Analysis of the Heat Flux Method for Measuring Burning Velocities

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr. R.A. van Santen, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op maandag 16 december 2002 om 16.00 uur

door

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Dit proefschrift is goedgekeurd door de promotoren:

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Printed by the Eindhoven University Press.

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Bosschaart, Karel J.

Analysis of the heat flux method for measuring burning velocities / by
Proefschrift. – ISBN 90-386-2744-0
NUR 961
Subject headings: premixed laminar flames / flat flames / lower alkanes / lower hydrocarbons / burning velocity / heat flux method
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Chapter 1

Introduction

1.1 The adiabatic burning velocity

The adiabatic burning velocity of a given fuel/oxidizer mixture is a key parameter governing a lot of the properties of combustion, for example the shape of a premixed flame. Therefore, a lot of effort has been undertaken in the past to measure this parameter accurately for several fuel/oxidizer mixtures, especially hydrocarbons because of their widespread use in domestic as well as industrial burners.

A problem with measuring the adiabatic burning velocity is that the shape of the flow and the flame appears to influence the burning velocity; this is the reason that a lot of early measurements showed a lot of scatter in the experimental data when plotted together in one graph. Flame cooling, curvature, strain and stretch appeared to be very complicated phenomena which are now a field of investigation on their own. To determine the adiabatic burning velocity, the flame should be as flat as possible, in ideal case one-dimensional. However, flat flames traditionally stabilize on a burner, which implies heat loss and therefore do not represent an adiabatic state. It is thus necessary to circumvent these problems in either case of a non-adiabatic (but flat) flame and adiabatic (but stretched) flame:

- In case of a stretched flame, experiments are performed at various stretch rates. These stretch rates can be plotted and extrapolated to zero stretch.
- In case of a burner stabilized flame, the flame can be tuned until it destabilizes, for example because the inlet velocity becomes higher than the adiabatic burning velocity. When the heat loss to the burner can be measured, the same can be done here: determine the heat loss as a function of the inlet velocity, and extrapolate the results to zero heat loss, which corresponds to an adiabatic state, with consequently adiabatic burning velocity.

Concluding, the desired state can only be reached by extrapolation. As generally known, extrapolations are always surrounded with uncertainties. This holds especially for the
Introduction

Due to stretch effects, the adiabatic burning velocity of methane/air was for a fairly long time reported to have its' maximum at 42 cm/s, but more recent experiments have revealed that 36 cm/s is a value that much better represents the burning velocity of a stretchless flame. In fact, when the old measurements are recalculated (extrapolated) using a more recent and insightfull stretch model, the results of the old measurements become lower and coincide with recent measurements.

For measuring burning velocities, a method is needed that does not need any extrapolation due to either stretch or heat loss effects and produces a flame that can practically be investigated in a laboratory. The heat flux method by van Maaren [43] provides such a method; in this work, the method will be further verified and improved, including an extension of the method to elevated temperatures and lower pressures.

1.2 Measurements

In this section, three methods for measuring the adiabatic burning velocity will be briefly described, after a short explanation of the adiabatic burning velocity: the counterflow method, the closed vessel method and finally the heat flux method that is used in this work and that will be extensively studied in later chapters.

The adiabatic burning velocity can be defined as the burning velocity of a fuel/oxidizer mixture in a tube, assuming that the flow is flat and that there is no heat exchange with the wall of the tube. Igniting the mixture at the open end of the tube will make a flame travel to the other (closed) end. Although this is a nice and simple way to explain the concept, it is clear that such a setup in practice would only poorly approximate the assumptions made: the flame front in the tube will be instable, and there will be effects near the wall causing disturbances from a flat flow profile as well. Furthermore, a flame that moves is not suitable in a situation where for example laser experiments should be performed in the flame. In the laboratory, a stabilized flame is preferred over an insta- tionary flame. However, stabilization of a flame generally implies heat loss to a burner or flame stretch.

1.2.1 The counterflow method

The counterflow method or opposed jet method is based on stabilization by counterflowing jets of fuel/oxidizer mixture, as shown schematically in figure 1.1. Because there is no interaction with a burner, these flames do not suffer from a heat loss problem. However, as can be seen in figure 1.1, the streamlines of the flow are not perpendicular to the flame front: these flames are necessarily stretched due to the straining flow of flue gases that need to flow to the side. By adjusting the distance between the outlet nozzles, the strain rate can be controlled. A larger distance between the nozzles will lead to a larger distance between the flame fronts, with a smaller strain rate as a result. By repeating the
1.2 Measurements

experiment at various strain rates, a correlation is found between burning velocity and strain rate which can be extrapolated to zero stretch. However, the results depend on the model used for this correction; a linear stretch model as initially applied by Law [29] gives higher results for the burning velocity than a more recent non-linear stretch model [46]. The latter appears to be consistent with present heat flux measurements.

1.2.2 The closed vessel method

The “closed vessel method” or generally called “combustion bomb” is another generally applied method to measure burning velocities. Unlike the counterflow method, it does not produce a flame in a stationary mode; instead, a volume (the combustion bomb) is filled with a known fuel/oxidizer mixture and subsequently ignited in the centre. A rotationally symmetric flame will propagate from the centre to the outside, burning the mixture. Using cameras and pressure probes, the process is recorded and analyzed afterwards to determine the burning velocity of the mixture. Also here, considerable corrections have to be performed before the laminar adiabatic burning velocity can be extracted from the experimental results. Obviously, the flame is stretched here as well, and because of the closed vessel where the flue gases cannot leave, corrections for the pressure increase also have to be taken into account.
1.2.3 The heat flux method

Originally, Botha and Spalding [4] had the idea of determining the heat loss necessary for stabilizing the flame by measuring the temperature increase of the water used for cooling the burner. They used a porous plug type burner where the plug is cooled with water. Practical problems are that the temperature increase of the cooling water is rather small, and that the adiabatic burning velocity still needs to be obtained by means of extrapolation to a zero heat loss, a situation that could not be created by this burner because the flame becomes instable and will blow off.

In 1993, van Maaren introduced the perforated plate burner, where a flame is stabilized on a brass plate of 2 mm thickness, perforated with a hexagonal perforation pattern of small holes. With an appropriately chosen perforation pattern, it can be shown that flames stabilized on this burner remain flat. Because the plate is rather thin, the temperature distribution in the burner plate approaches a one-dimensional distribution, only dependent on the radius. This temperature distribution can be measured by means of small thermocouples attached to the burner plate, and represents how well the flame is stabilized on the burner, because the temperature distribution actually corresponds to the heat loss from the flame to the burner. Measuring the heat loss this way is much more accurate than measuring the temperature increase of the cooling water. The second improvement upon the burner from Botha and Spalding is to heat the burner plate, more precisely, the burner plate is kept at a temperature of around 85 °C, which will cause the unburned gas mixture (at room temperature) to heat up when entering the burner plate. By doing so, the heat loss necessary for stabilizing the flame can be compensated by the heat gain of the unburnt gas mixture.

It can be shown that the temperature profile of this stabilized flame, when compared to a corresponding free flame, only deviates around the burner plate, and is unaltered elsewhere [13]. With this burner, it is therefore possible to create flat, stretchless, adiabatic flames in the laboratory. To find the adiabatic burning velocity, there is no need to extrapolate experimental results; in fact, the adiabatic burning velocity is found by interpolation, since flames where the unburnt gas velocity is only slightly higher than the adiabatic burning velocity still can be stabilized on this burner. When increasing the velocity, the flame will eventually blow off. The velocity where this happens depends on how much heat the unburnt gas mixture can gain from the burner plate and therefore it depends indirectly on the temperature of the burner plate, given by the temperature of the water flowing along the plate; a higher water temperature will cause a higher blow-off velocity.

