rate
- l mean-free path
- $l_{\rm c}$ characteristic heating length
- $l_{\rm p}$ inter-particle spacing
- m concentration calibration constant
- n number density of particles
- q heat of reaction
- $r_{\rm p}$ particle radius
- $S_{\rm L}$ burning velocity
- $S_{\rm L}^{\rm o}$ laminar burning velocity

- $S_{\rm u,ref}$ reference flame speed
- $T_{\rm ad}$ adiabatic flame temperature
- $t_{\rm c}$ characteristic combustion time
- $T_{\rm ig}$ ignition temperature
- $T_{\rm set}$ preset heating tube temperature
- $T_{\rm u}$ initial reactant temperature
- $U_{\rm jet}$ free stream flow velocity
- V voltage
- $V_{\rm o}$ nominal voltage
- x^* characteristic radiation absorption length
- $Y_{\rm u}$ mass fraction of deficient reactant

Chapter 1

Introduction

1.1 Overview

The need for more sustainable and zero-carbon emission energy production means finding an alternative fuel that could replace current fossil and hydrocarbon fuels. It has been proposed that metals could be used as an energy carrier and alternative fuel source due to their comparable energy densities to hydrocarbon fuels, making them applicable to large scale industrial power generation cycles (e.g. boilers and large heat engines) [1]. Traditionally, scientific studies on metal combustion have been limited in the context of accidental industrial explosions [2], and metalized solid rocket propellants [3]. Current scientific efforts at McGill, however, are primarily focused on characterizing the combustion of metal fuels in water, for clean hydrogen production, and in air under laminar flame conditions for further use in energetic devices burning metal fuels as recyclable energy carriers[4]. The realization of metal fuels applied to industrial and commercial applications would thus require reconciliation of the burning characteristics of metal-air flames for varying metal types [5–7], oxidizer compositions [5, 7], equivalence ratios [8], metal particle sizes [9, 10], flame geometries [5, 6, 8], and initial reactant temperatures. The focus of this thesis is to investigate the burning characteristics of metal-air flames under the influence of varying initial temperature. Experiments investigating these effects on metal flames are largely missing from the literature. There is an intrinsic value associated with initial temperature when it comes to power generation and system efficiency, particularly the effects on burning velocity and how those effects translate to heat and energy production. Understanding how metal flames behave under varying initial temperature conditions is a critical aspect towards enabling a future metal-fuel economy. The concept of preheating reactants in a combustion process through heat recuperation and/or regeneration has long been viewed as a highly practical means of saving fuel and reducing emissions [11]. By utilizing heat recuperation or regeneration processes, increasing the temperature of compressed air entering the combustion chamber can offset a certain amount of required fuel, which improves overall thermal efficiency. For reference, the US Department of Energy estimates fuel savings of 13-51% for natural gas combustion processes, depending on the amount of preheating [12].

Of more fundamental importance to dust flames and the effect of initial temperature, however, is the role of radiation heat transfer on flame propagation. Largescale industrial burners burning solid fuels may experience enhanced burning rates of dust flames due to radiation preheating. The goal of this work is thus to measure flame speeds in aluminum-air suspensions under varying degrees of preheat (emulating large-scale radiation absorption effects on a smaller, laboratory scale) and compare the experimental findings to previously developed qualitative dust flame models. The next sections will provide more background on radiation absorption in heterogeneous combustible mixtures, known preheat effects in gaseous flames, and a brief overview of modes of particle combustion (continuous regime of flame propagation), and the discrete regime of flame propagation, which are the basis of the qualitative models used for the theoretical comparison to the experimental results of this work.

1.2 Radiation Effects in Heterogeneous Flames

In a suspension of solid particles, the individual particles can emit and absorb radiation in a continuous fashion, making it possible for reactants to absorb thermal radiation. Whereas gaseous mixtures are mostly transparent to incident radiation, the radiation heat transfer in particulate suspensions may have a discernible effect on flame propagation through either radiative heat absorption or heat loss. Radiation transfer in particulate suspensions depends on the concentration of particles in suspension, the radiative and emissive properties of the particles, as well as the size of particles, and is generally described by the suspension's optical thickness, σ , which is detailed later in this section. The first to propose radiation heat transfer for heterogeneous combustion was Nusselt in 1924 [13]. Since then, the investigation of radiation heat transfer in particulate suspensions has been primarily focused on coal combustion [14-18]. Researchers claimed that comparable flame speeds between gaseous and coal flames could be justified, at least theoretically, by radiative heating of reactants in the flame preheat zone [15], suggesting that heat conduction is no longer the primary mechanism responsible for flame propagation [18]. Based on these theoretical assessments, models of particulate combustion involving radiation were developed and the results were compared to experimental data for small scale flame propagation in tubes [16].

Cassel, in one of the earliest studies of metal combustion, also assumed that radiation absorption in aluminum flames was a primary mechanism of flame propagation. [19]. Cassel made the assumption that aluminum flames dispersed in O₂/He and O₂/Ar mixtures would have burn rates controlled by oxygen diffusion to the particle surface (diffusive-regime). This would imply that the flame speeds, S, would scale with the mass diffusivity, \mathcal{D} , of each mixture, $S_{\text{He}}/S_{\text{Ar}} \approx \mathcal{D}_{\text{He}}/\mathcal{D}_{\text{Ar}}$. However, experimental results showed that $S_{\text{He}}/S_{\text{Ar}} < \mathcal{D}_{\text{He}}/\mathcal{D}_{\text{Ar}}$, implying that aluminum dispersed in O₂/Ar must have a greater contribution of radiation heat transfer than mixtures of O_2/He to account for the lower ratio of flame speeds. This was eventually disproved by Goroshin et al. [20], who also measured flame speeds of aluminum dispersed in O_2/He and O_2/Ar mixtures. Goroshin [20] observed a similar discrepancy between ratios of flame speeds and oxygen diffusivity, but by using spectroscopy techniques to identify the presence of micro-diffusion flames, was able to determine that aluminum flames dispersed in O_2/He burn in a regime where burn rates are controlled by reaction kinetics, $\dot{\omega}$, rather than diffusion of oxidizer. Thus the ratio of flame speed ratio is lower than predicted from oxidizer diffusivity because O_2/Ar mixtures have faster kinetic rates than O_2/He , thus the ratio of flame speeds is not dependent on varying degrees of radiative heat transfer, but rather on differing modes of particle combustion.

What was often missing in these early theoretical predictions of dust flames was consideration of the geometrical configuration of the flame itself. Earlier models often assumed one-dimensional, adiabatic scenarios that occasionally incorporated arbitrary and ambiguous correction factors or constants [15, 16]. It was also assumed that the physical systems were optically thick, generally meaning that the photon mean free-path, l, was much smaller than the particle size or distance between particles. This would result in more frequent photon collisions with fuel particles, and thus greater probability of radiation absorption. Furthermore, coal particles were considered to be perfectly absorbing, thus the assumption of negligible heat conduction was considered sensible in these earlier works, assuming optically thick suspensions [18]. For the case of stabilized metal flames, it has already been shown that the main mechanism for flame propagation is not radiation, but rather molecular heat conduction [5, 6, 8]. Rather, radiation might influence the flame by preheating reactants, but that stabilized flames in metal suspensions can propagate entirely without radiation absorption. A simple dimensional analysis of characteristic lengths for both radiation absorption and molecular heat conductivity can help elucidate the importance of radiation preheating as a mechanism for flame propagation. Comparing the characteristic lengths of both mechanisms will determine whether or not radiation effects are appreciable on the same scale as molecular heat conduction, and therefore distinguish between micro and macro scale thermal effects on reactants. The characteristic length of molecular heat conductivity can be determined from representative values of thermal diffusivity, α , and burning velocity, $S_{\rm L}$. For a heterogeneous mixture, α is typically expressed as [19]

$$\alpha = \frac{\lambda}{c_{\rm p}\rho + c_{\rm s}B} \tag{1.1}$$

where λ is the gas thermal conductivity, $c_{p,g}$ is the gas specific heat, ρ_g is the gas density, c_s is the particle specific heat, and B is the particle concentration in suspension. Typical values of thermal diffusivity range from 0.1-1.0 cm²/s, and measured burning velocities for aluminum flames are on the order of 30-50 cm/s [5, 6]. Estimating the length of the molecular heat conduction zone as α/S_L , the characteristic length falls on the order of 0.01 cm. This value can be directly compared to the estimated radiation absorption length in aluminum suspensions.

The radiation absorption length can be approximated in two ways, both yielding similar results. The first method uses temperature history measurements from large scale aluminum dust clouds performed by Julien et al. [8]. In dust clouds of approximately 2 m in width and 4 m in height, temperatures were measured of the reactant suspension up until the flame front arrival. Two distinct temperature changes were observed: 1) a very large and sudden temperature increase at the flame arrival, and 2) a more gradual increase in temperature that began approximately 150 ms prior to the flame arrival. The former is a result of molecular heat conduction at the flame front, and the latter indicates preheating due to thermal radiation absorption. The burning velocities measured by [8] were approximately 5 m/s, which corresponds to a radiation absorption length of about 75 cm.

The second method for estimating radiation absorption length involves the absorptivity of thermal radiation (wavelengths from 0.1 μ m - 100 μ m) of particles in suspension, and the photon mean free path, l, and the suspension's optical thickness, σ . The optical thickness, is defined as

$$\sigma = \int_0^{x*} \Gamma dx \tag{1.2}$$

where Γ is the extinction coefficient, or the fractional loss of intensity per unit length of the medium, and x^* is a characteristic length of the system. For a suspension of spherical particles, $\Gamma = n\pi r_p^2$, with n being the number density of particles in suspension, and r_p being the particle radius. A geometrical approximation for the extinction coefficient is used since the size of particles is generally larger than the wavelength of thermal radiation [21]. In an optically thin suspension ($\sigma \ll 1$), the photon mean free path is generally much larger than the characteristic dimensions of the medium, thus radiation absorption by the system is negligible. In the optically thick limit $(\sigma >> 1)$, the photon mean free path is much smaller than the characteristic dimensions of the medium, and thus radiation absorption can contribute to preheating of the reactants. Analogous to the extinction coefficient is the photon mean free path, $l = 1/\Gamma$. Assuming a suspension of 10 μ m particles with a concentration of 400 g/m³ and a characteristic burner length of 5 cm (a conservative value), the photon mean free path is approximately 4.5 cm, resulting in an optical thickness of 1.1. Aluminum particles have an absorptivity less than 0.1 in the thermal radiation wavelength region |22|, thus making the absorption length effectively greater than 45 cm and σ effectively less than 0.1. These predictions are in close agreement with the experimentally predicted radiation absorption lengths [8].

