# On the study of flames in aluminum and iron suspensions

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## Abstract

Despite its importance in industrial accidents and many technological applications, the field of dust combustion remains less understood in comparison to hydrocarbon combustion. The majority of the knowledge on dust combustion either comes from single particle experiments or from constant-volume combustion bombs. However, in the majority of real-life applications, dust combustion happens in dense suspensions, making the usefulness of the first of these approaches limited. As for combustion bombs, they typically only yield information about the pressure history and provide no information on flame structure and flame propagation mechanisms. The present experimental dissertation focuses on the investigation of optically accessible flames propagating in suspensions of metallic fuels using high-speed imaging and spectroscopy. It introduces two novel apparatus to study flames freely-propagating in aluminum suspensions. The first is a smallscale apparatus that uses transparent latex balloons of about 30 cm in diameter to contain the dispersed dust. The balloon expands maintaining isobaric conditions during the experiments. The second is a large-scale apparatus capable of producing conical clouds of aluminum powder on the order of meters in diameter. The present thesis also uses a recently introduced apparatus consisting of a dust Bunsen burner to study stabilized flames in hybrid metal-methane systems. Using these three techniques, this dissertation presents a large compendium of data on flames propagating in metal suspensions. The results on freely-propagating flames reveal for the first time the presence of thermo-diffusive instabilities in lean aluminum flames that are characterized by pulsating and spiral waves. The results also demonstrate that the flame speed in lean flames is weakly dependent on the oxygen concentration whereas the flame speed in fuel-rich flames is independent of the aluminum concentration. The experiments demonstrate that radiation heat transfer only plays a secondary role in the flame propagation mechanism even at large scales and also that it is possible to define the notion of burning velocity for dust flames. In the case of stabilized flames in hybrid mixtures and contrary to single particle theories, it is shown that metal fuel act as inert particles at low concentration in the methane flame and that a second, metal fuel flame front forms only above a critical concentration and couples to the methane flame. The above-mentioned findings highlight the importance to study dust combustion as a flame phenomenon.

## Abrégé

Malgré son importance dans plusieurs domaines, la combustion des poudres métalliques est toujours beaucoup moins étudiée que la combustion des carburants fossiles. Les expérimentations dans ce domaine sont généralement faites sur des particules individuelles ou dans des enceintes fermées. Toutefois, dans la majorité des applications, les particules brûlent à l'intérieur de denses suspensions, limitant par le fait même l'utilité des expériences faites sur des particules individuelles. De plus, les enceintes fermées ne produisent aucune information sur la structure de flamme ou les mécanismes de propagation de flamme. La présente dissertation expérimentale porte sur l'investigation de flamme qui se propage à travers de denses suspensions de poussières métalliques. Deux nouveaux appareils ont été créés afin d'étudier les flammes d'aluminium. Le premier fait usage de ballons en latex transparent de 30 cm de diamètre pour contenir la poudre dispersée. Le ballon s'agrandit en même temps que la propagation de la flamme, ce qui maintient des conditions isobariques à l'intérieur. Le second appareil est utilisé pour produire de larges nuages de poudres d'aluminium de forme conique mesurant environ 4 m de hauteur et 2 m de largeur. Cette thèse fait également rapport de l'utilisation d'un brûleur de type Bunsen récemment introduit afin d'étudier des flammes stabilisées dans des mélanges diphasiques de poudres métalliques et de méthane. Grâce à l'utilisation de ces trois techniques uniques, cette dissertation rapporte une grande base de données sur les flammes de combustibles métalliques. Les travaux sur les flammes nonstabilisées font état de la découverte d'instabilité thermo-diffusive, qui se manifestent sous la formes de pulsations et de spirales dans des mélanges pauvres en combustible. Les résultats démontrent également que les vitesses de flamme dépendent faiblement de la concentration en oxygène des mélanges pauvres en combustible alors que les vitesses de flammes sont indépendantes de la concentration d'aluminium dans les mélanges riches en combustible. De plus, les expériences démontrent que le transfert de chaleur par radiation ne joue qu'un rôle secondaire dans le mécanisme de propagation de flamme. Les travaux montrent qu'il est également possible de définir une vitesse fondamentale de flamme pour des mélanges de poudre. Pour ce qui a trait aux flammes stabilisées dans des mélanges diphasiques, les résultats indiquent qu'un front de flamme métallique se forme au de-là d'une certaine concentration

critique et que ce second front est couplé à la flamme de méthane. Toutes ces découvertes scientifiques ci-mentionnées prouvent qu'il est essentiel de traiter la combustion de poudres en tant que flamme et non uniquement par des particules individuelles.

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Je tiens à remercier mes parents, Carole et Jacques, pour leur support tout au long de mes études. Merci à Kim, qui a su géré mes moments les plus difficiles tout en finissant sa résidence. " Comprendre ce n'est point démontrer, ni expliquer. C'est accéder à la vision » -Antoine de St-Éxupéry

## **Contribution of Author**

#### Freely-propagating flames in aluminum clouds

I designed the balloon apparatus described in Julien et al. [1] and Julien et al. [2] and assembled it with the help of Maxime Julien. I also designed and assembled the field apparatus with the help of a group of undergraduate students led by Alex Wright doing their bachelor project. I performed the tests and analyzed the results for all balloon experiments with the help of James Vickery, Christopher Kowal and Justin Hayto. I wrote the software for processing the data. I also performed all field experiments myself with the help of Alex Wright and James Vickery, wrote the software for processing and analyzed the data.

#### Stabilized flames in hybrid metal-methane mixtures

The hybrid Bunsen dust burner was designed by Michael Soo and was assembled and tested by both of us. We ran all experiment together and analyzed the data published in Soo et al. [3]. I ran myself the next series of experiment figuring in Julien et al. [4] and developed the analytical model in it. I performed the experiments and analyzed the data in Julien et al. [5] and Sam Whiteley helped with the thermodynamic analysis.

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### **Chapter 1. Introduction**

#### **1.1 General Considerations and Motivation**

Combustion plays a central role in our daily life and is used for transportation, heating, electricity production, cooking, product manufacturing and many other applications. Modern society heavily relies on the combustion of gaseous and liquid hydrocarbon fuels and scientists have consequently invested a vast amount of efforts to study it. The field of combustion has made tremendous progress since Mallard and Le Chatelier [6], [7]. Complex chemical and thermodynamical models now exist that are able to predict hydrocarbon flame behavior for a wide variety of fuels and for many different applications [8][7]. These models are used to design the next generation of engines and combustors that will be more fuel efficient and less polluting.

Despite its importance in industrial explosions [9]–[13] and numerous technological application [14]–[18], the field of dust combustion still lags behind in terms of knowledge and understanding. Most experiments are performed in constant volume combustion bombs in an attempt to classify them according to the potential danger they represent in a specific environment [19]–[21]. Although useful for setting industry safety standards, these techniques remain ill-suited to provide fundamental scientific information on the combustion behavior of any type of powders.

There exists a wide array of different types of combustible dusts with different combustion properties [13]. Organic dusts, such as corn starch [20], flour [22], and cork [23], are composed of many different components and burn in a similar fashion to coal [24], [25]. They partially volatilize and burn in the gas phase, while leaving a charred core that burns with surface reactions. Plastics, such as poly methyl methacrylate (PMMA) [26], have low boiling or volatilization temperatures compared to their flame temperatures and their vapors mix with air to form a gaseous flame. Their combustion in that respect differs very little from the combustion of liquid hydrocarbon droplets [13].

Metal powders, unlike organic or plastic dusts, are pure substances with typically only one element present, which makes them more suitable for fundamental scientific studies. Refractory metals, such as iron, do not evaporate and burn only heterogeneously as surface reaction [27]. More volatile metals like aluminum or magnesium will evaporate [27], but since metal vapor-

oxygen reactions have very low activation energies, they will react immediately after evaporation and not mix with ambient air [28].

Metals are energetically dense [27], [29] and are thus frequently used as additives in propellants, pyrotechnics, explosives and other energetic materials [30]–[37]. Metals are being considered for fuel for solid-fuel hypersonic ramjets [16] and some researchers are even considering building a propellant mixture with only aluminum and water [38], [39]. Aluminum is used frequently in explosive formulations along with RDX or HTPB for condensed high-explosives [40] or for rocket propellants [41], [42]. Boron and beryllium are seen as the ultimate fuels since they have highest energy densities of all metals [43]–[46]. Beryllium, however has the problem of having extremely toxic oxides [47], which makes them ill-suited for any practical applications. Boron is still being considered as a potential fuel but burning it completely and efficiently still remains a challenge [48]. Magnesium combustion with carbon monoxide and carbon dioxide is of interest, among other things, for a potential missions to mars [49]–[51]. The Martian atmosphere is mainly constituted of carbon dioxide and carbon monoxide and has very little oxygen. Magnesium has a very low ignition temperature with carbon dioxide and would constitute an excellent rocket fuel combined with the CO<sub>2</sub> already present in the atmosphere.

Metal powders also have the potential to play a central role in the global energy market by becoming energy carriers. Metal powders are energetically dense, safe to handle with an almost infinite shelf life, making them the ideal energy carriers. Beach et al. [52] first proposed to use nano-powders as fuel injected in an internal combustion engine for transportation. However, injecting particles in an engine presents many technical problems. The Alternative Fuel Laboratory at McGill University proposes a different concept based on the combustion of micron-sized powder using a dust burner to produce heat [53]. The burner can be part of an external combustion engine to produce electricity or mechanical work or the heat can be used directly for process heating or simply heating buildings. Solid metal oxides are the only product of combustion and can be collected to be reprocessed. If renewable or nuclear energy is used to reprocess the metal oxides back into metal, the entire chain is carbon-free and environmentally friendly. Many metals are thus good candidates to be energy carriers and, since each element has different properties, the ideal candidate may differ depending on the application, which makes metal energy carriers very versatile. Other cycles using metal as energy carriers include burning the metal particle in a carbon

dioxide environment obtained from carbon sequestration and reprocessing the metal oxides using renewable energy sources [54].

The present manuscript-based thesis focuses on the combustion of micron-sized aluminum and iron particles in suspensions in different oxidizing environments. Aluminum, as mentioned above, is the most abundantly used metal in many energetic materials. Aluminum and iron are both extensively used industrially, which makes them prone to accidental explosions. Iron is also an ideal candidate for being an energy carrier due to its low cost, abundance and heterogeneous reactions that do not produce nano-sized oxides.

The first section of the thesis is composed of a literature and concept review of metal combustion. The review will first look at what has been accomplished on the combustion of single particles and will then focus on the state-of-the-art knowledge of flames propagating in suspensions. It will then be followed by a synthesis on the scope of the work performed in the course of this investigation. The 4 publications will then be presented in two different sections followed by a conclusion.

### 1.2 Literature and Concept Review of Metal Combustion

#### **1.2.1 Single Particle Combustion**

#### **1.2.1.1 Theory and Concepts**

The Glassman criterion [27] is used to determine whether a particle will burn in the vapor phase or at the particle surface and is based on the flame temperature and the boiling temperature of the metal. If the flame temperature is higher than the metal boiling point, then the metal can evaporate and burn in the vapor phase, as a micro-flame surrounding the particle. This micro-flame can have a radius that is several times the particle radius [55]. Some examples of vapor phase combustion metals include aluminum [56] and magnesium [49]. The second mode of combustion is called heterogeneous and happens when the flame temperature is lower than the boiling temperature of the metal [27]. In this case, all the reactions happen at the particle surface. In the case where combustion produces refractory metal-oxides, the flame temperature is limited by the boiling temperature of the oxide. If the combustion produces gaseous oxides, then the reactions at the surface of the particle produces sub-oxides in the gas phase which later condense into final oxides separate from the original core. When the reaction produces solid metal-oxides, then the products stay on the particle and the particle is bigger at the end then when it originally started. An example of the latter would be iron combustion. Thermodynamic solvers, such as Cantera [57] or NASA CEA [58], can be used to calculate the relevant temperatures to determine the phase of all products and the mode of combustion.

It was recognized by Glassman [59] and Bruzowsky and Glassman [60] that combustion of single particles of metals that burn in the vapor phase would burn in similar fashion to hydrocarbon droplets and follow the  $d^2$ -law [7]. The droplet is colder than the ambient gas and this gradient will cause heat to diffuse by conduction from the gas to the surface of the droplet. The heat will then move away from the surface to the interior of the droplet increasing its temperature and the rest will serve to gasify the liquid at the surface of the droplet. When the concentration of vapour is low in the surrounding gases, the vapour will be transported outwards, thus leaving place for more evaporation, implying that the combustion of droplets will be limited by diffusion of heat and mass. There are two asymptotic regimes in dust combustion, determined by the slowest rate in the system. The two competing rates are the rate of heat and species diffusion and the chemical reaction rate [61]–[63]. When the rate of heat diffusion is much larger than that of chemical reaction, the chemical reactions determine the combustion mode and is thus called kinetically-controlled regime. In those circumstances, the gas-phase temperature and particle temperature is essentially equivalent. Kinetically-controlled combustion typically happens for particles of smaller size [63]. When chemical reactions are slow in comparison to transport rates, than the combustion is diffusion-controlled. In that case, the particle temperature is significantly greater than the gas-phase temperature. Ignition is then defined as the transition from the kinetically-controlled regime to the diffusion controlled regime, a concept similar to that of thermal runaway [64], [65]. All particle combustion starts in the kinetic regime and, if the kinetics are fast enough, the particle ignites and burns in a diffusion-controlled regime. Figure 1.1 illustrates the difference in temperature profiles and oxidizer concentration for particles reacting in the diffusion regime versus particles reacting in the kinetic mode.



Figure 1.1 Temperature and oxidizer concentration profiles for particles reacting in diffusion and kinetic regimes.

Many mathematical models exist to describe combustion of single particles. The d<sup>2</sup>-law is used to correlate the burn time to the particle diameter [7]. King [66] developed a simplified model for combustion of magnesium particles in carbon dioxide where the particle reacts in two zones, where one zone is limited by transport properties and the other one by reaction kinetics. Mi et al.[67] have a model for ignition of amorphous boron agglomerates that happens in two stages. In the case of aluminum, Beckstead et al. [68] made a review of the different numerical model of single particle combustion. Early models assumed infinite kinetics, such that combustion of particles was controlled by transport properties [60], [69], [70]. Beckstead et al. [71] later elaborated on their own model that includes condensation of oxides after combustion.

#### **1.2.1.2 Experimental Methods**

A large amount of scientific studies on metal combustion was done on single particles. Single particles are ignited and the burn time, ignition temperature and some chemical kimetic rates are measured. One of the main methods of ignition is ignition by a hot flame [33], [72]–[75]. It has the advantage of being simple to implement but the temperature of the environment and the composition both depend on the initial mixture. Other methods include ignition by laser [76]–[79] and shock tubes [15], [63], [80]. These last two methods have the advantage of having independent mixture composition and temperatures.

The dependence of the burn time on the radius and the mode of combustion was verified experimentally [81][63]. Larger particles burn in a diffusion-controlled regime and follow the d<sup>n</sup>-law and smaller particles burn in a kinetically-controlled regime where the burn rate depends linearly on the particle diameter. Beckstead [56] gathered a compendium of data on aluminum burn times. He found that the exponent *n* correlating the burning time to the particle size *d* is  $n\sim1.5$ -1.8, slightly lower than 2. Bazyn et al. [63] showed evidence for the transition from a kinetically-controlled regime to a diffusion-controlled regime for an increasing size of aluminum particles. Badiola et al. [76] showed that small particles of zirconium and titanium have a linear dependence and compares to the results obtained for larger particles, where the exponent is much greater.

Burn time data has been gathered by Beckstead in 2005 for aluminum particles in different oxidizing mixtures [82]. The burn time of titanium [76], [83], [84] and zirconium [76] has been measured for different particle sizes and follow the same trend as aluminum. According to Beckstead et al. [68], aluminum kinetics has been measured in different oxidizers by Widener et

al. [71] and Bucher et al. [85]. More recently, aluminum kinetics has been measured in shock tubes by Servaites et al. [86].

#### **1.2.2 Flame propagation in dust clouds**

#### **1.2.2.1 Experimental Methods**

The majority of dust combustion experiments in clouds are performed in constant volume combustion bombs, where typically the measurements are only made with pressure transducers [19], [21], [87]. The maximum rate of pressure rise and maximum pressure are obtained from the pressure trace and this information is then used to classify dusts according to the danger they represent in industrial settings. Other parameters such as the maximum effective burning velocity, also obtained from the pressure trace, can also be used to classify dusts. Furthermore, these experiments are used to obtain the minimum ignition energy and flammability limits for a specific mixture of combustible dusts [88]. More recent works used hot-wire anemometry [89] and laser Doppler anemometry [87], [90] to measure the turbulence level in combustion bombs.

Combustion bombs still lack direct visual observation of flames and the non-isobaric conditions make it difficult to obtain fundamental parameters. Only a handful of studies investigated isobaric flame propagation in suspensions of metal particles using visual and optical methods. Cassel [91], [92] was one of the first to use a stabilized Bunsen flame to study flames in aluminum suspensions. He measured the burning velocity of flames in aluminum suspensions as a function of aluminum concentration. Ballal [93] used tubes in micro-gravity to study flame propagation through clouds of aluminum, magnesium and carbon. Boichuk [94] measured flame speed of flames in aluminum-boron binary mixtures and in pure boron in tubes. Sun et al. studied small-scale, unconfined freely-propagating flames in aluminum and iron [95]–[97]. Using laser light illumination and high-speed photography, they measured the flame speed as a function of concentration for different sizes of aluminum and iron particles.

McGill University has a long history of research in dust combustion. Goroshin et al. used a dust Bunsen burner [98] to measure the burning velocity of flames in aluminum cloud as a function of metal and oxygen concentration. Using the same apparatus, they used emission spectroscopy to measure flame temperatures [99]. Tang et al. and Goroshin et al. studied flame propagation through clouds of large iron particles using tubes in micro-gravity conditions [100]– [102]. Finally, Goroshin et al. [103] studied quenching distances of flames propagating through aluminum clouds using quenching tubes.

#### **1.2.2.2 Burning Velocity**

The burning velocity, defined as the speed at which an un-stretched flat laminar flame propagates through a quiescent mixture of unburned reactants, is the most fundamental property of any combustible mixtures that characterizes both the rate of combustion and the rate of the heat transfer from the flame zone to the unburned mixture [7]. By definition, the burning velocity is an asymptotic approximation and unavoidable effects such as flame stretch, heat loss, complex flow patterns, and residual turbulence all influence the experimental results. The different measurement techniques include, among others, Bunsen burners [104], flat-flame burners [105], outwardly expanding spherical flames [106], stagnation flame burners [107] and flames in tubes [108]. These measurements are essential for validating theoretical flame models that can now accurately predict flame dynamics and formation of pollutants in real systems. Some of the recent measurement techniques allow very accurate measurements of the burning velocity and flame structure, demonstrating excellent correlation with one-dimensional numerical flame models [8].

Flame speed is distinct from the burning velocity in the sense that it is not a fundamental parameter of a combustible mixture. It is the value that is directly measured in the laboratory and cannot be used as such for direct comparison between different methodologies. Figures 1.2 and 1.3 show the data available on flame speed for aluminum flames and for iron flames. They are obtained from different authors using different powder sizes and methodologies. Since they are not presented in terms of burning velocity, direct comparison is difficult to make between the different sets of data.



Figure 1.2. Flame propagation speed in iron dust cloud of different particle sizes and experimental methods [96], [101].



Figure 1.3. Flame propagation speed in aluminum dust cloud of different particle sizes, oxygen concentration and experimental methods [93], [94], [98].

#### 1.2.2.3 Diagnostics

Particle size distributions can be obtained with particle sizers, such as the Malvern Mastersizer, or with an optical or scanning electron microscope. Burnt particles can also be analyzed using microscopy after the experiments [85], [109]. The dispersion process and flame propagation can be imaged using high-speed imaging [1], [102]. The particle concentration is typically measured using a laser-absorption technique and the Beer-Lambert law [98], [110].

Spectroscopic methods can be used to investigate many properties of a flame; to determine to a certain extent the atomic and molecular composition of various zones in the flame, to obtain the temperature of the different species in the combustion zone and to attempt to quantify the radiation heat transfer at different points in time and space. Reif et al. from Ames Laboratory at Iowa State University [111]–[113] listed four different spectroscopic methods to obtain the information about temperatures in the flame. They are: the line reversal, the emission-absorption, the slope and the two-line methods. The two first methods require external lamps tuned to the desired frequencies whereas the latter methods only utilize the atomic lines of atoms already present or seeded in the flame. They clearly mention that this method actually measures only the temperature of the specific species emitting the lines and that a state of local thermal equilibrium is needed to conclude that the measured temperature is the flame temperature. In addition, laser light can be used instead of lamps to target more precisely a specific wavelength region, as is the case for measuring the concentration of NO in the flame zone [114].

Lewis et al. [115], [116] used the two-lines method with barium tracers to measure the flame temperature of aluminized explosives. This method can provide the temperature of the tracer, which is assumed to be in thermal equilibrium with the flame, given that the intensity of two peaks is measured and the values of the appropriate constants are available. In this case, the authors found the required constants from the National Institute of Standards and Technology [117]. The errors of their measurements range from 400 K to 1000 K and arise from the low signal to noise ratio from one of the barium lines.

Goroshin et al. [30] used optical pyrometry and spectroscopy to diagnose fireballs of metalized explosives, a multi-temperature environment. Assuming a blackbody profile for solid

emitters, pyrometry only requires two colours or wavelengths to be able to deduce the temperature, as long as those wavelengths do not overlap with emission bands of some of the gaseous species. They have been able to measure temperature with a precision of 100 K.

Goroshin [99], in collaboration with researchers from the University of Illinois, measured the solid phase temperature in aluminum dust flames by using Planck's law of blackbody radiation, and determined the gas phase temperature using AlO molecular bands. In order to find the temperature of the solid species, one needs to isolate the continuous part of the spectrum, cutting out the different peaks coming from atomic or molecular gases, such as the aluminium oxide bands and the sodium lines. In order to accurately locate the flame front, the authors scanned a horizontal cross-section of the Bunsen cone and assumed that it would be located at the highest intensity point. They have also extracted the temperature from the molecular AlO bands by fitting the data to the theoretical shape.

Lynch et al. [15], [118], also using Planck's law, determined the temperature of micron size alumina particles, while stating that alumina has an emissivity dependent on the square of the inverse of the wavelength at low temperatures and is roughly grey at around 3000 K. They also claim that this spectral dependence on the wavelength can produce errors in the range of 100 K to 1000 K and that the quality of the fit is not a good measure of the error. This method remains nonetheless very useful for measuring the flame temperature of solid fuels and might yield better results with particles that behave more closely to a real grey body. The findings of this work suggest that multiple temperature diagnostic techniques may be needed to ensure that systematic errors are minimized.