Using this burner, several fuel/oxidizer mixtures can be investigated and the adiabatic burning velocity can be determined. In the course of this work, it turns out that a lot of improvements are possible which, when applied to the basic design by van Maaren, yield more accurate results.
1.3 Laminar premixed flames

The flames used in this work are so-called laminar premixed flames: fuel and oxidizer are already completely mixed before they enter the reaction zone in the flame. The overall reaction for methane combustion reads

$$\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}. \quad (1.1)$$

The stoichiometric factor $s$ is defined as the ratio of oxygen and fuel in the overall reaction. From reaction (1.1), it can be seen that for methane $s_{\text{molar}} = 2/1 = 2$. When the factor is converted to a mass ratio, it reads $s_{\text{mass}} = 2 \cdot 32/(1 \cdot 16) = 4$ for methane, using the atomic weights of the oxygen and methane molecules, respectively. In general, the ratio of fuel and oxidizer in an unburnt gas mixture does not correspond to the stoichiometric ratio. Therefore, the ratio of fuel and oxidizer in a gas mixture is expressed using the equivalence ratio $\phi$, defined as

$$\phi = s_{\text{mass}} / (m_{\text{oxidizer}}/m_{\text{fuel}}) \quad (1.2)$$

A gas mixture with $\phi < 1.0$ is called a lean mixture, having an excess of air, while a mixture with $\phi > 1.0$ is a (fuel) rich mixture. The burning velocity $S_L$ depends strongly on the equivalence ratio, and has its’ maximum at slightly fuel rich conditions (typically at $\phi = 1.05$).

When an unburnt fuel/oxidizer mixture flow is ignited on a burner, several things can happen, depending on the magnitude of the unburnt gas velocity $v$ in comparison with the adiabatic burning velocity $S_L$. Assuming a uniform flow, if $v > S_L$, the flame will generally blow off, because the flame is not able to consume the fuel/oxidizer mixture fast enough to remain on the burner. If $v < S_L$, the flame approaches the burner and starts losing heat to it. Due to the heat loss and temperature decrease, reactions are slowed down and an equilibrium situation exists, where the flame remains in the same position: this flame is stabilized. However, when $v \ll S_L$, a situation can occur where the flame loses so much heat that the reaction can not be maintained, and the flame quenches. If the flame does not quench, it can enter into the burner, called flash-back.

Blow-off, quenching and flash-back are situations that are clearly to be avoided in practical burner systems. As seen from the above example, the adiabatic burning velocity $S_L$ is an important parameter for the flame behaviour.

1.4 Calculations

In our group, a code (ChemID [40]) is developed for simulating the combustion of a fuel/oxidizer mixture, where a lot of different conditions can be varied, for example the flame can be chosen to be a stabilized or a free flame. Also, a lot of available reaction schemes can be implemented, such as GRI [5], developed at Sandia Labs and highly optimized for natural gas combustion, or schemes proposed by Warnatz [48], that can be used more generally for higher hydrocarbons as well.
In this work, Chem1D calculations are used to compare with the experimental results. Since the flame in this work is made adiabatic, despite being stabilized, simulations in Chem1D are always performed as a free flame. Care should be taken when comparing experimental results with numerical results, because the parameters in the reaction schemes are generally optimized to yield published experimental data as good as possible. Because of the bias towards higher burning velocities as stretch effects were neglected in the past in most experiments, simulations have a tendency to predict too high burning velocities.

1.5 Scope of this thesis

In this work, the heat flux method by van Maaren [43] will be used as a basis for further development and improvement of measuring adiabatic burning velocities. Chapter 2 describes the basic principles of the heat flux method and the state of the experimental setup at the start of the project. Experiments are carried out to find aspects that need improvement. In chapter 3, the improvements are discussed in detail, leading to a new setup with enhanced performance as compared to the old one. Chapter 4 describes measurements using Coherent Anti-Stokes Raman Scattering (CARS), an advanced laser technique to determine temperatures, in some typical adiabatic flames \( \phi = 0.80, \phi = 0.90, \phi = 1.00 \) and \( \phi = 1.10 \) produced by the burner. The measurements confirm the good performance of the burner for providing adiabatic reference flames. Chapter 5 presents measurements of burning velocities in the improved setup for the lower alkanes methane, ethane, propane, \( n \)-butane and iso-butane at pressure \( p = 1000 \) mbar and temperature \( T = 295 \) K. For methane, also a set of measurements at elevated temperatures (295–370 K) is presented. In chapter 6, the method is extended to lower pressures, down to 100 mbar. The pressure dependence of a stoichiometric methane/air flame is determined using the extended setup. Systematic errors occurring at lower pressures are discussed.
Chapter 2

The heat flux method

2.1 Introduction

As pointed out in chapter 1, it is important to measure the adiabatic burning velocity accurately without a need for stretch correction.

The method pointed out in this chapter produces a flat flame, and was developed by de Goey and A. van Maaren [13], based on similar ideas as Botha and Spalding [4], who measured the temperature increase of water used to cool a porous plug burner, thereby gaining heat from the flame. By varying the unburnt gas velocity until no temperature increase is measured over the water flow, the adiabatic burning velocity can be determined. However, a practical problem with this setup is that the temperature increase of the water is rather small, resulting in a rather large uncertainty. Another problem is that the flame cannot be made effectively adiabatic; the flame will become unstable at the adiabatic condition and blow off. The adiabatic condition can therefore not be measured, but the adiabatic state needs to be determined by extrapolating the results at several burning velocities to the situation where no heat loss to the burner would occur. Nowadays, porous plug burners are still widely used for producing flat flames, for example when a reference flame is needed to test laser diagnostic techniques. Also, the measurement of flame properties such as the concentration profiles of intermediate species require well-defined flames to make a comparison possible with numeric models, which can be improved using the experimental results. However, it is not possible with porous plug burners to accurately determine the adiabatic burning velocity, and they can not be put in an adiabatic state, which would be the perfect reference situation. Furthermore, porous material tends to choke seeding materials used in LDV and PIV, both laser techniques to determine flow velocities. The use of these techniques is important to verify the flow field produced by the burner and hence the flatness of the flame.

The goal of this chapter is to describe the state of the heat flux setup at the start of this research. It will be used as the basis to improve the accuracy of the method in chapter 3. In section 2.2, the basic principles of the heat flux method are briefly discussed. The experi-
mental setup will be sketched in section 2.3, and an analysis will be made of the expected uncertainties in the experiment, especially the uncertainties arising from the Mass Flow Controllers. Furthermore, some experiments will be described to test the performance of the setup: measurement of the flue gas composition is used in section 2.4 to check the equivalence ratio $\phi$, since the calibration method based on gas meters is suspicious to yield systematic errors for some hydrocarbon flows. In section 2.5, infrared thermometry experiments will be used to check the rotational symmetry of the temperature distribution in the burner plate, since rotational symmetry is an essential assumption in theory. Finally, in section 2.6 some points of concern are briefly discussed, which will form the basis for a more thorough examination and improvement of the heat flux method in the next chapter of this thesis.

2.2 Principle

As already pointed out, the heat flux method is based on measuring the net heat loss from the flame to the burner and tuning the inlet velocity of the unburnt gas mixture to a value where no net heat loss to the burner is observed. This leads to an adiabatic state of the flame. In this section, the temperature distribution in the burner plate will be analyzed briefly, but first a qualitative overview is presented about the heat flux balance.