The three orders of magnitude difference between molecular heat conduction effects and radiative heat transfer signifies that, on a macro-scale, radiation can be a mechanism for flame propagation in particulate suspensions, but that on a microscale radiation contributes primarily to heat losses. It should also be noted that, even without considering the low absorptivity of aluminum particles, the suspension cannot definitively be considered optically thick, thus dismissing the primary role of radiation in dust flame propagation. The limiting factor then in characterizing radiation effects in heterogeneous combustion is not the ability to theoretically describe the physics, but rather the ability to obtain repeatable and measurable experimental results. There is no question that radiation heat loss is more prominent in small scale experiments, and that radiation absorption is more probable in large scale setups, but the reported values in literature and correlations made between those data and theoretical predictions only suggested the effects of radiation. It was eventually shown by Goroshin et al. [5, 20, 23] that the comparable flame speeds between gaseous flames and heterogeneous flames was due to particle ignition, or a transition from kinetically-limited combustion to diffusion-limited, and not necessarily radiation preheating. Thus, to develop a physically sound understanding of how radiation preheating might affect dust flame propagation, small-scale experiments should be performed where the initial reactant temperature can be independently controlled from radiation effects. Producing sound experimental data for initial reactant temperature dependencies on metal burning velocities can greatly assist in scaling radiation effects for larger-scale combustion applications.

Even after it was first suggested that radiation preheat effects were negligible in small-scale laboratory setups [5], there still remains an apparent absence in literature investigating solely the initial temperature effects on metal flames. The noteable exception comes from unpublished data from Goroshin et al. [24], however these experiments were performed using a total flame-surface-area method using a Bunsen flame, which is considered unreliable due to large temperature gradients across the flow. Julien [8] compared the results from [24] with freely-propagating aluminum dust clouds, and the radiative preheating effects in large scale dust clouds produced a similar increase in flame speed as seen for aluminum Bunsen flames. What is still missing, however, is reliable flame speed measurements under preheat effects and reconciliation between experimental results and basic theoretical/physical predictions for preheat of metal flames. This work aims to address this problem by utilizing small-scale controlled experiments where the effects of preheat on metal-air laminar flame speeds can then be used to reconcile radiation effects on much larger-scale and practical scenarios. Any radiation heat transfer in these small scale experiments would be attributed to heat losses and have no discernible effect on the laminar flame speed.

1.3 Effects of Initial Temperature: Gaseous Flames

The study of initial reactant temperature effects for gaseous flames has been studied since the mid-twentieth century, primarily for evaluating turbojet operational limits [25], and it was observed that flame speeds in gaseous mixtures increased with increasing initial temperature. The theoretical dependence of burning velocity on initial temperature was first compared to experimental results of preheat effects on methane, propane, and ethylene-air mixtures by Dugger [26], where good agreement was found between experimental laminar burning velocities and theoretical predictions from the thermal theory model developed by Frank-Kamanetskii [27] (< 20% difference). For reference, the experimental results for methane, propane, and ethylene flames from Dugger [26] are shown in Fig. 1.1, where a noticeable increase in flame speed is observed for increasing initial temperature. Now it is reasonable to assume that experimental results from seven decades ago are no longer as accurate



Fig. 1.1: Experimental flame speeds of methane, propane, and ethylene mixtures at varying initial temperatures [26].

compared to modern flame speed measurements, but the empirical relation established by Dugger [26] largely remains the state-of-the-art today, where the burning velocity is related to the initial temperature by a power law. Metghalchi and Keck [28] later proposed a direct correlation between burning velocity and initial temperature that could be expressed as

$$\frac{S_{\rm L}}{S_{\rm L,o}} = \left(\frac{T_{\rm u}}{T_{\rm u,o}}\right)^{\gamma} \tag{1.3}$$

Note that a similar pressure dependence can also be included in equation 1.3, but is omitted here since pressure effects are not considered in this work. It is important to emphasize that equation 1.3 is entirely empirically based. Most of the work found in literature focuses on better defining the scaling parameter, γ , which is now typically defined as a function of the mixture's equivalence ratio [29–38]. What is common amongst all these works, however, is that varying degrees of flame stretch are not considered when reconciling empirical power laws for preheat [29]. Recent experiments studying combustion in shock tubes studied even higher preheat temperature ranges (> 750 K) and found that in this elevated temperature range, experimental flame speeds deviate from the preheat law predictions, and that kinetic model predictions also diverge at higher temperatures [39]. While Ferris et al. [39] do not quantify the preheat law exponent for higher initial temperatures, it was found that the available kinetic model predictions had an average percent difference of 10.4% at temperatures above 500 K, compared to about 6.5% at temperatures ranging from 300 K to 500 K. To the authors knowledge, only one paper attempts to derive the preheat exponent from theory, albeit the power law form of the preheat law (Eq. 1.3) is assumed initially, thus the parametrization of γ is still dependent on an empirical correlation [40].

Despite the extensive work that has been performed for preheat effects on gaseous flames, there is still uncertainty regarding how γ should be defined [29], and there is a clear absence of any theoretical derivation of any preheat law from governing principles. Combustion textbooks may outline the temperature scalings from commonly applied flame theory models, but noticeably do not attempt to reduce the Arrhenius reaction term [41, 42]. Other textbooks may occasionally write-off physical explanations to an arbitrary term called the "preheat effect" [43]. In all, it is evident that the study of preheat effects on hydrocarbon flames by far surpasses work done in the field of heterogeneous combustion, but that there still exists a relatively high degree of uncertainty in the relevant work for gaseous flames, posing interesting questions beyond the scope of this thesis.

1.4 Qualitative dust flame models

1.4.1 Regimes of particle combustion

In combustible dust suspensions, the combustion of individual particles is fundamentally limited by two distinct processes: the diffusion of oxidizer to the particle surface (diffusive-regime), and the chemical reaction rate with the fuel particle (kineticregime) [44]. The critical transition of a particle burning in the kinetic-regime to the diffusive-regime is termed "ignition," and occurs when heat diffusion away from the particle can no longer overcome the increase in heat release from reaction kinetics, resulting in a sharp increase in temperature. The phenomena of flame front formation is analogous to particle ignition, but occurs independently of the mode of particle combustion, meaning that continuous flame fronts can be stabilized with particles burning either kinetically or diffusively. Figure 1.2 depicts the thermal structure of a particle burning in either the kinetic or diffusion limit.



Fig. 1.2: Depiction of kinetic and diffusion limits of particle combustion, showing profiles of both temperature and oxidizer concentration [45].

Aluminum-air flames burning in both kinetic and diffusive regimes were suggested by Goroshin et al. [20] by varying the diffusivity of the oxidizing gas mixture. Formally, the regime of particle combustion is defined by the Damköhler number (ratio of reaction time scale to diffusive time scale) and can be controlled by either decreasing the particle size, or equivalently, changing the mixture diffusivity (e.g. changing inert gas from Ar to He)[20]. In this work, air is used as the oxidizing gas, and previous work has shown that aluminum-air flames using the same size powder as in this work burns in the diffusive-regime [10]. However, in the context of preheating of dust suspensions, the dependence of flame speed on initial temperature may vary based on the mode of particle combustion. Since preheat effects have never been studied in either regime of combustion, the experimental burning velocities from this work are compared to theoretical predictions employing both kinetic and diffusive modes of combustion. The kinetic-regime is based on the assumption of kinetically reacting/evaporating aluminum droplets [27] and the diffusive-regime is based on the "box" reaction model [23].

Since the diffusive-regime model is primitive in its formulation, the derivation of the flame speed expression is provided in the subsequent section. The discrete regime of dust combustion [46] is also discussed in the context of preheat, providing a comprehensive discussion of preheat effects in aluminum-air flames. These considerations are further developed in Chapter 4.

Continuous theory derivation: diffusive-regime

The continuum dust flame model which assumes particles burn in a regime limited by oxidizer diffusion [23] is fundamentally based on the work of Mallard and LeChatelier [47], which assumes a heat flux balance at the ignition point of the mixture, typically defined by the ignition temperature, T_{ig} . The flame structure is depicted in Fig. 1.3, where the flame is broken into three regions: 1) preheat zone, 2) flame zone, and 3) post-combustion zone, where x is the flame propagation direction. Figure 1.3 depicts the flame temperature profile (red curve), and considers a negligible separation between the gas and solid phase temperatures, which has been observed in the case of rich dust flames [10]. The deficient reactant, Y, is shown as the blue curve and



Fig. 1.3: Flame structure of dust flame in continuous regime with constant heat release rate.

depicts the consumption of oxygen in the flame. The flame zone is characterized by a constant rate of heat release, W, and the thickness of the flame zone is a function of the combustion time, t_c , of the particles and the characteristic flame speed of the mixture. The start of the flame zone is controlled by the ignition temperature, T_{ig} , of the mixture.

The governing heat diffusion equation of the flame depicted in Fig. 1.3 is written as

$$\left(\rho_{\rm g}c_{\rm p,g} + Bc_{\rm s}\right)S_{\rm L}\frac{dT}{dx} = \lambda\frac{d^2T}{dx^2} + W \tag{1.4}$$

where $W = \frac{BQ}{t_c}$ and Q is the heat of reaction. Equation 1.4 has the following boundary conditions:

$$x=0,\ T=T_{\rm ig}; \quad x \to -\infty,\ T=T_{\rm u},\ \frac{dT}{dx}=0; \quad x=S_{\rm L}t_{\rm c},\ \frac{dT}{dx}=0$$

where

$$x < 0, W = 0;$$
 $0 < x < S_{\rm L}t_{\rm c}, W = \frac{BQ}{t_{\rm c}};$ $x > S_{\rm L}t_{\rm c}, W = 0$

Introducing the non-dimensional terms

$$\theta = \frac{T - T_{\mathrm{u}}}{T_{\mathrm{ig}} - T_{\mathrm{u}}}; \quad \xi = \frac{x}{S_{\mathrm{L}}t_{\mathrm{c}}}; \quad \kappa = \frac{S_{\mathrm{L}}}{\sqrt{\alpha/t_{\mathrm{c}}}}; \quad \mu = \frac{1}{1 + \frac{Bc_{\mathrm{s}}}{\rho_{\mathrm{g}}c_{\mathrm{p},\mathrm{g}}}} \frac{BQ}{(T_{\mathrm{i}} - T_{\mathrm{u}})\rho_{\mathrm{g}}c_{\mathrm{p},\mathrm{g}}} = \frac{T_{\mathrm{ad}}}{T_{\mathrm{ig}} - T_{\mathrm{u}}}$$

Equation 1.4 can be rewritten as

$$\frac{d\theta}{d\xi} = \frac{1}{\kappa^2} \frac{d^2\theta}{d\xi^2} + \mu \tag{1.5}$$

with the following boundary conditions

$$\xi = 0, \ \theta = 1; \quad \xi \to -\infty, \ \theta = 0, \ \frac{d\theta}{d\xi} = 0; \quad \xi = 1, \ \frac{d\theta}{d\xi} = 0$$

where

$$\xi < 0, \ \mu = 0; \quad 0 < \xi < 1, \ \mu > 0; \quad \xi > 1, \ \mu = 0$$

By solving Eq. 1.5 for each of the three zones of the flame, and matching the solutions at each boundary, the final flame speed expression is given as [46]

$$\frac{\kappa^2}{\mu} = 1 - e^{-\kappa^2}$$
(1.6)

To obtain an explicit equation for flame speed, Lambert Function, $W_{\rm o}$ is used as shown in [48]. The explicit, non-dimensional, expression is given as

$$\kappa^2 = W_o \left(-\mu e^{-\mu}\right) + \mu \tag{1.7}$$

In dimensional form, the flame speed for dust flames burning in the diffusive regime is thus expressed as

$$S_{\rm L}^2 = \left(\frac{\alpha}{t_{\rm c}}\right) \left[W_{\rm o}\left(-\mu e^{-\mu}\right) + \mu\right] \tag{1.8}$$

The effects of preheat on laminar dust flames burning in diffusive-regime are assessed in Chapter 4, based on the formulation of Eq. 1.8.

