Laser Diagnostics of Combustion-Generated Nanoparticles
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Chapter 2

Flames and gas burners

Aggregate growth and volume fraction were studied in 1-D premixed burner-stabilized flames. This chapter details the burners and flow control system that were used for the experiments presented in this work.
2.1. Introduction

Combustion can take place under a wide variety of conditions, ranging from violent explosions to the orderly burning of gas at the kitchen stove. Regardless of the system, complex chemical and physical processes typically take place at short time scales and high temperatures, making it challenging to examine them in detail. To study the growth of combustion-generated nanoparticles in a laboratory setting a well-controlled combustion environment is desired, preferably one that is easily accessible for diagnostic tools.

Over decades of combustion research diffusion and premixed flames have both been popular objects of study. These flames differ in how the oxidizer and fuel combine. In diffusion flames the fuel and oxidizer are mixed during the combustion process, and flame propagation is controlled by diffusion. These systems can have only a fuel supply, relying on ambient air as oxidizer, or otherwise have a separate fuel and oxidizer flow, such as in counterflow diffusion flames where these flows oppose each other to produce a pure diffusion flame. Premixed flames on the other hand, are flames that result from the combustion of a premixed blend of fuel and oxidizer. The premixing allows for establishing a homogeneous mixture with well-controlled and defined composition, which is commonly expressed in terms of the fuel equivalence ratio \( \phi \): the ratio of the actual fuel/oxidizer mole ratio \( X_{\text{fuel}}/X_{\text{ox}} \) to that at stoichiometric conditions:

\[
\phi = \frac{X_{\text{fuel}}/X_{\text{ox}}}{X_{\text{fuel,stoich}}/X_{\text{ox,stoich}}},
\]

where the stoichiometric proportions are such that fuel and oxidizer are present in the mixture in the proportions given by the balanced chemical equation describing combustion (e.g. Eq. (1.14) for hydrocarbon fuel and oxygen). Conditions are said to be fuel-lean or fuel-rich in the cases of excess fuel (\( \phi > 1 \)) or deficient fuel (\( \phi < 1 \)), respectively. The adiabatic flame temperature of premixed flames is a function of \( \phi \), where the temperature generally has a maximum around \( \phi = 1 \). This is illustrated for a premixed methane/air flame in Figure 2.1.

Another important distinction that can be made is between flames with a turbulent gas flow and those with a laminar gas flow. When the flow is turbulent, chaotic velocity fluctuations result in an irregular flow that is the sum of an average motion and these variations. In laminar flow the gas follows smooth flow lines that do not interfere with one another. As a result, this type of flow is much simpler to simulate in detail. Combining laminar flow conditions with the homogeneity of the premixed gas flame allows for
establishing a type of flame that is especially well-suited (and oft-used) for studying combustion processes because of its relative simplicity: the flat laminar (1-D) premixed flame.

### 2.2. Flat Laminar Premixed Burner-Stabilized Flames

Flat, laminar, premixed flames yield conditions that are especially amenable to analysis because of their 1-D character, which means that the conditions only change along the axis of the flame. The laminar nature of these flames also means that it is possible to study processes as function of time by measuring axial profiles, since it is fairly straightforward to convert the heights above the burner (HAB) to a corresponding residence time ($t_{r,eX}$). In these flames most of the chemical processes typically occur in a relatively thin (and well-defined) interfacial region that separates the unburned and burned gases (Figure 2.2). In this flame front, the fuel is rapidly oxidized, leading to a steep gradient in both temperature and species concentrations. Because combustion is generally a multi-step process, the region is also rich in intermediate species. In the laboratory frame, the flame front propagates with velocity $v_{exit} - v_L$, where $v_{exit}$ is the velocity with which the cold gas exits the burner and $v_L$ the free-flame laminar burning velocity, which is a function of $\phi$ as shown for a premixed methane/air flame in Figure 2.1. We can now distinguish three different scenarios: In cases where the exit velocity exceeds the laminar burning velocity ($v_{exit} > v_L$) the flame front will be driven downstream, resulting in blow-off, where the flame is blown away and eventually extinguishes. If both are equal ($v_{exit} = v_L$), the flame
front is stationary in space. In this case, the flame will be essentially adiabatic (neglecting radiative heat losses). And if the exit velocity falls short of the burning velocity \( v_{\text{exit}} < v_L \), the flame front will propagate upstream towards the burner deck. This is a scenario that in some cases could result in flashback, where the flame propagates back into the equipment or supply line, which in the worst case could end in an explosion.