#### 1.2.2.4 Radiation Heat Transfer

Solid particles, as opposed to gaseous molecules, emit and absorb radiation in a continuous fashion. Radiation heat transfer can thus be significant in terms of heat loss in the reaction zone but also can contribute to the flame propagation mechanism. Radiation emitted from the reaction zone and from the combustion products can propagate through the reaction zone and pre-heat the reactants. The flame speed is thus faster since the flame propagates in a pre-heated mixture. The amount of heat exchanged by radiation depends on the size of the dust cloud, the type of particles and the size and size distribution of particles. A photon must travel several mean free paths before being absorbed [119], which means that small clouds will see radiation as pure heat loss . Viskanta

and Mengüç [120] claim that radiation heat transfer becomes substantial at characteristic combustion lengths of about 1m in gaseous fuels, suggesting that this characteristic length could be smaller for dust clouds.

Joulin et al. from the Laboratoire d'Énergétique et de Détonique in Poitier, France [121]– [123], used the method of asymptotics to study gaseous flames laden with inert particles, where the inert particles can transfer heat from the burnt zone to the unburnt reactants via radiation. They show that the addition of inert particles to a gaseous fuel-oxidizer mixture will promote flame propagation and that the flames may be more resistant to quenching. Their model of radiation is based on the Milne-Eddington approximation of the radiative transfer equation [119]. Some models even predict that radiation can be the main driving mechanism for flames propagating within particulate clouds [124], [125].

#### 1.2.2.5 Models

Goroshin et al. [103] developed a model for calculating the flame speed in metal clouds as a function of equivalence ratio. Aluminum was assumed to burn heterogeneously, that is with no pre-mixed aluminum-vapor air mixture, due to the very low activation energy of metal-vaporoxygen reactions [28], [126]. In this model, the flame propagates only by molecular heat diffusivity. The model is divided in two zones, fuel lean and fuel rich, which allows for two simple analytic solutions for calculating the flame speed that depends, among other things, on the ignition temperature and particle burn time. Based on this model, Goroshin et al. [127] created a new model for binary mixtures with two different sizes of particles. In any real applications, powders have a size distribution and combustion and ignition properties of powders depend on the particle size.

Huang et al. [128] published a model similar to that of Goroshin et al. [103] for the combustion of nano-aluminum powder, which they state burn in a kinetically-controlled mode and yet still use ignition temperature that exists only for diffusion-controlled regimes [65]. Goroshin et al. [129], [130] and later Tang et al. [131] developed a model on discrete flame propagation. It assumes that particle burn time is very fast compared to the diffusion of heat, which means that the flame propagates from one particle to the other in a discrete rather than continuous fashion.

Recent work by Soo et al. [65] show that models based on ignition temperature and burn time may be inadequate since they don't take into consideration the effect of ensemble of particles. The model shows that the onset of chemical reactions critically depends on the particle concentration.

#### 1.2.2.6 Flames in hybrid mixtures and double reaction fronts

Flames in hybrid mixtures are flames propagating through mixtures containing fuels of two different phases, typically a solid phase fuel and a gaseous or liquid fuel. Commonly studied mixtures include methane and coal [132]–[134] or organic dusts mixed with methane [23]. Slurry fuels that mix hydrocarbons and solid particles are sometimes envisaged as combustibles for airbreathing propulsion devices due to their high energy content [35]. Soo et al. [3] investigated stabilized aluminum-methane-air flames using a dust Bunsen burner. Palecka et al. [135] studied quenching distances in hybrid mixtures of aluminum and methane. Detonations in hybrid mixtures are also studied [136]–[139] for their applications in metalized propellants and explosives.

Flames that arise from two fuels with sufficiently different reaction mechanisms can have two distinct reaction zones [3], [135], [140]. Khaikin et al. [141] explored the idea of two consecutive reactions in a gas phase, with three different species. The first species turns into the second one, which turns into the third one. In their example, the two reactions have distinct reaction mechanisms, which explains why two flame front can exists. Such phenomenon are only observed in exotic gaseous mixtures, such as the CH<sub>4</sub>-NO<sub>2</sub>-O<sub>2</sub> mixtures observed in Branch et al. [140] or reactive systems composed of very different fuels such as mixtures of metals powders and hydrocarbon fuels [3], [135].

#### **1.3 Scope of present thesis**

The traditional approach to study metal combustion is, as previously mentioned, to perform single particle experiments. However, combustion of metal powders in any pratical application always happens in dense suspensions, such that it is often difficult to extrapolate the information obtained from those experiments to a real-life scenario. Although ignition temperatures and particle burn times are sometimes used in analytic models, those parameters remain insufficient to fully describe dust combustion phenomena. The single particle approach completely ignores the collective effects in a flame, which requires a certain concentration of dusts in suspension. A dust flame propagates through a cloud via diffusion of heat and cannot, as such, be explained with single particle theory alone. Dust combustion thus needs to be treated as a wave phenomenon, similarly to a gaseous flame. With this treatment come the different concepts usually associated to gas combustion: burning velocity, flammability limit, flame stability, flame structure, turbulent combustion and many others. It is only possible to study dust combustion in a complete fashion when it is treated as a flame and, thus, experiments must be thought and designed with that idea in mind.

In this respect, combustion bomb experiments have the advantage of being conducted in dense suspensions, normally having a central ignition and then a more or less spherical flame propagation. However, in the majority of cases, the pressure history is the only measurement and they have no optical access, which makes it impossible to assess the uniformity of the dust clouds and the flame shape, two important parameters to study properly flame phenomenon.

It quickly becomes apparent that it is necessary to develop new tools to look at the various phenomena occurring in a dust flame. As listed in the previous section, only a handful of publications used visual means to observe flames in metal suspensions. The experimental data available on dust flames is consequently limited. Building a large compendium of data using new techniques at different cloud sizes will help to build a strong scientific foundation.

Furthermore, powders, unlike gases, have very different characteristics depending on who manufactured it. A powder with the same metal content and same mean particle diameter can burn differently due to a different size distribution or particle morphology. In that regard, the same batch of aluminum powder, Ampal 637, produced by Ampal, NJ, USA, has been used since 1991 at

McGill University, allowing for direct comparison and creating a complete database. Some of the same techniques were also used to characterize the combustion behavior of iron, but data remains limited to flames in tubes.

In continuation of this effort, the present work studies combustion of metal powders, aluminum and iron, in suspensions in different geometries, scales and oxidizing environments using stabilized and freely-propagating flames. Three novel experimental methods are thus used or introduced in the present thesis, methods that will prove to be versatile and adaptable to different powdered solid fuels. They consist of a hybrid dust-gas Bunsen burner, a small-scale balloon apparatus and a field apparatus producing large-scale clouds. The hybrid Bunsen burner was first introduced in Soo et al. [3] and is based on a design used previously for pure dust flames by Goroshin et al. [98]. The following two apparatus were designed specifically for studying freely-propagating dust flames and are introduced later.

A large compendium of data is obtained with these three experimental apparatus that has been published in four different articles. The diverse concepts studied include: flame speed, burning velocity, radiation heat transfer, flame front formation, particle regime of combustion, flame instabilities, discrete flame propagation and flame temperature. The three different experimental methodologies are complimentary by allowing the comparison between different geometries. Furthermore, it is difficult with the balloon experiment to perform experiments with very fuel rich mixtures due to the settling of powder and the difficulty to see inside the flame but it is very easy to go to very fuel lean concentrations. On the other hand, it is difficult to stabilize a lean flame on the Bunsen burner but experiments can be performed at very rich conditions.

Dust combustion in realistic applications happen in many different oxidizing environments. Dust explosions can happen in pure air but also in an environment containing a certain fraction of combustible gases such as methane or hydrogen. Explosion in coal mines usually involve a mixture of solid coal and methane gas in air. Also, aluminum particles in propellants burn in a combination of different oxidizers at high temperature that arise from the combustion of the main matrix. This diversity of oxidizing environments needs to be represented in scientific studies with basic, controlled experiments. The different oxidizing environments can also be used to look at different flame properties by modifying certain parameters, such as the chemical reaction rate, by changing the type of oxidizer, or the molecular heat diffusivity, by changing the inert diluent.

The four publications in the present manuscript-based dissertation are divided in two sections: 1) Freely-propagating flames in aluminum dust clouds and 2) Metal dust flames in the products of hydrocarbon combustion. The experimental findings are explained in light of existing theories or with simple models that highlight the basic physical nature of the various phenomena.

## **Chapter 2. Effect of Scale on Freely Propagating Flames in Aluminum Dust Clouds**

#### 2.1 Introduction on freely-propagating flames in aluminum clouds

Chapters 2 and 3 look at freely-propagating flames in aluminum clouds for different oxidizing mixtures. The publications introduce two novel experimental methodologies to study dust combustion. The first is called the balloon experiment and is an isobaric variation on the isochoric combustion bombs commonly used for testing of different industrial powders. The latex balloon expands with the flame propagation such that constant pressure is maintained. The transparent balloon also allows full visual access to the entire event, from dust dispersion to the end of the flame propagation. The second apparatus is used to generate large-scale clouds and is used in field tests outside McGill University. It produces a vertical column of dust roughly 4m high and 2m wide. The two different apparatus allow for the comparison of different geometries and different scales.

The laminar burning velocity, as mentioned previously, is a fundamental parameter in gas combustion [7]. It is a unique property of a mixture that depends on its initial composition, pressure and temperature. It is related to its reactivity and energy content. Other parameters, such as the turbulent burning velocity, can be described using the laminar burning velocity. Accurate measurements of the laminar burning velocity thus become essential to characterize any combustion systems. A distinction must thus be made between the burning velocity and the laminar flame speed which depends, among other things, on stretch, flow rates and geometry [142].

In contrast to gaseous flames, the question remains if the very concept of a fundamental burning velocity exists for flames in particle suspensions. This partly comes from the difficulty of obtaining a perfectly laminar suspension of solid particles, required for burning velocity measurements. Dust particles rapidly settle in a quiescent environment and, in order to maintain the dust in suspension, an ascending laminar flow or some level of flow turbulence is required. For large particles that are tens of microns or more in size, the flow velocity that is required to counteract particle settling may even exceed the flame burning velocity. Thus, performing dust combustion experiments in a wide range of particle sizes ultimately requires a microgravity environment [102], which is costly and time consuming.

Furthermore, due to possibility of heat transfer from the flame to the fresh unburned mixture by radiation, dust flames are also more sensitive to the system scale than gaseous flames. Radiation emitted from condensed particles in the flame zone and the post-combustion zone can propagate through the flame and pre-heat the reactants, effectively transferring heat from the products to the reactants. However, photons must travel several mean free paths before being absorbed, which means that dust clouds must be sufficiently large for radiation to effectively play a role. In small-scale clouds, radiation is simply heat loss and cannot participate in the flame-propagation mechanism.

The effect of turbulence is carefully studied by varying the ignition delay time between the end of dispersion and ignition. This delay time has to be optimized according to the geometry and dispersion mechanism. A purely laminar flow is impossible to achieve under normal gravity conditions, but introducing delay times can bring the measurement sufficiently close to zero turbulence intensity to allow the comparison between different methods.

As shown in section 1.1, data exist on the flame propagation speed in aluminum dust clouds but no effort has been made yet to reconcile it and confirm the existence of the notion of burning velocity in dust clouds. The two different scales and geometries in the present dissertation allow for a direct comparison of the burning velocity. This approach is thus similar to what is done for gas flames.

# 2.2 Publication: Effect of scale on freely propagating flames in aluminum dust clouds, *Journal of Loss Prevention in the Process Industry*

# Effect of Scale on Freely Propagating Flames in Aluminum Dust Clouds

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#### Abstract

The majority of experimental tests done on combustible dusts are performed in constant volume vessels that have limited or no optical access. Over the years, McGill University has been developing alternative experimental techniques based on direct observation of dust flames, yielding reliable fundamental parameters such as flame burning velocity, temperature and structure. The present work describes two new experimental set-ups allowing direct observation of isobaric and freely propagating dust flames at two sufficiently different scales to test the influence of scale on dust flame phenomena. In the laboratory-scale experiments, a few grams of aluminum powder are dispersed in transparent, 30 cm diameter latex balloons that allow for full visualization of the spherical flame propagation. In the field experiments, about 1 kg of aluminum powder is dispersed by a short pulse of air, forming a conical dust cloud with a total volume of about 5 m<sup>3</sup>. High-speed digital imaging is used to record the particle dispersal and flame propagation in both configurations. In the small-scale laboratory tests, the measured flame speed is found to be about 2.0±0.2 m/s in fuel-rich aluminum clouds. The burning velocity, calculated by dividing the measured flame speed by the expansion factor deduced from thermodynamic equilibrium calculations, correlates well with the previously measured burning velocity of about 22–24 cm/s from Bunsen dust flames. Flame speeds observed in field experiments with large-scale clouds, however, are found to be much higher, in the range of 12±2 m/s. Estimations are presented that show that the presumably greater role of radiative heat transfer in larger-scale aluminum

flames is insufficient to explain the six-fold increase in flame speed. The role of residual largeeddy turbulence, as well as the frozen-turbulence effect leading to large-scale dust concentration fluctuations that cause flame folding, are discussed as two possible sources for the greater flame speed.

#### 1. Introduction

The ever increasing role of modern technologies based on metal powders, such as powder metallurgy, chemical processing, plasma spraying, etc., and the rapidly increasing scale of metal powder production are overshadowed by the increased human and material cost of accidents caused by metal dust explosions [13]. In spite of the strong impetus to implement state-of-the-art preventive measures to mitigate accidents, the progress in this field has been relatively slow in comparison to other branches of preventive science. The slow progress in prevention of metal dust explosions reflects the relatively underdeveloped state of combustion science in this field in contrast to the impressive progress achieved in understanding the physics and chemistry of homogeneous gas flames.

The primary reason for the slow progress in dust combustion science is rooted in the difficulties of extracting the fundamental combustion parameters, such as ignition temperature, burning velocity, flame quenching distance and flame structure, from laboratory experiments with metal dust clouds. Traditionally, most dust combustion tests are performed in constant volume vessels. Though convenient for empirical testing, constant-volume bombs have limited or no optical access, and the pressure rise is the only parameter typically measured in most experiments. The pressure history provides limited insight into the dust flame propagation since the deduction of the flame speed from the rate of pressure rise is neither accurate nor representative if the flame propagation deviates from the ideal picture of a spherically symmetric laminar flame [143], [144]. Some experiments have demonstrated that the residual turbulence induced in the mixture during the dust dispersal phase may have a considerable influence on flames ignited with short delay times after dispersal [90], [145]. Furthermore, the implementation of modern flame diagnostic techniques, such as emission and laser-absorption spectroscopy, is required to elucidate the flame structure and verify equilibrium calculations of flame temperatures against experimental values, which is difficult to accomplish in constant volume bombs.
An array of experimental set-ups allowing for visual observation of flames in dust and hybrid combustible gas-dust clouds has been developed at McGill University over the past two decades. They are based on experimental methods that have proven to be successful in gas flame research and include Bunsen dust burners [3]-[5], [98], [99], counter-flow dust burners (under development), as well as dust flames propagating in transparent tubes and narrow channels [101], [135]. These set ups have permitted an accurate measurement of the burning velocities [98], flame quenching distances [103] and spectroscopic diagnostics of the dust flame structure [99] in dust and hybrid combustible gas-dust mixtures [4], [5]. A large series of dust combustion experiments were performed at low gravity on board a parabolic flight aircraft [101], [102]. By eliminating particle sedimentation and natural convection, microgravity conditions have permitted the observation of laminar dust flames for a very wide range of particle sizes. The current paper presents two new experimental systems developed to investigate the effects of scale on the flame propagation in combustible dust clouds. The first apparatus, which is similar to the one recently reported by Skjold et al. [146], allows the laboratory observation of isobaric spherical flames in dust clouds dispersed in transparent latex balloons with an initial volume of about 14 litres. The second apparatus permits the creation of unconfined dust clouds with a total volume in the range of 5-10 m<sup>3</sup>.

#### 2. Experimental Methods and Results

#### 2.1 Small-scale spherical dust flames in transparent latex balloons

Figure 2.1 shows a photograph of the experimental apparatus, including the dispersion and ignition systems (the control unit, mixing tank and safety housing are not visible). The balloon is placed on the neck of the balloon holder, which has three different ports: one for inflating the balloon, one for dispersing the powder and one for the igniter. At the start of a test, the balloon is inflated through a solenoid valve controlled by a remote timer. Once the balloon reaches the desired size, about 30 cm in diameter, a calibration image is taken. The powder, placed in a receptacle within the dispersion unit, is then injected into the balloon. The injection is initiated by the opening of a second solenoid valve, causing a high-pressure gas jet to impinge on the powder surface, lofting the powder, and entraining it into the flow through a perforated cap and into the balloon. This method results in a uniform dispersion of the powder throughout the balloon. The two-phase flow is initially turbulent, with prominent, large-scale vortices moving primary along the wall of the balloon. A delay is applied to allow the turbulence to decay before igniting the mixture by discharging a capacitor through a 100 micron thick tungsten wire positioned at the center of the balloon. A small, yet unavoidable, amount of powder is deposited on the surface of the balloon during the powder dispersal process, making the effective concentration somewhat lower than the one calculated based on the initial powder mass and the volume of the inflated balloon. It is estimated that the amount of deposited powder does not exceed 10% of the initial powder weight in the receptacle.

The transparent balloon allows for the imaging of all experimental stages with a high-speed camera, including powder dispersal, ignition, and the subsequent isobaric flame propagation. The dust dispersal process, with the balloon uniformly backlit with a diffuse light source, is recorded at 300 frames per second using a Photron SA5 camera. The flame propagation process is recorded with the same camera typically at 5,000 frames per second.



Figure 2.1. Small-scale apparatus.

This method of measuring flame speed is first validated using methane-air mixtures of various equivalence ratios. The contour of the flame on the high-speed movie is traced for every frame and the radius is taken to be the average distance between the contour and the center-of-mass. The flame speed is equal to the slope of the curve, which is found by linear regression. Conservation of mass allows the calculation of the 1D laminar burning velocity,  $S_L$  [7] using  $S_L = S_f(\rho_b/\rho_u)$ , where  $S_f$  is the flame speed, and  $\rho_b$  and  $\rho_u$  are the burned and unburned gas densities, respectively. The density of the gas before and after combustion is found using the chemical equilibrium solver Cantera [57]. As shown in Fig. 2.2, the burning velocities are in good agreement with other literature values measured with spherical flames [147]–[149].



Figure 2.2. Burning velocity vs. equivalence ratio for methane-air mixtures compared to results from other freely-propagating spherical flames.

Tests with stoichiometric methane-air mixtures are performed to determine the minimum delay time required between the powder dispersal process and ignition. A pulse of pre-mixed methane-air instead of air is introduced into the balloon with no powder to study the effect of turbulence on the flame speed. The results are shown in Fig. 2.3 and the dashed line represents the laminar flame speed. It can be seen that approximately 5 seconds are required for the effect of turbulence to be negligible. This delay time is found to be a good compromise between the decay of turbulence and minimal settling of the powder.



Figure 2.3. Methane flame speed as a function of ignition delay time. The dashed line represents the laminar flame speed.

Laboratory-scale experiments with aluminum powder are carried out with Ampal aluminum powder (Ampal 637, Ampal, NJ), which has a Sauter mean diameter  $d_{32}$  of about 5.6 microns. An electron microscope picture of the powder and the particle size distribution can be found in a recent publication [4]. The same batch of Ampal powder has been used in previous experiments with stabilized Bunsen aluminum flames [98]. This allows for direct quantitative comparison with the burning velocities obtained in this work. Figure 2.4 shows still frames during the dispersal of 0.5 g of aluminum powder within the latex balloon. The final dust mass concentration is about 75 g/m<sup>3</sup>.



Figure 2.4. Dispersal of 0.5 g of aluminum within a transparent balloon. Though fully dispersed at the time of 1.44 s, an additional delay is applied prior to ignition to allow the turbulence to decay.

Figure 2.5 shows the flame propagation through an aluminum dust cloud with a concentration of about 500 g/m<sup>3</sup>. The images are processed the same way as for the methane flames. A typical result for the average radius as a function of time is shown in Fig. 2.6, with the slope corresponding to the flame speed.



Figure 2.5. Characteristic aluminum flame propagation for a powder concentration of 500 g/m3.



Figure 2.6. Flame front radius as a function of time for flame propagation in an aluminum-air mixture.

The flame speed as a function of aluminium concentration is shown on Fig. 2.7. The burning velocity is obtained by multiplying the flame speed by the ratio of the burnt and unburnt densities and is shown in Fig. 2.8 with solid square symbols and compared to the results found by Goroshin et al. [98] on the Bunsen burner, corresponding to the open circle symbols. The results are in good agreement with burning velocities on the order of 20 cm/s.



Figure 2.7. Measured flame speed for various aluminum concentrations.



Figure 2.8. Measured flame speed for various aluminum concentrations from present investigation compared with previous work using the same powder, but with a stabilized Bunsen aluminum dustair flame.

#### 2.2 Field experiments with large-scale dust clouds

Figure 2.9 shows the dust dispersal apparatus specifically designed for the field tests. The apparatus can disperse up to 1 kg of metal powder within 2-3 seconds, creating a large dust cloud with an average aluminum dust concentration close to the stoichiometric value, i.e., 300 g/m<sup>3</sup>. The lightly compacted column of aluminum powder is held in a cylindrical metallic cartridge and is pushed up as a whole towards the dispersal nozzle by a pneumatic piston at a constant rate. The dust is dispersed at the base of the nozzle by a sonic annular air jet, referred to as an air-knife, from a 0.5 mm annular slot. Figure 2.10 shows the powder dispersal process. The dispersed powder forms a vertical dust cloud with a conical shape that is about 4 m tall and up to 2 meters wide at the top, as shown on Fig. 2.10. The cloud is ignited by a small 2–3 g charge of black powder placed in an open metal tube, immediately after the dispersal air is cut-off by a solenoid valve. The powder dispersal and flame propagation processes were visualized with a Photron SA5 highspeed camera operating at 1,000 frames per second. Fig. 2.11 shows a series of single frames at different times illustrating the flame propagation through the dust cloud. A single frame from Fig. 2.11 is shown in Fig. 2.12 to identify the different regions of the flame. Convection of the dust cloud due to the ambient wind conditions during the field trials, even for low wind speeds, made it impossible to introduce a significant delay time between the dispersal and ignition events.



Figure 2.9. Photograph of field test apparatus and schematic of powder dispersal unit.



Figure 2.10. Dispersal of aluminum dust to form a conical-shaped dust cloud.



Figure 2.11. Flame propagation for cloud shown in Fig. 2.10.



Figure 2.12. Still frame of the aluminum flame (top) propagating upwards, taken from Fig. 11 at a time of 200 ms after initiation of flame propagation; narrow flame in the lower part of the flame is the remnant of the black powder charge. The dashed line indicates the center of the cloud.

The progression of the flame front can be determined by tracing the location of the leading edge of the flame. Light scattered from the aluminum particles ahead of the flame makes it difficult to precisely determine the front boundary and this issue is accounted for in the experimental uncertainty. Figure 2.13 shows the vertical progression of the flame front for the trial shown in Fig. 2.11. Figure 2.14 shows the position of the flame front as a function of height for a vertical cross-section. The flame speed is found by a linear fit through these data points. As shown in Fig. 2.15, the average flame speed at different horizontal positions across the cloud varies by an insignificant amount.