1.4.2 Discrete theory

While traditional flame theory assumes that reactions occur in a continuum (i.e. heat is uniformly spread throughout the mixture) [49], heterogeneous systems have localized heat sources in particles. Most studies of heterogeneous combustion assume that the flames propagate based on continuous theory, but it has been proposed that dust flames may propagate in a discrete nature under conditions where the burning time of individual particles is much shorter than the heat diffusion time between particles [46]. Recent evidence of discrete flame propagation has been observed in iron flames burning in oxygen-xenon mixtures in microgravity conditions [50], and it was shown that this discrete nature can render flame speeds independent of oxygen concentration or particle burning rates, and that the inter-particle spacing of these heterogeneous systems strongly influences the flame speed.

The flame speed in discrete theory is expected to have a dependence of $S_{\rm L} \propto \alpha/l_{\rm p}$, where $l_{\rm p}$ is the inter-particle distance. An explicit expression for the flame speed in discrete theory has not yet been found, however the above scaling has been observed from solving the analytical expression for the discrete model [46] as well as in experiments [50]. The discreteness of a heterogeneous mixture is defined by the discreteness parameter, $\tau_{\rm c} = t_{\rm c} \alpha/l_{\rm p}^2$, where $\tau_{\rm c} \ll 1$ is considered to be the discrete limit. When modeling discrete flames, $t_{\rm c}$ is modeled as a δ -function. As the discreteness parameter for a given heterogeneous mixture is increased, the discrete theory predictions eventually coincide with predictions from continuous theory [46]. The effects of preheat in the discrete regime will be considered in the discussion (Chapter 4) to provide a comprehensive comparison to the experimental results from this work.

Chapter 2

Experimental Methods

2.1 Description of Preheat Apparatus

2.1.1 Overall description

The experimental setup built for this work is shown schematically in Fig. 2.1, and is based on previous dust flame burners used at McGill [5, 6]. A piston cylinder is filled with aluminum powder which is fed upwards to the dispersion system using a stepper motor that precisely controls the feed rate of powder being delivered. Despite variable force loading in the piston and cylinder during dispersion, the stepper motor is designed to maintain a constant feed rate. An "airknife" provides a sonic flow of air which continuously removes a small layer of powder, creating a turbulent two-phase flow. The two phase flow is then laminarized and heated through a 1 m long, highlypolished, stainless steel tube with a diameter of about 2 cm, enveloped by a series of three 400 W ceramic heaters. Each heater is individually temperature controlled with a K-type thermocouple in contact with the tube wall. The apparatus is preheated to a constant temperature prior to each experiment. The heated flow exits the conical bottom nozzle, having a diameter of about 12.7 mm, and is met by an opposed flow of ambient air from a concentrically placed top nozzle. A remotely controlled



Fig. 2.1: Depiction of experimental apparatus: (left) image of burner and supporting structure; (middle) schematic of counterflow preheat burner; (right) schematic of stabilized flat flame.

propane-air ignition torch is used to ignite the aluminum-air mixture, forming a flat flame between both nozzles. The ignition torch is immediately shut-off once a selfsustained flame is formed. An upward flow of inert nitrogen gas is used to shield the flame from external contaminants and to reduce the prevalence of vortices at the flow periphery. An emergency off switch is built into the apparatus' control box which stops the stepper motor, closes all pneumatic valves to stop gas flow, shuts off ignition torch, and turns off the ceramic heaters.

2.1.2 Dispersion system

The newly designed dispersion system assembly is shown in greater detail in Fig. 2.2. The stepper motor not only saves space and weight to the entire apparatus, but can also be easily controlled from a computer, along with all other control and diagnostic



Fig. 2.2: Metal powder dispersion system: (left) picture of dispersion system including stepper motor assembly, piston cylinder, and "airknife" assembly; (right) schematic of dispersion system assembly

systems. The assembly is built such that the bottom plate, upon which the motor is mounted, may translate up or down to allow for removal of the piston between experiments. The motor rod is fitted with a self-aligning end which pushes on the brass piston. By maintaining relatively loose tolerances, the piston can be loaded and unloaded easily and the stepper motor assembly ensures alignment with the piston under variable loading conditions. The stepper motor rod has an effective length of 4 inches. The piston is fed upwards at a rate of about 0.04 in/s, resulting in a total dispersion time of just over 1.5 minutes.

All aluminum-air preheat experiments used spherical H-2 powder produced by Valimet (Stockton, CA). The particle arithmetic mean diameter (d_{10}) , measured using a laser scattering method with a Horiba LA-920, was approximately 3.5 μm . The particle size distribution is shown in Fig. 2.3. To prevent agglomeration and ensure



Fig. 2.3: Particle size distribution and SEM image of Valimet H2 Aluminum powder. Particle sizing results obtained using Horiba LA-920.

efficient combustion during experiments, the aluminum powder is dried in a vacuum oven at about 500 K for 4-6 hours to remove any excess moisture that may have accumulated on the particles during storage.

2.1.3 Length of heating tube

Obtaining a controllable and relatively uniform temperature profile of the metal suspension at the nozzle exit highly depends on the length of the heating tube. In the case of heterogeneous mixtures, the heating tube must be straight to avoid excess pressure losses and particle settling. Only for gaseous mixtures could the heating tube be looped or coiled to maximize the heating length. The required heating tube length can be determined from a simple dimensional analysis using the onedimensional heat conduction equation. The characteristic heating time, τ , can be approximated as $\tau \simeq l_c^2/\alpha$, where l_c is the characteristic length (tube inner radius), and α is the mixture thermal diffusivity. Assuming a tube diameter of 0.870 in and α of 2.14e-5 m²/s, τ is about 5.6 s. Accounting for a typical flowrate of 300 cc/s, this corresponds to a tube length of about 4.4 meters. This gives a rough estimate of how long the heating tube should ideally be, but certain lab and practical constraints limit the tube from being this long. Ultimately, a meter long tube was chosen and results will show that the exit flow temperature profile is relatively uniform within the center flow region of interest within \pm 5-10 K.

2.1.4 Preheat temperature measurements

The temperature of the aluminum-air suspension was determined by measuring the temperature of the gas devoid of particles at the exit of the bottom nozzle. Due to strong particle adhesion to the thermocouple probe, direct temperature measurements of the particle suspension soon become unreliable. It is thus assumed that the temperature of the suspension closely matches the temperature of the gas alone. This assumption is primarily based on the probability of enhanced radiative heat absorption within the suspension of metal particles, as well as greater thermal inertia of the suspension when flowing through the unheated section of the apparatus. These effects largely compensate for the lower thermal diffusivity of the suspension compared to the gas. The preheated temperature of the gas is measured at the exit of the bottom nozzle using three bare-wire K-type thermocouples with diameters of 0.127 mm, 0.254 mm, and 0.381 mm. To correct for measurement error due to variable heat losses from each thermocouple, temperature measurements from the three thermocouples are extrapolated to zero-junction to obtain the absolute temperature of the gas.

Figure 2.4 shows the radial temperature profile of the suspension for four different preset tube-wall temperatures (T_{set}) of 373 K, 474 K, 523 K, and 573 K. For each T_{set} , the exit flow temperature exhibited a top-hat profile in the center flow region, approximately ± 2 mm from the nozzle center. The temperature of the flow in this center region did not deviate by more than ± 10 K in both space and time. While the effects of heat loss are noticeable near the flow periphery at higher tubewall temperatures (see Figure 2.4), only center-line flow velocities are used for flame speed measurements, thus temperature gradients near the nozzle edge do not affect the experimental results and the initial temperature is taken from the center-line measurement.



Fig. 2.4: Radial temperature profiles of aluminum suspension at varying tube-wall temperatures.

2.2 Diagnostics

The preheat counter-flow metal dust burner consists of two main diagnostic setups: 1) laser attenuation to monitor aluminum dust concentration throughout experiments, and 2) Particle Image Velocimetry (PIV) to capture the flow of particles through the flame front. The diagnostic setups are shown schematically in Fig. 2.5.

The dust concentration monitoring setup is comprised of a 5 mW 632 nm collimated red laser and a corresponding photodetector with a narrow band-pass filter centered at 632 nm, which filters out the bright luminescence from the aluminum



Fig. 2.5: Schematic of laser diagnostic systems, including PIV and dust concentration monitoring.

flame. The laser light passes through the center of the particle-laden flow field at the exit of the bottom nozzle. The light attenuation, caused by scattering from the aluminum particles, is measured using the photodetector, and related to the dust concentration using the Beer-Lambert Law, which is written as

$$ln\left(\frac{V_{\rm o}}{V}\right) = mB \tag{2.1}$$

where V_{o} is the nominal voltage produced by the 5 mW red laser, V is the attenuated voltage, B is the dust concentration, and m is the calibration constant. The calibration is performed by dispersing dust particles into a high-collection filter while simultaneously monitoring laser attenuation, weighing the filter before and after dispersion, and then calculating the resulting dust concentration. The dust concentration and laser attenuation results are then fitted to Eq. 2.1 to obtain the calibration constant. Figure 2.6 shows the dust concentration calibration data, where the shaded region represents the 95% confidence interval, and the dotted lines represent the prediction bands at two standard deviations. The calibration constant, m, was approximately $0.007 \text{ m}^3/\text{g}.$



Fig. 2.6: Concentration calibration results showing the line of best fit, 95% confidence interval (shaded), and prediction bands at two standard deviations (dotted).