Figure 2.2. Schematic of the structure of a 1-D premixed flame.

The flames used in this work are so-called burner-stabilized flames. Provided that the channels of the burner deck are narrow enough that the flame cannot propagate through them (the flame would be quenched due to excess heat loss from the flame to the channel walls), the flame front will still tend to propagate upstream when \( v_{\text{exit}} < v_L \), but flashback is prohibited. Instead, heat will be transferred to the burner by conduction, resulting in a lowered flame temperature. This principle can be exploited to control the flame temperature: in the present work the flame temperature was varied by changing the mass flux of the fuel/air mixture through the burner, which determines the degree of stabilization and thereby the amount of heat transferred to the burner [1–4]. This provides a means to control flame temperature without changing the composition of the gas mixture, as it requires neither changing the fuel equivalence ratio \( \phi \), nor dilution of the premixed gas with an inert species such as \( \text{N}_2 \). The effect of exit velocity on flame temperature is illustrated in Figure 2.3 for rich, stoichiometric and lean methane/air flames. The properties of the 1-D burner-stabilized flames are determined by just the fuel equivalence ratio \( \phi \), pressure, initial temperature, and the exit velocity [5], which is why the conditions in these
flames can be varied in a straightforward manner. In addition, it is possible to calculate the flame structure by numerically solving the set of governing equations.

**2.3. Calculating the structure of flat laminar premixed flames**

The description of flat laminar premixed flames is based on the 1-D conservation equations that govern their behavior. In fact, various software packages have been developed that are able to calculate the flame structure by numerically solving these equations using the proper boundary conditions. To facilitate the analysis of the experimental results in this work, one-dimensional flame calculations were performed using the code from the Cantera suite [6] with the GRI-Mech 3.0 chemical mechanism [7] for methane-based flames (see, for example, Figure 2.3). For ethylene-based flames the set of one-dimensional conservation equations of mass, gas phase species and energy was solved with the chemical-kinetic San Diego mechanism [8].

Neglecting the effects of viscosity, radiation and external forces, the governing equations for a 1-D steady flame at constant pressure can be written as follows [5,9].

**2.3.1. Overall conservation of mass**

Because chemical reactions do not affect the total amount of mass, the mass flux, \( \dot{M} \), is independent of the axial distance from the burner surface, \( x \). Therefore, the conservation of
total mass states:

\[
\frac{d}{dx} (\rho v) = \frac{d}{dx} (\dot{M}) = 0 ,
\]

(2.2)

where \( \rho \) is the total mass density, and \( v \) the mean mass flow velocity.

### 2.3.2. Conservation of species mass

Due to chemical reactions, the mass fractions of individual species \( i \) change in time at mass production rate \( R_i \). This means that in contrast to the conservation equation for total mass, this equation for a particular species has a source term. In addition, each species has a diffusion velocity \( V_i \) relative to the mean mass flow velocity, which is caused by the species’ concentration gradient (Fickian diffusion) and the thermal gradient (Soret effect):

\[
V_i = \frac{1}{\rho_i} \left( \frac{c^2}{\rho} \sum_j M_{ij} D_{ij} \frac{\partial X_i}{\partial z} - \frac{D_{ij}^T}{T} \frac{\partial T}{\partial z} \right),
\]

(2.3)

where \( \rho_i \) and \( M_i \) are the mass density and molar mass of species \( i \), \( D_{ij} \) are multicomponent diffusion coefficients, \( X_i \) is the species’ mole fraction and \( D_{ij}^T \) is the thermal diffusion coefficient. The conservation equation of species mass can be written as

\[
\frac{d}{dx} [Y_i \rho (v + V_i)] = R_i ,
\]