Figure 2.13. Flame front progression over time.



Figure 2.14. Flame front progression for a vertical section of the flame.



Figure 2.15. Calculated flame speed along the horizontal front.

In total, six successful trials were performed in the field when the flame propagated without interruption from the bottom to the top of the cloud. The tests were performed with the spherical industrial aluminium powders H-5 and H-10 (Valimet Inc, CA) having median particle diameters  $d_{50}$  of 8.0 µm and 12.0 µm, respectively. The average residual vertical velocity of the powder jet after flow cut-off and ignition can be easily deduced from the video images and is found to be around 0.2 m/s. This value has already been subtracted from the measured flame speeds shown in Table 2.1.

Trial Number	Flame Speed(m/s)	Aluminum Powder
1	13	H-5
2	12	H-5
3	13	H-5
4	10	H-5
5	14	H-10
6	10	H-10

 Table 2.1: Flame speed in large-scale aluminum dust clouds

#### 4. Discussion

As mentioned above, the good agreement between the burning velocities derived from experiments with small-scale aluminium clouds having characteristic sizes from cm's (Bunsen dust flames) to tens of cm's (balloon experiments) confirms the applicability of the burning velocity notion towards small-scale dust flames. The absence of an increase in velocity with an increase in the scale of the flame over this range indicates that the effects of radiative heat transfer are negligible for small-scale dust clouds. Indeed, estimations show that the free path length of radiation in a stoichiometric aluminium dust cloud with Ampal aluminium powder is around 10 cm and that the absorption length is probably even larger, so that the absorption of radiation emitted by the flame and combustion products in the laboratory-scale dust clouds is effectively negligible. The radiation in such clouds acts essentially as a heat loss mechanism, similar to gas flames [7] and, thus, can only lead to a decrease in flame speed.

However, the characteristic size of the dust cloud in the field experiments is much larger than the effective radiation absorption length; thereby ensuring that the radiation emitted by the aluminium flame front and the hot condensed combustion products will be absorbed by the fresh unburnt dust suspension. Thus, at first glance, the observed six-fold increase in flame speed in the field tests in comparison to the laboratory experiments might be considered as evidence that the flame is driven by radiative heat transfer. Simple estimations shown below, however, clearly demonstrate that the radiation alone is insufficient to explain the observed difference in flame speeds. Recent calculations [150] of the integral emissivity coefficient  $\varepsilon$  from an infinite optically-thick layer of 0.5 micron aluminium oxide particles, which are the primary radiation emitters in aluminium flames, estimates its value at about 0.3 at 3000 K. The flame at this temperature can then emit a maximum radiation flux  $W = \varepsilon \sigma T^4$  of about  $W = 1.4 \times 10^6 \text{ W/m}^2$ . Because the particle residence time within the radiation heating zone  $t_r = l/V$  (where l is radiation absorption length and V is the flame speed) is at least an order of magnitude longer than the characteristic time of the heat exchange between 5 micron particles and the gas, the suspension is uniformly heated by the absorbed radiation as a whole. Thus the maximum temperature increase of the aluminium suspension due to radiation absorption can be estimated from the energy balance between the enthalpy of the incoming dust flow and radiation flux, ie.,  $\Delta T = \frac{\varepsilon \sigma T^4}{(C_a \rho_a + C_s \rho_s) V}$ . The estimations show that at the observed flame speeds of 10-12 m/s, the radiation preheating of the mixture would not exceed 100 K. Such a small preheating is unable to provide a sufficient increase in the aluminium flame burning rate, irrespective of whether the particles burn in a kinetic or diffusive mode. This suggests that some other mechanism(s) besides radiative heating may be responsible for the observed high-speed flames in the field tests.

One possible mechanism is associated with the residual large-scale eddy turbulence within the dust cloud [151]. The high-speed videos of the dust dispersal process in the field tests provide clear evidence of the formation of large-scale eddies generated by the high-speed submerged dust dispersal jet. Unlike the small-scale turbulence that quickly dissipates after the termination of the dispersal flow due to viscous momentum losses within two-phase media, the large eddy turbulence is more persistent. The motion of the eddies continues for several seconds after the powder is dispersed albeit with diminishing flow speeds. As was demonstrated in the theoretical work by Kagan and Sivashinsky [152], even low-speed large-eddy turbulence is capable of more than an order of magnitude increase in the flame speed largely due to the increase of the flame surface area.

Another process that might lead to the increase of the flame propagation speed is specific to dust combustion and may be referred to as a "frozen turbulence" effect. Large eddies created during the dust dispersal process with a submerged jet are accompanied by the entrainment of large amounts of surrounding air into the resulting dust cloud [153]. This leads to a stratification of the dust concentration within the jet with alternating areas of high and low dust concentration. Such stratification persists long after the decay of any turbulence due to the effectively zero diffusivity of the particulate fuel. A complex pattern of dust concentration fluctuations results in a spatially fluctuating burning interface which may lead to the appearance of a corrugated flame having an average flame speed greater than that of a freely propagating flat flame.

Of course, without direct experimental verification the proposed explanations of the effect of "live" and "frozen" large-scale eddy turbulence as a possible cause for the observed flame speed increase are unsubstantiated. One possible verification procedure would be to introduce longer delay times from the end of dust dispersal to the time of ignition of the cloud, giving the dynamic or "live" large-eddy turbulence additional time to decay. This would, however, require performing the experiments with unconfined dust clouds within a large-scale enclosure that would eliminate the influence of the weather (in particular the wind) on the stability of the dust cloud. Direct measurements of the temperature history at various locations within the cloud are also required to confirm estimations of the absence of a noticeable radiative preheating in the flame. Such experiments are already under preparation stage and will be performed in the near future.

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# **Chapter 3. Freely-Propagating flames in aluminum clouds**

### **3.1 Chapter Introduction**

The work presented in chapter 3 follows directly and builds on what has been published in the Journal of Loss Prevention in the Process Industry and shown in chapter 2. The same apparatus have been used in both experiments: the balloon apparatus and the field apparatus. The balloon apparatus in chapter 2 was tested with methane-air flames to validate the methodology, because the values of burning velocity for methane flames have been accurately measured with different methodologies and by many research groups. Also, only results of aluminum in air were presented in chapter two and compared to results obtained by Goroshin et al. on a Bunsen burner [98]. The work presented in chapter 3 follows what has been done and explores the role of oxygen concentration, aluminum concentration and inert diluent on the flame propagation.

The large-scale experiments and the results presented in chapter 2 were preliminary experiments aimed at testing the new apparatus and measuring the flame propagation speed for two types of aluminum powders. The flame speeds obtained in large-scale experiments were significantly greater than those obtained for small-scale experiments in balloons. A few different hypothesis were presented in chapter 2, namely the role of radiation in reactants pre-heating and the role of turbulence.

The work presented in chapter 3 aims at verifying those hypothesis. The previous experiments were performed outdoors, in the field, with no wind protection, which made it impossible to have a delay time between the end of the dispersion process and ignition. Also, due to wind conditions, the cloud was rarely straight and would often be tilted, making it difficult to insert thermocouple probes inside the cloud. For those reason, a new experimental facility was used where experiments can be performed indoors. This new facility allowed for easy implementation of thermocouple probes inside the cloud and allowed the introduction of a delay time before ignition.

The results will demonstrate that radiation heat transfer is not the main driving mechanism in dust flames. It is shown that radiation indeed pre-heats the reactants, thus enhancing the burning velocity, but the temperature increase is limited to around 150 K above initial temperature and heat conduction is the dominating effect in flame propagation. Furthermore, this effect of radiation can

only happen if the cloud is large enough for heat to be re-absorbed and the effects of radiation are negligible if the cloud is small.

# **3.2** Publication: Freely-Propagating flames in aluminum clouds, *Combustion and Flame*

## Freely-propagating flames in aluminum dust clouds

Philippe Julien, James Vickery, Samuel Goroshin, David Frost, Jeffrey Bergthorson

#### Abstract

The free propagation of isobaric flames through aluminum dust clouds is investigated in an extensive series of experiments using two facilities with different scales. In small-scale laboratory experiments, spherical flame propagation occurs in aluminum dust clouds contained within 30cm-diameter latex balloons, whereas in large-scale tests, flames propagate vertically through unconfined aluminum dust clouds with a vertical scale of about 4 m. The balloon experiments are performed with suspensions of aluminum powder in oxygen mixed with nitrogen, argon, or helium with various concentrations of oxygen and aluminum. It is found that stable flame propagation is only observed for aluminum concentrations near stoichiometric to rich conditions. Pulsating and spiral-like flames are discovered in fuel-lean mixtures, and flames with cellular patterns occur in very-fuel-rich suspensions. The burning velocities in the stable propagation regime derived from the balloon experiments correlate well with data previously obtained with stabilized Bunsen-type flames. The flame speed of stable flames is found to be a strong function of the heat conductivity of the gas mixture. In addition, the oxygen concentration has a strong influence on the flame speed for fuel-rich mixtures but dependence is reduced for fuel-lean mixtures. In the large-scale experiments, the burning velocity is estimated to be about two times larger than for the small-scale experiments. The increase in burning velocity is attributed to preheating of the unburned mixture by radiation from the condensed-phase combustion products. The degree of preheating, determined with an array of fine thermocouples, is found to be in the range of 150-200 K. The propagation of stable flames is discussed in light of existing qualitative dust flame models, whereas the pulsating flame propagation regime observed is interpreted in terms of the thermo-diffusive instability theory developed for high Lewis number flames in gases and solid reactive powder mixtures.

#### 1. Introduction

Suspensions of combustible particles in an oxidizing media are ubiquitous in industry, agriculture, transportation and propulsion technology [9], [11], [13], [14], [20], [22]. Though often amalgamated together under the term "combustible dusts", solid fuels are very diverse, ranging from very volatile organic substances, such as plastics, flour, sugar or cornstarch, to refractory materials, such as carbon (graphite) or iron that do not volatilize or evaporate. Organic dusts have melting and volatilization temperatures well below their flame temperature, such that their combustion behavior differs little from the combustion of hydrocarbon droplets. The evaporation or decomposition of the organic volatile fuel and hydrocarbon sprays in the flame preheat zone might lead to the formation of a continuous flame sheet in the case of small particles and large fuel concentrations or, for large particles in fuel-lean mixtures, result in the combustion of particles surrounded by individual diffusion micro-flames [154]. Complex fuels, such as coal, contain both volatile and refractory substances and burn partially in the vapor phase by volatilization while leaving a charred core that burns heterogeneously.

Irrespective of the boiling temperature of the metal, the extremely fast and non-activated reaction kinetics of metal vapors with oxygen precludes formation of a premixed metal-vapor mixture in the flame preheat zone. [28], [126]. This excludes complex mixed heterogeneous/homogeneous flame regimes typical for combustion of solid and liquid hydrocarbon fuel suspensions which, combined with the fact that metals are pure elemental substances with well-defined properties, available in a wide range of particle sizes, makes flames in metal suspensions well-suited for the academic study of heterogeneous dust flames. Among all metals, aluminum is of special interest since it is often used as an energetic additive to propellants, explosives and pyrotechnics.

In contrast to hydrocarbon flames, the field of dust combustion remains vastly underdeveloped. This is partly due to the experimental difficulty of obtaining a laminar suspension of solid particles which is required to measure the fundamental combustion parameters, such as the burning velocity. Dust particles rapidly settle in a quiescent environment, and, in order to maintain the dust in suspension, an ascending laminar flow or some level of flow turbulence is required. For large particles that are tens of microns or more in size, the flow velocity that is required to counteract particle settling may even exceed the flame burning velocity. Thus, performing dust combustion experiments over a wide range of particle sizes ultimately requires a microgravity environment [102]. Furthermore, the combustion behavior of a dust suspension depends on the particle morphology and size distribution, which makes it difficult to compare experimental data obtained from different research groups using dissimilar powders. Due to the large flame thicknesses and the possibility of heat transfer from the flame to the fresh unburned mixture by radiation, dust flames are also more sensitive to the system scale than gaseous flames.

The vast body of literature on dust combustion is mostly based on experiments in closed bombs with no visual access, where the pressure history within the vessel is the only parameter measured. This experimental technique is primarily used to empirically classify the explosivity of dusts based on the rate of pressure rise, in accordance with the explosion hazard scale, while leaving the scientific questions of the flame structure and flame propagation mechanism unresolved. Only a small number of experimental groups, using different techniques, have provided direct measurements of the flame propagation speeds from which the burning velocity can be extracted. For example, Cassel employed stabilized Bunsen-type flames [91], Ballal et al. [93] performed experiments with flat flames in a tube in microgravity, and Sun et al. [95]–[97] explored freely-propagating flames at very small scales. For the past 20 years, researchers at McGill University have systematically used visual observation of metal dust and hybrid hydrocarbon/metal-dust flames stabilized on Bunsen burners [3]-[5], [98], propagating in tubes in normal and microgravity environments [100], [101], [135], and, more recently, spherically expanding in transparent latex balloons [1], to determine flame speeds and flame structure. The systematic use of the same batch of aluminum powder in the different experiments has facilitated the accumulation of a unique dataset of aluminum dust flame properties such as burning velocity, flame quenching distance, and flame spectral characteristics. This comprehensive compendium of data allows for the direct comparison of properties using different methods to fully characterize the combustion properties and flame structure.

As a continuation of this systematic work, the present study introduces two new experimental facilities allowing the observation of freely-propagating dust flames with different scales [1]. The first laboratory-scale apparatus uses transparent latex balloons to observe nearly-constant-pressure spherically-expanding flames up to 30 cm in diameter [146]. The aluminum is

suspended within the balloon by a pulsed dispersal system in different gaseous mixtures of oxygen with nitrogen, argon or helium. Special care is taken to minimize the influence of the residual turbulence induced by the dust dispersal process by introducing an ignition delay time of appropriate length. The second apparatus creates aluminum dust clouds that are about 2 m wide and 4 m high inside a large-scale indoor experimental fire tower. The flame is initiated at the bottom of the cloud with a pyrotechnic igniter. A grid of thermocouples of different sizes placed inside the dust cloud is used to measure the level of long-range preheating of the dust mixture through the radiative flux ahead of the flame. The burning velocity results from the laboratory and larger scale experiments are compared with the data previously obtained from stabilized Bunsen-type dust flames [98]. Pulsating and spiral instabilities in spherical aluminum flames are discovered in fuel-lean mixtures and are discussed in reference to the general thermo-diffusive theory of flame stability developed for gaseous flames and condensed systems [155]–[157].

#### **2. Experimental Methods**

#### 2.1 Small-scale flames in balloons

The transparent latex balloons have a diameter of about 30 cm and volume of about 14 L when inflated prior to injection of the powder (Fig. 3.1). As the flame propagates, the balloon expands, maintaining essentially isobaric conditions up until it bursts with a pressure rise that is less than 0.01 bar. The aluminum powder is initially placed in a hemispherical cup at the bottom of a cylindrical dispersion unit that has a maximum capacity of 8 g of powder. The powder is fluidized within the cylindrical chamber by an impinging pulse of high-pressure gas. The particles become entrained in the flow, and the aluminum-gas mixture travels upward through a hemispherical cap before entering the pre-inflated balloon. The cap is pierced with multiple holes to separate the two-phase flow into many particle-laden jets that move up through the center of the balloon. The suspended particles recirculate within the balloon, mixing with the gas mixture until a uniform gas-particle mixture is created within the balloon, as shown in Fig. 3.2. The powder suspension is then centrally ignited by a heated tungsten wire following a 4 s delay after the initial powder injection to allow the initial turbulence to decay, as described in a previous publication [1]. The dust dispersal and flame propagation processes are recorded using a high-speed Photron SA5 videocamera, operated at 4,000-7,500 frames per second. Neutral density filters are used to attenuate the light intensity of the intensely luminous flames at high dust concentrations. A

photodiode and a microphone, installed near the balloon and synchronized with the camera, monitor the history of the flame brightness and the acoustic waves emitted by the flame, respectively. More details on the design and operation of the apparatus are given in a previous publication [1].



Figure 3.1. Schematics and photograph of the laboratory apparatus for observation of spherical dust flames in transparent latex balloons.



Figure 3.2. Still frames of the dispersion of 4g of aluminum powder in the latex balloon apparatus for a final concentration of approximately 200 g/m<sup>3</sup>.

In most dust combustion experiments within closed vessels, it is usually assumed that the dust is uniformly dispersed throughout the vessel volume without any powder deposition, and hence the dust concentration is calculated by simply dividing the mass of the dust sample by the inner volume of the vessel. However, some portion of the powder does not remain in suspension but, rather, accumulates on the vessel wall or settles to the bottom of the chamber prior to ignition. In the present experiment, some degree of powder deposition also occurs, and hence a calibration is performed to correlate the mass of the dust sample initially within the dispersion unit with the actual amount of dust in suspension at the moment of ignition. A rigid acrylic sphere with a similar size and volume is used in place of the latex balloons in conjunction with a laser light-attenuation probe to calibrate the dust concentration [3]–[5], [98]. The probe consists of a 633 nm red laser and a photodiode with a narrow-bandpass filter corresponding to the wavelength of the laser. The powder is dispersed as usual but not ignited. The powder concentration is derived from the photodiode output signal using the Beer-Lambert law, which states that the logarithm of the light attenuation corresponds to the powder concentration multiplied by a constant. This constant, which depends on the distance traveled by the laser and the type of powder used, has been determined in previous experiments using the same powder [3], [4]. Figure 3.3 shows a typical time history of the dust concentration determined within the suspension during and after the dust dispersal process.



Figure 3.3. Time history of the aluminum dust concentration in the balloon measured by the laser light attenuation probe.



Figure 3.4. Experimentally measured concentration of the aluminum in suspension at the moment of ignition (4 s after the start of dispersion) as a function of the amount of aluminum dust initially placed in the dispersion unit. The shaded area represents the 95% confidence interval of the fit,the solid line the least-square fit and the dashed line is the estimate of the aluminum concentration obtained assuming that the entire dust sample remains in suspension.

As can be seen from the concentration measurements and high-speed photographic records of the dispersal process (see Fig. 3.2), the probe initially records a very high dust concentration as the multiphase flow jets move through the center of the balloon where the probe is positioned. The ascending multiphase flow then impinges on the balloon wall and is deflected outwards and downwards near the balloon wall. The large-scale vortical motion that is induced cascades down to smaller-scale turbulent eddies that uniformly distribute the dust throughout the balloon volume. The dust concentration continues to decline following dispersion due to powder settling. The graph in Fig. 3.4 shows the result of dust concentration measurements at the moment of cloud ignition, which is set at a delay time of 4 seconds, as a function of the amount of aluminum dust placed within the dispersion receptacle. As can be seen, the measured concentration correlates with, but is considerably below, the calculated values assuming all the dust remains in suspension at the moment of ignition. The difference increases with the weight of the dust sample and reaches almost a factor of two for large masses of powder.

#### 2.2 Large-scale unconfined flames

Combustion experiments in large-scale aluminum dust clouds are performed using the dust dispersal device previously developed [1] and shown in Fig. 3.5 below. The apparatus is essentially a scaled-up version of the dust dispersal unit used with our laboratory Bunsen burner, as described by Soo et al. [3] and Julien et al. [4], and can create a large uniform column of suspended powder. Up to 1 kg of aluminum powder is initially loaded into the cylindrical cartridge having an inner diameter of about 5 cm and length of 30 cm. During the dispersal process, the powder column is displaced upwards at constant speed by a pneumatic piston and is progressively de-agglomerated and entrained into the vertical air flow generated by an impinging sonic annular air jet (or air-knife) at the top of the cartridge. All of the powder within the cartridge is dispersed within a time of less than 1 second, as shown in Fig. 3.6, creating a vertical dust cloud about 4 m tall and 2 m wide near the top.

Initial tests were performed at an outdoor test site [1], but it was necessary to initiate the flame propagation promptly during the latter stages of the dispersal process to avoid the displacement of the dust cloud by the ambient wind conditions. To provide a sufficient delay time between powder dispersal and ignition to allow the turbulence within the multiphase cloud to decay, quiescent ambient conditions are required. Hence, the present experiments were performed

indoors in the large-scale fire tower at the Fire Research Laboratory of the National Research Council of Canada (Mississippi Mills, Ontario, Canada). The tower is approximately 10 stories (35 m) high and has about 200 m2 of floor area. Two large, variable-area openings at the tower base allow the intake of outside air for ventilation and prevent any pressure build up during the flame propagation. The combustion products are vented through openings in the ceiling connected to a powerful ventilation system, which is operated only after the combustion event is completed to avoid disturbing the cloud formation and flame propagation.

Cloud ignition is achieved with a small 2 g charge of black powder placed at the cloud base, which is initiated by an electrically-heated bridge wire. The ignition charge is placed on a mast to vary the height as the ignition delay times are adjusted. Another mast with two rows of bare junction K-type thermocouples with three different bead sizes (0.075, 0.0125 and 0.25 mm) is placed close to the dispersal unit, with the thermocouple arms extending into the dust cloud axis to record the temperature history within the cloud during the passage of the flame. A Photron SA5 videocamera was used to record the flame propagation at 2,000 frames per second. The camera record and temperature measurements were synchronized using a photodiode signal from the ignition event.



Figure 3.5. Schematics and photograph of the experimental rig for the large-scale dust cloud combustion tests.



Figure 3.6. Still frames of dust dispersion process for large-scale tests.

#### 2.3 Aluminum powders and gaseous mixtures

Three different types of aluminum powders were used in the present investigation. The laboratory experiments in latex balloons were performed with Ampal 637 (Ampal Inc., NJ) aluminum powder that is comprised of nodular-shaped particles, as shown in the SEM image in Fig. 3.7. The large-scale experiments were performed using either H-5 or H-10 aluminum powder manufactured by Valimet Inc. (Stockton, CA), which have a relatively spherical morphology as shown in Fig. 3.7. The large-scale experiments required large quantities of powders, such that the amount of Ampal 637 available was insufficient. The particle size distributions of Valimet H-5 and H-10 powders were obtained using a Malvern Mastersizer 2000 are shown in Fig. 3.7, and have considerable overlap with the particle size distribution of Ampal 637 powder.

The various test series within the balloons were performed with oxygen concentrations ranging from 15% to 100%. The oxygen is diluted with nitrogen, argon or helium to have different heat capacities and diffusivities while keeping the concentration of aluminum and oxygen constant. Oxidizing mixtures are prepared in a mixing tank by partial pressure.



Figure 3.7. Electron microscope photographs and particle size distributions of Ample 637 and Valimet H5 and H10 aluminum powders.

#### 3. Results

- 3.1 Spherically-expanding flames in balloons
- 3.1.1 Regimes of flame propagation

Different regimes of flame propagation are observed in the present experiments, and the type of regime depends primarily on the fuel equivalence ratio, i.e., on the oxygen and aluminum concentrations. Mixtures in the vicinity of stoichiometric concentrations exhibit stable propagation of a smooth flame expanding radially outwards after central ignition. Figure 3.8 shows still frames from a stable flame experiment, with an aluminum concentration of about 370 g/m3 in air.



Figure 3.8. Flame front propagation in near-stoichiometric suspension in air at aluminum dust concentration of about 370 g/m3. Stoichiometric concentration of aluminum in air is about 320 g/m<sup>3</sup>.