The PIV setup consists of a 5 W, 532 nm green continuous laser (Dragon Laser), and optical elements to form a laser sheet that illuminates a cross-section of the flow field. The optics consist of a Galilean telescope which expands the beam to encompass the flame and upstream flow field, along with a cylindrical lens that forms a thin laser sheet at the center of the flow field. A Photron SA5 highspeed camera, filming at 4000 fps and fitted with a 532 nm narrow bandpass filter, is mounted perpendicular to the PIV laser setup, and captures the reflected light from the cross-section of illuminated aluminum particles. Image pairs are then processed in DaVis (LaVision), which tracks the displacement of individual particles between frames to produce a velocity vector map. These vector maps are subsequently processed in MATLAB, where the center-line velocities are used to obtain the velocity profile. Images of this process are seen in Fig. 2.12 and described in section 2.4.

2.3 Validation of experimental setup

2.3.1 PIV validation: cold flow

Prior to performing aluminum-air or methane-air experiments, experimental results for cold stagnation flow were compared to an analytical model for impinging laminar jets to validate the basic features of the experimental apparatus and PIV technique [51]. The cold stagnation flow axial velocity profile is well characterized by an error function and a strain rate parameter which depends only on the Reynolds number (Re) [51]. Prescribing the experimental flow conditions and parameters to the cold stagnation flow model, the analytical model is then compared to the PIV cold flow results, seeded with a small amount of 5 μ m alpha-alumina (Al₂O₃), averaged over 500 frames along the center line of the flow, as shown in Fig. 2.7. The comparison in Fig. 2.7 shows good agreement between experimental and analytical results, indicating that the PIV technique accurately captures the particle motion from the bottom nozzle exit to the stagnation plane, and that effects of Stokes drag are negligible.

2.3.2 PIV validation: preheated methane-air flame speeds

Methane-air flames were also seeded with 5 μ m alpha-alumina (Al₂O₃). Stretched burning velocities, $S_{u,ref}$, at equivalence ratios of $\phi = 0.9$, 1.0, and 1.2 were measured at initial gas temperatures of about 293 K, 353 K, 438 K. The stretched burning velocity is determined by finding the local minimum of the flow profile corresponding to the flame position, as shown in Fig. 2.8. At each temperature, experiments were



Fig. 2.7: Averaged experimental cold stagnation flow profile compared with analytical model [45]

performed for multiple stretch rates, K, which is defined as the velocity gradient 2 mm upstream of the flame.

Experimental values of $S_{u,ref}$ were extrapolated to zero-stretch to obtain the laminar burning velocity, S_{L}^{o} , using stagnation flame models obtained from the GRI 3.0 kinetic mechanism. An example comparison between an experimental methane-air flat flame flow profile and a simulated flat flame flow profile is shown in Fig. 2.8. The poor agreement shown between the GRI 3.0 simulation results and experimental data in the post-flame region in Fig. 2.8 is likely caused by lowered inert particle count due to decreased density of the gas. Unreliable particle tracking and averaging of near-zero velocities in the post-flame region consequently reduces the average velocity, resulting in such an apparent deviation from the GRI 3.0 simulation results. For the purposes of this work, the post flame region is not critical in determining $S_{u,ref}$, and therefore any post-flame discrepancies are neglected.



Fig. 2.8: Averaged experimental counterflow methane-air flame profile ($\phi = 1.0$, no preheat) compared with simulation results obtained using the GRI 3.0 kinetic mechanism.

Figure 2.9 shows a comparison of multiple flow profiles for experimental and simulated methane-air flames ($\phi = 1.0$) across multiple stretch rates for constant initial temperature. An increase in stretch rate shifts the flame position further away from the bottom nozzle, and generally results in an increase in flame speed. There is good agreement between experimental results and GRI 3.0 predictions up until the flame position, and while post-flame agreement is generally poor, the experimental results do seem to converge to the same stagnation surface, which qualitatively matches with GRI 3.0 predictions. Figure 2.10 demonstrates the effects of preheat on the flame profile, at approximately the same stretch rate, for increasing initial temperature. The flame position shifts upstream with preheat, which results in a faster reference flame speed. There is also generally good agreement in flame position and flame speed between experimental and simulated preheated methane-air flat flames.

The uncertainty in experimental flow velocities in Figs. 2.9 and 2.10 is defined by the standard deviation of the mean flow velocity. Since the results are averaged over approximately 1000 data points, the uncertainty is on the order of 0.1 cm/s and cannot be represented graphically. In Chapters 3 and 4, Figs. 3.2 and 4.2, respectively,



Fig. 2.9: Averaged experimental counterflow methane-air flame profiles at $\phi = 1.0$ and $T_{\rm u} = 300$ K for stretch rates of K = 342 1/s (red), 365 1/s (blue), and 402 1/s (black), compared with GRI 3.0 stagnation flame simulations at the same stretch rates (solid lines).

instead use the standard deviation of the measured flow velocities to define the uncertainty in order to more realistically depict the spread of the data and accuracy of the measurement technique being used. A more general discussion regarding uncertainty in flame speed measurements is provided in Chapter 3.

In the extrapolation to zero-stretch technique [52, 53], it assumed that the deviation between experimental and simulated stretched flame speeds is also applicable at flames of zero-stretch, thus this deviation can be applied to free-flame simulations using GRI 3.0 mechanism to obtain the experimental $S_{\rm L}^{\rm o}$. The experimental and simulated flame speeds from Figs. 2.9 and 2.10 are plotted in Fig. 2.11 for each equivalence ratio and simulated values for unstretched flames are shown on the vertical axis at zero-stretch. The average deviation between stretched experimental and simulated flame speeds is applied to $S_{\rm L}^{\rm o}$ from simulations, resulting in the experimental value of $S_{\rm L}^{\rm o}$ that is used for validating the experimental setup.



Fig. 2.10: Averaged experimental counterflow methane-air flame profiles at $\phi = 1.0$ and $K \approx 410$ 1/s for initial temperatures of $T_{\rm u} = 293$ K (black), 353 K (blue), and 438 K (red), compared with GRI 3.0 stagnation flame simulations at the same initial temperatures (solid lines).



Fig. 2.11: Extrapolation of stretched methane-air burning velocities to zero-stretch for $\phi = 0.9$, 1.0, and 1.2 and $T_{\rm u} = 293$ K (\blacksquare), 353 K (\square), and 438 K (\blacksquare). Simulated flames are represented by triangles.

2.4 Flame speed measurements in aluminum-air

mixtures

Aluminum-air suspensions were preheated to temperatures of about $T_{\rm u} = 300$ K, 361 K, 443 K, 481 K, 524 K. The reference flame speeds and stretch rates for counterflow aluminum-air flames were obtained in a similar manner as methane-air flames. However, whereas the seeding particles in methane-air flames can be traced through the flame front and up to the stagnation plane, the aluminum particles vaporize and form nano-metric oxide products, which have a greater tendency to scatter light. Thus, particle tracking is not feasible downstream of the flame. This difference in PIV diagnostics is apparent when comparing the images and velocity vector fields in Figs. 2.12a.ii and b.ii.



Fig. 2.12: Comparison of aluminum-air and methane-air flame speed measurements. (a.i/b.i) Flat aluminum/methane flames. (a.ii/b.ii) Left: PIV image showing illuminated aluminum/alumina particles; Right: Processed velocity vector field of counterflow aluminum/methane flame. (a.iii/b.iii) Representative velocity profile of flat aluminum/methane flame.

Ideally, the stretch rate for all preheated aluminum-air flames would have been kept constant to limit the effects on flame speed to only the initial temperature. However, stabilizing counter-flow aluminum-air flames across a wide range of flowrates is not feasible given the current limitations in achieving consistent and stable dust dispersion. Therefore, faster flame speeds must be stabilized at higher stretch rates. Furthermore, corrections due to stretch for aluminum-air flames have not been performed since a theory for stretched dust flames does not yet exist. Stretch effects in dust flames will likely differ from gas flames due to particle inertia and the considerably thicker combustion zones, on the order of the flame preheat zone [23], due to particles burning in the diffusive regime. It is thus assumed that effects of stretch in dust flames are consistent across all initial temperatures.

It has also been previously shown in aluminum dust flames that flame speeds in fuel-rich suspensions are insensitive to fuel particle concentrations, due mainly to a negligible change in oxygen concentration and increased reaction surface area in rich flames [8]. Therefore, aluminum dust concentrations were kept above stoichiometry $(B_{\rm st} \approx 305 {\rm g/m^3})$, in order to eliminate a dependence of flame speed on dust concentration. On average, aluminum concentrations ranged between 325 g/m³ and 375 g/m³.

Flame spectra were obtained for aluminum-air flames, using a 100 μ m fiber optic cable and Ocean Optics USB 4000 spectrometer. However, the fitting of the flame spectra to Planck's Law, within the range of 410 to 850 nm, resulted in an uncertainty of \pm 200 K for flame temperature. For the purposes of this thesis, such a large and unavoidable uncertainty rendered flame temperature measurements unsuitable for analysis, and thus are not included in this work.

2.4.1 Experimental procedure for aluminum-air flames

This section describes the general procedure used for conducting preheated counterflow aluminum-air flame experiments. The ceramic heater temperature controllers are first set to the desired tube-wall temperature ¹. The dispersion piston is removed during this time to prevent premature heating/ignition of the aluminum powder. Once the apparatus reaches steady-state temperature (usually within ≈ 30 minutes), the spacing between the bottom and top nozzle is readjusted to account for thermal expansion of the apparatus. All diagnostic setups (concentration and PIV) are also adjusted accordingly. The preheated gas temperature is then measured at this time. The flowrates of air supplied to the bottom and top nozzles are set using electronic mass flow controllers (MFCs) at about 400 cc/s. The stepper motor feed rate is set to 0.04 in/s

The dispersion piston, filled with aluminum powder, is then inserted into the bottom of the "airknife". The ventilation system is turned on to capture the combustion products. The pneumatic valves are opened to allow air flow to both nozzles and the stepper motor is activated to begin dispersion of powder. The concentration of powder is monitored in real-time and allowed to gradually ramp-up to fuel-rich conditions, at which point the ignition torch is activated to ignite the aluminum-air mixture. Once a stable, self-sustained flame is visible, the high-speed camera is triggered and records for approximately 1-2 seconds. After the camera has finished recording, all air lines are closed and the stepper motor is retracted to its initial position.