(2.4)

where \( Y_i \) is the species’ mass fraction. Since chemical reactions neither form nor destroy mass, it follows that \( \sum R_i = 0 \). As noted before, the combustion process is typically not a simple single-step reaction as reaction equations like Eq. (1.14) might suggest. The stoichiometric combustion of methane for example involves tens of chemical species and hundreds of elementary reactions. Chemical mechanisms describe the set of elementary reactions and corresponding rates involved in a combustion process from reactants to products. For instance, the widely-used GRI-Mech 3.0 chemical mechanism which is optimized to model natural gas combustion contains 325 reactions and 53 species [7].
2.3. Calculating the structure of flat laminar premixed flames

2.3.3. Conservation of energy

The chemical reactions in combustion result in the release of heat, giving rise to a temperature gradient. The equation for the conservation of energy states:

\[
\frac{d}{dx} \left[ \sum_i Y_i \rho_i H_i (v + V_i) - \lambda \frac{dT}{dx} \right] = 0 ,
\]

where \( H_i \) is the specific enthalpy of species \( i \), and \( \lambda \) the thermal conductivity coefficient of the mixture. In this equation, the first term describes the change of enthalpy due to the flow of species, and the second term describes the heat flux caused by the transport of energy due to the temperature gradient. For gas mixtures, \( \lambda \) can be calculated from the thermal conductivities of the individual components, \( \lambda_i \), with reasonable accuracy using the empirical law \[5,10\]:

\[
\lambda = \frac{1}{2} \left[ \sum_i X_i \lambda_i + \left( \sum_i \frac{X_i}{\lambda_i} \right)^{-1} \right] = 0 .
\]

2.3.4. Ideal gas equation of state

The system of equations is complemented by the ideal gas law, which for a gas mixture can be written as:

\[
p = \rho R T \sum_i \frac{Y_i}{M_i} = 0 ,
\]

where \( R \) is the gas constant. Combined with the previous conservation equations we now have a system containing \( (z + 2) \) linearly independent equations, where \( z \) is the number of species in the flame. With the proper choice of boundary conditions, and because \( V_i \) is a known function of temperature and species concentrations \[11\], this is sufficient to solve for the unknown parameters: \( T, \rho, v \) and \((z - 1)\) independent parameters from the set \( \{Y_i\} \).

2.3.5. Boundary conditions

For solving the system, we distinguish between two different scenarios: adiabatic, freely propagating flames, and burner-stabilized flames. Although the governing equations are the
same, the boundary conditions differ [11]. In the case of burner-stabilized flames, $M$ is fixed, while the temperature and mass flux fractions are specified at the cold boundary, and vanishing gradients are imposed at the hot boundary.

Freely propagating flames require a different approach, since $M$ must be determined as part of the solution. Therefore, a different boundary condition or removal of a degree of freedom is required to solve the problem. This can be accomplished by fixing the location of the flame by specifying the temperature at one point, the requirement being that this point is chosen such that the temperature and species gradients are close to zero at the cold boundary. Note that by determining $M$ we also find $V_L$, as this will be equal to the velocity of the gas mixture at the cold boundary in the solution.

2.4. Gas burners

Producing the flat laminar premixed burner-stabilized flames described above requires the use of specially designed flat-flame burners. Over the course of the research presented in this work, two types of flat-flame burner (detailed below) were used to stabilize the 1-D premixed flames. To facilitate performing measurements at different positions in the flame, each burner is mounted on a positioner (Parker), allowing it to translate along three perpendicular axes with $\sim 0.1$ mm precision. This way the burner is the only required moving part in the experimental setups described in 0.

2.4.1. McKenna Flat Flame Burner

The commercially available McKenna Flat Flame Burner (Figure 2.4) [12] has been a staple in combustion research for decades [13]. A porous sintered matrix burner disk made of either bronze or stainless steel (6 cm diameter) is contained in a stainless-steel housing (in turn fastened into the main body). The plate contains an Archimedean spiral cooling circuit for water flow which minimizes radial temperature gradients. The fuel mixture (premixed oxidizer and fuel) is introduced into the bottom of the housing and distributed evenly through the burner. Inert gas can be passed through a coaxial shroud ring to shield the flame from the outside environment and stabilize it above the sintered disk. Cavities in the housing below the sintered burner plug and shroud ring ensure a smooth fuel flow by mitigating any pressure surges. The McKenna burner offers reproducible flame conditions that are also highly repeatable with different burners of the same design [14]. For this reason, these laminar flow burners have become more or less ‘the’ standard for researching
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Figure 2.4. Overview of the McKenna Flat Flame Burner [12] (left), reprinted from www.flatflame.com, retrieved December 20, 2018. Reprinted with permission. And a rich ethylene/air flame stabilized above the McKenna burner (right).