Several unstable combustion regimes were observed in both very fuel-rich mixtures and fuel-lean mixtures. On the rich side, flames have exhibited cellular patterns on their surface. In fuel-lean suspensions, the flame instabilities are classified into the following four categories, listed in order of decreasing aluminum concentration starting from stoichiometric conditions: i) decaying pulsating flames (pulsations with diminishing amplitude), ii) regular pulsating flames (pulsations with constant amplitude), iii) pulsating flames accompanied by spiral patterns formed on the flame surface, and iv) spiral flames.

Flames with decaying pulsations, followed immediately by pulsations, are the first forms of instabilities that are observed as the concentration of aluminum is decreased below the stoichiometric value. The first regime is referred to as "decaying pulsations" on the graph of Fig. 3.10 below. In both cases, pulsations start immediately after ignition and are characterized by brief periods of intense luminosity followed by an apparent extinguishing of the flame where the brightness of the flame is reduced by almost an order of magnitude. At aluminum concentrations only slightly below the stoichiometric value, the pulsations are weak, and the flame often starts to propagate steadily after only a few pulsating periods. As the aluminum concentration is decreased still further, the pulsations become more intense and persist until the flame reaches the balloon wall. Figure 3.9 shows still frames from two periods of such a pulsating flame.



Figure 3.9. Still frames illustrating two periods of a pulsating aluminum flame in lean aluminum suspension in 60%O<sub>2</sub>/40% Ar gas mixture and aluminum concentration of about 280 g/m<sup>3</sup>.

At very low aluminum concentrations, near the lean flammability limit, a second type of thermo-diffusive instability is observed. Spiral waves, often referred to in the literature as spin combustion, can be clearly observed on the flame front. For extremely lean mixtures, when the flame speed becomes comparable to, or lower than, the flow speed induced by the buoyancy of the hot combustion products, the flame propagates upwards in the form of rotating spirals. The spirals appear to start and stop at different locations, and multiple rotating spirals can be observed simultaneously. A spiral flame is shown in a video in supplementary materials. When the mixture has an aluminum concentration between the values associated with the pulsation and spiral regimes, a combination of these two types of instabilities can be observed simultaneously. The flame pulsates, with the clear formation of spiral patterns on the flame surface during the burning phase.

Figure 3.10 presents the mapping of the different combustion regimes as a function of aluminum and oxygen concentrations in gaseous mixtures of oxygen with helium, nitrogen or argon. The horizontal dashed lines crossing the different columns indicate stoichiometric aluminum concentrations for each specific oxygen concentration. The present experimental setup allows for a maximum aluminum concentration of about 550 g/m3, such that fuel-rich conditions are only possible in mixtures with oxygen concentration below 30%. As can be seen from Fig. 3.10, most fuel-rich mixtures, as well as fuel-lean mixtures with fuel equivalence ratios above 0.8, exhibit stable flame propagation. As the aluminum concentration is lowered below this value, the flame generally first starts propagating with decaying pulsations. As the concentration is decreased the pulsations grow stronger and persist until the flame front reaches the balloon wall. As the dust concentration is reduced even further, pulsations are followed by pulsations with spirals and, finally, purely spiral flames. It is interesting to note that spiral flames occur more frequently in nitrogen-oxygen mixtures while the combination of spirals and pulsations occurs more frequently in helium-oxygen mixtures.



Figure 3.10. Map of the different regimes of combustion observed for variable oxygen and aluminum concentrations for several inert diluents.

#### 3.1.2 Propagation speed of stable flames

The propagation speed of stable flames is determined from the high-speed video records. As the flame is not always spherically symmetrical, the contour of the flame front on each frame was fit with an ellipse. The mean flame radius is then defined as the average distance from the edge of the ellipse to its center-of-mass. The flame radius is plotted as a function of time and a leastsquares fit to the data is used to find the slope of the line giving the flame speed, S\_f=dr/dt [24]. The experimental data points of flame speed in air in the stable flame propagation regime are

shown in Fig. 3.11 for different mass concentrations of aluminum in suspension. As can be seen from Fig. 3.11, in fuel-lean mixtures, which corresponds to the portion of the curve left of the dashed line that represents stoichiometric conditions, the flame speed increases relatively sharply with an increase in aluminum concentration.

Figure 3.12 shows the measured flame speeds as a function of aluminum concentration in argon-oxygen mixtures at three different oxygen concentrations of 15, 20, and 30%. As can be seen, in fuel-lean mixtures the flame speed increases linearly with aluminum concentration, within the scatter, but is relatively insensitive to the oxygen concentration in the mixture. At all oxygen concentrations, the flame speed reaches an approximate plateau level in rich mixtures, and the average plateau value is larger for mixtures with larger oxygen content. This demonstrates a relatively strong dependence of the flame speed on oxygen concentration for fuel-rich mixtures.

The dependence of the flame speed on aluminum concentration in 3.15 % oxygen mixtures with different gaseous inert diluents (N<sub>2</sub>, Ar, He) is shown in Fig. 3.13. At equal aluminum concentrations, the lowest flame speed is observed in oxygen-nitrogen mixtures followed by slightly higher speeds in mixtures with argon. In contrast, helium increases the flame speed more than three times in comparison to argon-diluted mixtures. The flame speeds are observed to be quite insensitive to the concentration of aluminum for rich mixtures, as observed previously [98].



Figure 3.11. Flame speed at different aluminum concentrations in air for stable flames.



Figure 3.12. Flame speed versus aluminum concentration in argon mixtures with different oxygen content for stable flames.



Figure 3.13. Flame speed versus aluminum concentration in 15% O<sub>2</sub> and 85% N<sub>2</sub>, Ar or He for stable flames.

#### 3.1.3 Pulsation frequency and average flame speed of pulsating flames

The flame front in the pulsating regime is also tracked by fitting an ellipse to the front on the images, and the radius is taken to be the average distance between the center of mass and the edge of the ellipse. Figure 3.14 shows an example of the flame radius tracked as a function of time for a pulsating flame. It can be seen that for very brief periods of time, the flame propagates at extremely high speeds separated by a longer phase where the flame radius effectively does not change with time. The average flame propagation speeds of the pulsating flames, obtained from a linear fit to the data, are shown in Fig 3.15 for three different inert gas diluents with an oxygen concentration of 60%. The results demonstrate that the average flame propagation speed in the pulsating regime increases only with aluminum concentration and, surprisingly, is largely independent of the heat and mass diffusivity of the mixture, which differs by a factor slightly larger than two between helium and argon mixtures. This behavior is strikingly different from a stable flame propagation regime, where the flame speed strongly depends on the thermal diffusivity of the mixture increasing by almost factor of four when argon in mixture with oxygen is replaced by helium (Fig. 3.13) for flames in 15% oxygen.



Figure 3.14. Time dependence of the radius of the pulsating flame in 60% O<sub>2</sub> and 40% Ar with an aluminum concentration around 280 g/m<sup>3</sup>.



Figure 3.15. Average propagation velocity of the pulsating flame versus aluminum concentration in 60% O<sub>2</sub> and 40% N<sub>2</sub>, Ar or He.

A typical variation of the pulsating flame brightness recorded by the photodiode is shown in Fig. 3.16, superimposed with the acoustic pressure signal recorded by the microphone. It is evident that both traces coincide in frequency and are in-phase, indicating that acoustic pulsations are induced by the pulsating flame. Figure 3.17 presents an example of the light emitted from a flame with decaying pulsations undergoing transition from the pulsating mode to a stable flame propagation mode.


Figure 3.16. Typical light and sound pressure signals from pulsating flame (60% O<sub>2</sub> and 40% Ar mixture, aluminum concentration around 420 g/m<sup>3</sup>).



Figure 3.17. Typical light signal from a flame with decaying pulsations (42% O<sub>2</sub> and 58% Ar mixture, aluminum concentration about 450 g/m<sup>3</sup>).

Figure 3.18 illustrates the dependence of the frequency of flame oscillations on the aluminum concentration in fuel-lean mixtures of 80% oxygen diluted with either argon or helium. The dependence of the flame oscillation frequency on aluminum concentration under different concentrations of oxygen in argon-oxygen mixtures is illustrated in Fig. 3.19 for 42%, 60%, and 80% oxygen. As can be seen, in both cases, the frequency increases approximately linearly with aluminum concentration, while neither the oxygen concentration nor the type of inert gas exhibit any substantial influence on the oscillation frequency. Pulsation frequencies do not noticeably change in helium mixtures, which have much higher sound speed. Furthermore, experiments were performed for different balloon sizes, enclosure sizes and balloon thicknesses and yielded the same frequency for a given aluminum concentration.



Figure 3.18. Dependence of the flame pulsation frequency on aluminum concentration in 80% O<sub>2</sub> and 20% Ar or He.



Figure 3.19. Dependence of the flame pulsation frequency on aluminum concentration in O<sub>2</sub>-Ar mixtures with varying O<sub>2</sub> concentrations of 42%, 60% and 80%.

# 3.2 Large-scale experiments

#### 3.2.1 Flame propagation speeds

In total, 18 successful trials were performed using the experimental set-up described in section 2.2. Selected still frames from high-speed movies of the flame propagation event through the dust cloud are shown in Fig. 3.20. The top row shows images of the flame initiated with zero ignition delay time after dispersion. The bottom row shows a flame propagation event initiated with a 0.4 second delay following the end of the dust dispersion process. Because the cloud continues to move upwards after the powder dispersal stops, the position of the ignition charge for the longest ignition delays is raised to 1 m above the dispersion nozzle, while, for zero-delay ignition, the igniter was positioned next to the dispersion nozzle exit. Attempts to increase the ignition delay time beyond 0.4 seconds were unsuccessful as the flame either did not propagate through the whole length of the cloud or was increasingly asymmetrical, indicating the development of strong fuel concentration gradients. The average aluminum concentration in the cloud is estimated by dividing the mass of the dispersed powder by the volume of the cloud at the end of dispersal process, derived from video images, and is found to be close to stoichiometric conditions for all large-scale tests.



Figure 3.20. Still frames of flames ignited without delay (top) and with 0.4 seconds delay (bottom) after the end of the dust dispersion process for Valimet H-5 powder and a concentration around stoichiometry.

The procedure for obtaining the flame propagation speed from the high-speed movies is described in detail in [135] and is based on tracking and averaging the flame movement through individual columns of vertical pixels of the images. Some fraction of the observed flame propagation velocity is induced by the buoyancy forces lifting the combustion products upwards. The buoyancy-induced flame speed is estimated by tracking the upward movement of the combustion products after the flame reaches the top of the cloud, which was found to be in the range of  $2.5 \pm 1$  m/s. The average flame speed values measured in H-5 and H-10 aluminum dust clouds at different ignition delay times, reduced by the speed induced by buoyancy, are shown in Fig. 3.21. The error bars are the sum of the standard deviations of the flame propagation in large dust clouds is strongly influenced by the initial turbulence induced by the dust dispersal process. However, as can be seen from Fig. 3.21, the influence of turbulence is significantly reduced with a delay time between the end of the powder dispersal and the ignition event of 0.3-0.4 seconds.



Figure 3.21. Flame speed as a function of mixture ignition delay time in dust clouds of H-5 and H-10 Valimet aluminum powders for aluminum concentrations around stoichiometry.

# 3.2.2 Mixture pre-heating by radiation

A typical result illustrating the temperature history in the dust cloud prior to the arrival of the flame front, recorded by the array of three thermocouples of different sizes, is shown in Fig. 3.22. Starting from the bottom curve to the top, the three temperature traces represent the output signals from thermocouples with junction diameters of 0.25, 0.125 and 0.075 mm, respectively. The top temperature trace is derived by extrapolating the temperature signals from thermocouples at each moment in time to the signal that would be produced by a "zero-sized junction" thermocouple with no thermal inertia, indicative of the gas-phase temperature. The two different slopes of the gas temperature curve indicate preheating of the reactants by the absorbed radiative flux emitted by the flame and the combustion products, followed by the rapid heating via molecular heat diffusion with the arrival of the flame front. The maximum temperature attained by the mixture due to radiative heating is indicated in Fig. 3.22 by a dashed line and was below 200 °C in all experiments. The test facility was not heated and, therefore, the initial temperature of 0 °C corresponds to the room temperature during the tests.



Figure 3.22. Temperature traces as a function of time for different size thermocouples ahead of the flame front (dashed lines). The solid line represents signal extrapolation to "zero-size" thermocouple. Powder H-5, 0.3 sec ignition delay time and an aluminum concentration around stoichiometry.

# 4. Discussion

Detailed modeling and quantitative numerical analysis must be performed to explain the various physical phenomena observed in the present work and will be the subject of a subsequent publication. However, some qualitative explanations of the observed phenomena and trends based on physical considerations can be discussed. The flame speed dependence on dust cloud parameters in the stable flame-propagation regime are interpreted using some of our previously-published qualitative dust-flame models. The physical interpretation of the observed unstable combustion regimes is based upon thermo-diffusive instability theory developed for the description of similar phenomena for gaseous and condensed-phase mixtures. Large-scale tests are interpreted using a basic hydrodynamic model to obtain the burning velocity, and the effect of radiation is discussed in the context of pre-heating of reactants.

# 4.1 Stable flame propagation4.1.1 Flame speed and burning velocity

Similarly to flames in gas mixtures, the burning velocity of a spherically-propagating, constant-pressure dust flame can be found by simply dividing the measured flame speed by the expansion coefficient, defined as the ratio of the density of unburned mixture to the density of combustion products [158]. For any given aluminum concentration, this ratio can be calculated using an equilibrium code, such as Chemical Equilibrium with Applications (CEA) developed by NASA [58], that calculates both equilibrium temperatures and the number of moles of gaseous combustion products. The burning velocities derived from the balloon experiments for mixtures in 20% oxygen diluted with argon are shown in Fig. 3.23 in comparison to the data obtained previously from experiments with Bunsen dust flames for the same batch of Ampal-637 aluminum powder [98] in argon and 21% oxygen. As can be seen from Fig. 3.23, the burning velocities obtained from the two different experiments are in agreement, as was shown for aluminum-air flames in a previous publication [1]. The agreement between two different experimental methods with different geometries implies that the notion of burning velocity as a fundament physical-chemical parameter also applies for flames in metal suspensions, similar to gas flames.



Figure 3.23. Comparison of the burning velocities derived from balloon experiments and Bunsentype dust flames [98] in argon mixed with 20% O<sub>2</sub> for balloons and 21% O<sub>2</sub> for Bunsen flame.

#### 4.1.2 Dependence of the burning velocity on aluminum and oxygen concentration

The effect of aluminum concentration on the flame burning velocity at different levels of oxygen concentration is illustrated in Fig. 3.24 with argon being the inert diluent. Again, the burning velocities are obtained from the data of Fig. 3.12 by multiplying the flame speed by the expansion coefficient, which is also obtained with an equilibrium solver. The solid lines shown represent the trends of the flame speeds for the three different oxygen concentrations.



Figure 3.24. Dependence of burning velocity in aluminum suspensions on fuel concentration at different concentrations of oxygen diluted with argon.

As evident from Fig. 3.24, the dependence of the burning velocity with increasing aluminum concentration demonstrates the same qualitative behavior at all oxygen concentrations. The flame velocity increases with aluminum concentration in lean mixtures and then plateaus after crossing the stoichiometric value exhibiting very low sensitivity to dust concentration in fuel-rich mixtures. This behavior is different to flames in gaseous fuel mixtures where the dependence of the flame speed on the fuel equivalence ratio is more or less symmetrical around the stoichiometric value. There are two major reasons for this distinctive feature of dust flames. First of all, the flame temperature decreases less significantly with an increase of the fuel concentration in fuel-rich solid suspensions than in gases. This is because an increase in solid-fuel concentration only increases the specific heat of the mixture without diluting the oxygen concentration, since the solid particles occupy a negligible volume. Thus, the calorific value of a rich dust mixture is defined solely by

the oxygen concentration and not the fuel. The second reason is that the rate of aluminum particle combustion in the diffusive-combustion regime is not very sensitive to the reduction in bulk flame temperature, due to the formation of micro-diffusion flames around each particle with each flame temperature at the stoichiometric value. In fact, a larger reaction surface area in rich mixtures actually leads to a faster reaction rate, compensating for the decrease in flame temperature and, thus, keeping the value of flame speed relatively constant.

As can be seen from Fig. 3.24, the seemingly weak dependence of the burning velocity on oxygen concentration in fuel-lean mixtures is the most striking result observed in the present study for stable flames in aluminum suspensions. Regardless of the aluminum particle combustion regime, i.e., kinetic- or diffusion-limited, the particle reaction rate is proportional to the oxygen concentration. In accordance with the basic theory of diffusion-reaction waves in a reacting continuum [159], the propagation speed of the front is proportional to the square root of the reaction rate, which is equivalent to the square root of the oxygen concentration. The only reasonable explanation for the observed flame reduced sensitivity to oxygen concentration is the recently-developed theory of discrete flame propagation [130], [131], [160]. This theory predicts that in a system with fast-reacting, spatially-discrete heat sources, inter-source heat diffusion controls the flame propagation rate, resulting in a decrease in sensitivity of the flame speed on reaction time of the particles with oxygen. Based on this theory, the estimations provided in a previous publication [161] have actually predicted the results experimentally observed here. As the concentration of aluminum increases, the inter-particle spacing decreases and the discrete flame effects diminish. In fuel-rich mixtures, the amount of burned aluminum also rises proportionally to the oxygen content resulting in higher flame temperatures and, correspondingly, higher flame speeds for higher oxygen concentrations.

## 4.1.3 Effect of the gas molecular transport coefficients on the burning velocity

As in gaseous flames, the burning velocity in solid suspensions is roughly proportional to the square root of the heat diffusivity of the gas multiplied by the reaction rate. In addition, the rate of particle combustion in the diffusive combustion regime is proportional to the diffusivity of oxygen towards the micro-flames surrounding each particle. Combining these two factors gives the surrounding  $S_{L,\text{He}}$  /  $\sqrt{(\alpha D)_{He}/(\alpha D)_{He}}$  for the dependence of the huming velocity.

the expression  $\frac{S_{L,He}}{S_{L,Ar}} = \sqrt{\frac{(\alpha D)_{He}}{(\alpha D)_{Ar}}}$  for the dependence of the burning velocity,  $S_{L,R}$ 

in terms of the heat diffusivity  $\alpha$  and mass diffusivity of oxygen D for helium and argon as inert gases (they have equivalent heat capacities) [98]. This predicts a 3.9 fold flame speed increase for mixtures in 15% oxygen. As can be seen from the flame speed data in Fig. 3.13, the ratio between the flame speeds in argon and helium is around 2.9. Perhaps this discrepancy could be explained by uncertainty in the measured values; however, a lower experimental ratio of burning velocities in helium-oxygen and argon-oxygen mixtures was also observed in experiments with stabilized aluminum Bunsen dust flames [98]. This trend of discrepancies points towards a different mode of particle combustion depending on whether oxygen is diluted with argon or helium. Particle combustion in argon mixtures is controlled by the diffusion of oxygen towards the diffusion microflame surrounding each particle and the experimental evidence indicates that a heterogeneous kinetically-controlled reaction at the surface might be the limiting reaction stage in helium mixtures due to their higher molecular heat and mass transfer coefficients [100]. In the asymptotic case of kinetically-controlled combustion, the flame speed depends on heat diffusivity only. Any intermediate (partial) dependence on oxygen diffusivity would indicate a transient particle combustion regime [65].

# 4.1.4 Effect of cloud geometry and radiation heat transfer on the burning velocity in large-scale aluminum dust clouds

In order to derive the burning velocity from the flame speed measured in the present largescale experiments, one has to account for the specific geometry of the axial flame in a cylindrical cloud. After combustion, the gas expands due to the increase in temperature and the change of mean molecular weight. Depending on the geometry, this expansion effectively acts as a piston displacing the reactants and surrounding air so that the flame moves faster in the laboratory frame than the fundamental burning velocity. In the case of a spherical flame with central ignition, as in the balloon experiments, the combustion products are self-confined, and the burning velocity is obtained by multiplying the flame speed by the ratio of the densities of the burnt and unburnt mixtures. For clouds with an approximately cylindrical geometry, as in the present field experiments, the effect of gas expansion is different. Feng et al. [162] and later Kaptein and Hermance [163] developed an analytical model to calculate the expansion coefficient for flames propagating in methane-air layers within underground mine galleries. By extending their analysis to the present axi-symmetrical and practically unconfined conditions, the model predicts that the observed flame speed is related to the burning velocity by the expression  $S_b = S_f \sqrt{\rho_b / \rho_u}$ . The burning velocity, calculated using this expression from the flame speed data with a maximum ignition delay time of 0.4 s, is in the range of about 45±10 cm/s, which is more than twice the flame burning velocity of about 20 cm/s from the experiments with small-scale laboratory Bunsen flames [98] and flames in balloons [1].

Unlike combustible gas mixtures that are largely transparent to radiation, suspensions of solid fuel particles can efficiently absorb the thermal radiation emitted by the flame and the combustion products [16]. In dust flames, radiation goes from being a source of heat loss to a mechanism of heat transfer from the flame and combustion product to the unburned fuel mixture. Numerous theoretical models of flames that include radiation heat transfer in suspensions of various solid fuels, or even gas fuels laden with inert particles, have predicted radiation to be an important, or even dominant, flame propagation mechanism capable of increasing the flame speed by more than an order of magnitude in comparison to flames driven by molecular heat conductivity alone [121], [122], [164], [165]. In practice, however, no noticeable effects of radiation have been observed during laboratory testing of dust suspensions, including the present experiments in latex balloons, suggesting that the scale of the laboratory flames is insufficient for efficient absorption of the radiative heat flux. The mean free path of a photon in a stoichiometric aluminum cloud can be estimated to be on the order of 4-5 cm. However, most of this radiation is scattered and not absorbed by the particles. The estimated absorption cross-section of a micron-size aluminum particle in the 2-5 micron wavelength region, characteristic of aluminum flame thermal radiation, is below 0.1 [166]. Correspondingly, the absorption length of radiation in an aluminum cloud is at least an order of magnitude greater than the mean free path of photons. Indeed, as can be seen from the thermocouple traces in Fig. 3.22, in a large dust cloud, the suspension starts to be heated by radiation 150 ms prior to the flame arrival. With a flame propagation speed in this case of about 5 m/s, this time corresponds to a distance of about 50-100 cm, larger than the scale of a flame propagating through a balloon of 30 cm diameter and much larger than the Bunsen flame which has a characteristic dimension of 1-2 cm.

The effect of the initial temperature on the burning velocity in aluminum suspensions was previously measured by Goroshin et al. [16] and a 2-fold increase was observed for the 170 K

increase in initial temperature shown on Fig. 3.22. Using an initial value of about 20 cm/s, the burning velocity of a flame propagating through a cloud of aluminum powder at 440 K would be on the order of 40 cm/s, which is comparable to the value obtained from the present field experiments once the expansion coefficient and buoyancy-induced velocity are taken into consideration.