¹Particle ignition within the 1 m heating tube can occur at wall temperatures of ≈ 600 K (lower than cloud ignition temperature). This may lead to rapid burning of the column of powder within the dispersion piston, resulting in the piston becoming dangerously hot.

Chapter 3

Results

3.1 Methane-air validation results

Laminar burning velocities of methane-air flames as a function of initial temperature are shown in Fig. 3.1, with reference to the GRI 3.0 free-flame simulations. The resulting power law scaling for all three equivalence ratios was approximately $S_{\rm L}^{\rm o} \propto T_{\rm u}^{1.9}$, which is in good agreement with established power law relations from literature [29] and free-flame simulations. These results are also shown as a function of equivalence ratio in Fig. 3.2, where the error bars represent the standard deviation of the measured flame speed. There is a noticeable systematic difference between the experimental methane-air flame speeds and the simulation results. This could be partially attributed to the use of 5 μm alumina particles, rather than smaller 1 μm particles, as used in previous work [53]. The estimated effects of Stokes drag for 5 μm alumina particles suggested that particle slip in the gaseous flow field could partially account for the apparent deviation between experimental and simulated results. However, the experimental setup is not optimized for gas flame experiments, thus all experimental gas flame results are solely intended as proof-of-concept. Additionally, a relatively large disparity in experimental flame speeds for gaseous flames under preheat still exists in the literature [29], where the preheat power law exponent may deviate between 1.6 and 2.0 depending on the type of experiment performed and what diagnostics where available at the time. Thus, for the purposes of this work, it can be stated that the experimental apparatus and diagnostic techniques function as intended, based on the experimental methane-air preheated flame speed results. To the authors knowledge, these are the first results for preheated methane-air flame speeds using a counter-flow flat flame burner.



Fig. 3.1: Validation results of preheated methane-air flames at $\phi = 0.9$, 1.0, and 1.2, compared to GRI 3.0 kinetic mechanism predictions.



Fig. 3.2: Experimental preheated methane-air flame speeds compared to free-flame GRI 3.0 simulations at multiple equivalence ratios. Error bars represent one standard deviation of the zero-stretch flame speeds.

3.2 Aluminum-air flame speed results

Aluminum-air flames were successfully stabilized across a range of initial reactant temperatures from 300 K to 524 K. Flame speeds were obtained by averaging the local minimum of the flow velocity profile obtained from 100-200 PIV images. Flame speeds obtained from each experiment are shown with respect to initial temperature in Fig. 3.3. It is interesting to note that previous reported flame speeds from aluminum counter-flow flames under ambient conditions using 5.6 μ m particles were approximately 30-35 cm/s [6]. Flame speeds in this work at ambient conditions were about double (≈ 65 cm/s) due to smaller average particle size (larger reaction surface area). Flame speeds essentially double when increasing the initial temperature by about 225 K, which demonstrates a lower sensitivity in flame speed to initial temperature with reference to the data from unpublished work reported in [24]. Fitting a power law to the results in Fig. 3.3 results in $S_{\rm L} \propto T_{\rm u}^{1.1}$.



Fig. 3.3: Flame speeds of aluminum-air suspensions at different initial temperatures of the unburned mxiture.

It was also observed that flame speeds in fuel-rich suspensions remained generally constant with respect to dust concentration, even at higher initial temperatures, as shown in Fig. 3.4. These results, however, are limited to a narrow range of concentrations when compared to previous studies of aluminum-air flames in fuel-rich suspensions [8]. The average uncertainty in concentration caused by fluctuations during the dispersion process is approximately ± 16 g/m³, and is not expected to affect the flame speed results under varying degrees of preheat. It should be noted that while preheating the dust suspension does not alter the particle concentration, the gas (oxidizer) density does decrease, which effectively increases the equivalence ratio of the mixture.



Fig. 3.4: Flame speeds of aluminum-air suspensions at different fuel-rich concentrations of aluminum.

Whilst no theory for stretched dust flames exists in the literature, comparing measured stretched rates with simple predictions based on flowrate and changes in initial temperature will determine whether the experimental strain rates are consistent with known hydrodynamic effects. The strain rate can be approximated as $K \approx U_{jet}/d_n$,



Fig. 3.5: Measured aluminum-air flame stretch rates for various initial temperatures. Red dotted line represents estimated strain rate.

where U_{jet} is the free stream flow velocity at the exit of the nozzle, and d_n is the distance between the nozzle and the flame. The free stream velocity is directly proportional to the initial temperature, assuming a fixed a mass flowrate of the dust suspension for all experiments. Due to the intense luminosity of the aluminum-air flame, tracking the flame front is not feasible and thus the limiting assumption is made that d_n is constant for all experiments and about 8 mm. The measured strain rates as a function of initial temperature are shown in Fig. 3.5. The dashed line in Fig. 3.5 represents the estimated strain rate at a given initial temperature for the mass flowrate used for all aluminum-air experiments. The predictions show good agreement with experimental measurements, indicating that accurate measurement of strain rates for metal flames are feasible, even at elevated initial temperatures. As previously mentioned, aluminum-air flame speed measurements are not corrected for stretch and are presented in this thesis solely as experimental results. However, the unknown effects of stretch in dust flames are a prominent aspect of uncertainty in the

final analysis of preheat effects on aluminum-air flames, as is discussed near the end of Chapter 4.

3.3 Uncertainty in aluminum-air flame speed measurement

Flame speed measurement uncertainty arises from mixture impurities, variances in equivalence ratio or fuel loading, imaging resolution, or agglomerations. For gaseous flames, variances in parameters such as equivalence ratio or mixture purity can be quantified with relative ease, and these variances can be used to perturb numerical simulations (e.g. GRI 3.0 mechanism or Aramcomech 3.0)[39]. The effect of each individual parameter uncertainty on the numerical flame speed is then applied to the experimental measurements. Albeit, an often controversial subject for gaseous flames is the assumption that numerical gas flame simulations do not introduce any additional error [54]. This implies that uncertainty quantification for gaseous flame speed measurements may in fact be larger than currently reported values.

In the case of metal flames, fluctuations in fuel loading (aluminum concentration) are monitored, but since no accurate numerical models currently exist for metal flames, the effect of each parameter on the flame speed cannot be reasonably quantified. The uncertainty for aluminum-air flames is therefore quantified by the standard deviation of the mean of the measured results. This is assumed to account for overall variations in the measurement technique, which includes experimental fluctuations due to particle loading and video processing methods using DaVis particle tracking software. Ultimately, the uncertainty in aluminum-air flame speed measurements is not significant when considering the mean value of the data, and may be on the order of 0.1 cm/s to 1 cm/s. Albeit, this does not suggest that experimental aluminumflame speed measurements from this work are absolute since obvious measurement limitations are still prevalent, particularly with regards to flame geometry (hydrodynamic stretch effects) and measurement techniques and software used. The final results in Chapter 4 actually show the standard deviation of the measurements, as oppose to the standard deviation of the mean, to more appropriately show the spread of the measurements that are typically observed in dust flame experiments.

Chapter 4

Discussion

In order to explain the physical mechanisms responsible for the observed flame speed sensitivity to preheat in aluminum-air flames, the discussion section is divided into three parts. The first section discusses the effects of preheat on flame temperatures and kinetic rates in aluminum-air flames. The second section will attempt to physically explain the observed experimental trend in flame speed under preheat effects by considering only the two continuous models, invoking the kinetic and diffusive regimes of particle combustion. The role of variable ignition temperatures and the *collective effect* [19] are discussed. The third section includes analysis using discrete theory and the looks at the influence of preheat effects on dust flames in the realm of a varying discreteness parameter. The effects of radiation preheating are not discussed in this section, as it was mentioned in section 1.2 that radiation preheating only affects dust flames in large-scale dust clouds. The only radiation effects in the small-scale experiments performed in this work are attributed to heat losses.

4.1 Sensitivity of $T_{\rm ad}$ to preheat

The strong dependence of $S_{\rm L}$ on $T_{\rm u}$ for methane-air flames, shown in Fig. 3.1, is generally attributed to an increase in the mixture heat diffusivity in the flame preheat zone, and a dependence of Arrhenius kinetic rates on temperature in the combustion zone. The heat diffusivity of a gaseous mixture typically scales as $\alpha \propto T_{\rm u}^{1.5}$, and the Arrhenius law exhibits an exponential dependence on temperature as $\dot{\omega} \propto e^{-E_{\rm A}/RT_{\rm ad}}$. The reader should note, however, that the effects of heat diffusivity and reaction rates do not fully account for the observed increase in flame speeds in gaseous flames. Combustion textbooks usually only attribute preheat effects to α and $\dot{\omega}$ (or $T_{\rm ad}$) [41], but do not consider other fundamental factors, such as heat needed to reach the start of the reaction zone of the flame. In general, the literature does not discuss the physics of preheat for gaseous flames, and almost exclusively aims to simply find the *trend* of preheat effects on flame speeds. It is not the goal of this thesis to fully reconcile these claims for gaseous flames, but merely to elicit them as these are important considerations, especially when attempting to understand the lesser-known physics of metal flames.

The dependence of $S_{\rm L}$ on $T_{\rm ad}$, in the case of gaseous flames, is strongly felt through the Arrhenius term, and for gaseous flames $T_{\rm ad}$ can be approximated as $T_{\rm ad} \approx T_{\rm u} + (q/c_{\rm p}) Y_{\rm u}$, where q is the chemical heat release, $c_{\rm p}$ is the specific heat, and $Y_{\rm u}$ is the mass fraction of the deficient reactant [41]. Figure 4.1 shows the calculated dependence of methane-air flame temperatures on $T_{\rm u}$, calculated with CANTERA using the NASA thermodynamic database [55]. The CANTERA $T_{\rm ad}$ calculations account for product dissociation in the flame zone (mainly H₂O and CO₂), which has the effect of lowering $T_{\rm ad}$, but the approximation that $T_{\rm ad}$ increases due to a corresponding increase in $T_{\rm u}$ is a reasonable estimate for the purposes of this discussion.