2.4.2. Home-made burner

The other burner used in this work is home-made, similar to the one used by Mokhov and Levinsky [3]. Its main feature is a 6 cm diameter ceramic-tile burner deck (Schwank)—mounted atop the cylindrical burner housing—with perforations of \( \sim 1.3 \) mm in diameter, spaced 0.5 mm apart in a honeycomb pattern. The large perforation size (compared to the sintered disk of the McKenna burner) makes the burner more suitable for measurements involving siloxanes (Figure 2.5) because it prevents the deck from getting clogged up very rapidly, while the deck can also easily be replaced when the perforations do become...
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constricted; in the work described in this thesis the deck was replaced well before any visible narrowing of the perforations occurred. The unburned gas is introduced into the bottom of the housing trough two opposing inlets in the cylinder side wall. The housing is filled with glass beads which serve the purpose of homogenizing the gas flow before it passes through the burner deck, preventing the emergence of the velocity differential that might otherwise develop in the pipe flow. A tubular chimney with diameter of 80 mm is placed downstream to suppress flow instabilities and stabilize the flame above the burner deck.

Figure 2.5. Methane/air flame with siloxane admixture stabilized above the home-made burner, the laser beam appears brighter in the flame due to scattering by silica particles (left), and comparison between a burner deck after prolonged use and a new one (right). Note that for the measurements described in this thesis, the burner deck was replaced well before any visible narrowing of the perforations occurred.

2.5. Gas handling system

A schematic of the gas handling system that was used to create the desired gas mixture and feed it to the burner is shown in Figure 2.6. The bulk of the system consists of Swagelok fittings, connectors and tubing, which allows for easy modification to suit the requirements of any specific experiments. Dry, filtered air was supplied by an oil-free compressor while other gases were supplied from cylinders with purity of at least 99.7%. The bubbler system used to add hexamethyldisiloxane, C₆H₁₈Si₂O (abbreviated as L₂), to the gas mixture for experiments involving siloxane admixture is described separately below. The sections of tubing in the system are of sufficient length to ensure homogeneous mixing of all gases before reaching the burner.

In this work, the flow rates of the gases were set using Alicat MC-series mass flow controllers with a specified accuracy of ±1% full scale. The flow rates in this work were always higher than 10% of full scale of the flow controllers used for their measurement. Additionally, the flow rates were measured by Bronkhorst Hi-Tec EL-FLOW® flow meters.

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(accuracy of 0.1% full scale + 0.5% of reading). Differences between the measured and set values of flows were less than 2%, in the working range from 9 to 40 SLPM (298 K, 1 atm). It is interesting to note that the devices operate based on different measuring principles: the Alicat controllers are based on measuring the pressure differential across an internal restriction, which is proportional to the gas’s volumetric flow and viscosity, while the Bronkhorst meters measure the temperature differential along a heated capillary tube, which depends on the gas’s mass flow and heat capacity.

2.6. Siloxane addition through bubbler system

While siloxanes occur naturally in biogas, the concentrations of different siloxane species can vary wildly depending on the source [15–18]. However, in order to perform repeatable measurements for a variety of conditions, we need precise control over the concentration of silica in the flame. This is best accomplished by introducing silicon into an otherwise ‘clean’ flame ourselves. Many previous studies of silica formation have used silane (SiH₄) as the source of silicon. But given the pyrophoric nature of this compound, complete premixing of the silicon source with the fuel-air mixture is problematical and the introduction of SiH₄ instead occurred diffusively (see for example [19] and references therein). This gives rise to uncertainties in the actual local concentrations of silica precursors. The use of siloxanes, which are relatively stable in air, opened the door to premixed studies with well-defined local concentrations, as summarized in [20]. Therefore, the most obvious approach to introducing silicon into the flame is by simply doping siloxanes in the premixed mixture made up of ‘pure’ components.