### 4.1.5 Unstable flames

Contrary to acoustic oscillations previously observed in tubes [167], [168], pulsations in balloons are observed only in fuel-lean mixtures and are the strongest near the lean flame propagation limit indicating that their physical nature is very different from acoustic coupling. Similar pulsating flames in fuel suspensions have only been observed and reported once, for flames in suspensions of large PMMA particles in microgravity [26], [169]. Those authors considered the pulsations to be caused by periodical preheating of the fresh mixture by flame radiation. This, however, is an unlikely explanation since, as was discussed above, radiation cannot be sufficiently absorbed by the unburned mixture in small-scale dust clouds and primarily acts as a heat-loss mechanism. The effects of radiative heat transfer should also increase with fuel concentration, whereas pulsating flames are observed only in fuel-lean mixtures and are replaced by stable flame propagation when the fuel concentration approaches stoichiometric conditions. Thus, the observed pulsating and other unstable flame-propagation regimes are most probably the manifestation of thermo-diffusive instabilities, characteristic of flames with Lewis numbers deviating from unity [141], [156].

Near stoichiometric concentrations, the diffusion of heat through the flame in the suspension is balanced by the diffusion of oxygen, resulting in Le numbers close to unity and steady flame propagation [7], [170]. According to flame stability theory, thermo-diffusive instabilities appear when this balance is broken, i.e., when the diffusion of either heat or mass begins to dominate over the other. For fuel-rich dust suspensions, the Lewis number is smaller than unity, which results in a cellular structure of the flame front [170]. Cellular flames have been observed in fuel-rich iron dust mixtures of small iron particle sizes during microgravity experiments by Tang et al. [101] as well as in the present balloon experiments when the aluminum concentration is above 500 g/m3. Increasing the dust concentration beyond the stoichiometric value does not change the heat conductivity of the mixture because the particles occupy a

negligibly small volume. However, the heat diffusivity of the mixture does decrease with an increase in powder concentration due to the increase in heat capacity and density of the overall suspension. This effect yields Lewis numbers below unity for fuel-rich mixtures, causing the formation of cellular flames.

For fuel-lean dust mixtures, the gradient of oxygen concentration across the flame is small and the diffusion of oxygen does not substantially affect the flame structure. The Lewis number becomes very large due to the zero diffusivity of metal particles in suspension, and a different type of instability arises. These instabilities take the form of pulsations, target patterns, or spiral waves, and have been observed in numerous systems that support reaction-diffusion waves [171]–[173]. For combustion systems, the criterion for the onset of pulsating instabilities has been established by Joulin and Clavin and can be written as follows:  $\beta$ (Le-1)>16, with  $\beta$  being the Zeldovich number [165]. In other words, pulsating and spiral-wave instabilities are possible only for systems with sufficiently large Lewis numbers, high activation energy and low flame temperatures. These types of instabilities have been mostly observed in condensed systems [37], [174]–[176] and rarely for gaseous flames due to the difficulty in creating combustible gaseous mixtures satisfying the instability criterion [158], [177]–[179].

A qualitative map of the different flame propagation regimes observed in the present experiments for aluminum suspensions as a function of the oxygen and aluminum concentrations is shown in Fig. 3.25.



Figure 3.25. Map of the flame propagation regimes within fuel-oxygen concentration coordinates.

As can be seen from Fig. 3.25, the structure of the map of the flame propagation regimes generally follows the criteria for stable/unstable flame propagation predicted by flame thermodiffusive instability theory. However, a number of the phenomena observed in the present work still lack a clear physical explanation. For example, the flame trajectories in the pulsating regime shown in Fig. 3.14 indicate that brief periods of rapid flame movement are followed by comparatively-long periods of flame stagnation. The behavior within this flame propagation regime is difficult to rationalize with laminar flame theory. Also, the independence of the average flame propagation speed on the heat diffusivity of the gas mixture observed for pulsating flames and presented in Fig. 3.18 also seemingly contradicts the very nature of a flame driven by molecular heat diffusivity. One possible explanation may be that the observed pulsating phenomenon is closer to a series of consecutive thermal explosions, as described by the nonstationary thermal explosion theory developed first by Frank-Kamenetskii [64]. Each explosion is followed by a period of thermal relaxation, where the mixture burning rate falls effectively to zero. The combustion products after the explosion act like a hot wall, at a temperature close to the adiabatic value, that heats the reactants in the adjacent layer of the mixture until another thermal explosion event occurs inside the layer of unburned mixture bordering the combustion products from the previous explosion. Further work will be needed to clarify the physical mechanisms responsible for all of the flame propagation regimes shown in the regime map in Fig. 3.25.

## 5. Conclusion

The present work reports a large set of experimental data on isobaric, freely-propagating flames in aluminum dust clouds, ranging in scale from tens of centimeters to several meters, that was obtained with two experimental facilities. The main highlights of this experimental work are the following:

- Stable propagation of an unperturbed spherical flame was only observed in the vicinity of the stoichiometric concentration. Pulsating, spiral and combined spiral-pulsating flames were observed in fuel-lean mixtures and the formation of a cellular pattern on the flame front was evident in fuel-rich dust clouds. The appearance of unstable combustion generally follows the predictions of thermo-diffusive flame stability theory corresponding to pulsating flame instabilities at large Le numbers (fuel-lean dust suspensions) and cellular instabilities for Le numbers below unity (fuel-rich clouds).
- For the stable flame propagation regime in fuel-lean mixtures, the flame speed is quite insensitive to the oxygen concentration. For fuel-rich suspensions, the flame speed is insensitive to an increase in aluminum concentration. The first observation can be explained in terms of the discrete flame theory that takes into account inter-particle heat transfer. The latter observation is primarily a consequence of the insensitivity of the particle combustion rate to flame temperature in the diffusive regime.
- The burning velocity derived from flame propagation speeds in balloons correlates well with previously measured values from stabilized aluminum Bunsen flames whereas the value of the burning velocity observed in large-scale dust clouds is larger by almost a factor of two. The increase in burning velocity is attributed to pre-heat of the reactants by radiation emitted from the combustion zone and combustion products, a phenomenon that only occurs when the size of the cloud is sufficiently large for self-absorption of the radiation.

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# 3.3 Discussion on freely-propagating flames in aluminum suspensions

# **3.3.1 General considerations**

Two novel apparatus were introduced in the publications shown in chapters 2 and 3 to study freely-propagating flames in aluminum suspensions. The data presented looked at the flame propagation speeds in different oxidizing environments and at different scales and geometries. The effect of radiation was studied by measuring the temperature of the reactants ahead of the flame front with thermo-couples. The burning velocity was obtained for the two different geometries in air and compared to data previously obtained by Goroshin et al. [98] on a Bunsen burner. Discrete flame propagation was observed in stable fuel lean flames. Furthermore, thermo-diffusive instabilities, that took the form of spiral and pulsating waves, were discovered in sufficiently fuel lean mixtures. The very nature of thermo-diffusive instabilities, described in more details below, tend to indicate that those pulsating and spin instabilities would not be unique to aluminum flames but could potentially be observed for most metal dust systems. The work presented in this chapter on freely-propagating flames in aluminum clouds confirms the need to use fundamental experiments reflecting the reality of dust combustion in real life applications to capture all physical phenomena. Those various phenomena observed require the use of imaging techniques and would not be observable in single particle experiments.

Furthermore, in fuel lean flames, the previous chapter reports the observation of discrete flame propagation. This deduction comes from the rather weak dependence of the burning velocity on the oxygen concentration in fuel lean mixtures. In both fuel lean and fuel rich cases, the flame propagates via the diffusion of heat since heat sources are discrete and localized in space. In fuel lean cases, the term discrete refers to the fact that particle reaction time is much greater than heat diffusion time and thus the heat production rate has little impact on the flame propagation speed. In the case of fuel rich mixtures, the particle reaction time is not significantly faster than the heat diffusion time and thus plays a role in the flame propagation speed. Another term found in litterature for discrete flame propagation is percolation.

The results presented in this chapter tend to demonstrate that it is possible to define the notion of burning velocity for dust flames. The comparison between spherical flames and Bunsen

flames for mixtures in argon and in nitrogen with 21% oxygen are in good agreement. Furthermore, when considering all potential factors influencing the flame propagation speed such as turbulence and radiation heat transfer, it appears that it is possible to reconcile data obtained in clouds of different scales.

The results also seem to indicate that radiation only plays a secondary role in the flame propagation in the large-scale dust clouds presented in the publications (about 2 m in width). Radiation indeed pre-heats the flame but only around 150 K above the initial temperature. For small-scale flame, such as the flames in the balloon experiments, radiation only plays the role of heat loss. This means that, unlike some of the models cited previously, the flame still propagates via molecular heat transfer. This suggests that a different modeling approach could be used, where radiation heat transfer is decoupled from the flame code. Radiation could be treated as a mechanism to pre-heat the reactants, which increases the flame speed when compared to the initial temperature by faster heat diffusion and chemical kinetics.

# 3.3.2 Instabilities

Before discussing thermo-diffusive instabilities in more detail, it is important to rule out acoustic waves as the source of the pulsations. In the case of acoustic coupling, as seen previously in flames in tubes [167], [168], the acoustic wave emitted by the flame bounces back on the closed end and interferes with the flame creating a pulsation. In this case, the frequency of oscillation will depend on the length of the tube and also on the speed of sound of the mixture. However, the diverse tests performed in the balloons show otherwise. The pulsation frequency was found to be independent of the size of the balloon, the size of the enclosure, the elasticity of the balloon (tests performed with double and triple layers of balloons) and the speed of sound of the mixture (frequency was identical for argon, nitrogen and helium as diluent). These observations, combined with the observation of spirals, led to the conclusion that the present phenomenon must be different than pulsations caused by acoustic coupling.

Flames propagate by the molecular diffusion of heat and oxygen. Near stoichiometric concentrations, the diffusion of heat is balanced by the diffusion of oxygen, resulting in Le numbers close to unity and steady flame propagation [7]. In accordance with flame stability theory, thermo-diffusive instabilities appear when this balance is broken, i.e., the diffusion of either heat or mass begins to dominate over the other. For fuel-rich dust suspensions, the Lewis number is

smaller than unity, which results in a cellular structure of the flame front. This type of instability has been the object of many studies in gaseous systems [7]. Such instabilities have also been observed in rich dust flames for small iron particle sizes by Tang et al. [100] during microgravity experiments with iron dust flames. As previously mentioned, increasing the dust concentration beyond the stoichiometric value does not change the gaseous compositions of the mixture since the particles occupy a negligibly small volume. However, the increased dust concentration does increase the heat capacity of the mixture, which leads to a decrease in the heat diffusivity and eventually a decrease of the Lewis number to values well below unity for substantially fuel-rich mixtures, causing the formation of flame cells.

For fuel-lean dust mixtures, the gradient of oxygen concentration across the flame is small and the diffusion of gaseous species does not affect the flame structure. The Lewis number becomes very large and a different type of instability arises. These instabilities take the form of pulsations, target patterns, or spiral waves, and have been observed in numerous systems that support reaction-diffusion waves [172]. For combustion systems, the criterion for the onset of pulsating instabilities has been established by Joulin and Clavin and can be written as follows:  $\beta(Le - 1) > 16$ , with  $\beta$  being the Zeldovich number [165]. In other words, pulsating and spiralwave instabilities are possible only for systems with sufficiently large Lewis numbers and activation energy. These instabilities have been observed rarely for gaseous flames due to the difficulty in creating a mixture that satisfies the criterion and in which a flame can propagate [177]– [179].

However, any lean dust mixture with low fuel volatility will have a high Lewis number, since the limiting reactant has essentially zero diffusivity (Le  $\rightarrow$  infinity), which should make pulsating instabilities very common in dust flames. Despite their likelihood, they have only been observed and reported once, for flames in suspensions of large PMMA particles in microgravity [26], [169]. The authors considered the instabilities to be caused by radiative heat transfer. This is an unlikely explanation since radiation cannot be sufficiently absorbed by the unburned mixture in small-scale flames and primarily acts as a heat-loss mechanism. Radiative effects also increase with fuel concentration, due to an increase in optical thickness, whereas pulsating flames are reported only in fuel-lean mixtures.

Pulsating flame instabilities in combustion systems were first experimentally observed in condensed energetic systems by Merzhanov and Borovinskaya [175]. Shkadinskii et al. [180] later developed a first numerical model of flames in condensed systems that explain the observed pulsating instabilities. Later a simplified analytical approach was further developed by Matkowsky and Sivashinsky [156] and showed that, in the absence of reactant diffusion, the flame propagation can indeed be unstable and propagate in a pulsating manner.

In spite of intensive study, the pulsating flame phenomenon still lacks a clear qualitative physical explanation. The slope of a flame trajectory on a radius vs time plot normally gives the flame speed. One can observe on Fig. 3.14 brief periods of extremely rapid flame movement, alternating with long periods when the flame essentially does not move. The very large slopes of the flame trajectories during the rapid movement periods correspond to flame speeds in the range of tens of meters per second, which are difficult to explain even if one takes into account the preheating of the fuel mixture during the periods when the flame is stagnant. The observed independence of the average flame propagation speed on heat diffusivity for pulsating flames seemingly contradicts the very nature of a flame largely driven by molecular heat diffusivity. Thus, the observed phenomenon is much closer in appearance to a series of consecutive thermal explosions as described by the non-stationary thermal explosion theory developed first by Frank-Kamenetskii [64]. Each explosion is followed by a period of thermal relaxation, where the mixture burning rate falls effectively to zero. The combustion products after the explosion act like a hot wall at a temperature close to the adiabatic value that heats the reactants in the adjacent layer of the mixture until another thermal explosion occurs inside the layer of unburned mixture bordering the combustion products from the previous explosion.

Using the physical interpretation given above, it is possible to derive an analytical expression for the ignition delay and, thus, pulsation frequency. Treating the initiation of the reaction as the ignition of an unconfined mixture by a hot surface, the ignition delay time is given by an expression developed by Law [7]. The frequency is then taken to be the inverse of the delay between consecutive ignitions:

$$t = \frac{\rho C_p (T_{ad} - T_i)^2 T_a}{2T_{ad} \pi B_c e^{\frac{-T_a}{T_{ad}}} q Y}$$

The delay term depends, among other things, on the adiabatic flame temperature. A greater adiabatic flame temperature gives a shorter delay time or a larger frequency. This is consistent with the experimental data observed. For fuel lean cases, increasing the concentration of aluminum increases the heat released which increases the flame temperature and shortens the delay time. As can be seen, the heat conductivity is absent from the expression, implying that the frequency is independent of the heat diffusivity of the gas. Indeed, experimentally there appears to be no difference in frequency between flames with mixtures containing argon or helium and also no difference as noted above in the average flame speed. Since this consecutive-ignition process is not technically the propagation of a flame front, but rather a series of thermal explosions, it is misleading to refer to the average flame speed. Since the thermal explosion event is by itself a very fast event in comparison to the ignition delay time, the average apparent flame speed should be the distance from the burned products at which thermal explosion occurs in the layer of fresh mixture multiplied by the frequency of the event. Again, this gives a result that does not depend on the heat diffusivity of the mixture.

The spiral waves reported in this paper are also a manifestation of the same pulsating instabilities. They have first been observed by Merzhanov and co-workers in condensed systems [175], [181]. They have been since observed in many different condensed systems such as thermites [174] and combustion synthesis [182]. It has been mathematically shown that spiral waves or spin combustion can be obtained using the same model as for pulsating flames but with a cylindrical geometry [183], [184]. They have also been recently observed in hydrogen-air, hydrogen-oxygen and butane-oxygen-helium systems at elevated pressures [157], [179].

# **Chapter 4. Combustion of Aluminum Suspensions in Hydrocarbon Flame Products**

# 4.1 Introduction to stabilized metal flames in hydrocarbon products

The following two chapters present the two publications pertaining to stabilized flames in hybrid hydrocarbon-metal mixtures. The first article focuses on aluminum-methane mixtures and the second one on iron-methane mixtures. As mentioned previously, aluminum is a common additive in many energetic materials, such as propellants and condensed explosives. In a typical propellant, the matrix, composed mainly of high explosives and binders, burns first producing heat and a wide range of oxidizers, like carbon dioxide, water and chlorine compounds. In the second step, aluminum burns in this hot oxidizing environment, which results in extra energy generation and thus an increased total energy density for the propellant [185]. Hybrid aluminum-methane flames are a simplified system used to model the two-step combustion process of actual propellants. This simple system allows the study of different parameters in a controlled environment.

When studied from a single particle point of view, one would introduce a single aluminum particle in the methane flame and measure whether the particle would burn or not. In the case where the particle fails to ignite, standard single particle theory would state that introducing more particles in the flame would only decrease the methane flame temperature by increasing the heat capacity, which takes you further away for the ignition temperature. However, the experimental results shown below demonstrate the opposite: after a certain critical concentration of aluminum powder, a second flame front forms in the aluminum cloud and couples to the first methane front. This indicates that aluminum combustion in the product of hydrocarbon combustion also needs to be treated as a frontal phenomenon.

Aluminum flames have higher temperatures then methane flames and are thus much brighter. This makes it difficult to visualize both flame fronts. Furthermore, combustion of aluminum particles happens in the gas phase, which involves evaporation of aluminum and chemical reactions in the gas phase. For those two reasons, it is interesting to work with iron particles instead. Iron flame temperatures are similar to methane flame temperature, which makes it possible to observe the two flame fronts. Iron burns heterogeneously, which simplifies the physics by removing gas-phase combustion and all sub-oxides in the vapor phase. Iron is thus an ideal fuel to use in a model system that studies flame propagating in hybrid mixtures.

Hybrid mixtures are a convenient way of introducing different oxidizers than oxygen and increasing the initial mixture temperature. The different oxidizers have different chemical reaction rates, which can shift the regime of combustion between a kinetically-controlled regime and a diffusion-controlled regime.

# 4.2 Combustion of Aluminum Suspensions in Hydrocarbon Flame Products, *Journal of Propulsion and Power*

# Combustion of Aluminum Suspensions in Hydrocarbon Flame Products

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# Abstract

Stabilized aluminum flames are studied in the products of methane combustion. A premixed methane-air Bunsen flame is seeded with increasing concentrations of micron-size aluminum powder, and scanning emission spectroscopy is used to determine the flame temperature via both the continuous and AlO spectra. The flame burning velocity is measured and the condensed flame products are collected and analyzed for unburned metallic aluminum content. It was observed that, below a critical concentration of about 120g/m<sup>3</sup>, aluminum demonstrates incomplete oxidation with a flame temperature close to the methane-air flame. Below the critical concentrations, the flame burning velocity also decreases similar to a flame seeded with inert SiC particles. In contrast, at aluminum concentrations above the critical value, an aluminum flame front rapidly forms and is coupled to the methane flame. The flame temperature of the coupled methane-aluminum flame is close to equilibrium values with aluminum as a reactant and the flame burning velocity remains flat for increasing aluminum concentrations. A simple theoretical estimation, which assumes that the aluminum reaction rate is controlled by the kinetic evaporation of aluminum, adequately predicts the critical concentration range at which the aluminum flame front can be coupled with the methane flame.

# **1. Introduction**

Combustion of metal particulate suspensions in the products of hydrocarbon flames occurs in metalized slurry fuels [35], metalized propellants [186], [187], solid and fuel-air metalized explosives [138], [188], in technological processes including reactive particle spray deposition [189] and the synthesis of nano-oxides [190], as well as in industrial accidents. The extensive literature accumulated over more than fifty years of research on metal combustion is primarily dedicated to the experimental study and theoretical modeling of the ignition and combustion of a single isolated metal particle, including the effect of different pressures, temperatures and oxidizing environments [61]. Due to experimental limitations, the majority of studies were performed with relatively large particles, ranging from tens to even hundreds of microns in size; whereas, in practical applications, the size of particles is often in the micron-size range. Recent work has pointed out that the extrapolation of results obtained for large particles to particles of smaller size might not always be appropriate due to a possible change in the combustion regime with a reduction in particle size; that is, a transition from combustion controlled by the diffusion of oxygen or other oxidizing gases to a combustion mode limited by the reaction kinetics [63].

The present study investigates yet another factor that impedes the application of the isolated single particle approach for the prediction of metal combustion characteristics in real systems with large metal content. The combustion of metal particles in such systems occurs within relativelydense dust clouds and, therefore, can be a frontal phenomenon analogous to a gas flame. The experimental results presented in this paper demonstrate that the formation of a flame front within a metal particle cloud and the subsequent characteristics of the combustion front cannot be predicted by direct extrapolation of data obtained with isolated single particles. The generation of heat within the dust flame front and the consumption of the oxidizer not only continuously modify the combustion environment around the burning particles, but also influence the flow conditions upstream of the metal flame front via molecular or turbulent diffusion of heat and gaseous species. Due to heat transfer to the flow upstream of the metal dust combustion front, the conditions for particle combustion may be sustained without relying solely on the heat provided by the hydrocarbon flame, as would be the case for a single particle. In fact, metal dust flames in micron-sized suspensions can self-stabilize in a cold flow, without any hydrocarbon fuel source, with flame speeds comparable to those of hydrocarbon fuels. This technique was first demonstrated by Cassel [91] and reproduced in more recent work [98], [99].

In the current investigation, the formation of a stabilized, aluminum dust-cloud flame in the products of a hydrocarbon flame is studied experimentally by seeding premixed methane Bunsen flames with micron-sized aluminum particles. The first results of this investigation unambiguously demonstrated that, as the concentration of aluminum particles increases, an aluminum dust flame forms rapidly above some critical value of metal mass loading [3]. In the present work, the combustion characteristics of the metal dust flame are studied for flames with and without excess oxygen, and are investigated with the use of more accurate and detailed flame diagnostics. In particular, spatially-resolved emission spectroscopy is synchronized with optical dust concentration monitoring, allowing the direct correlation between flame temperature and aluminum mass concentration. In addition to the condensed phase temperature derived from the continuous spectra, a temperature is also obtained by fitting the emission spectrum of AlO, a gas phase intermediate, to a simulated spectrum. Comparison of the solid phase and AlO temperatures is used to shed light on the combustion mechanism. The dependence of the burning velocity, or laminar flame speed, of the mixture as a function of aluminum particle concentration is compared with similar measurements with inert silicon carbide (SiC) particles to determine the concentration at which the heat release from the aluminum combustion significantly influences the flame speed. The condensed flame products are also collected at different alumium loadings, corresponding to different combustion regimes, before and after the formation of an aluminum flame front. Products are chemically analyzed to determine the fraction of aluminum remaining and transmission electron microscopy (TEM) is used to determine the particle morphology. Finally, a simplified theoretical estimation, based on the Frank-Kamenetskii approach, is presented to describe the conditions under which the methane and aluminum flames may be coupled. The aluminum particle concentration for which coupling is predicted to occur is consistent with the experimental results. A key characteristic of the new theoretical estimation is that the aluminum combustion is considered to be kinetically limited by the aluminum evaporation rate.