In figure 2.1, the general idea of the heat flux balance is depicted. A cross section of a very small part (3 holes) of the burner plate is shown, where the streamlines of the gas flow are sketched on the left side, showing that the flow is flattened by the pressure drop of the flame front. The right side of the figure indicates the heat balance that occurs everywhere in the burner plate; the horizontal arrows represent the heat gain of the unburnt gas mixture by the burner plate, while the vertical arrows show the heat loss from the flame to the burner plate, necessary for stabilizing the flame. Summed over the burner plate as a whole, the total heat gain of the flame is defined as $\Phi_u$, while the total heat loss is defined as $\Phi_f$. The net difference between the heat loss and the heat gain, $\Phi_f - \Phi_u$, is responsible for the temperature distribution that is observed in the burner plate by means of the set of thermocouples. The flame is effectively adiabatic when the heat loss equals the heat gain, resulting in a zero net heat flux and therefore a constant temperature across the burner plate.

The resulting temperature profile of the stabilized flame as compared to a free flame is shown schematically in figure 2.2. The burner plate is situated from 0 to $x_p$, and has a temperature profile $T_p$ in axial direction. Due to the heat received by the flame, the temperature of the burner plate is slightly higher at the downstream side of the plate. In section 3.3.5, this temperature gradient will be investigated in more detail. Because of the good conduction of the burner plate material this gradient is rather small compared to the gradient in the gas temperature. Since $T_p$ is larger than the temperature of the gas mixture entering the burner plate, the gas mixture is heated by the burner plate near the inflow. According to numerical research by Rook [38], most of the unburnt gas heating occurs near the inflow for velocities in the range of interest. While passing the burner plate, the gas mixture eventually gains a higher temperature than the burner plate,
2.2 Principle

Figure 2.1: The heat flux balance: close-up of a part of the burner plate. Left side: sketch of the streamlines, right side: the heat fluxes occurring; under and in the burner plate: heat gain by the unburnt gas mixture, above the burner plate: stabilizing heat loss from the flame to the burner plate. Typical temperatures are indicated.

Figure 2.2: The temperature profile of a free flame (line, $T_{\text{free}}$) compared to the temperature profile of a flame stabilized on the burner plate (dashed, $T_{\text{stab}}$). $T_p$ indicates the temperature of the burner plate.
because of upstream heat conduction from the flame to the unburnt gas mixture. In case of a stabilized adiabatic flame, the heat gain equals the heat loss and the temperature profile from \( x_p \) on will be the same as in the case of a free flame; this shows that the temperature profile due to the presence of the burner plate is only affected around the burner plate. Therefore, the influence is expected to be negligible since no reactions take place at the relatively low temperatures in this region, and the resulting flame will be a good substitute for a free flame.

To analyze the heat flux balance in the burner plate quantitatively, we will consider the energy equation in cylindrical coordinates, without tangential contribution assuming rotational symmetry:

\[
- \frac{\partial}{\partial x} \left[ \lambda_{p,x}(r) \frac{\partial T_p(x, r)}{\partial x} \right] - \frac{1}{r} \frac{\partial}{\partial r} \left[ \lambda_{p,r}(r) r \frac{\partial T_p(x, r)}{\partial r} \right] = \alpha(x) [T_g(x, r) - T_p(x, r)],
\]

(2.1)

where \( T_p \) is the temperature of the burner plate, \( T_g \) the temperature of the gas, \( \lambda_{p,x} \) is the thermal conductivity of the burner plate in axial direction \( x \), while \( \lambda_{p,r} \) is the thermal conductivity in radial direction \( r \), and \( \alpha \) is the volumetric heat transfer coefficient (in W m\(^{-3} \) K\(^{-1} \)) between the gas and the burner plate. The heat conductivities in radial and axial direction are different because of the perforation pattern of the burner plate.

Integrating equation (2.1) over the burner plate thickness from \( x = 0 \) to \( x = h \) yields

\[
- \frac{1}{r} \frac{\partial}{\partial r} \left[ \lambda_{p,r}(r) r \frac{\partial T_p(x, r)}{\partial r} \right] \bigg|_{x=0}^{x=h} = \int_0^h \alpha(x) [T_g(x, r) - T_p(x, r)] dx \\
+ \lambda_{p,x} \frac{\partial T_p}{\partial x} \bigg|_{x=h} - \lambda_{p,x} \frac{\partial T_p}{\partial x} \bigg|_{x=0} = q(r),
\]

(2.2)

where \( q \) is the net heat transfer from the gas to the burner plate, corresponding to the previously mentioned \( \Phi_J - \Phi_u \). In case of a 1D flame, \( q \) is not dependent on \( r \). Defining the average plate temperature

\[
\overline{T}_p(r) = \frac{1}{h} \int_0^h T_p(x, r) dx
\]

(2.3)

and combination with equation (2.2) yields

\[
- \frac{1}{r} \frac{d}{dr} \left[ \lambda_{p,r}(r) r \frac{dT_p(r)}{dr} \right] = \frac{q(r)}{h}.
\]

(2.4)

Assuming that the conduction coefficient \( \lambda_{p,r} \) does not depend on temperature, and therefore not on \( r \), equation (2.4) can be solved easily:

\[
\overline{T}_p(r) = T_{cent} - \frac{q}{4\lambda h} r^2.
\]

(2.5)

The temperature distribution in the burner plate appears to be a parabola, with the center of the burner plate as the symmetry axis.
However, in general the conduction coefficient $\lambda_e$ depends on temperature, and can be written as

$$\lambda_e(T) = a + b \cdot T,$$  \hspace{1cm} (2.6)

where the subscript denotes brass, the material used for the burner plate. For brass, $a = 73.1 \text{ Wm}^{-1} \text{K}^{-1}$ and $b = 0.160 \text{ Wm}^{-1} \text{K}^{-2}$. The temperature range in which the burner plate operates with a flame stabilized on it is $350 \text{ K}$ to $450 \text{ K}$, leading to a conduction coefficient varying from $129 \text{ Wm}^{-1} \text{K}^{-1}$ to $145 \text{ Wm}^{-1} \text{K}^{-1}$. However, in a single experiment the difference between the maximum and minimum temperature is usually not more than $40 \text{ K}$, which reduces the variation in the conduction coefficient to only $6 \text{ Wm}^{-1} \text{K}^{-1}$, corresponding to a relative variation of $5 \%$.

Since the burner plate is perforated, an effective conduction coefficient $\lambda_{p,e}$, already used in previous equations, is introduced to account for the perforation pattern:

$$\lambda_{p,e}(T) = \varepsilon \cdot \lambda_e(T).$$  \hspace{1cm} (2.7)

The constant $\varepsilon$ depends on the perforation pattern and was investigated in detail by Sonnenmans [41] numerically and confirmed by van Maaren [43] experimentally. Solving equation 2.4 again with the temperature dependent conduction coefficient results in

$$\overline{T}_p(r) = -\frac{a}{b} + \left[ q \left( \frac{R^2 - r^2}{2h\varepsilon} \right) + \left( \frac{a}{b} + T_R \right)^2 \right]^{\frac{1}{2}}.$$  \hspace{1cm} (2.8)

To compare the difference between equation (2.5), where a constant conduction coefficient is assumed, and (2.8) an example of a resulting temperature distribution is shown in figure 2.3, where typical values are substituted in both equations. The net heat flux $q$ is equal in both cases, as well as the temperature at the edge of the burner plate ($r = 15 \text{ mm}$). This situation may occur in practice, although the net heat flux and therefore the temperature difference between maximum in the centre of the plate and minimum at the edge of the plate is rather high; even in this situation, the deviation from a parabola is minimal, and it can be concluded that in all practical situations the simplified equation (2.5) can be safely applied.