In this work, L² was used as silica precursor. Its combustion can be represented by the overall reaction:
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\[ C_6H_{18}Si_2O \ (g) + 12O_2 \ (g) \rightarrow 6CO_2 \ (g) + 9H_2O \ (l) + 2SiO_2 \ (s) \ . \quad (2.8) \]

Owing to its low saturation pressure, L2 cannot easily be inserted into the fuel stream directly. Instead, it was added to the unburned fuel/air mixture by passing a fraction of the fuel flow through the bubbler system shown in Figure 2.6 [21] containing liquid L2 with a purity of >98.5% (Sigma-Aldrich 52630 FLUKA). The mole fraction of L2 in the unburned gas mixture can be calculated from the relative volume flows and pressure as

\[ X_{L2} = \left( \frac{P_{L2}}{P_{Bub}} \right) \left( \frac{Q_{Bub}}{Q_{Total}} \right) \ , \quad (2.9) \]

where \( P_{L2} \) is the (temperature dependent) vapor pressure of L2, \( P_{Bub} \) is the pressure in the bubbler system, and \( Q_{Bub} \) and \( Q_{Total} \) are the standard volumetric flow through the bubblers and of the gas mixture through the burner, respectively. Weighing the siloxane cylinder before and after a few hours of operation has shown that for normal operating conditions \( P_{L2} \) is close to that of saturated vapor (5.59 kPa at 298 K [22]). All measurements were performed at the same temperature (298 K) and pressure (295 kPa) inside the bubblers. Mole fractions of L2 in the total fuel/air mixture ranging from 150 to 800 ppm were obtained by varying the fraction of fuel passing through the bubbler system, with an estimated day-to-day reproducibility of better than 10%. The low concentration of L2 means that the number of moles in the gas mixture does not change significantly during combustion due to its presence. However, oxidation of one L2 molecule produces two SiO\(_2\) molecules, so in the case of a stoichiometric methane/air mixture for example we can consider \( X_{SiO_2} = 2X_{L2} \), since the total number of moles does not change during complete combustion of methane:

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \ . \quad (2.10) \]

In the rest of this work we will only refer to the concentration of Si in the combustion products unless specifically stated otherwise.

References

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\[6\text{C}_6\text{H}_{18}\text{Si}_2\text{O} (g) + 12\text{O}_2 (g) \rightarrow 6\text{CO}_2 (g) + 9\text{H}_2\text{O} (l) + 2\text{SiO}_2 (s) \quad (2.8)\]

Owing to its low saturation pressure, L cannot easily be inserted into the fuel stream directly. Instead, it was added to the unburned fuel/air mixture by passing a fraction of the fuel flow through the bubbler system shown in Figure 2.6 [21] containing liquid L with a purity of >98.5% (Sigma -Aldrich 52630 FLUKA). The mole fraction of L in the unburned gas mixture can be calculated from the relative volume flows and pressure as

\[\chi_L = \frac{\rho_P L}{\rho_P B} \cdot \frac{Q_B}{Q_T} \quad (2.9)\]

where \(\rho_P L\) is the (temperature dependent) vapor pressure of L, \(\rho_P B\) is the pressure in the bubbler system, and \(Q_B\) and \(Q_T\) are the standard volumetric flow through the bubblers and of the gas mixture through the burner, respectively. Weighing the siloxane cylinder before and after a few hours of operation has shown that for normal operating conditions \(\rho_P L\) is close to that of saturated vapor (5.59 kPa at 298 K [22]). All measurements were performed at the same temperature (298 K) and pressure (295 kPa) inside the bubblers. Mole fractions of L in the total fuel/air mixture ranging from 150 to 800 ppm were obtained by varying the fraction of fuel passing through the bubbler system, with an estimated day-to-day reproducibility of better than 10%. The low concentration of L means that the number of moles in the gas mixture does not change significantly during combustion due to its presence. However, oxidation of one L molecule produces two SiO\(_2\) molecules, so in the case of a stoichiometric methane/air mixture for example we can consider \(\chi_{SiO_2} = 2\chi_L\), since the total number of moles does not change during complete combustion of methane:

\[\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (2.10)\]

In the rest of this work we will only refer to the concentration of Si in the combustion products unless specifically stated otherwise.

References


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