# 2. Experimental details

## Dust Burner

A schematic of the hybrid gaseous-dust fuel burner is shown in Fig. 4.1. The burner was specifically assembled for the current experiments on methane-aluminum mixtures and has several new design elements compared to the previous dust burner that was used to study stabilized pure aluminum dust flames [98]. The new apparatus has the capability of dispersing a variety of micron-sized powders in any gaseous mixture. The premixed methane-air flow is seeded with aluminum particles using a dust dispersion system described previously [3], [98], [99], [103]. The powder is continuously fed via a syringe-type feeder and dispersed using a supersonic jet from an annular 50 micron slot. The initially highly-turbulent flow is expanded in a low angle conical diffuser and laminarized in a 60 cm long, 2.2 cm inner diameter flow tube before exiting through a conical nozzle with an exit diameter of 12 mm. The co-flow assembly surrounding the nozzle provides a coaxial flow of air or inert gases at the same speed as the combustible mixture. The flow rate through the nozzle is regulated by diverting part of the flow through a side tube using an ejector system (see Fig. 4.1). The ejector was calibrated using pure oxygen as the main flow and nitrogen as an ejecting flow and measuring the oxygen concentration at the exit of the bypass tube. The combustible flow is ignited at the nozzle exit by a remotely-operated propane-oxygen torch.



Fig. 4.1 Schematics of the dust burner (left) and set up for calibrating the light attenuation probe (right).

# Aluminum Powder

The Ampal 637 micron-sized aluminum powder used in the present experiments is composed of spheroidal or nodular aluminum particles having a Sauter mean diameter ( $d_{32}$ ) of about 6.5 µm. This powder came from the same large batch that was used in previous experiments with aluminum dust cloud flames [98], [99], [103]. The consistent use of the same powder allows the results for the hybrid mixtures obtained in the current paper to be quantitatively compared to the previous results for pure aluminum-air flames. The scanning electron microscope (SEM) image of the powder shown in Fig. 4.2 illustrates the size and morphology of the particles. Fig. 4.2 also shows the particle size distribution obtained with a Malvern Mastersizer 2000.



Fig. 4.2 SEM photograph (left) and volumetric particle size distribution (right) of Ampal-637 aluminum powder.

# Dust concentration measurements and monitoring

The concentration of aluminum particles in the flow is continuously monitored by a laser light attenuation probe. A 5 mW diode laser emits a beam that is expanded through cylindrical lenses and collimated to a 3x6 mm rectangular-shaped laser sheet before being transmitted directly through the burner nozzle, as shown in Fig. 4.1B. The rectangular slits on the nozzle walls are covered with transparent, high-temperature, optically-clear Teflon tape and the special nozzle geometry, which includes a wider cone angle above the slit, prevents dust deposition on the inner side of the tape. After attenuation from the dust flow, the laser beam is focused onto a photodiode, which is protected from the intense flame illumination by a narrow bandpass filter of the same wavelength as the laser light (633 nm) and a spatial filter. The signal from the photodiode is recorded by a data acquisition system.

The laser-light-attenuation probe is calibrated by pulling the two-phase flow through a stack of several fine particulate filters using a vacuum, and collecting the dust for approximately 5 seconds. The dust concentration in the flow is calculated by dividing the mass of aluminum by the total volume of the gas that passed through the nozzle for the same period of time. The light attenuation probe calibration for the aluminum powder used in the present experiments is shown

in Fig. 4.3, which also includes the two-sigma prediction band for measurements (dash lines) and the uncertainty band for the resulting calibration curve (shaded area).



Fig. 4.3 Calibration of the light attenuation probe versus dust concentration. Dash lines show the prediction band for new measurements and the shaded area indicates the uncertainty (3 standard deviations) for the resulting calibration.

### Flame Photography and Spectroscopy

A high-resolution digital camera equipped with a macro lens and a variable neutral density filter is used to image the flames. The camera hot-shoe adapter is connected to a battery to generate a signal at the time of the photograph that can be correlated, on the data acquisition record, with a particular value of aluminum dust concentration. A high-speed digital video camera allows the flame behaviour in the transition regime to be monitored with a framing rate of 300 frames per second.

Spatially-resolved flame emission spectra are obtained using an opto-mechanical scanning system similar to the one used in our previous work for the study of aluminum dust flames [98]. The telescopic system focuses the magnified flame image on the film plane of a SLR camera with a magnification ratio of 1:1.5. The fiber optic cable installed in the center of the image plane of the SLR camera transmits the optical signal to a miniature diffraction spectrometer. The scanning of the flame image across the entrance of the telescopic system is performed by a rotating flat mirror and a step motor. The step signal driving the motor triggers the spectrometer acquisition

and allows the spectrum acquired at each step to be correlated with the instantaneous aluminum mass concentration. The spatial resolution of the system varies between 0.15 mm and 0.6 mm to accommodate the different flame luminosities and different spectrometers used. Two Ocean Optics Inc. miniature spectrometers with fiber optic inlets are used. The first, an Ocean Optics USB-4000 spectrometer, with a spectral resolution of 2.5 nm and a spectral range from 350 nm to 1100 nm, has no entrance slit and is coupled to a 100  $\mu$ m fiber optic cable. Data from this spectrometer is analyzed to derive the flame temperature from the continuous part of the spectrum. The second spectrometer, an Ocean Optics HR-4000, with a spectral resolution of up to 0.02 nm in the range of 200 nm-1100 nm (depending on the grating installed), has an entrance slit of about 8 microns and is coupled to a 600  $\mu$ m optical fiber. This spectrometer provides the necessary spectral resolution to fit an AlO vibrational band to a temperature. The top view of the optical diagnostic set up is shown in Fig. 4.4.



Fig. 4.4 Schematic of the optical diagnostic apparatus.

The position of the flame front is located by the maximum intensity of the spectral signal determined from each set of scans across the flame cone. The temperature of the condensed emitters in the flame front is derived by fitting the continuous part of the spectra to Planck's law

of blackbody radiation. As in Ref. [99], it is assumed that the prime emitters of the continuous spectra are aluminum oxide particles whose spectral emissivity is assumed to be proportional to the inverse of the square of the wavelength  $(1/\lambda)^2$ . The estimated accuracy of the method is approximately ±50 K at low flame temperatures and about ± 150 K at high temperatures.

Temperatures of the gaseous aluminum sub-oxide, AlO, are derived by fitting the spectrum of the AlO  $\Delta v = -1$  band obtained with the high-resolution spectrometer to a theoretically calculated spectrum as described in detail in Ref. [191]. This particular band of AlO is chosen due to the sensitivity of its shape to temperatures typically encoutered in aluminum combustion. The AlO temperature derived is close to the peak temperature in the system [192].

#### Gas flow and oxygen concentration

The gas flow through the system is controlled using needle valves and rotameters that are calibrated with a digital flow meter within 2% accuracy. For the ejector calibration, the oxygen concentration in the flow is measured with an oxygen analyzer having an accuracy of roughly 0.2%. Two different gas compositions are used in the present experiments. The first gas mixture is a stoichiometric methane-air mixture. The second mixture has identical flow rates of oxidizer and methane, but the air is replaced by a mixture of 26% oxygen and 74% nitrogen. Thus, after methane combustion, the first composition produced a flow of combustion products without any free oxygen, whereas the second composition generated a product flow with 5% of remaining free oxygen. This allows the effect of free oxygen on the combustion of aluminum in hydrocarbon combustion products to be determined. This enriched oxygen mixture is used to keep the flow rates identical (required for consistent dust dispersion) and to maintain similar methane flame temperatures.

# 3. Experimental Results and Discussion

### Qualitative observations of the aluminum-methane flame at different aluminum concentrations

The qualitative behaviour and structure of the flame in the hybrid methane-aluminum mixture at different aluminum concentrations is analyzed using digital high-resolution images and high-speed movies synchronized with the dust concentration monitoring system. Figure 4.5

contains images of the different flame structures observed as a function of aluminum concentrations. As seen from the images in Fig. 4.5, the flame structure changes drastically with an increase in aluminum concentration. A 3.0 neutral density filter was employed at high aluminum concentrations to distinguish the flame structure, such that the actual changes in the flame appearance are greater than what is depicted by the images in Fig 4.5. At low mass concentrations, below 100 g/m<sup>3</sup>, the flame appears yellow in color, with no cone arising from the aluminum combustion zone. The appearance of the methane-aluminum flame at this aluminum concentration range is not different from the flame seeded with inert SiC powder. As the concentration of aluminum particles increases to roughly 120-140 g/m<sup>3</sup>, a bright white spot emerges first at the tip of the flame and, as the concentration increases further to about  $180 \text{ g/m}^3$ , a very bright front with a well-defined outer border indicating aluminum combustion moves down along the flame cone, eventually stabilizing just a few millimetres above the rim of the methane flame. This process is illustrated with the still frames shown in Fig. 4.5 (bottom). A similar aluminum front formation behaviour is observed in methane mixtures containing 5% of free oxygen. In this case, the appearance of the aluminum flame front can be seen at somewhat lower dust concentrations.



Fig. 4.5 Flame images at different concentration of aluminum (top) and still frames from highspeed recording of aluminum front formation process (bottom).

#### Flame spectra and temperature

Typical flame spectra acquired before and after the formation of the aluminum dust flame front (at low and high aluminum concentrations) are presented in Fig. 4.6. As can be seen from Fig. 4.6, the flame demonstrates a weak signal of the AlO band sequence at low aluminum concentrations. In contrast, after the formation of the aluminum combustion front at higher aluminum concentrations, the AlO molecular bands are strong in emission and are similar to spectra from pure aluminum dust-air flames [12]. At concentrations above 200 g/m<sup>3</sup>, strong non-ionized aluminum vapor atomic lines can be seen at 394.40 nm and 396.15 nm [117].



Fig. 4.6 Flame spectra before (low aluminum concentration, 80 g/m<sup>3</sup>, number 1) and after the formation of aluminum flame front (high aluminum concentration, 250 g/m<sup>3</sup>, number 2), in products of methane combustion containing 5% of free oxygen content.



Fig. 4.7 Temperature of condensed emitters in methane-aluminum flames with (26% O<sub>2</sub>), and without (21% O<sub>2</sub>), free oxygen in the combustion products.

The results of the temperature measurements for condensed-phase emitters as a function of aluminum concentrations in a stoichiometric methane-air flame and in the methane mixture with 5% of free oxygen) are presented in Fig. 4.7. The temperature measurements confirm the observed qualitative behavior of both flames as the aluminum concentration is increased. There is a sharp rise in the flame temperature at concentrations around 150-175 g/m<sup>3</sup>, which corresponds to the observed formation of the aluminum flame front. As shown in Fig. 4.8, the flame temperature changes from a temperature typical of a methane flame loaded with inert particles to a flame temperature close to temperatures predicted by equilibrium calculations with aluminum as a reactant. From the photographic video evidence illustrated in Fig. 4.5, it is apparent that, for every particular point on the Bunsen-flame cone, there is a rapid bifurcation-type transition associated with the formation of the aluminum dust combustion flame front. In spite of this sudden, stepwise flame-front formation, measurements within a narrow range of aluminum concentration produce intermediate flame temperatures situated between the two combustion modes. However, these temperatures are not associated, as high-speed videos show, with any transitional phenomenon. Rather, they arise from spectra acquired over a long integration time, during which the two combustion regimes were both present during the measurement interval.

Measurement of the characteristic AIO temperatures can only be performed for hightemperature flames that have strong enough AIO emission so that the  $\Delta v = -1$  band (see Fig. 4.6) can be resolved. The results are presented in Fig. 4.8 together with the condensed-phase temperature and thermodynamic calculations of the adiabatic flame temperature. Figure 4.8 demonstrates that, before the formation of the aluminum flame front, the heat released from the relatively-slowly oxidizing aluminum has little effect on the flame temperature, which remains close to that of the methane flame. Only after the formation of the aluminum flame front does the flame temperature approach the predicted thermodynamic equilibrium value. The gaseous and condensed-phase temperatures are effectively equivalent considering the accuracy of the temperature measurements, which are estimated to be  $\pm 120$  K for the condensed phase temperature and  $\pm 100$  K for the AIO temperatures.



Fig. 4.8 Temperature of the condensed emitters (solid squares) and the gas phase temperature (open diamonds) derived from AlO molecular spectra in comparison to the temperature obtained from the constant-pressure thermodynamic calculations (solid line).
#### Analysis of condensed combustion products

Condensed combustion products from the methane-aluminum flame are collected on a thick horizontal copper plate positioned at about 20 mm above the flame tip for approximately 5-15 seconds. The cold metal surface is a relatively efficient collector of particles from the hot combustion flow due to a strong thermophoretic force moving particles along the temperature gradient towards the plate surface [193]. From 5 to 10 exposures (plates) were required to collect a sample mass sufficient for chemical analysis. Due to the relatively long collection time, product samples cannot be linked to a particular value of aluminum concentration but only to some concentration range, as identified in Table 4.1, corresponding to slow aluminum oxidation (50-100 g/m<sup>3</sup>), establishment of the aluminum flame front (150–200 g/m<sup>3</sup>) and aluminum-rich flames  $(200-300 \text{ g/m}^3)$ . The product samples were analyzed for metallic aluminum content via the NaOH digestion method. The results of the analysis are presented in Table 4.1 for the two different oxygen concentrations, with theoretical values obtained from the equilibrium calculation (in parentheses).

Table 4.1 Troduct Analysis			
	Aluminum Content		
Sample/concentration	21% Oxygen	26% Oxygen	
range			
Original Powder	98.9	98.9	
50-100 g/m <sup>3</sup>	25.6 (0.0)*	0.5 (0.0)*	
150-200 g/m <sup>3</sup>	0.9 (0.0)*	0.2 (0.0)*	
200-300 g/m <sup>3</sup>	7.4 (4.1)*	2.9 (1.3)*	

Table	4.1	Product	Analysis
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\* Values calculated using an equilibrium solver

The original sample contains 98.9% aluminum, indicating a very thin oxide layer on its surface. As can be seen from Table 1, even in the case with no free oxygen (21% O<sub>2</sub>), the degree of conversion of aluminum to oxide reaches 75% even without the formation of the aluminum flame front. It is practically complete for mixtures with 5% of free oxygen (26% O<sub>2</sub>). The slow, non-frontal oxidizing reaction stretches over a long downstream distance and contributes little, as mentioned before, to the flame temperature. The TEM photographs of the collected products in this concentration range reveal that they are dominated by the heavily oxidized aluminum particles with traces of submicron spherical aluminum oxide present. In contrast, the product composition of aluminum combustion in the frontal regime is dominated by submicron (d<0.1 µm) aluminum oxide particles and the degree of aluminum conversion to oxide is close to 100%. Metallic aluminum can again be found in aluminum-rich mixtures above the stoichiometric concentration in accordance with thermodynamic predictions [3]. The presence of unburned metallic aluminum with oxygen in the ambient air is minimal during the collection process.

#### Burning velocities of aluminum-methane mixtures

The total flame surface area method is used to obtain flame burning velocities in aluminummethane-air mixtures. Hence, the known volumetric flow rate through the nozzle is divided by the surface area of the inner flame cone to obtain the burning velocity [98]. Each flame image is linked to a particular value of dust concentration using timing marks produced by the camera output on the data acquisition system record. The procedure is first tested by comparing data obtained for pure methane-air and aluminum-air mixtures with results published in literature. The burning velocity of the stoichiometric methane-air mixture is found to be about  $36\pm2$  cm/s, in good agreement with data in the literature obtained with the same method [158]. The burning velocity in a pure aluminum flame is found to be  $20\pm3$  cm/s at an aluminum concentration of roughly 400 g/m<sup>3</sup>, in agreement with previous measurements performed for the same aluminum powder but on a different burner [98]. The burning velocities in stoichiometric methane-air ( $0.095CH_4 + 0.190O_2 + 0.715N_2$ ) and methane mixture with 26% of oxygen ( $0.095CH_4 + 0.235O_2 + 0.670N_2$ ) seeded with aluminum and inert silicon carbide powders at different concentrations are presented in Fig. 4.9 (the data from the plot on the left was first published in [3]).



Fig. 4.9 Burning velocities of methane flames seeded with different concentrations of aluminum and silicon carbide (SiC) powders. Left: 21% O<sub>2</sub>, right: 26% O<sub>2</sub>.

As can be seen, both aluminum and silicon carbide suspensions in either gaseous mixture first exhibit a decrease in the flame speed with increasing solid phase concentration. The obvious explanation for the lower methane flame speed when it is seeded with inert particles is that the specific heat of the gas-solid mixture increases, resulting in lower flame temperatures. The somewhat stronger decline of the burning velocity in silicon carbide suspensions can be attributed to the smaller SiC particles  $(1-5 \,\mu\text{m})$  in comparison to aluminum and, as a consequence, a smaller difference between the particle and gas temperatures within the reaction zone. At silicon carbide concentrations above 170 g/m<sup>3</sup>, the flame starts to extinguish in both gaseous mixtures. The flame quenching starts with the opening of the flame tip. The opening progressively widens with the increase of the SiC concentration until a value of approximately 250 g/m<sup>3</sup>, at which point most of the mixture escapes unburned. In contrast, in mixtures with aluminum particles, the flame burning velocity stops decreasing after the aluminum flame front is formed and the tip of the flame remains closed even at aluminum concentrations up to 400 g/m<sup>3</sup>. The observed plateau of the burning velocity with respect to aluminum concentration indicates a coupling between the methane and aluminum combustion fronts. Upon coupling, heat is transferred from the aluminum flame front to the methane flame front, which promotes the methane flame propagation. Without this heat transfer, the methane flame speed would keep decreasing until the flame quenches, as it occurs

when inert particles are seeded in the flames. The coupled flames may be analogous to a so-called control regime, discussed in previous studies of binary dust mixtures, in which the slower burning, but more energetically potent, component defines the burning velocity of the linked fronts, even though it is positioned behind the faster primary flame front [127].

#### Theoretical estimation of the required aluminum concentration for flame coupling

Due to the complexity of the flame in a hybrid mixture consisting of two interacting methane and aluminum combustion fronts, development of a complete non-steady theoretical model of the combustion process is beyond the scope of the present paper. Instead, here we develop a simple theoretical estimation of the minimal concentration of aluminum in suspension for which the methane and aluminum combustion fronts may be coupled into a single flame structure. The obvious criteria for such a linkage would be the ability of the aluminum dust flame front to propagate in the methane combustion products with a speed equal to or exceeding the speed of the product flow from the primary methane flame front. In this estimation, the methane and aluminum dust combustion that the joint methane-aluminum front has a somewhat greater speed than a pure methane flame seeded with inert particles. Such an approximation is acceptable for determining the mechanism and concentration at which coupling occurs, but cannot predict the resulting flame speed of the hybrid flame front.

The burning velocity of the methane-air mixture seeded with inert aluminum particles and the flow speed of the products are calculated with the open-source combustion software Cantera [57] using the reduced mechanism drm-19 developed by Kazakov and Frenklach<sup>1</sup>. In these calculations, the particles and gas are assumed to be in thermal equilibrium. The flow speed of the methane combustion products with inert aluminum particles,  $S_{b,methane}$ , is shown in Fig. 4.10, denoted by a solid line, and decreases with higher particle loading, as expected.

<sup>&</sup>lt;sup>1</sup> http://www.me.berkeley.edu/drm/

The burning velocity of the aluminum dust flame is estimated assuming that the small aluminum particles used in the present experiments burn in the methane combustion products in the kinetic mode, i.e., the burning rate is limited by some reaction kinetics, rather than diffusion of the oxidizers towards the particle surface, as indicated in a previous study [63]. This assumption is based on the set of observations of these flames that indicates that the transition from slowburning to frontal combustion of the aluminum front happens at a critical concentration where the kinetic rate of reaction becomes fast enough to enable flame coupling. The nature of the kinetic resistance in the high-temperature aluminum flames encountered in the present work remains open for discussion. The calculated adiabatic flame temperature of the linked methane-aluminum flame is close to, or even exceeds, the aluminum boiling point (2792 K). The experimentally-measured flame temperatures, although somewhat lower, are also close to the aluminum boiling point. Estimates show that, near the boiling point, the evaporation rate of an aluminum droplet considerably exceeds the rate of heterogeneous reactions published in the literature [86]. Moreover, aluminum evaporation likely occurs in the kinetic regime because of the small particle size and the fact that the very rapid non-activated nature of the reaction of aluminum vapor with oxidizers [28] prevents accumulation of the aluminum vapor at the droplet surface. Thus, it is assumed that the effective aluminum reaction rate,  $\dot{\omega}$ , corresponds to the kinetic evaporation mass flux from the total surface area of aluminum particles per unit volume. The evaporation rate,  $R_{e}$ , per unit surface area in the kinetic regime is given by:

$$R_{\rm e} = \alpha_{\rm e} \sqrt{\frac{m_{\rm Al,atomic}}{2\pi k_{\rm B} T_{\rm b}}} P_{\rm v} \tag{1}$$

where  $T_b$  is the droplet temperature,  $\alpha_e$  is the coefficient of evaporation,  $m_{Al,atomic}$  is the atomic mass of aluminum and  $k_B$  is the Boltzmann constant [194]. For a pure aluminum droplet, the coefficient of evaporation should be close to unity, as aluminum is composed of single atoms which makes the liquid easier to evaporate than, for example, a polar molecule like water [195]. However, part of the aluminum droplet surface does not participate in the evaporation as it is covered by a liquid aluminum oxide cap, as was observed in previous work [61]. Thus, estimates provided in the present paper consider  $\alpha_e$  as an unknown parameter in the range, for sake of argument, from 0.2–1. The vapor pressure,  $P_v$ , can be found using the Clausius-Clapeyron relationship:

$$P_{\rm V} = A e^{\frac{-h_{\rm V}}{RT_{\rm b}}} \tag{2}$$

where the activation energy,  $h_v = 294$  kJ/mol, is the latent heat of aluminum vaporization, A = 3.1 x10<sup>10</sup> Pa is the pre-exponential factor and R is the universal gas constant [196]. The total reaction rate,  $\dot{\omega}$ , can then be obtained by multiplying the expression (1) by the total surface area of aluminum droplets per unit volume:

$$\dot{\omega} = \frac{3B\alpha_{\rm e}A}{r_{\rm o}\rho_{\rm Al,s}} \sqrt{\frac{m_{\rm Al,atomic}}{2\pi k_{\rm B}T_{\rm b}}} e^{\frac{-h_{\rm V}}{RT_{\rm b}}} , \qquad (3)$$

where  $r_0$  is the initial radius of the aluminum particle, B (g/m<sup>3</sup>) is the mass concentration of aluminum suspension in methane combustion products and  $\rho_{Al,s}$  is the solid aluminum density. In the present formulation, the flame in the aluminum suspension with the burning rate controlled by the kinetics of aluminum evaporation is no different from a gaseous flame with a one-step firstorder Arrhenius-type reaction. Thus, a known Zel'dovich-Frank-Kamenetskii type analytical expression [197] can be derived for estimating the burning velocity of an aluminum flame in methane combustion products. The present analysis was done assuming that the fuel (aluminum particles) had zero diffusivity which leads to the temperature dependence in the expression below:

$$S_{\rm u} = \sqrt{\frac{3\sqrt{2\pi}}{Ze} \left(\frac{T_{\rm u}}{T_{\rm b}}\right)^2 \left(\frac{\lambda_{\rm b}}{\rho_{\rm b} c_{p,\rm b}}\right) \frac{A\alpha_{\rm e}}{r_{\rm o} \,\rho_{\rm Al,s}} \sqrt{\frac{m_{\rm Al,atomic}}{2\pi k_B T_{\rm b}}} e^{\frac{-h_{\rm v}}{RT_{\rm b}}}$$
(4)

where the Zel'dovich number, Ze, is given by the expression:

$$Ze = \frac{h_{\rm v}(T_{\rm b} - T_{\rm u})}{RT_{\rm b}^2} \tag{5}$$

the heat conductivity,  $\lambda_b$ , the density,  $\rho_b$ , the heat capacity,  $C_{p,b}$ , and the flame temperature,  $T_b$ , in the expression (4) are all obtained from Cantera using an equilibrium calculation. The initial

temperature,  $T_u$ , is obtained from the flame speed calculation for the methane flame loaded with inert aluminum particles. The results obtained for different values of evaporation coefficient  $\alpha_e$  are plotted in Fig. 10 with dash lines.