### 2.3 Experimental setup

The experimental setup for the heat flux method at the start of the project, shown in figure 2.4, consists of the perforated plate burner at the core of the setup, with Mass Flow Controllers to provide the burner with a gas flow. The Mass Flow Controllers and the thermocouples in the burner plate are, via an interface with RS232 communication, attached to a PC, where the experiment can be fully controlled. The experimental setup consists of the following main parts:

- The burner, described in detail in section 2.3.1, consists of a plenum chamber, burner head and burner plate with thermocouples attached. To ensure correct temperatures for every part of the burner, two thermostat baths are used; one for
keeping the burner plate “hot” at approximately 85 °C, the other for keeping the plenum chamber at room temperature, assumed to be equal to the mixture temperature. The temperature of the hot water is chosen as high as practically possible; with a bath temperature of 90 °C to 95 °C, the temperature at the burner plate is typically around 85 °C, which is lower than the bath temperature due to cooling of the hoses from the thermostat controller to the burner plate. When a higher temperature would be needed, for example to stabilize super-adiabatic flames or to measure burning velocities with a higher initial temperature, the heating medium would have to be replaced by a medium that has a higher boiling temperature than water, for example silicon oil. The cold water is kept at room temperature, typically 20 °C. This is the effective inlet temperature of the gas mixture. When burning velocities of gas mixtures with a higher initial temperature would be measured, the temperature of this thermostat bath, as well as the temperature of the pipes from the MFC’s to the burner, would have to be increased to the corresponding initial temperature.

- The Mass Flow Controllers on the mixing panel provide the burner with a mixture of fuel and oxidizer. Buffering vessels are placed before the MFC’s, in order to damp pressure variations from the supply side. The pressure in the buffering vessels is 3 bar, which reduces to atmospheric pressure when the gas passes the MFC. Air is supplied from a pressurized air line, while fuel is taken from a gas cylinder. All gases are filtered before entering the MFC’s to avoid contamination. The mixing panel is equipped with several fuel MFC’s, in order to be able to use two fuel MFC’s at a time when a hydrocarbon mixture, e.g. methane/propane, is investigated. Another use of the extra lines is the possibility to switch to an MFC better suited for the demanded gas flow; as a rule of thumb, MFC’s should not be used under 10 % of their maximum capacity for maintaining the desired accuracy.
2.3 Experimental setup

The MFC’s are calibrated using a gas meter; when a calibration is performed, the burner is replaced by the gas meter. In section 2.3.2, an analysis of the expected uncertainties arising from the MFC’s is presented. More details about the calibration procedure are treated in appendix G. Mixing of the fuel and air flows takes place at a T-shape connection of small diameter (8 mm) pipes and continues on the way to
the burner for several meters.

- An interface between the experiment and the PC. The interface communicates with the PC via an RS232 serial line, and according to the commands received from the PC reads out the thermocouple voltages or sends setpoints, in the form of a voltage from 0 to 5 V, to the MFC’s. Two interfaces can be used with the setup; the MultiLab interface designed and built at TUE, and the ADAM interface from Advantech. In both setups, a stabilized external power supply from Delta Elektronica is integrated into the interface to provide the power for the MFC’s.

- The PC is a standard Pentium based computer at 200 MHz, running LabVIEW from National Instruments, taking care that important parameters can be controlled easily: the setpoints of the MFC’s are calculated from the velocity and equivalence ratio input from the user. The thermocouple readouts for measuring the radial temperature profiles in the burner are monitored continuously (typical sample rate is 1 Hz) and displayed graphically, while a parabolic fit through the radial temperature profile is promptly calculated and displayed as well. Ambient conditions are taken from an external thermometer and barometer respectively, and are entered manually into the LabVIEW program.

In the following, parts of the setup will be discussed in detail; in section 2.3.1, the burner will be discussed, while section 2.3.2 treats the gas flow control and an analysis of the accompanied uncertainties.

### 2.3.1 The burner

The burner is shown schematically in figure 2.5. Three parts are essential for its’ use as a tool to measure adiabatic burning velocities:

1. The orifice provides a nearly uniform outflow profile.

2. The burner consists of a perforated plate of 30 mm diameter stabilizing the flame. The plate is cooled or heated (depending on the operation condition) by a cooling or heating jacket.

3. Thermocouples attached to the burner plate measure the temperature distribution from which the net heat flux from the flame to the burner can be determined.

The orifice of the burner head is chosen in such a way that, in combination with the plenum chamber, the flow profile at the outlet is nearly uniform. The burner plate forms a flow resistance which removes the small deviations inevitably occurring since the design is made for a restricted range of flow velocities. When a flame is stabilized on the burner, the pressure drop is even higher, resulting in a flat flow profile for an extended range of flow velocities. However, care should be taken that around the edges of the burner, significant deviations occur; this problem was investigated in detail by van Maaren [45] with LDV. The result of this research is that a so-called 1D area can be
defined in the flow, where the resulting flame can safely be considered a flat flame. A typical value for this 1D area in a 30 mm burner plate is a diameter of 20 mm.

The burner plate itself is very carefully designed. Since a flat flame should be obtained, care should be taken that the perforation pattern consists of holes that are sufficiently small to revert the flow into a uniform profile after passing the burner plate. Here, the flame also acts as a pressure drop helping the flow to become properly flat again. The diameter of the holes that is needed to produce a flat flame for a given fuel/oxidizer mixture is mainly determined by the velocity of the unburnt gas flow and therefore by the range of burning velocities of the mixture. Since high flow velocities form the critical limit, the maximum burning velocity determines the maximum hole diameter that should not be exceeded for obtaining a flat flame. A procedure to numerically determine the maximum hole diameter is described by de Goey[12]. From this analysis, it follows that for burning velocities in the range 10–50 cm/s, a hole diameter of 0.5 mm is sufficiently small to produce a flat flame.

The thermocouples used in the burner plate are of type T (Copper — Constantan). The diameter of the thermocouple wires is 0.1 mm, chosen small enough to avoid disturbances to the flow profile in the orifice. Also, the thermocouples need to be small to be able to attach them in one of the holes in the burner plate. Several aspects of the thermocouples will be considered in more detail in chapter 3. The thermocouples are manufactured from thermocouple wires and attached directly into the burner plate.
2.3.2 Gas Flow Control

The gas flows into the burner are provided by Mass Flow Controllers (Bronkhorst Hi-Tec). The functioning of these devices is based on the temperature decrease of the gas along a narrow duct parallel to the main flow. Because of this principle, the MFC’s deliver a mass flow rate, rather than a volumetric flow rate; furthermore, this mass flow rate does not depend on small variations of pressure and/or temperature of the device. The best accuracy is achieved when the MFC’s are calibrated shortly before the measurements are carried out with a third-order polynomial function to correct for any non-linear effects in the device and the electronic circuits. In this way, the uncertainty will be \( \phi/BD \% \) per MFC, provided the controller is used in a range above \( \phi/BD/BC \% \) of its maximum flow rate. Since the gas mixture entering the burner is a mixture of at least two gas flows, uncertainties add up. To estimate the resulting uncertainty in the equivalence ratio \( \phi \) and the burning velocity \( C_4 \), the equations for \( \phi \) and \( C_4 \) in the most simple case, where only air and fuel are mixed, are considered:

\[
\phi = s_{mass} \times \frac{q_{\text{fuel}}}{F_0 q_{\text{air}}} \\
6.0 \times 10^4 \times p \phi S_L = \left( \frac{q_{\text{air}}}{M_{\text{air}}} + \frac{q_{\text{fuel}}}{M_{\text{fuel}}} \right) 
\]