Metal flames may exhibit a similar dependence of thermophysical properties on temperature, as seen in gaseous flames, but aluminum-air flame temperatures (also shown in Fig. 4.1 using FactSage thermochemical software [56]) remain practically unchanged with an increase in initial mixture temperature. Thus, aluminum-air flames are likely to exhibit a much weaker dependence on reaction kinetics than gaseous flames. The insensitivity of aluminum-air flame temperatures to preheat is explained by the presence of refractory oxides in the flame zone, primarily Al_2O_3 . Glassman [57] was the first to propose that metal flame temperatures would be limited by the metal oxide's dissociation temperature if the available heat (difference between the



Fig. 4.1: Calculated adiabatic flame temperatures for methane-air and aluminum-air stoichiometric mixtures at different temperatures of the unburned mixture.

heat of reaction and the rise in enthalpy required to raise the products from the initial temperature to the volatilization temperature of aluminum) was not sufficient to entirely vaporize the oxide. Calculated temperatures in Fig. 4.1 show that aluminum-air flame temperatures are approximately 3500 K, or near the dissociation temperature of Al_2O_3 . Thus, in a diffusion-limited combustion regime, individual aluminum particles would burn near this oxide vaporization-dissociation temperature, independently of the surrounding gas temperature. This distinguishable aspect of aluminum dust flames may suggest a weak kinetic reaction rate dependence on temperature.

Furthermore, studies on the combustion of single aluminum particles have also suggested a weak dependence of particle combustion time on temperature [58]. Seminal works on single particle combustion have shown decreasing ignition delay times for particles injected into a high temperature, high pressure gas flow, yet these particles generally exhibited constant burn times [59]. This could be an indication that even in dense clouds of particles, the overall burn time may be independent of the temperature of the surrounding gas. It should be noted, however, that most studies involving single particles are performed at elevated pressures (e.g. shock tubes) which may not be directly comparable to flames at ambient pressures.

The independence of reaction rates on temperature is a distinguishable feature of aluminum-air flames and is extended to both continuous and discrete models of flame propagation. The next sections outline the dust flame models, while accounting for constant flame temperatures and constant reaction rates, and will be simplified to temperature dependent scalings to elucidate the role of preheating on flame speeds in dust suspensions.

4.2 Preheat effects: continuous flame theory

4.2.1 Preheat effects: kinetic-regime

The modeling of kinetically reacting aluminum particles is fundamentally described by the expression for flame speed developed by Zeldovich and Frank-Kamenetskii [44], which does not employ the concept of a fixed ignition temperature, but rather depends on the Arrhenius reaction rate term, as well as the transport of energy through the diffusion of species and heat. The expression, as presented by Law [41], and modified here for heterogeneous combustible mixtures, is written as

$$S_{\rm L}^2 = \frac{2\alpha {\rm Le}\mathcal{K}}{r_{\rm p}\rho_{\rm g} {\rm Ze}^2} e^{\frac{-E_{\rm A}}{{\rm R}T_{\rm ad}}}$$
(4.1)

where Le is the Lewis number, \mathcal{K} is the pre-exponential factor, $r_{\rm p}$ is the particle radius, R is the universal gas constant, $E_{\rm A}$ is the activation energy, and Ze is the Zeldovich number. A Lewis number (ratio of heat to mass diffusion) of unity is assumed to simplify the analysis. For gaseous mixtures, \mathcal{K} is a density-weighted collision reaction rate with units of g/m³ – s. For heterogeneous flames however, \mathcal{K} should be a densityweighted regression rate to account for the particle size, and thus have units of $\frac{m}{s} \frac{g}{m^3}$. Thus, the combined term $\mathcal{K}/r_{\rm p}\rho_{\rm g}$ is usually defined as constant for a given combustible mixture [41].

The Zeldovich number is written as $\text{Ze} = E_A (T_{\text{ad}} - T_u)/RT_{\text{ad}}^2$ and represents the heat required to raise the mixture from T_u to T_{ad} , normalized by T_{ad} . The Zeldovich number is fundamentally the product of two terms. The first is a temperature term dependent on the chemistry of the mixture and written as E_A/RT_{ad} , which is the activation temperature normalized by the flame temperature. The second term is a heat balance and is written as $(T_{\text{ad}} - T_u)/T_{\text{ad}}$. This concept is similar to μ , which appears in the diffusive-regime flame speed expression (Eq. 1.8), except that reaction onset in kinetic theory occurs near T_{ad} , or one Zeldovich interval below T_{ad} [41], instead of at T_{ig} . Since $\dot{\omega}$ is constant due to constant T_{ad} , Eq. 4.1 can be simplified to

$$S_{\rm L}^2 \propto \frac{\alpha \dot{\omega}}{{\rm Ze}^2} \approx \frac{\alpha}{{\rm Ze}^2}$$
 (4.2)

Note that the appearance of Ze^2 , instead of simply Ze, in Eq. 4.2, is based on the assumption of a first-order heterogeneous reaction rather than zero-order reaction. However, in terms of flame speed sensitivity to initial temperature, there is negligible difference in assuming either Ze or Ze².

Based on Eq. 4.2, the flame speed for particles burning in the kinetic regime is dependent on preheat due to an increase in the thermal diffusivity of the suspension and a lowering of the required heat needed to reach one Zeldovich interval below $T_{\rm ad}$. Since $\alpha = \lambda / (\rho_{\rm g} c_{\rm p,g} + B c_{\rm s})$, the effect of raising the initial temperature causes an increase in λ and a decrease in $\rho_{\rm g}$. The specific heats of the gas and solid particles are effectively constant across the initial temperature range in this work, and B is also kept nearly constant for all experiments. The temperature at which α is evaluated at is critical in modeling any combustion system, and can greatly affect theoretical predictions. In this work, a first approximation is used where the increase in α through the flame preheat and reaction zones is compensated for by an increase in flow speed of the fuel-air mixture within the flame zone due to decrease in gas density. The increased flow speed would have the tendency to slow the diffusion of heat upstream, thus it is reasonable to evaluate α at simply $T_{\rm u}$. This assumption is made for all models in this work.

The reader should also note that the assumption of constant B for all experiments is based on the concentration measurements presented in Fig. 3.4. It may also be realistic to expect the dust concentration to diminish with preheat as gas expansion causes particle spacing to increase, however it is incorrect to assume that B would drop proportionally to $\rho_{\rm g}$ (maintaining a constant ϕ) with increasing $T_{\rm u}$. The case of constant ϕ was tested for all dust flame models and produced insignificant changes in the qualitative results for all models, and thus are omitted from this work.

4.2.2 Preheat effects: diffusive-regime

As outlined in section 1.4.1, the combustion of solid metal particles controlled by oxygen diffusion to the particle surface necessitates particle ignition, or a transition from the kinetic-regime of combustion to the diffusive-regime. This ignition event occurs at the particle ignition temperature. In the diffusive-regime model, the heat release rate is constant in the flame zone, and the burning rate of the particle is governed by a characteristic combustion time, t_c , rather than an Arrhenius reaction rate, $\dot{\omega}$. Equation 1.8 is written again here for convenience:

$$S_{\rm L}^2 = \left(\frac{\alpha}{t_{\rm c}}\right) \left[W_{\rm o}\left(-\mu e^{-\mu}\right) + \mu\right] \tag{1.8}$$

It should be emphasized that μ has a similar definition to Ze, used in the kineticregime model, however μ is more sensitive to changes in initial temperature since the difference in temperature is defined as $T_{ig} - T_u$ and not $T_{ad} - T_u$, as defined in the Zeldovich number. This implies that preheated flames burning in the diffusive regime are much closer to reaction onset than flames burning in the kinetic-regime, and thus more sensitive to preheat.

The assumption of constant t_c can be made in the diffusive regime since there is negligible separation between gas and solid phase temperatures in fuel-rich dust flames [10]. In the diffusive regime, the characteristic combustion time is defined as $t_c = r_p / \mathcal{D}C_g$, where r_p is the particle radius, \mathcal{D} is the mass diffusivity of the oxidizer, and C_g is the oxidizer concentration surrounding the particle. Both \mathcal{D} and C_g are temperature dependent, however, at a constant $T_{\rm ad}$, oxidizer diffusion rates and concentration are nearly constant. The Lambert function term, $W_o(-\mu e^{-\mu})$, also changes negligibly with preheat compared to μ , thus the analytical flame speed expression for dust flames in the diffusive regime can be simplified to

$$S_{\rm L}^2 \propto \frac{\alpha \mu}{t_{\rm c}} \approx \alpha \mu$$
 (4.3)

From Eq. 4.3, the effect of $T_{\rm u}$ on $S_{\rm L}$ is partially felt through the change in thermal diffusivity of the mixture, much like the kinetic-regime model, and the temperature dependent term μ , which can be physically interpreted as representing the energy required to heat the mixture from $T_{\rm u}$ to $T_{\rm ig}$ in the flame preheat zone. This would imply that preheating the dust suspension simply reduces the required heat needed to reach the ignition point, thus the rate of flame propagation through the mixture must increase (left-hand side of Eq. 1.4) to balance the constant heat flux from the combustion zone (right-hand side of Eq. 1.4). What remains unknown, however, is a value for T_{ig} for a given aluminum-air suspension. For single aluminum particles T_{ig} is approximately 2000 K, or near the melting point of Al₂O₃. In a dense cloud of particles, T_{ig} can reach temperatures as low as 900 K, near or slightly below the melting point of aluminum, due to what is termed the *collective effect* [19]. The *collective effect* describes the self-heating of particles in a dense suspension, effectively shielding the particles from heat loss to the surroundings. This has the effect of lowering ignition temperatures in dust suspensions by several hundred degrees [60]. However, since it still remains unclear what T_{ig} should be for a dense suspension of aluminum particles, a range of values are used, as shown in Fig. 4.2.

4.2.3 Comparison of continuous flame theory with experimental results

The theoretical models described in the previous sections are used to calculate normalized flame speed sensitivities to initial temperature, and are directly compared with the averaged aluminum-air flame speed results from this work in Fig. 4.2. All flame speeds are normalized with respect to ambient conditions where $T_{\rm o} = 300$ K. The noticeable decreased sensitivity of aluminum flame speeds to temperature compared to methane flame speeds was previously mentioned in Chapter 3, and it is now evident from Fig. 4.2 that this decreased sensitivity is attributed to an independence of kinetic reaction rates to initial temperature for aluminum flames. Both dust flame models capture this weakened sensitivity to initial temperature for aluminumair flames, keeping in mind the qualitative nature and simplicity of both models. The dotted line in Fig. 4.2, representing the kinetic regime preheat predictions, falls just slightly below the diffusive regime prediction for $T_{\rm ig} = 2000$ K. This could suggest that preheat effects in aluminum-air flames are independent of the mode of particle

Fig. 4.2: Comparison of sensitivity of experimental aluminum-air dust flame speed on initial mixture temperature with results for methane-air flame and theoretical predictions considering a) kinetically reacting particles, b) particles burning in the diffusion regime.

combustion, at least if ignition temperatures are near the aluminum oxide boiling point.