Fig. 4.10 Calculated flow speed of methane products from Cantera (solid lines) and estimated burning velocity of aluminum dust flame (dashed line, from bottom to top,  $\alpha_e = 0.2, 0.4, 0.6, 0.8, 1.0$ ) controlled by aluminum evaporation rate.

As discussed above, the aluminum concentration value corresponding to the intersection of the methane products flow speed with the predicted speed of an aluminum flame can be interpreted as the minimal concentration at which the methane and aluminum flame fronts became coupled. The estimated concentration changes from around 70 g/m<sup>3</sup> to 150 g/m<sup>3</sup> with a change in the evaporation coefficient from 1 (top curve) to 0.2 (bottom curve). The simple theoretical approach used here predicts the observed coupling of the aluminum and methane flame fronts within a concentration range consistent with the experiments and, therefore, supports the assumption that the aluminum burning rate is controlled by the aluminum vaporization rate.

#### 4. Conclusion

Historically, the reaction dynamics of metal particles in hot oxidizing flows, produced by the combustion of hydrocarbons in various energetic systems including metalized solid and liquid propellants and explosives, has been studied and modeled as a combustion process involving isolated individual particles. The implicit assumption behind this approach is that the transition from individual-particle combustion towards combustion of a metal suspension, or ensemble of particles, characteristic of real systems would not significantly change the underlying combustion physics. The present work has demonstrated that this approach is inadequate for heavily-metalized systems that rely on the metal for the bulk of the energy output and, thus, require relatively dense dust clouds. Thus, knowledge of the ignition temperature and combustion times of individual aluminum particles is insufficient for the prediction of the combustion dynamics of aluminum suspensions at high dust concentrations. For example, aluminum particles large enough to burn in the diffusive mode might be unable to ignite at the relatively low temperatures of some hydrocarbon combustion products but effective aluminum combustion might be established if the conditions are right for the formation of an aluminum flame front. Similarly, the combustion time for the kinetically-reacting small aluminum particles, which is controlled by relatively slow surface reactions at temperatures characteristic of hydrocarbon combustion, will be replaced by the much faster kinetics of aluminum evaporation at the high dust-flame temperatures that are produced by burning the aluminum itself.

Modeling of metal combustion in heavily-metalized energetic systems must consider the possibility of laminar or turbulent frontal combustion in the metal suspensions generated by the burning, or detonating, energetic system. The present work has demonstrated that, for a flame in a hybrid methane-aluminum mixture, the dust-combustion front may also influence the hydrocarbon flame; thus, a proper theoretical model has to analyze these two fronts as a coupled flame structure.

The main results of the present work are highlighted in the points below:

- It is observed that, at some critical aluminum concentration, the aluminum flame front becomes coupled to the hydrocarbon flame, corresponding to a change in the aluminum reaction mode from relatively-slow oxidation to a fast combustion process.
- The temperature of the aluminum flame, derived from the continuous part of the spectrum and from AlO molecular bands, is close to the thermodynamically-predicted values with aluminum as a reactant; whereas, before the formation of the aluminum front, the temperature derived from the continuous spectra is close to the temperature of the methane flame with aluminum as an inert additive.
- The burning velocity of the methane-aluminum flame decreases with an increase in aluminum concentration prior to the formation of the aluminum flame front and attains a plateau value thereafter. In comparison, the flame speed of a methane flame seeded with inert SiC particles similarly decreases, but then extinguishes at high particle concentrations.
- A theoretical estimate for the propagation speed of an aluminum flame propagating in methane combustion products, with the reaction rate controlled by the kinetic evaporation of aluminum, can adequately predict the minimal concentration at which the methane and aluminum flames become linked.

# Acknowledgements

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# **Chapter 5: Flame structure and particle-combustion regimes in premixed methane-iron-air suspensions**

# **5.1 Chapter Introduction**

Chapter 4 presented the results obtained with aluminum-methane-oxygen-nitrogen mixtures on a Bunsen burner. The results clearly demonstrate that an aluminum flame front forms above a critical concentration in the combustion products of hydrocarbons. However, due to the brightness of the aluminum flame, it is difficult to visually observe both fronts at the same time.

The work presented in chapter 5 is based on the previous work presented in chapter 4, but replaces aluminum with iron particles as the metal fuel. Iron is not used as an energetic material but burns heterogeneously, which simplifies the chemistry by removing vapor-phase reactions and sub-oxide formation. Furthermore, the iron flame temperature is similar to that of the methane flame temperature, which makes it possible to observe the two flame fronts. The results presented below will demonstrate that the flames behave in a similar fashion whether the metal fuel is aluminum or iron.

# 5.2 Publicaton: Flame structure and particle-combustion regimes in premixed methane–iron–air suspensions, *Proceedings of the Combustion Institute*

# Flame structure and particle-combustion regimes in premixed methane-iron-air suspensions

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#### Abstract

Flame structures and particle combustion regimes are studied in hybrid fuel mixtures of methane and iron using a modified Bunsen burner with two different oxidizing environments. The first is a stoichiometric methane-air mixture, in which the iron reacts with the hot gaseous combustion products in a kinetically-controlled regime; the second is a lean methane-oxygen-nitrogen mixture, allowing iron to react with the excess oxygen in a diffusion-controlled regime. The particle seeding concentration is monitored using laser attenuation and varies from 0 - 350 g/m<sup>3</sup>. Burning velocities are obtained from flame photographs and condensed phase temperatures are determined from particle emission spectra via polychromatic fitting of the spectra to Planck's law of blackbody radiation. High-speed imaging is also used to qualitatively characterize the different flame structures. Results are also compared to a methane flame seeded with inert silicon carbide particles instead iron. It is shown that, independent of the combustion regime, a critical concentration of iron powder is required to form a coupled flame from in the combustion products of the methane flame. Furthermore, after the dust flame formation, a double front structure separated by a dark zone is observed in the kinetic regime, whereas the two flames overlap and form a single Bunsen cone in the case of the diffusion regime.

#### **1. Introduction**

Multi-front reactive waves are complex phenomena that are known to occur in a variety of different systems. Two or more reactive fronts can interact by different physical mechanisms,

including diffusion and convection of either heat or active species, and through radiative heat transfer. Double detonation fronts have been studied for reactive particle-laden gases [136], [138]. Similar phenomena have been observed in systems undergoing self-propagating high-temperature synthesis [198], metalized propellants [187] and also figure into proposed novel nuclear reactor concepts [199]. A simple system to study multi-front phenomena consists of mixtures containing two fuels that have very different activation energies and reaction mechanisms. Deflagrations in such mixtures have been studied theoretically [103], [141] and experimentally for CH<sub>4</sub>-NO<sub>2</sub>-O<sub>2</sub> mixtures [200] and hybrid aluminum-methane mixtures [3].

For aluminum-methane-air mixtures, previous studies have demonstrated that an aluminum flame front may form in the products of the methane combustion with micron-sized aluminum particles reacting in a kinetically-controlled regime [3]. In this case, the aluminum flame front forms only above a critical particle concentration and is believed to be coupled to the methane flame front. However, due to the intense luminosity of the aluminum flame it is not possible to directly observe the methane flame front once the aluminum flame has formed. In addition, aluminum typically burns in the vapor phase and produces a large quantity of sub-oxides which increases the complexity of the problem by introducing other potential limiting factors, such as the rate of evaporation [4]. For these reasons, a different particulate fuel is selected to simplify the investigation of multi-front reactive waves. Iron is a suitable candidate as it burns purely heterogeneously by surface reactions. The iron-air adiabatic flame temperature is on the order of the methane flame temperature, which allows the observation of both flames simultaneously. It has also been shown that iron can burn in either a diffusion-controlled or a kinetically-controlled regime depending on, among other things, the oxidizing environment [100].

The present study investigates stabilized flames with a double-front structure in hybrid mixtures of iron and methane and focuses on the effect of the particle combustion mode on this flame structure and its propagation speed with different oxidizing mixtures. The kinetically-controlled regime is observed in the products of methane-air combustion, whereas the diffusion regime is observed when the mixture contains excess oxygen. The gases are seeded with micron-sized iron powder with a particle concentration varying from zero to 350 g/m<sup>3</sup>. Flames are directly observed with high-speed imaging and burning velocities are obtained using an estimate of the flame surface area from the flame photographs. Emission spectroscopy is used to determine the

temperature of the condensed-phase species in the flame. The results are then compared to that of a methane flame seeded with inert silicon carbide (SiC) particles. In the kinetically-controlled regime, an iron flame front forms above a critical concentration and couples to the methane flame, even though the particles do not ignite. In the case of the diffusion-controlled regime single particles do ignite, even at the lowest concentrations, but again form a distinct iron flame front above a critical concentration.

#### 2. Experimental Methods

#### Iron Powder and Gaseous Mixtures

The iron powder used in the present investigation was produced by Alfa Aesar. The Sauter mean diameter of the particles is  $d_{32} = 2.20 \,\mu\text{m}$  with a volume-weighted size distribution obtained from a Malvern Mastersizer shown in Fig. 5.1. Figure 5.2 shows an SEM photograph of the powder, indicating the spherical morphology of the powder.



Figure 5.1. Iron particle size distribution.



Figure 5.2. Scanning electron micrograph of iron powder.

Two different gaseous mixtures are used: the first is a stoichiometric methane-air mixture in which, after the methane flame, there is no excess oxygen; in the second case, all flow rates are kept identical but the air is replaced with the modified mixture made up of 26% oxygen and the balance nitrogen, which has little effect on the flame temperature and the operation of the dust dispersion system. The resulting mixture corresponds to an equivalence ratio of 0.8, which leaves approximately 5% excess oxygen after the methane has been fully consumed.

#### Dust Burner and Diagnostics

Experiments are performed with a Bunsen burner designed to operate with gaseous and dust fuels. Detailed schematics of the apparatus can be found in previous publications [3]. The powder is fed from a reservoir to the burner by a piston and is dispersed by the gas mixture through an air-knife. The resulting two-phase flow is laminarized in a 60-cm-long tube and ignited at the exit of the nozzle.

The dust concentration is monitored by laser attenuation. A beam passes through the twophase mixture through a slit in the nozzle covered with high-temperature, high-optical clarity tape. The Beer-Lambert law is used to correlate the laser attenuation with the dust concentration. The system is calibrated separately for every type of powder [98]. An Ocean Optics USB 4000 spectrometer coupled with a 100-micron optical fiber is used to obtain emission spectra from the dust flame. Spatial resolution is achieved in one dimension by coupling the optical fiber to a telescope focused on a rotating mirror reflecting the image of the flame. The Bunsen cone is scanned with a step motor attached to the mirror. The flame front is located by the point of maximum emission intensity [99]. Flame images and videos are acquired with a high-resolution digital camera and a high-speed video camera operating at 300 frames per second. A variable neutral-density filter is used to reduce the intensity of the light emitted by the flame [3]. The intensity of the filter is changed according to the luminosity while keeping the exposure time and f-number the same. All optical systems are linked to the particle concentration monitor to correlate the time of the picture, video or spectrum with its corresponding dust concentration.

#### **3. Results and Discussion**

#### Flame spectra and temperature

Flame emission spectra are acquired over the range of particle concentrations in both types of methane flames. The integration time varies with the dust concentration and temperature. Shorter integration times are required for high particle loadings due to the greater number of emitters. The two oxidizing environments produce distinctively different spectra, as illustrated in Fig. 5.3.



Figure 5.3. Emission spectra for both stoichiometric methane-air and enriched-oxygen-methane cases at an iron concentration of approximately 200 g/m3.

The lower spectrum in Fig. 5.3 is obtained from iron particles in the stoichiometric methane-air flame. The spectrum is composed solely of continuous blackbody radiation, without any atomic lines or molecular bands. By contrast, the top spectrum, from the methane-lean mixture, exhibits molecular bands between 550 nm and 650 nm on top of the continuous spectrum. Those bands are present even at low iron concentration and are thought to be attributed to an electronic transition of iron oxide, FeO, identified from the spectrum produced by West and Broida [201]. The temperature is obtained by fitting the continuous part of the spectra to Planck's law of blackbody radiation [99], assuming that iron particles behave as grey bodies. The accuracy of the temperature measurements is estimated to be  $\pm 120$  K. Measurements are taken in the midway between the base and the tip of the flame and the temperature can vary over the height of the cone, with the tip being the hottest part. Results are shown in Fig. 5.4, with the open squares reflecting the stoichiometric case and closed squares the enriched-oxygen case.



Figure 5.4. Iron particle temperatures as a function of iron concentration in both oxidizing environments.

There is a significant difference in particle temperature depending on the oxidizing environment. The methane flame temperature without iron loading in both cases is approximately 2200 K. The particle temperature in the methane-air flame is close to the methane-flame temperature at low particle concentration and slowly decreases with increasing concentration. The particle temperature in the oxygen-enriched mixture, however, has a relatively constant value near 2600 K, even at low particle concentration, which is about 400 K greater than the methane adiabatic-flame temperature.

#### Burning velocities

The burning velocities are obtained from photographs of the flame. The contour of the Bunsen cone is traced on a touch-sensitive screen, fitted with a seventh-order polynomial and rotated to obtain the total surface area, A. The volumetric flow rate,  $\dot{V}$ , is then divided by A to obtain the burning velocity,  $S_L$  [7]. The burning velocity as a function of particle concentration is shown in Figs. 5.5 and 5.6.



Figure 5.5. Burning velocities as a function of dust concentration. The gaseous mixture is stoichiometric methane-air.



Figure 5.6. Burning velocities as a function of dust concentration. The gaseous mixture has 5% excess oxygen.

Figure 5.5 shows the results in air and Fig. 5.6 shows the result in enriched-oxygen. The results are also compared with the values obtained with silicon carbide particles. The stoichiometric methane-air burning velocity is about 35 cm/s, which agrees with literature values [158]. The burning velocity when calculated with the GRI-30 mechanism [202] in Cantera [57] gives a value 51 cm/s in the excess oxygen case, which agrees with the experimental results.

Silicon carbide particles are used as a heat sink in the methane flame, increasing its effective heat capacity. This decreases the flame temperature and, in turn, decreases the burning velocity. This trend can be observed in both gaseous environments. In small quantities, iron particles behave in a similar fashion and reduce the burning velocity. In the stoichiometric case, the flame speed appears to plateau at a particle concentration of about 250 g/m<sup>3</sup>, near the maximum value for which the flame was stable, as discussed below. The plateau appears to occur sooner for the excess-oxygen flame, at a concentration of about 100 g/m<sup>3</sup>. It is suspected that the steepness of the burning velocity is due to the discrepancy of particle size. The iron particles range from 1 to 3  $\mu$ m whereas the average SiC particle is 6  $\mu$ m. This difference in size implies that the SiC particles do not reach thermal equilibrium within the methane reaction zone and thus have a reduced impact on the methane flame, compared to iron, for the same particle loading.

#### Stoichiometric methane-air flame: No excess oxygen

The flame temperatures indicate that the iron burns in a kinetically-controlled regime when introduced into the stoichiometric methane-air flame. The absence of oxygen after the methane flame means that the iron particles must react with the combustion products of methane: water vapor and carbon dioxide. Water molecules diffuse quicker than oxygen molecules yet the reaction rate is most likely slower than with oxygen, which would explain why the chemical reaction rates control the combustion. The particle temperature at low iron concentrations is very close to the adiabatic flame temperature of 2220 K. This does not necessarily imply that the particles burn in a kinetically-controlled regime since the predicted thermodynamic equilibrium iron-air temperature (without methane) is comparable at about 2250 K [11]. In a diffusion-controlled regime, the particle temperature is independent of the particle loading and does not follow the gas-phase temperature. However, as can be seen in Fig. 5.7, the particle temperature follows the thermodynamic prediction (solid line) for the methane-air mixture including iron particles, further

indicating that the particle and bulk gas temperatures are equal and that the particles are reacting in the kinetically-controlled regime.



Figure 5.7. Measured iron-particle temperature and calculated equilibrium temperature for the stoichiometric methane-air case.

Figure 5.8 shows images of iron-methane-air flames at three different iron concentrations. Depending on the concentration, the stabilized flame has one of three different appearances. Flame A has a low concentration of about 80 g/m<sup>3</sup> and only one Bunsen cone is visible. The light observed comes from the blackbody radiation emitted by hot iron particles in the flame. This alone is not a sign of combustion. At these low concentrations, particles will oxidize in the hot environment but neither ignition nor flame front formation is observed. Flame B has an intermediate iron concentration of about 200 g/m<sup>3</sup> and two distinct Bunsen cones are visible. The thin inner cone is the methane flame and the thick outer one is the iron flame. The two cones are separated by a dark zone, in which there is no flame. After leaving the first flame, the gas expands causing the local iron concentration to decrease, which is why less light is observed in that region. The second cone is the iron flame front, which causes the particles to heat up again and emit more light. This double-front structure happens only above a certain critical concentration, which coincides with the point of the iron flame front formation. This critical concentration, found from the flame speed data and high-speed videos, is situated at around 200 g/m<sup>3</sup>. The dust flame front is separated from the

methane flame front, which means that the particles still absorb heat from the methane reaction zone. However, a leveling off of the burning velocity is observed at this point (see Fig. 5.5), which implies that enough heat is transferred from the iron flame to the methane flame to compensate for the heat absorbed and the flames must be coupled. Furthermore, a methane flame loaded with a similar concentration of SiC particles quenches, which indicates that the methane flame could not exist at these particle loadings without being supported by the energy released from the iron flame.



Figure 5.8. Iron-methane-air flames: (a) Low particle concentration (~80 g/m3) showing no iron flame front formation; (b) intermediate particle concentration (~150 g/m3) showing a double flame front; (c) high iron concentration (~325 g/m3) showing flame instabilities.

Finally, Fig. 5.8c is taken in the high concentration range of about 325 g/m<sup>3</sup>. The flame becomes unstable and cellular due to thermo-diffusive instabilities. These instabilities occur when the flame is deficient in the more mobile reactant, changing the Lewis number of the mixture [7]. Increasing the particle concentration will not vary the amount of gaseous reactants since the gas flow rates are unchanged and the particles occupy an insignificant volume compared to the gases. Thus, an increase in particle concentration will not decrease the concentration of oxidizers, the species actually diffusing in the mixture. An increase in particle concentration will increase the overall heat capacity of the mixture, which in turn affects the heat diffusivity and decreases the

Lewis number. When the Lewis number is sufficiently small, the structure becomes cellular [7]. A similar cellular structure has been observed for pure iron flames in microgravity [100].

#### Enriched-oxygen-methane Flame: 5% Excess Oxygen

The experimental results suggest that, with 5% excess oxygen in the methane flame, iron particles ignite and burn in a diffusion-controlled regime. The particle temperature, even at low concentrations, is about 400 K above the methane adiabatic flame temperature. Furthermore, the temperature remains constant across the concentration range, further indication that the particles ignite and that the particle and bulk-gas temperatures separate. The gas-phase temperature cannot be measured directly by emission spectroscopy, but the iron particles can be replaced with inert SiC particles. The temperature results are shown in Fig. 5.9. As expected, the temperature at low SiC concentrations is close to 2220 K and decreases with an increase in particle loading. This figure also shows equilibrium thermodynamic calculations performed for different iron concentrations. The solid line is the calculation performed for the enriched-oxygen-methane mixture including iron. The measured particle temperature is always above that of the calculated equilibrium temperature of the iron-methane-oxygen mixture.



Figure 5.9. Emission temperature measurements for iron and silicon carbide particles in enrichedoxygen-methane mixture and comparison to thermodynamic equilibrium predictions.

Figure 5.10 shows two flame images taken at two different concentrations for the enriched oxygen case. Image A has a low iron concentration and only the methane flame is visible. It is also possible to see single iron particles burning, after ignition, including the characteristic micro-explosion at the end of the particle track. The heat required to bring the particle up to the ignition temperature comes from the methane flame and the particles may react with the 5% excess oxygen, in addition to the water vapor and carbon dioxide. Image B is taken at a concentration of about 150 g/m<sup>3</sup>. In this image, only one Bunsen cone is visible in the diffusion regime, which is the coupled combustion front consuming both methane and iron. The formation of the iron flame front coincides with the levelling off of the burning velocity, which occurs at lower concentrations than in the methane-air case. Furthermore, the formation of the dust flame front is clearly visible in high-speed images and is a distinct phenomenon from a mere increase of igniting particles in the flow.



Figure 5.10. Iron-methane-enriched-oxygen flames: (a) low concentration (~25 g/m3) with no dust flame front; (b) high concentration (~140 g/m3) with a coupled flame and one visible Bunsen cone.

#### Flame front formation

These experiments have shown that the formation of a dust flame front in the hydrocarbonair flame products is independent of the regime of particle combustion and is analogous to what can be observed in a gas phase mixture. A minimum concentration of iron particles is required for the heat-release rate to be sufficient to sustain the propagation of the iron flame. In this respect, single particle models are insufficient to completely describe the observed results, as they ignore the effect of feedback from the reaction of neighboring particles on increasing the local temperature above the methane product temperature. This description of flame front formation applies to any reactive particulate system, whether it is a pure dust cloud [98] or for hybrid mixtures of gaseous and solid fuels [3].

In the kinetically-controlled regime, iron particles at low concentration will oxidize in the flame but the reaction rate will be too slow to form a flame front. The iron flame will form only when there is at least a critical number of iron particles, such that the overall heat released from the dust cloud is sufficient to propagate a flame at a speed that matches the speed of the methane-flame products. For the structure to be stable, the two fronts must be coupled, which can only happen through the exchange of heat between the two reaction zones, which is reflected, among other things, in the leveling off of the flame speed [4]. This situation is illustrated with Fig. 5.11a, where the two heat release zones are separated from each other and the temperature plateau between reaction zones corresponds to the dark region. This phenomenon has been previously discussed for flames in hybrid mixtures of aluminum and methane in air. This regime has been denoted a *control* regime [197], where the second flame front effectively controls the speed of the first flame, observed by the levelling off of the flame speed. It has also been discussed in the case of binary mixtures of dusts [127].