In these equations, the stoichiometric factor \( s_{mass} = 4 \) (for methane/air) and the air factor \( f_{O_2} = 0.2315 \) (clean Eindhoven air) are used. The temperature \( T \) of the gas mixture and the cross sectional area \( A \) are defined just below the burner plate, before the mixture is heated. The mass flows \( q_x \) are defined as

\[
q_x = S_x Q_{\text{max},x} \rho_{0,x}.
\]

Here, \( S_x \) is the MFC setpoint, \( Q_{\text{max},x} \) is the maximum mass flow rate of the MFC in L/min and \( \rho_{0,x} \) is the density of component \( x \) at normal conditions \( \rho_0 = 101325 \) Pa and \( T_0 = 273.15 \) K. The constant \( 6.0 \times 10^4 \) in equation (2.10) compensates for the use of the conventional unit L/min; 1 L/min equals 1 L/min at normal conditions \( T_0 \) and \( \rho_0 \), and therefore represents a mass flow, usually given in kg/s.

To estimate the resulting errors in \( \phi \) and \( S_L \), a straightforward analysis using partial derivatives leads to the estimates of the errors \( \Delta \phi \) and \( \Delta S_L \):

\[
\frac{\Delta \phi}{\phi} = \frac{\Delta q_{\text{fuel}}}{q_{\text{fuel}}} + \frac{\Delta q_{\text{air}}}{q_{\text{air}}} \\
\Delta S_L = \frac{F_0 T}{6.0 \times 10^4 \times p A} \left( \frac{\Delta q_{\text{fuel}}}{M_{\text{fuel}}} + \frac{\Delta q_{\text{air}}}{M_{\text{air}}} \right)
\]

The uncertainties for both MFC’s \( \Delta q_{\text{fuel}} \) and \( \Delta q_{\text{air}} \) are estimated from deviations during calibration. At the start of the project, gas meters were used to perform the calibration, but since this method has some limitations in accuracy as well as the gases that can be used, it was later replaced by a Flow Piston Prover setup. Both methods determine the gas flow by a volume measurement method, and are described in more detail in appendix G. With the Flow Piston Prover setup, a typical uncertainty of \( \Delta q = 5 \times 10^{-3} \times Q_{\text{max}} \) was
observed in the operating range of 0.1Q_{\text{max}} to Q_{\text{max}}. This uncertainty includes the reproducibility on a short term (minutes), as well as a long term (weeks between subsequent calibrations) basis. This leads to a typical uncertainty of 1%, or ±0.01, for equivalence ratios of interest of ~ 1.0. For equivalence ratios other than 1.0, the error is larger, because the relative errors in both mass flows increase when producing smaller flows. (For comparison, the typical uncertainty using the old gas meter setup is ±0.03.) According to equation (2.13), the error in $S_L$ is caused for the largest part by $\Delta g_{\text{air}}$, because the air flow is typically 10 times larger than the fuel flow (assuming methane as fuel). Both equations (2.12) and (2.13) show that it is important to choose appropriate dimensions for the MFC’s to keep the errors small, because an overdimensioned MFC will introduce a large $\Delta q$.

### 2.4 Flue gas CO$_2$ measurements

Using the gas meter calibration method and the analysis of the previous section, the typical uncertainty in $\phi$ turns out to be ±0.03, which is relatively large. Also, the calibration of some hydrocarbons, in particular propane, causes problems when using the gas meter because propane dissolves in the oil that is used in the gas meter. Therefore, the flue gas is analyzed by means of a CO$_2$ analyzer, capable of measuring the CO$_2$ concentration of a gas mixture. This method of checking $\phi$ is independent of the calibration of the Mass Flow Controllers and is thus very suitable to serve as a second check. Disadvantage of the method is that it only provides a result in lean flames, because in rich flames there will be a considerable amount of CO. The $\phi$ check has been carried out in lean methane/air as well as lean propane/air flames.

When the equivalence ratio $\phi$ of a CH$_4$/air flame should be determined from the CO$_2$ concentration, the following overall reaction has to be considered:

$$\text{CH}_4 + 2n \text{O}_2 + 2n \left( \frac{1}{f_{\text{O}_2}} - 1 \right) \text{N}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2 \text{O} + 2(n - 1) \text{O}_2 + 2n \left( \frac{1}{f_{\text{O}_2}} - 1 \right) \text{N}_2$$

(2.14)

Here, the non-reacting nitrogen part is taken into account because the analyzer measures the CO$_2$ concentration relative to the total amount of flue gases — except for the water vapour, which is filtered out before the flue gases enter the analyzer. The oxygen fraction in air is denoted by $f_{\text{O}_2}$, and $2n$ is the number of oxygen molecules present at the beginning of the reaction. As can be seen from the reaction, the CO$_2$ molar fraction $X_{\text{CO}_2}$ indicated by the analyzer is given by

$$X_{\text{CO}_2} = \frac{1}{1 + 2(n - 1) + 2n \left( \frac{1}{f_{\text{O}_2}} - 1 \right)} = \frac{f_{\text{O}_2}}{2n - f_{\text{O}_2}}.$$  \hspace{1cm} (2.15)

Using (2.15) to find an expression for the equivalence ratio $\phi = 1/n$ yields

$$\phi = \frac{2}{f_{\text{O}_2} \left( 1 + \frac{1}{X_{\text{CO}_2}} \right)}.$$ \hspace{1cm} (2.16)
For propane, this analysis leads to

\[
\phi = \frac{5}{f_{\alpha_2} \left( 2 + \frac{3}{X_{CO_2}} \right)}.
\]  

(2.17)

The results of the flue gas measurements are shown in figure 2.6, where two MFC’s were used, both with methane as well as propane, in another experiment. Typical deviations from the perfect line are ±0.05, consistent with the error analysis in 2.3.2 (using the old calibration method), when also the uncertainty of the CO\textsubscript{2} measurement is taken into account. The good reproduction of the measurements is also consistent with the observed behaviour of the MFC’s. A remarkable fact is that the methane and propane measurements appear to behave differently, as if a different systematic error occurs in the flue gas measurements. This can be attributed to the gas meter calibration procedure, where considerable problems occurred with propane dissolving in the oil of the gas meters, leading to a significant change of the oil level in the gas meter. It has been tried to avoid this effect as much as possible by flushing the gas meter for a long time with propane, assuming that in the end the oil will be saturated with propane. Since the amount of propane dissolving in the oil depends on the flow velocity of the propane, this method is not expected to be very accurate. In figure 2.6 it can be seen that the propane measurements yield significant higher values for \( \phi \) than the methane measurements. This is consistent with the hypothesis that propane dissolves significantly in the process of calibration; since the amount of propane measured during calibration is less than the actual value, the MFC’s will consequently be set to a setpoint that is too high, resulting in a too rich flame. Also, the measurements appear to reproduce slightly worse in the case of propane, which can be explained by the rather inaccurate assumption that oil saturates during the calibration.

The conclusion of the flue gas analysis is that with the gas meter calibration equipment, it is not possible to do an accurate calibration of MFC’s with propane, while also the methane calibration is limited in the sense that the reproducibility would allow for a better calibration. These observations have led to the purchase of the new Flow Piston Prover calibration equipment, described in appendix G, allowing for a more accurate calibration, and eliminating problems with hydrocarbon flows. In the remainder of this work, the equivalence ratio \( \phi \) of the flames is determined by the MFC setpoints; the CO\textsubscript{2} flue gas measurements are not used anymore.