The deviation between the kinetic and diffusive regimes arises mainly due to a lowering of the ignition temperature of the mixture due to the *collective effect*. However, within the measurement uncertainty for flame speeds, it cannot be stated with any confidence that assuming $T_{ig} = 900$ K is statistically more accurate than assuming $T_{ig} = 2000$ K. While there is no direct evidence experimentally that the ignition temperature in the present aluminium flames is at or near 900 K, the fact that the diffusive regime predictions show a greater than linear trend in flame speed versus initial temperature, much like the experimental data, suggests that ignition temperatures in dust flames may be considerably lower than previously expected, and warrants further investigation.

Measuring the cloud ignition temperature is not yet feasible for stabilized metal flames. The only experimental observations from this study that may plausibly have demonstrated an ignition temperature near or below 900 K in dense aluminum suspensions were a series of high-temperature experiments where the wall temperature of the heating tube exceed 600 K. At the onset of the dust dispersion process for each dust flame experiment, a highly dense suspension of particles initially flows through the apparatus, which may briefly enhance the self-heating of particles through the heating tube. In these instances, instead of a stabilized flame, the dust flow autoignited within the heating tube. Auto-ignition of the aluminum-air was observed repeatedly for tube wall temperatures ranging from 600 K to 673 K, although such low ignition temperatures are likely due to combined effects from agglomerates within the flow and high particle concentrations. These observations are by no means conclusive but could suggest that reaction onset in dense clouds of particles could be decoupled from chemical restrictions, such as melting temperature, and may otherwise depend on other physical factors such as the particle density of the mixture. It has only been observed in cases of nano-metric aluminum particles (< 10 nm) that the melting temperature was below what is predicted at the micro-scale (Puri and Yang, 2007), and therefore dependent on geometry rather than chemical properties. The smallest H-2 aluminum particles from this work were measured in the range of hundreds of nanometers, therefore size-dependent melting temperatures of H-2 aluminum particles are not expected, but the collective effect in dense clouds of particles may still result in unique physical phenomena that have not been properly observed experimentally.

The relatively good agreement between experimental measurements and diffusive regime predictions only suggests that such low ignition temperatures in aluminiumair flames are possible, but further experimental and modelling work are required to better understand preheat effects in aluminum suspensions. Preheated aluminium-air flames of larger particle size may also affect the ignition temperature and thus the sensitivity of flame speed to initial temperature.

4.3 Preheat effects: discrete flame theory

In contrast to modeling aluminum-air flames as comprised solely of continuous heat sources, assuming the presence of discrete spatial and temporal heat sources may elucidate different physical phenomena in the context of preheat effects in dust flames. The sensitivity of aluminum-air flame speeds to preheat in the discrete regime, assuming $T_{ig} = 2000$ K, is shown in Fig. 4.3, and is directly compared with the continuous model predictions. Like the continuous regime, the discrete regime model still considers the heat required for ignition of the particles as an influential factor in the preheat effect, however for the sake of analysis, variable ignition temperatures are not considered in this section, instead focusing mainly on the influence of the discreteness of the system. To model the discrete regime, the particle combustion time (t_c) is modeled as a δ -function, such that the characteristic heat diffusion time between particles is what governs the rate of flame propagation, whereas in the continuous regime $t_c \approx 0.5$ ms, which is the reported combustion time for H2 aluminum particles [61]. The sensi-

Fig. 4.3: Comparison of sensitivity of experimental aluminum-air dust flame speed on initial mixture temperature assuming discrete and continuous flame propagation and $T_{ig} = 2000$ K.

tivity of flame speed on the mixture thermal diffusivity in discrete flames $(S_{\rm L} \propto \alpha)$ is greater than what is traditionally observed in continuous flames $(S \propto \sqrt{\alpha})$ [50], which strongly contributes to the large increase in flame speed at higher temperatures predicted by the discrete model.

Figure 4.3 shows that the experimental results fall in between the continuous and discrete predictions, which could be evidence that the preheat effect in aluminum-air flames is partially influenced by discrete effects. In Fig. 4.2, the continuous theory (diffusive-regime) predictions approached the experimental results for lower ignition temperatures, implying that the role of the *collective effect* could partially explain the preheat effect in aluminum-air flames. However, in Fig. 4.3, the ignition temperature is fixed at 2000 K, thus neglecting the *collective effect*. This means that the discreteness of the system, defined by the discreteness parameter $\tau_c = t_c \alpha / l_p^2$, strongly influences the flame speed sensitivity to preheating. To illustrate how the discreteness of the system effects the flame speed sensitivity to preheat, and how the discrete model eventually converges to the continuous model (for $\tau_{\rm c} > 1$), discrete model predictions are plotted in Fig. 4.4 for discreteness parameters ranging from $\tau_{\rm c} \rightarrow 0$ $(t_{\rm c} \rightarrow \delta \text{ function})$ to $\tau_{\rm c} = 4.60 \ (t_{\rm c} = 0.5 \text{ ms})$, where $\tau_{\rm c}$ is represented as an average value across all initial temperatures. Figure 4.4 thus shows that the aluminum-air flames from this work may propagate in a regime comprised of both continuous and discrete heat sources. It still remains unclear, however, why the flame speed dependence on thermal diffusivity changes from $\sqrt{\alpha}$ to α when transitioning from continuous to discrete. This question will need to be addressed in a future study.

The assumption of discrete flame propagation in the context of preheating poses additional theoretical and physical questions that are beyond the scope of this thesis. A sensitivity analysis of the continuous and discrete flame models may reveal underlying physical properties that could explain the increased sensitivity observed in discrete flames. The main takeaway from this section then, is that consideration

Fig. 4.4: Comparison of sensitivity of experimental aluminum-air dust flame speed on initial mixture temperature for different discreteness parameters.

of discrete effects in dust flames is equally as valid as considering the *collective effect* for purely continuous models. Consideration for discrete effects in stabilized laminar dust flames is simply a logical progression in heterogeneous flame theory, and has helped explain interesting physical phenomena in previous work involving stabilized dust flames [7].

Chapter 5

Conclusion

This work has demonstrated the first systematic investigation of the effects of initial temperature on flame speeds in aluminum-air flames. A novel dust flame burner was designed and built, capable of preheating dust-suspensions to controllable temperatures up to 524 K. Results showed that flame speeds in aluminum-air suspensions are less sensitive to increasing initial temperature than gaseous flames. The presence of refractory oxides during aluminum combustion has the effect of dampening the sensitivity of the flame temperature and reaction rates to preheat.

In continuous heterogeneous flame theory, the flame speed is influenced by an increase in the thermal diffusivity of the mixture and a decrease in the heat required to reach the ignition point, which greatly depends on the *collective effect* in dense suspensions. However, theoretical predictions for both kinetic and diffusive regimes suggested that preheated aluminum-air flames exhibit similar dependencies to initial temperature, regardless of the mode of particle combustion, given the experimental uncertainties. In discrete theory, the flame speed sensitivity on heat diffusion is felt much more strongly, and the flame propagation no longer depends on the combustion time of the particles and instead is more strongly influenced by the rate of heat diffusion between localized heat sources. Discrete model predictions showed that the

aluminum-air flames may be partially discrete which may account for the observed flame speed sensitivity to preheat.

The findings from this work will help to further advance the fundamental understanding of aluminum and metal combustion, and promote research in modeling of both continuous and discrete heterogeneous flame theory. This initial study of preheated heterogeneous laminar flames could eventually help promote better designs of large scale dust combustion systems susceptible to preheat from radiation absorption effects or heat recovery systems.

5.1 Future Work

Future studies would involve reevaluating current dust flame models and reconciling the concept of ignition temperature in the diffusive regime and activation energy asymptotic analysis used to describe reaction onset in kinetic theory. A flame front may form in dust flames, irrespective of the mode of particle combustion, therefore a more detailed mechanism of how a dust flame propagates is needed to reconcile flames in both regimes of combustion. Preheat studies also should be performed for different metals, such as iron. The lack of vapor-phase combustion in iron flames means that the flame temperature may not be limited as in aluminum flames, which could lead to higher sensitivities of flame speeds to preheat. Also, observed discrete effects in stabilized iron flames [7] could provide further insight into the physical mechanisms in discrete flames under the effects of preheat. The effects of hydrodynamic stretch have also not been investigated for metal flames and may influence experimental flame speed measurements, particularly at higher temperatures. It is also of interest to find the minimum oxygen concentration required to sustain a dust flame at varying degrees of preheat [61].

Bibliography

- J.M. Bergthorson, S. Goroshin, M.J. Soo, P. Julien, J. Palecka, D.L. Frost, and D.J. Jarvis. Direct combustion of recyclable metal fuels for zero-carbon heat and power. *Applied Energy*, 2015.
- [2] Rolf A. Eckhoff. Dust Explosions in the Process Industries. Gulf Professional Publishing, 2003.
- [3] Alon Gany and Leonard H Caveny. Agglomeration and ignition mechanism of aluminum particles in solid propellants. *Proceedings of the Combustion Institute*, 17(1):1453–1461, 1979.
- [4] Jeffrey M. Bergthorson. Recyclable metal fuels for clean and compact zero-carbon power. Progress in Energy and Combustion Science, 68:169–196, 2018.
- [5] S. Goroshin, I. Fomenko, and J. H S Lee. Burning velocities in fuel-rich aluminum dust clouds. *Symposium (International) on Combustion*, 26(2):1961–1967, 1996.
- [6] Philippe Julien, Sam Whiteley, Michael Soo, Samuel Goroshin, David L. Frost, and Jeffrey M. Bergthorson. Flame speed measurements in aluminum suspensions using a counterflow burner. *Proceedings of the Combustion Institute*, 36(2):2291–2298, 2017.
- [7] Michelle McRae, Philippe Julien, Santino Salvo, Samuel Goroshin, David L. Frost, and Jeffrey M. Bergthorson. Stabilized, flat iron flames on a hot counterflow burner. *Proceedings of the Combustion Institute*, 37(3):3185–3191, 2019.
- [8] Philippe Julien, James Vickery, Samuel Goroshin, David L. Frost, and Jeffrey M. Bergthorson. Freely-propagating flames in aluminum dust clouds. *Combustion and Flame*, 162(11):4241–4253, 2015.
- [9] François David Tang, Samuel Goroshin, Andrew Higgins, and John Lee. Flame propagation and quenching in iron dust clouds. *Proceedings of the Combustion Institute*, 32:1905–1912, 2009.
- [10] Michael J. Soo, Keishi Kumashiro, Samuel Goroshin, David L. Frost, and Jeffrey M. Bergthorson. Thermal structure and burning velocity of flames in nonvolatile fuel suspensions. *Proceedings of the Combustion Institute*, 36(2):2351– 2358, 2017.