It is important to distinguish between particle ignition and flame front formation. Particle ignition refers to a specific phenomenon: the particle transitioning from kinetic-oxidation to diffusion-controlled combustion, causing a separation of the particle from the bulk-gas temperature. When introduced into the excess-oxygen flame, iron particles heat up and ignite after an induction time, which depends on the particle size. At low concentrations, this ignition occurs after the methane flame and the particles act merely as heat sinks within the reaction zone, decreasing the pure gas flame temperature, without contributing to the flame propagation. This is

represented by Fig. 5.11b, where the heat release from the ignited iron particles happens far from the flame and is spread over a large distance, reflecting the range in particle-induction and burn time for the variable particle sizes in the iron powder. As the dust concentration increases, increased heat release from surrounding particles leads to a feedback mechanism, and locally higher temperatures than in the low-concentration case, which causes the particles to ignite closer to the methane flame. At the critical concentration, the heat released by the iron particles will be enough to form a flame front. In such a case, the iron reaction zone is small and must overlap with the methane reaction zone; hence only one flame is visible. This is denoted a *merging* flame regime [197] and is represented by Fig. 5.11c.



Figure 5.11. Different combustion regimes observed in this study: (a) kinetic regime with iron flame front; (b) diffusion regime with no flame front; (c) diffusion regime with flame front.

#### 4. Conclusion

The flame structure of methane-iron-air flames is investigated for particles reacting in the diffusion-controlled or kinetically-controlled regimes through the use of different oxidizing mixtures. In the kinetic regime at low particle concentrations, iron slowly oxidizes in the hot combustion products of methane and an iron flame front only forms above a critical concentration and couples to the methane flame. Finally, at high concentrations, the flame structure exhibits instabilities due to thermo-diffusive effects caused by the increase in the overall heat capacity of

the mixture. The second case, with diffusion-controlled particle combustion, where single iron particles ignite in the hot combustion products and burn with a temperature close to their own adiabatic flame temperature, an iron flame front is also seen to form and merge with the leading methane flame above a critical particle concentration. Detailed modeling of the phenomena observed requires further knowledge of high-temperature iron kinetics with oxygen, water and carbon dioxide. These rates are currently unknown and determination of these reaction rates should be the focus of future studies.

These results demonstrate that it is possible to form a stabilized flame front in a reactiveparticle suspension whether the particles are reacting in a kinetically-controlled or diffusioncontrolled regime or, likely, even in a regime where both kinetics and diffusion play equal roles. For a flame front to form, the rate of heat release by the particles must be sufficient to stabilize the reaction wave within the dust suspension, which requires that the resulting flame speed of the metal front in the local oxidizing environment be equal to the local flow velocity. These metalhydrocarbon-air flames provide a relatively clean and simple system in which to study the stability and physics of multi-front reactive waves.

#### Acknowledgement

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### 5.3 Discussion on stabilized metal flames in hydrocarbon products

The two articles presented in chapters 4 and 5 discussed stabilized Bunsen flames in hybrid metal-methane systems. The first article focused on aluminum and the second on iron powder. Both experiments have the same main finding: a critical concentration of dust is required for the formation of the metal front in the product of combustion of methane. When introduced at low concentration, the powder takes heat from the methane flame, which slows down its burning velocity, and reacts too slowly to contribute to the flame propagation. However, when the concentration is sufficiently great, the surface area of all particles becomes large enough and the resulting flame temperature sufficiently hot, producing an aluminum flame speed that matches the flow speed of the combustion products of the methane flame.

This coupling happens independently of the regime of combustion. In the case of the aluminum flame, it is proposed that the combustion of particles is limited by the kinetic rate of evaporation, making it a kinetically-limited regime just the same as a chemical kinetic rate. In the case of iron powder, the particles burn in a kinetic regime when no excess oxygen is present and burn in a diffusion controlled regime when excess oxygen is present.

In the case of particles burning in the diffusion-controlled regime, the particle temperature will be greater than the gas-phase temperature and will approach the adiabatic stoichiometric temperature. This phenomenon can be observed on Fig. 5.9, where the measured temperature of iron particles is constant with particle concentration. The measured temperature is above the predicted thermodynamics temperature, a discrepancy explained by the relative uncertainty of the measurements which can be on the order of 100 K to 200 K.

# 6. Concluding Remarks

# 6.1 Synopsis

Traditionally, dust combustion is studied by performing single particle experiments and obtaining basic information such as ignition temperature, burn time and chemical reaction rates. However, real-life scenarios involving dust combustion always happens in dense suspensions, which makes the use of data obtained from single particle experiments limited. The other approach to study dust combustion, which takes place in particle clouds, is to use constant-volume combustion bombs. This second approach, however, also yields limited results due to the difficulty in imaging the dust dispersion process and the flame propagation. Furthermore, these experiments typically yield only the pressure history, which is not always representative of the event. This situation calls for new experimental methodologies that will allow for the construction of a large data-base that will help better characterize and understand dust combustion.

The present experimental, manuscript-based thesis investigates flame propagation in suspensions of aluminum and iron particles in different oxidizing mixtures. It introduces two new apparatus and uses a recently developed apparatus for the study of flames propagating through metal suspensions. The thesis presents a large compendium of data on flames in different metal suspensions and oxidizing mixtures. The work confirms the need to study dust combustion in clouds rather than with single particle experiments and reinforce the need to visually look at the flame propagation. Different methodologies were developed to compare flames with diverse geometries and conditions.

# 6.2 Contributions to the advancement of the field

Many contributions have been made to the advancement of the field of dust combustion. There were significant technical development, and scientific findings.

#### The main technical achievements include:

- Creation of a balloon apparatus that allow the observation of spherical, freely-propagating isobaric spherical flames in latex balloon.
- Creation of a field apparatus for producing large-scale clouds.
- Development of a methodology to compare the flame speed from flames with different geometries
- A large compendium of data on flame propagation speed for iron and aluminum flames in different oxidizing environments and geometries.

#### The main scientific findings of the work include:

- A critical concentration of dust is required for the formation of a flame front in the combustion products of a hydrocarbon flame, whereas a single particle will not ignite in this hot oxidizing environment. This indicates the necessity of considering cloud combustion when discussing dust combustion.
- The formation of the metal flame front is independent of the regime of combustion. The proposed model of aluminum combustion in methane flames stipulates that the kinetic evaporation of aluminum is the limiting rate. In the case of hybrid iron-methane flames, the regime depends on the amount of excess oxygen. However, in all cases, the formation of a flame front is observed above a certain critical concentration.
- The coupling mechanism between the metal flame and the hydrocarbon flame is through exchange of heat. The solid particles heat up and take heat from the methane flame, which has for effect to lower the methane burning velocities. On the other hand, the second flame front produces heat which can diffuse to the first front, which creates the coupling.
- Spherical, freely-propagating aluminum flames are only stable in the vicinity of stoichiometric concentrations. Very rich flames have cellular instabilities whereas

sufficiently fuel lean flames have pulsating and spiral instabilities. Those instabilities are thermo-diffusive in nature and are attributed to the zero diffusivity of solid fuel.

- The observation of a discrete flame propagation mode in lean aluminum flames in mixtures of 15%, 20% and 30% oxygen diluted with argon. This observation validates the previously predicted existence of discrete flames, which states that the combustion time of particles is very short in comparison to the heat diffusivity, which yields a flame propagation rate that is weakly dependent on the oxygen concentration.
- Flame propagation speed in rich aluminum clouds is independent of aluminum concentration. This result, also observed in earlier work by Goroshin et al. [98], can be attributed to two factors. First, adding more fuel (in the solid form) does not remove any oxygen present. This addition of fuel will simply increase the heat capacity of the mixture, but will be compensated by the increase in total surface area. The second reason is that the rate of combustion of aluminum will be determined locally by the micro-diffusion flame which always happens at stoichiometry and is, thus, insensitive to the global flame temperature.
- Radiation heat transfer plays a role only when the flame is sufficiently large. Even in clouds that are a couple of meters in diameter, the radiation heat transfer only plays a secondary role in the flame propagation mechanism by pre-heating the reactants with radiation emitted from the flame zone and the post-combustion zone. The main driving mechanism for the flame must still be molecular heat transfer.
- The results tend to show that it is possible to define a fundamental burning velocity for dust flames. Results are in good agreement for flames in air and in argon when the comparison is performed between Bunsen flames and freely-propagating spherical flames. In the case of flames propagating in large columns of dust, the results indicate that it would be possible to reconcile the values obtained with small-scale values when taking the effect of radiation into account.

# 6.3 Direction of future research

The present thesis reported the use of different experimental techniques to study flames propagating in dust suspensions. Flames in hybrid mixtures were investigated using a stabilized flame on a Bunsen burner. Future research direction needs to investigate flames in hybrid mixtures in different geometries and sizes. This approach can include using the balloon apparatus to study freely-propagating flames in a spherical geometry.

The effect of the different oxidizers in flames in hybrid mixtures can be investigated by replacing methane by a different gaseous fuel. For example, hydrogen can be used to produce an oxidizing environment containing only water or carbon monoxide for an environment with only carbon dioxide. Other types of oxidizers that are present in propellants can also be seeded in various amount either in the Bunsen burner or in the balloon apparatus.

The present dissertation claims that the zero diffusivity of metal fuels is responsible for pulsating and spiral instabilities. This tend to indicate that those types of instabilities would be present in flames propagating in all types of metal fuel. Future research should investigate this statement by replacing aluminum by different types of metal powders, such as iron or magnesium.

The scientific findings reported in this dissertation have been explained using combustion theory and previous modelling efforts. However, a comprehensive modelling effort is required to explain the various observed phenomena. A 2-dimensional model of flames propagating is required to reproduce the instabilities reported in chapter 3, including the spiral flame propagation. Also, the modelling approach cannot impose the regime of combustion as an initial parameter but rather should be a result of the computation that depends, among other things, on the type of particles, type of oxidizers and concentrations of fuel and oxidizer. This modeling approach can also be extended to cover flames in hybrid mixtures of gaseous and solid fuels.

# **Appendix A: Dust Bunsen burner**

#### Apparatus

The hybrid dust burner, shown on Fig. 4.1, and some experimental techniques are described in this section in more detail. The powder cartridge is composed of a cylindrical tube and a Teflon piston with a disc of felt at the top for pushing the powder. The felt is used to remove all the powder from the walls and preventing blockage as the piston is moving upwards. A steel rod moved by a mechanical actuator is screwed into the piston and pushes it slowly upwards. The sifted metal powder is loaded initially in the cartridge, but not compacted. The powder is pushed towards the air-knife, located at the top of the piston. The sonic methane-air flow lofts the powder into suspension and the two-phase flow is entrained towards the nozzle in a 60 cm-long tube that laminarizes the flow. The mixture is ignited at the top of the nozzle with an oxy-propane torch. The co-flow used in all experiments was air and was mainly used to make an envelope around the flame that entrains the combustion products up towards the ventilation unit. Due to the difficulties of stabilizing dust flames, it was not possible to use an inert co-flow such as nitrogen or argon.

Two different rotameters are used to control the oxidizer and methane flow rates. The gas fuel used 99.9% pure methane and the oxidizer used is dry air or a 26% oxygen/74% nitrogen mixture. The rotameters were calibrated before the experiments using a flow-meter located after the air-knife.

#### Diagnostics

The different diagnostics, shown on Fig. 4.4, are composed of a dust concentration measurement system, an emission spectroscopy system and a digital single-lens reflex camera. The DSLR camera is a Canon 60D and is used with a variable neutral density filter. The filter intensity is controlled manually and is constantly changed during the experiment to adapt to the changing light intensity. The flame starts relatively dim when it is only a methane flame at the beginning and ends up being an extremely bright flame at the end when aluminum burns and the concentration is in the order of 500 g/m<sup>3</sup>. The exposure time is kept constant for all pictures. The camera is mounted on an 80/20 frame and attached to the main frame of the burner and is parallel with the flame.

Two Ocean Optics fiber optic spectrometers are used to acquire emission spectra of the flame, as discussed in Julien et al. [4]. The system allows for spatial resolution of the emission spectroscopy to acquire spectra only from the flame front. A telescope is focused on the flame front through a flat mirror that rotates around a vertical axis to be able to horizontally scan the flame front. A modified SLR camera is mounted on the telescope, which replaces the lens normally used, which achieves high spatial resolution. A fiber optic connector was inserted on the door at the back of the camera, such that the fiber optic is inserted where a 35 mm film would normally be used. The fiber optic only captures a central portion of the image normally captured by the film.

#### Dust Concentration Measurements

The dust concentration is monitored at all times with a laser light attenuation probe and synchronized with the other diagnostics. A red 632nm laser passes through a slit in the nozzle and is captured with a photodiode. The powder concentration is calculated using the Beer-Lambert law,  $\ln\left(\frac{V_0}{V}\right) = -Bk$ , where V<sub>0</sub> is the initial voltage, V is the measured voltage, B is the powder concentration and k is the proportionality coefficient. This coefficient will depend on the distance traveled by the laser and the type of powder used. To calibrate the probe, the powder is collected in a cold flow using filters with a vacuum system that captures the powder for a certain amount of time. Knowing the volumetric flow rate, the average concentration of powder during that time is correlated to the light attenuation. The different curves for aluminum 637, iron 1-3 micron and silicon carbide is shown in Fig. A1 and the slopes of the curves are the coefficient of proportionality k.



Figure A1. Different laser-attenuation probe calibration curves and data for the three different powders: Ampal 637 (Al), SiC and Fe.

#### Temperature Measurements

The condensed phase temperature is obtained from emission spectra from the flame. As written in the papers, the spatially resolved spectrometer scans horizontally the Bunsen cone and acquires a spectrum at every position. The spectrum with the highest intensity corresponds to the flame front itself. To obtain the condensed phase temperature, polychromatic pyrometry techniques are used. The molecular bands and atomic lines are removed from the continuum and only the continuum is left, which can then be fitted the Planck's law of blackbody radiation. Planck's law of radiation is approximated in the wavelength region of interest by  $\ln\left(\frac{i_{\lambda,T}\lambda^5}{\epsilon(\lambda,T)}2\pi C_1\right) = \frac{C_2}{\lambda T}$ , with  $C_1=0.5954\times10^{-10}$  m K. Iron is a grey emitter and the emissivity  $\epsilon$  is independent of the wavelength. For aluminum, the majority of emitters are nano-sized aluminum oxides, for which the emissivity depends on the inverse square of the wavelength [99]. Figure A3 shows an example of a spectra for a hybrid iron-methane-air flame and figure A4 shows the fit to obtain the temperature.



Figure A2. Spectra of an iron-methane-air flame, with an iron concentration of about 200 g/m<sup>3</sup>.



Figure A3. Temperature fit of the spectra shown in figure A2, for a temperature of around 2100K.

# **Appendix B: Balloon apparatus**

#### Apparatus

The balloon apparatus, shown on Fig. 2.1 and Fig. 3.1, is described in more detail in the following section. The powder is initially placed inside the dispersion unit in a semi-spherical container. The container can hold up to 7g of uncompacted aluminum Ampal 637 powder, which has a packing density of roughly 1g/cm<sup>3</sup>. The powder is dispersed using an air pulse that lasts 0.8s at a pressure of 65 PSI. The gaseous mixtures are premixed in a mixing tank using partial pressure methods. The mixing is done 24 hours in advance to allow complete mixing of the tank. After dispersion, the powder is then entrained in a <sup>1</sup>/<sub>4</sub>" stainless steel tube that leads to the balloon holder. The latex balloon is initially placed around the balloon holder and inflated to the desired size prior to the powder dispersion. A 3 inch wide and 2 inch high PVC tube is placed around the balloon holder to prevent the balloon from moving and gives it a spherical shape.

Ignition is achieved with a heated tungsten wire coated with a nitrocellulose film. To realize the film, shotgun powder is dissolved in acetone to make a viscous paste in which the wire is dipped and then dried. The tungsten wire is then placed inside the two stainless steel tubes for the ignition holder. The ignition stick is composed of a ceramic tube, glued inside a <sup>1</sup>/<sub>4</sub>" stainless steel tube. The ceramic tube has two holes, in which small hollow stainless steel tubes are inserted. At the bottom of each tube, a copper wire is inserted and held in place by squeezing the stainless steel tube. The copper wire is then attached to a thermocouple connector for easy installation. The top of the ignition stick has then two hollow stainless steel tubes sticking out, in which the tungsten wire is inserted. The center hole of the balloon holder is used for the ignition stick. A piece of electrical tape is stuck on top of the balloon and then the balloon is inflated. The electrical tape serves as temporary seal. After balloon inflation, the ignition stick is inserted fully inside the balloon and sealed using a Swagelok fitting. Finally, the flame is ignited 4s after the beginning of the powder dispersion.

The entire apparatus is placed inside a ventilated enclosure made of polycarbonate panels. The transparent panels allow for full visualization of the experiments and procure protection. The entire
procedure is remotely controlled with a control box. Flame and dispersion images are acquired with a Photron SA5 camera at frame rates between 1000 and 5000 frames per second.

#### Flame speed processing

In order to obtain the flame speed of flames freely-propagating in balloons, it is necessary to track the radius of the flame as a function of time. For methane flames, a code automatically locates the front and calculates the radius. However, for aluminum flames, the trace must be made manually. The light emitted from the flame is intense and light is scattered from the particles ahead of the flame, which produces a diffuse flame front making it difficult to locate it. Furthermore, the flame is not always symmetrical and there is frequent and uneven deposition of powder in patches which blocks the light. For all those reasons, it is difficult to have a code automatically trace the flame front. Both the automatic and manual tracing methods were compared for a methane flame and the results agreed very well, as can be seen from Fig B1.



Figure B1. Manual vs automatic trace for a methane flame for the radius of the flame as a function of time. The slope of the linear fit is equivalent to the flame speed in m/s.

# **Appendix C: Field apparatus**

The field apparatus or large-scale apparatus, shown on Fig. 2.9 and Fig. 3.5, is described in more detail below. The dispersion system is similar to that of the hybrid Bunsen dust burner. The powder is initially loaded in the cartridge and a pneumatic piston moves the column of powder towards the dispersion nozzle. The cartridge can hold up to 1 kg of aluminum powder at a packing density of 1g/cm<sup>3</sup>. Air is delivered to the air-knife with 4 half-inch brass tubes. A compressed air tank is filled to the desired pressure, which was around 70 PSI for the current study. The powder dispersion lasted for 0.8 s and the ignition delay time was between 0 s and 0.4 s.

The initial series of trials were performed at the Canadian Explosive Research Laboratory (CERL) in Nepean, Ontario, at their outdoor testing facility. However, the presence of wind made it difficult to achieve a vertical column of dust unaltered by wind. The second series of tests were performed at the Fire Research Laboratory of the National Research Council of Canada in Mississipi Mills, Ontario. Figures C1 to C4 show pictures of the layout of the apparatus at CERL and at NRC and the thermocouple mast.



Figure C1. Layout of dispersion system at CERL.



Figure C2. Ignition charge and main unit at CERL.



Figure C3. Layout of dispersion system at NRC.



Figure C4. Thermocouple mast at NRC.

### Appendix D. Expansion coefficient in a column of dust

The analysis to obtain the burning velocity from the flame speed for the cylindrical geometry is similar to the one performed by Feng et al. [162] for a layer of premixed methane-air in a mine gallery. Kaptein et al. [163] later made some small modifications on the model by adding the effet of buoyancy in Bernouilli's equation. However, their results give a burning velocity that tends to infinity as the gallery height goes to infinity, which is unphysical. To simplify the problem, the effects of buoyancy were removed in the experimental data by subtracting the speed of the plume of oxides, formed during combustion, from the flame speed.

Modifications were brought to the model of Feng et al. to move from the 1 dimensional problem to a 2 dimensional problem with axisymmetric conditions. In Feng's analysis, it was performed for a height of gallery m. The flame is stationary at station 2/3 is treated with a jump relation. The gas flows in at velocity  $u_1 = u_1'$ , which is equivalent to the flame speed. The burning velocity, which is what is sought after, is then the velocity at station 2,  $u_2$ . Figure D1 shows a diagram of the problem.



Figure D1. Schematic for hydrodynamic model.

The variables used are P,  $\rho$ , A, u, that stand for pressure, density, radial distance and velocity, respectively. The system uses conservation of momentum and Bernouillis equation.

The equations used between sections 1' and 4' are, in order, continuity and Bernouilli :

- $\lim_{m \to \infty} (\rho_1(m-1)A_1^2 u_s) = \lim_{m \to \infty} (\rho_1(mA_1^2 A_4^2)u_4')$
- $P_1 + \frac{1}{2}\rho_1 u_s^2 = P_4 + \frac{1}{2}\rho_1 u_4'^2$

Section 1 to 2, continuity and Bernouilli's equation:

- $\rho_1 u_s A_1^2 = \rho_2 u_2 A_2^2$
- $P_1 + \frac{1}{2}\rho_1 u_s^2 = P_2 + \frac{1}{2}\rho_2 u_2^2$

Flame, section 2 to 3, continuity and Bernouilli's equation:

- $\rho_3 u_3 A_3^2 = \rho_4 u_4 A_4^2$
- $P_3 + \frac{1}{2}\rho_3 u_3^2 = P_4 + \frac{1}{2}\rho_4 u_4^2$

Section 3 to 4, continuity and Bernouilli's equation:

- $\rho_2 u_2 A_3^2 = \rho_3 u_3 A_4^2$
- $P_2 + \rho_2 u_2^2 = P_3 + \rho_3 u_3^2$

Overall conservation of momentum:

•  $\lim_{m \to \infty} ((P_1 + \rho_1 u_s^2) m A_1^2) = \lim_{m \to \infty} (P_4 m A_1^2 + \rho_4 u_4^2 A_4^2 + (m - A_4^2) \rho_1 u_4'^2)$ 

Subject to the following conditions

$$P_4 = P_4'$$

 $A_2 = A_3$ 

$$\rho_1 = \rho_2$$

$$\rho_3 = \rho_4$$

$$\varepsilon = \frac{\rho_3}{\rho_1} = \frac{T_1}{T_3}$$

The conditions mean that, in order listed, there is no pressure difference between the combustion products and the surroundings, the area between section 2 and 3 must match, there is no density difference between the two areas before the flame and the two areas after the flame and the ratio of densities before and after the flame is equal to the ratio of temperatures. The limit is taken as m goes to infinity since the column of dust was unconfined in the present experiments, which gives

$$u_1 = u_1' = u_4$$

Solving the system gives a similar result to that obtained by Feng et al., that is

$$S_b = S_f \sqrt{\varepsilon}$$
 with

$$\varepsilon = \frac{T_3}{T_1}$$

## **Appendix E – Calculation of mean free path**

The mean free path l can be estimated using geometric considerations [119]. Defined as the average distance travelled by a photon before it hits a metal particle in suspension, which is different from the absorption length, it can be calculated using the particle number density N, and particle cross-section, C. The probability P that a photon encounters a particle is

$$P = NC$$

The particle density is obtained from the powder concentration *B*, which is, if taken at around stoichiometry in air,  $314g/m^3$ .

$$N = \frac{B}{V\rho}$$

With *V* being the volume

$$V = \frac{4}{3}\pi r^3$$

And  $\rho$  the density, 2700 g/m<sup>3</sup>, *r* the radius which is in the region of 1 to 10 microns. The mean free path is then

$$l = \frac{1}{P} = \frac{4\rho r}{3B}$$

For a particle of 1 micron in size, the mean free path is on the order of 1.2cm and it is 12cm for particles of about 10 microns in size.

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