### 2.5 Infrared thermometry experiments

Since the temperature distribution in the burner plate is determined by measuring the temperature in very small spots at the burner plate, it is essential that the temperature distribution in the burner plate is rotationally symmetric — a disturbance in the rotational symmetry will lead to a systematic error in the measured adiabatic burning velocity. Such disturbances could be caused by a (local) bad thermal conduction between the burner plate and the burner head. Therefore, care should be taken when mounting the burner plate in the burner head; the plate should fit firmly in the head and if possible,
Figure 2.6: Determination of $\phi$ by measurements of CO$_2$ concentration in the flue gases of lean methane/air flames (left) and propane/air flames (right). Horizontal axis: $\phi$ calculated from MFC setpoints, vertical axis: measured $\phi$. The line $y = x$ indicates the situation where both methods of determining $\phi$ coincide. Different markers denote different MFC's used.
thermal grease should be used. This is tested using infrared thermometry experiments on the burner plate.

In this section, the basic principles of infrared thermometry will be briefly described, focusing on the experiments in the burner. The experimental setup is shown and the results are presented.

**Infrared experiment setup**

All bodies radiate dependent on temperature; at temperatures of our interest, ranging from room temperature to 150°C, the radiation is mainly in the infrared range. The temperature effect can be used to investigate temperature differences. The precise relationship between infrared intensity and temperature is very complicated, since the reflectivity of the monitored surface is important as well. For this reason, the measurements on the burner plate will be limited to qualitative measurements rather than absolute measurements. For determining temperature differences and hence the rotational symmetry, this is sufficient.

The infrared thermometry setup used is an AGA liquid nitrogen cooled infrared detector, expanded with an interface to convert the analogue measurements to digital pictures which are stored and analyzed with a PC. This is schematically shown in figure 2.7.

To interpret the results measured by the equipment, we will briefly analyze the basic
process that leads to the results. The Stefan-Boltzmann law states that the total energy $E$ emitted by a radiative body is given by

$$E = \varepsilon \sigma T^4,$$

(2.18)

with $\sigma$ the Stefan-Boltzmann constant and $\varepsilon$ the emissivity. Since the burner plate under investigation mainly radiates in the infrared range, it is a good approximation to assume that the camera, only sensitive in the infrared, will detect all radiation; in fact, both frequency ranges match each other. Since we are interested in temperature differences, we will consider two intensities: one reference intensity $I_{\text{ref}}$ belonging to a constant temperature $T_{\text{ref}}$ on the burner plate. The other intensity $I$ corresponds to a measurement where a flow disturbs the constant temperature, resulting in a temperature profile $T_{\text{ref}} + \Delta T(r)$, where $\Delta T(r)$ is the disturbance, assumed to be small (typically 200 K) in comparison to the reference temperature of 370 K. The intensity detected by the camera is proportional to the energy emitted as well as a factor $g$ accounting for the material properties and the ratio of holes/material, i.e. the porosity of the burner plate:

$$I_{\text{ref}} = \varepsilon \sigma g(r, \phi) T_{\text{ref}}^4$$

(2.19)

for the reference measurement and

$$I = \varepsilon \sigma g(r, \phi) (T_{\text{ref}} + \Delta T(r))^4$$

(2.20)

for the actual measurement. The factor $g$ depends on position, but is the same in both the reference and actual measurement, and therefore will cancel when the measured intensity $I$ is divided by the reference measurement $I_{\text{ref}}$:

$$S = \frac{I}{I_{\text{ref}}} = \frac{(T_{\text{ref}} + \Delta T(r))^4}{T_{\text{ref}}^4}. $$

(2.21)

Since $\Delta T(r)$ is small with respect to $T_{\text{ref}}$, equation (2.21) can be simplified to

$$\frac{I}{I_{\text{ref}}} = 1 + 4\frac{\Delta T}{T_{\text{ref}}},$$

(2.22)

showing that if a measurement is divided by the reference measurement, the intensity shows a linear dependency on the temperature difference $\Delta T$, the quantity of interest. This property will be used further on.

### 2.5.1 Infrared results

To investigate the rotational symmetry of the burner plate, infrared measurements are carried out in two situations:

- The case when no air flow is present; only the water flow in the heating jacket is used to bring the burner plate to a temperature of 90 °C. This is the reference picture and should make clear how irregularities in the surface of the material disturb the infrared signal, so that subsequent measurements can be accordingly corrected.
• Only an air flow is present without flame, which will cool down the burner plate. If the burner plate shows a rotationally symmetric (and parabolic) temperature distribution, it can be safely assumed that this is also the case when a flame is stabilized above the burner.

A few experiments with a flame above the burner were performed as well, but those measurements were not successful due to the excessive radiation caused by the flame, which makes the radiation from the burner plate practically invisible. Infrared filters would be needed to block this radiation by the flame (mainly caused by water and carbon dioxide).

In figure 2.8, the results of the experiments are shown. In the first picture, where only the burner plate is heated up by the water jacket without any flow present, some disturbances can be seen in the burner plate around the spots where thermocouples are attached to the burner plate. Since at a thermocouple position, a hole is blocked with the material of the burner plate (seen from above) the effective reflective surface is larger, leading to a larger intensity around the thermocouple spots. A larger intensity is also seen at the edges where no perforation pattern is present. Also, local differences in the polishing of the material, likely to be present after handling of the burner plate to attach the thermocouples, can lead to disturbances in the infrared intensity distribution.

On the second picture 2.8b an air flow is present through the hot burner plate. Approximately the same disturbance pattern can be seen around the thermocouple positions. To obtain a picture representing temperature differences, the ratio $\frac{S}{C_1}$ is taken from the two pictures, in accordance with equation (2.22). Here, $I_{rot}$ is the infrared intensity found in the reference picture where no flow is present. The resulting picture 2.8c does not show the irregularities anymore, except near the edges where due to large gradients in the intensity and possible misalignment of pixels some artifacts can be seen. Nevertheless, the normalized intensity appears very smooth and rotationally symmetric in the burner plate.

In figure 2.9ab, two cross sections through the burner plate are made, showing the normalized intensity as a function of either horizontal or vertical pixel number. Both profiles are passing the middle of the burner, and show a rather smooth curve, symmetric with respect to the centre of the burner plate. In figure 2.9c, all normalized pixel intensities are shown as a function of distance to the middle of the burner plate. Some scatter is seen, but the profile clearly forms a parabola.

**Conclusions from the IR experiments**

It can be concluded from the experiments that the temperature distribution in the burner plate is sufficiently rotationally symmetric. The infrared method looks promising for measuring the temperature distribution in the experiment with a flame as well, but these experiments are hampered by the fact that appropriate filters should be used to block the radiation from the flame itself to disturb the signal originating from the burner plate. Actually, only a small window would remain after excluding all excessive radiation, which could cause the signal to be too small to yield accurate results.
The setup as described in this chapter has been used successfully to do measurements of burning velocities [43]. Using flue gas measurements, it has been shown that another calibration method for the MFC’s is necessary to improve accuracy. However, it turned out that there are still some difficulties, limiting the accuracy and causing problems to reproduce the results found earlier. As an example, a typical measurement in an existing burner head is shown in figure 2.10. Since it is known from the infrared measurements that the temperature distribution is rotationally symmetric, it can be concluded that the performance of the thermocouples should be improved. Measurements are needed in which a parabolic fit can be made while the scatter of the thermocouple measurements remains within reasonable boundaries (a few Kelvin).