- [11] F J Weinberg. Combustion Temperatures: The Future? Nature, 233(0):239–241, 1971.
- [12] U.S. Department of Energy. Energy Tips Process Heating. Combustion Technology Manual, (November), 2007.
- [13] W. Nusselt. No Title. V.D.I, 68(124), 1924.
- [14] D.T. Smoot, I.D.; Pratt. Pulverized Coal Combustion and Gasification. Plenum Press, New York, 1979.
- [15] Robert H. Essenhigh and Joseph Csaba. The thermal radiation theory for plane flame propagation in coal dust clouds. Symposium (International) on Combustion, 9(1):111–125, 1963.
- [16] John L Krazinski, Richard O Buckius, and Herman Krier. COAL DUST FLAMES: A REVIEW AND DEVELOPMENT OF A MODEL FOR FLAME PROPAGATION. Progress in Energy and Combustion Science, 5:31–71, 1979.
- [17] D R Ballal. Flame Propagation Through Dust Clouds of Carbon, Coal, Aluminium and Magnesium in an Environment of Zero Gravity. Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences, 385(1788):21– 51, 1983.
- [18] B. Deshaies and G. Joulin. RADIATIVE TRANSFER AS A PROPAGA-TION MECHANISM FOR RICH FLAMES OF REACTIVE SUSPENSIONS. 46(4):561–581, 1986.
- [19] Hans M. Cassel. Some fundamental aspects of dust flames. Bureau of Mines, (6551), 1964.
- [20] Samuel Goroshin, Jorin Mamen, Andrew Higgins, Tim Bazyn, Nick Glumac, and Herman Krier. Emission spectroscopy of flame fronts in aluminum suspensions. *Proceedings of the Combustion Institute*, 31 II(2007):2011–2019, 2007.
- [21] John R. Howell, Robert Siegel, and M. Pinar Mengüç. *Thermal Radiation Heat Transfer*. CRC Press, Boca Raton, 5th edition, 2011.
- [22] J Bartl and M Baranek. Emissivity of aluminium and its importance for radiometric measurement. *Measurement Science Review*, 4(3):31–36, 2004.
- [23] S. Goroshin, M. Bidabadi, and J. H.S. Lee. Quenching distance of laminar flame in aluminum dust clouds. *Combustion and Flame*, 105(1-2):147–160, 1996.
- [24] Samuel Goroshin, Andrew Higgins, and Michael Kamel. Powdered metals as fuel for hypersonic ramjets. 37th Joint Propulsion Conference and Exhibit, (August 2014), 2001.
- [25] O.W. Childs, J. H.; McCafferty, R.J.; Surine. NACA REPORT No. 881. NACA, (881), 1947.

- [26] G.L. Dugger. Effect of Initial Mixture Temperature on Flame Speed of Methane-Air, Propane-Air, and Ethylene-Air Mixtures. *National Advisory Committee for Aeronautics*, 14(8):399–405, 1952.
- [27] J. B. Zeldowitsch and D. A. Frank-Kamenetzki. 1938 ACTA PHYSICOCHIM-ICA U.R.S.S. VOL IX. No. 2. Acta Physicochimica, IX(2):131–140, 1938.
- [28] Mohamad Metghalchi and James C. Keck. Burning velocities of mixtures of air with methanol, isooctane, and indolene at high pressure and temperature. *Combustion and Flame*, 48(C):191–210, 1982.
- [29] A. A. Konnov. The effect of temperature on the adiabatic laminar burning velocities of CH4-air and H2-air flames. *Fuel*, 89(9):2211–2216, 2010.
- [30] S. P. Sharma, D. D. Agrawal, and C. P. Gupta. The pressure and temperature dependence of burning velocity in a spherical combustion bomb. *Symposium* (*International*) on Combustion, 18(1):493–501, 1981.
- [31] Toshio Iijima and Tadao Takeno. Effects of temperature and pressure on burning velocity. Combustion and Flame, 65(1):35–43, 1986.
- [32] R. Stone, A. Clarke, and P. Beckwith. Correlations for the laminar-burning velocity of methane/ diluent/air mixtures obtained in free-fall experiments. *Combustion and Flame*, 114(3-4):546–555, 1998.
- [33] S. Y. Liao, D. M. Jiang, and Q. Cheng. Determination of laminar burning velocities for natural gas. *Fuel*, 83(9):1247–1250, 2004.
- [34] Kenji Takizawa, Akifumi Takahashi, Kazuaki Tokuhashi, Shigeo Kondo, and Akira Sekiya. Burning velocity measurement of fluorinated compounds by the spherical-vessel method. *Combustion and Flame*, 141(3):298–307, 2005.
- [35] R. T.E. Hermanns, A. A. Konnov, R. J.M. Bastiaans, L. P.H. de Goey, K. Lucka, and H. Köhne. Effects of temperature and composition on the laminar burning velocity of CH4+ H2+ O2+ N2flames. *Fuel*, 89(1):114–121, 2010.
- [36] Vladimir A. Alekseev, Moah Christensen, and Alexander A. Konnov. The effect of temperature on the adiabatic burning velocities of diluted hydrogen flames: A kinetic study using an updated mechanism. *Combustion and Flame*, 162(5):1884– 1898, 2015.
- [37] D. P. Mishra. Effects of initial temperature on the structure of laminar CH4-air premixed flames. *Fuel*, 82(12):1471–1475, 2003.
- [38] Yi Wu, Vincent Modica, Bjorn Rossow, and Frédéric Grisch. Effects of pressure and preheating temperature on the laminar flame speed of methane/air and acetone/air mixtures. *Fuel*, 185:577–588, 2016.

- [39] Alison M. Ferris, Adam J. Susa, David F. Davidson, and Ronald K. Hanson. High-temperature laminar flame speed measurements in a shock tube. *Combus*tion and Flame, 205:241–252, 2019.
- [40] Xinlu Han, Zhihua Wang, Shixing Wang, Ronald Whiddon, Yong He, Yu Lv, and Alexander A. Konnov. Parametrization of the temperature dependence of laminar burning velocity for methane and ethane flames. *Fuel*, 239(November 2018):1028–1037, 2019.
- [41] Chung K. Law. Combustion physics. 2006.
- [42] Stephen R. Turns. An Introduction to Combustion: Concepts and Applications. McGraw Hill Education, New Delhi, third edition, 2012.
- [43] Kenneth K. Kuo. *Principles of Combustion*. 2nd edition, 2005.
- [44] D. A. Frank-Kamenetzki. Diffusion and Heat Exchange in Chemical Kinetics. Princeton University Press, 1955.
- [45] Michael Soo, Xiaocheng Mi, Samuel Goroshin, Andrew J Higgins, and Jeffrey M Bergthorson. Combustion of particles, agglomerates, and suspensions – A basic thermophysical analysis. *Combustion and Flame*, 192:384–400, 2018.
- [46] S Goroshin, J H S Lee, and Yu Shoshin. EFFECT OF THE DISCRETE NA-TURE OF HEAT SOURCES ON FLAME PROPAGATION IN PARTICULATE SUSPENSIONS. Symposium (International) on Combustion, 27:743–749, 1998.
- [47] M.M. Mallard and Le Chatelier. Étude sur la combustion des mélanges gazeux explosifs. J. Phys. Theor. Appl, 1(1):173–183, 1882.
- [48] Jan Palecka, Samuel Goroshin, Jeffrey M Bergthorson, Samuel Goroshin, and M Bergthorson. Propagation and quenching of dual-front flames in binary-fuel mixtures mixtures. *Combustion Science and Technology*, 2202, 2018.
- [49] Ya. B. Zeldovich, G. I. Barenblatt, V. B. Librovich, and G. M. Makhviladze. The Mathematical Theory of Combustion and Explosions. Consultants Bureau, New York, 1985.
- [50] Jan Palecka, Jessica Sniatowsky, Samuel Goroshin, Andrew J Higgins, and Jeffrey M Bergthorson. A new kind of flame : Observation of the discrete flame propagation regime in iron particle suspensions in microgravity. *Combustion and Flame*, 209:180–186, 2019.
- [51] Jeffrey M. Bergthorson, Kazuo Sone, Trent W. Mattner, Paul E. Dimotakis, David G. Goodwin, and Dan I. Meiron. Impinging laminar jets at moderate Reynolds numbers and separation distances. *Physical Review E - Statistical*, *Nonlinear, and Soft Matter Physics*, 72(6):1–12, 2005.

- [52] F N Egolfopoulos, N Hansen, Y Ju, K Kohse-Höinghaus, C K Law, and F Qi. Advances and challenges in laminar fl ame experiments and implications for combustion chemistry. *Progress in Energy and Combustion Science*, 43:36–67, 2014.
- [53] J D Munzar, B Akih-kumgeh, B M Denman, A Zia, and J M Bergthorson. An experimental and reduced modeling study of the laminar flame speed of jet fuel surrogate components. *Fuel*, 113:586–597, 2013.
- [54] Antoine Durocher, Philippe Versailles, Gilles Bourque, and Jeffrey M. Bergthorson. Impact of Kinetic Uncertainties on Accurate Prediction of NO Concentrations in Premixed Alkane-Air Flames. Combustion Science and Technology, 0(00):1–27, 2019.
- [55] David G. Goodwin, Raymond L. Speth, Harry K. Moffat, and Bryan W. Weber. Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes. https://www.cantera.org, 2018. Version 2.4.0.
- [56] C.W. Bale, E. Bélisle, P. Chartrand, S.A. Decterov, G. Eriksson, A.E. Gheribi, K. Hack, I.H. Jung, Y.B. Kang, J. Melançon, A.D. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer, and M-A. Van Ende. Factsage thermochemical software and databases - 2010-2016. www.factsage.com, 2016. Calphad, vol. 54, pp 35-53, 2016.
- [57] Irvin Glassman and Richard A. Yetter. Combustion. Combustion, page 92101, 2008.
- [58] M. W. Beckstead. Correlating aluminum burning times. Combustion, Explosion and Shock Waves, 41(5):533–546, 2005.
- [59] A.F. Belyaev, Yu. V. Frolov, and A.I. Korotkov. Combustion and Ignition of Particles in Finely Dispersed Aluminum. *Combustion, Explosion and Shock Waves*, pages 323–329, 1968.
- [60] A N Zolotko, Ya I Vovchuk, V G Shevchuk, and N I Poletaev. Ignition and Combustion of Dust – Gas Suspensions. Combustion, Explosion and Shock Waves, 41(6):611–621, 2005.
- [61] Michael Soo, Samuel Goroshin, Nick Glumac, Keishi Kumashiro, James Vickery, David L Frost, and Jeffrey M Bergthorson. Emission and laser absorption spectroscopy of flat flames in aluminum suspensions. *Combustion and Flame*, 180:230–238, 2017.