In the next chapter, care is taken to understand the underlying problems. One of the aspects is the attachment and performance of the thermocouples; in the old setup, thermocouples were soldered into a hole of the burner plate. This implies that the thermocouple is not in direct contact with the burner plate, but that an intermediate material is present which can influence the measurement, either thermally by an isolation effect or electrically by disturbing the thermocouple voltage. Since thermocouple voltages are very small (typically a few mV), this is a serious concern.

As shown in figure 2.2 in this chapter, a vertical temperature gradient in the burner plate exists. When thermocouples are not attached at the same height, a systematic error will occur. It was estimated by van Maaren [43] that the temperature difference of the downstream and upstream side of the burner plate is a few K. Although this is small in comparison with the radial temperature differences, an analysis will be carried out in the next chapter that enables to correct for these systematic errors, resulting in a smaller uncertainty for the adiabatic burning velocity.

Furthermore, when measuring the adiabatic burning velocity in a given fuel/oxidizer mixture, it is observed that not always the same results are found when the experiment is repeated in a couple of hours. It appears that the balances of heat fluxes present in and around the burner head can take a long time to settle down to a stationary state, resulting in a shift of the measured burning velocity.

These difficulties are treated in more detail in chapter 3, leading to an improved design of the heat flux setup, which can be used to determine burning velocities with a better accuracy than the old setup, while reproducibility of the results is ensured.
Figure 2.8: Results of the infrared measurements. From upper left to lower right: a) reference signal $I_{\text{ref}}$ when no flow is present, b) signal $I$ with flow, c) the ratio of the signals $S = I / I_{\text{ref}}$. 
2.6 Discussion

Figure 2.9: Cross sections of the IR intensity ratio $S$ through the burner plate

(a) Horizontal cross section. Markers: measurements, line: parabolic fit.

(b) Vertical cross section. Markers: measurements, line: parabolic fit.

(c) Intensity as a function of radial position $r$
Figure 2.10: Measurement of the temperature distribution in an old burner head. Deviations from the parabolic profile are considerable and it can be expected that the measurement results suffer from systematic errors.
Chapter 3

Improvements of the heat flux method

3.1 Introduction

When doing measurements with the burner at the start of this research, as described in chapter 2, several problems were observed. First of all, the temperatures indicated by the thermocouples did not yield a nice parabolic distribution, as expected and described in section 2.2. Instead, temperature distributions such as in figure 2.10 were obtained. Obviously, these are troubling the evaluation of the measurements; it can be expected that a systematic error exists in the measured adiabatic burning velocities. Cleaning of the burner head and attachment of new thermocouples did not solve the problem. Therefore, an investigation is performed of the errors that occurred and improvements are carried out to obtain acceptable temperature distribution measurements.

Several error sources are considered in this chapter. Two separate groups of improvements are considered: improvements concerning the burner head, discussed in section 3.2, and improvements concerning the thermocouples, discussed in section 3.3. The analysis of the burner head deals with the heat flux balances present in the burner head, while the thermocouple improvements consist of both a construction part and a correction method to account for the vertical temperature gradient that is present in the burner plate. Eventually, the analysis leads to a burner design and measurement method that produces reliable results for the adiabatic burning velocity. The improved setup will be used in chapter 5 to perform burning velocity measurements in several lower alkanes, and in chapter 6 it will be used as a basis for the low pressure version of the heat flux setup.
3.2 Burner head

Several aspects of the heat fluxes present in the burner head are analyzed in this section. Starting with the observation of instationary effects on a large time scale (1 hour) in section 3.2.1, the necessity for a new burner head design becomes clear. Instationary warming up of the burner as a whole occurs because of a bad thermal isolation between the hot and cold parts of the burner. The consequence is that it will last a fairly long time (typically 1 hour) until the burner system has reached its equilibrium state. With the introduction of the new burner head in section 3.2.2, the heat flux balances in the burner head are described. In sections 3.2.3 and 3.2.4, these heat fluxes are studied in more detail, and comparisons between the old and new version are presented.

3.2.1 Instationary warming up of the burner

While doing experiments with the perforated plate burner, it has been observed that measurements were reproducible very well within a few minutes. However, when repeating the same experiments a few hours later or on another day, the results were often significantly different. To investigate the cause of this effect, the burner has been observed for a couple of hours, all the time with the same flame stabilized on it ($\phi = 0.80, \nu = 22 \text{ cm/s}$). In figure 3.1, the parabolic coefficient of the temperature fit is shown as a function of time (a.u.). It appears that the parabolic coefficient and therefore the net heat flux is changing significantly during this period. When measuring adiabatic burning velocities, this change would correspond to a difference of about 2 cm/s in the measured burning velocity, which is a major concern. Once the heat flux has become stable (situation 1), the

Figure 3.1: The parabolic coefficient ($K/\text{mm}^2$) as a function of time (number of samples which roughly corresponds to seconds) after switching on the burner equipment. The equivalence ratio and velocity of the unburnt gas mixture remained the same during the time of this experiment.
3.2 Burner head

flame can be changed to another equivalence ratio and/or velocity (situation 2) without observing such a long time constant for stabilization. Also, changing the flame back from situation 2 to situation 1 shows the heat flux seen in situation 1 within minutes. Therefore, it can be concluded that the warming up time at the start of an experiment is related with heat fluxes that are not within the burner plate itself. The large time constant in the order of hours indicates that a large mass is involved in the process. This appears to be the supporting construction of the burner: initially, it was not very well isolated from the burner and tends to heat up slowly, by heat “leaking” from the hot water jacket to the rest of the construction. During the instationary phase of heating up burner parts, the hot wall of the burner head also traverses a trajectory, causing the heat transfer from the hot wall to the unburnt gas mixture to be varying in time. This effect is held responsible for the observed shifting of the net heat flux measured in the burner plate.

Therefore, it is important to minimize this effect, by avoiding the warming up of the burner support construction to occur. The first attempt was to provide the top of the burner head with a cooling jacket, but this appeared to be insufficient; without a thermally isolating layer somewhere in the burner head, the resulting heat flux from a hot to a cold water jacket is very large. As a consequence, the water jackets significantly exchange heat and change temperature, which is not the goal of these jackets.

The conclusion from this experiment is that a new burner head should be constructed where the hot part is kept thermally isolated from the rest of the burner head and especially the large support construction. The result is the improved burner head which will be discussed in the next section. In the following sections, the heat fluxes present in the new burner head are analyzed.

The surface where the heat transfer from the burner head to the unburnt gas mixture occurs is reduced this way as well. It has not been reduced to zero however, because there remains a hot part of the burner head which transfers heat to the cold gas.

3.2.2 Heat flux balances in the burner head

As pointed out in the previous chapter, the edge of the burner plate should be kept constant at a relatively high temperature (typically 85°C) for a heat flux to occur from the burner plate to the unburnt gas mixture. This is accomplished by means of a cooling/heating jacket1. Since the remaining parts of the construction should be kept cool (room temperature), this induces heat fluxes within the construction from hot to cool parts, as indicated in figure 3.2. This shows the newly constructed burner head with an isolating ceramic Macor ring and additional cooling jacket at 20°C. Macor is a ceramic material, and has a low heat conductivity in comparison to brass. This material can be processed very well, which is necessary for shaping it into the form of an orifice.

Heat fluxes 3, from the upper part of the burner head to the lower part and 4, from the burner head to the unburnt gas mixture, as well as 5, from the burner head to the supporting construction, are undesired because of the following reasons:

---

1 Depending on the mode of operation, the jacket is either cooling or heating. A better name would be “constant temperature” jacket.
30 Improvements of the heat flux method

Figure 3.2: Schematical representation of the heat fluxes occuring in the burner head. 1: heat flux from flame to burner plate. 2: heat flux from burner plate to unburnt gas mixture (inside burner plate). 3: heat flux from upper (hot) part of the burner head to the lower (cold) part. 4: heat flux from burner head to unburnt gas mixture. 5: heat flux from burner head to support construction.

- A heat flux to the burner head and subsequently to the rest of the supporting construction (heat flux 5) will have a large time constant (typically one hour) because of the amount of mass that is heated up; this is inconvenient when doing measurements in stationary flames.

- The heat from the hot to the cool part of the burner head (flux 3) is taken from the waterflow that is supposed to keep the edge of the burner plate at a constant temperature. A large heat flux in the burner head consequently leads to a disturbance of the rotational symmetry of the burner plate, since the waterflow is from one side of the burner plate edge to the other.

- The heating up of the burner head causes heat transfer from the heated part to the unburnt gas flow (flux 4). This effectively means that the initial temperature of the unburnt gas mixture is not well known anymore. In fact, the initial temperature will be higher near the edge of the burner plate, where the mixture was heated up.

In the following, these aspects will be studied and the magnitude of the undesired heat fluxes is determined or estimated, to be sure that the effects are negligible, or that the burner has to be adapted on some parts. The analysis is supported by some test measurements.
3.2 Burner head

3.2.3 Heat flux from the hot to the cold part of the burner head

The upper part of the burner head is heated to 85 °C, while the lower part should be kept at room temperature (20 °C). Ideally, only the burner plate has a temperature of 85 °C, but heating up the surroundings is inevitable. The macor ring should provide some isolation so that the lower part of the burner head can be kept cool without a large heat flow in the burner head, resulting in a temperature gradient in the burner plate. Since the heat conduction coefficient of brass is much higher than that of macor, the largest part of the temperature gradient will be across the macor ring. Assuming that the gradient is across this ring, we can calculate the heat flow from the upper to the lower part of the burner head:

\[ P = \lambda_v A \frac{\Delta T}{\Delta x} \]

\[ = 1.46 \text{ W/(m} \cdot \text{K)} \cdot \frac{\pi}{4} \left( (6.6 \cdot 10^{-3})^2 - (3.5 \cdot 10^{-3})^2 \right) \cdot \frac{65 \text{ K}}{3 \cdot 10^{-3} \text{ m}} \]

\[ = 78 \text{ W}. \] (3.1)

where \( \lambda_v \) is the heat conduction coefficient of macor, \( A \) the surface of the ring perpendicular to the heat flow (horizontally) and \( \Delta T/\Delta x \) the temperature gradient over the ring in vertical direction. Knowing the heat flow \( P \), the water flow can now be calculated with

\[ v = \frac{P}{\rho A_{\text{jacket}} c \Delta T_{\text{water}}}. \] (3.2)

Here, \( v \) is the velocity of the water, \( \rho \) the density, \( c \) the specific heat capacity. The surface \( A \) is the cross section of the heating jacket, and \( \Delta T_{\text{water}} \) is the temperature drop of the water when it has passed the heating jacket. This temperature drop should, of course, be as small as possible. For the moment, we take \( \Delta T_{\text{water}} = 1 \text{ K} \) as the acceptable maximum temperature drop. For \( A_{\text{jacket}} = 2 \cdot 5 \cdot 4 \cdot 10^{-3} \text{ m}^2 \) is substituted, since the heating jacket consists of two parallel channels. This leads to \( v = 0.47 \text{ m/s} \), corresponding to a flow of \( \rho A_{\text{jacket}} v = 0.018 \text{ kg/s} \) or \( 1.8 \cdot 10^{-5} \text{ m}^3/\text{s} \). This flow is the minimum requirement to fulfill the demand that the temperature drop in the hot water running through the hot burner part does not exceed 1 K, using the isolating ceramic ring.

When the ceramic isolation would not be present, like in the previous version of the burner head, the heat flux from the hot to the cold part of the burner head would be considerably larger (by a factor \( \lambda_{\text{brass}} / \lambda_v = 86 \)) and consequently the required minimal water flow is raised by the same factor, reaching a level that is not possible for the present thermostat controllers in combination with the small water channels to provide.

To verify the above analysis, test experiments were carried out in two burner heads; one set in an “old style” burner head without thermal isolation and another set in a “new style” burner head with the ceramic isolation ring. In both experiments, the unburnt gas flow is set to zero. Note that an ideal result would be that all thermocouples would indicate the same temperature of the water because there is no forced convection through the burner plate. The unisolated burner head is cooled by a separate cooling jacket, in order to avoid an excessive heating of the unburnt gas flow as well as reducing the time
Figure 3.3: The reversal of the water flow direction in the upper heating jacket shows that the water is cooled down on its way from the entrance to the exit of the jacket. Top: old burner head. Bottom: isolated burner head. Not only the temperature in the isolated case is higher, also the differences between the indicated temperatures are smaller.

for the system as a whole to reach a stationary state. Each measurement set consists of carrying out a temperature distribution measurement in the burner plate twice: one with the original direction of the water flow, the other with the water flow direction reversed. In figure 3.3, it is clearly seen that a pattern occurs when comparing both experiments, which is much more amplified in the old style burner head. Also, the isolated burner head has a higher temperature as a whole, as expected. The trend seen is that those thermocouples that indicated a temperature above the average in the first experiment, show a lower temperature in the second experiments when the water flow is reversed, and vice versa. The differences between the indicated temperatures are larger for thermocouples that are closer to either the entrance/exit of the heating jacket. This is shown in figure 3.5, where the temperature difference for each thermocouple is plotted as a function of the
3.2 Burner head

x-coordinate indicated in figure 3.4, a coordinate that is supposed to be proportional with the temperature drop of the water in the heating jacket (i.e. going from the entrance to the exit of the jacket). In the middle of the burner plate, at $x = 15\text{ mm}$, the difference is zero, which can be expected since the burner head is rotationally symmetric. It is clearly seen that a correlation exists between the x-coordinate and the observed temperature difference per thermocouple. This shows that the water flow from entrance to the exit of the jacket significantly cools down, disturbing the rotational symmetry of the temperature distribution. This further indicates the need for the ceramic isolation ring, where the effect is still seen, but at an acceptable level.

Another conclusion that can be drawn from these experiments is that the thermocouples are able to detect very small temperature differences, down to $1.0\text{ K}$. Although the magnitude of the indicated temperature seems to deviate a lot among the different thermocouples, the reversal of the heating flow, and thereby the reversal of the temperature gradient, can be observed with the thermocouples.

![Figure 3.4: The configuration of the thermocouple positions with respect to the entrance and exit of the heating jacket. The x coordinate is defined as going from the entrance to the exit of the heating jacket.](image-url)
3.2.4 Heat flux to the unburnt gas mixture

To decide whether the heat fluxes in the burner head are significantly disturbing the measurements, we need to compare the heat fluxes within the burner head with the net heat flux from the flame to or from the burner plate. This net heat flux to/from the burner plate can be calculated using the results of van Maaren [43]:

\[ P(r) = 2\pi r h e \lambda \frac{dT}{dr}, \quad (3.3) \]

where \( h \) is the thickness of the burner plate and \( e \lambda \) the effective heat conduction coefficient. Substituting a parabolic temperature profile \( T = a_2 r^2 + b \) in equation (3.3), we find

\[ P(r) = 4\pi r^2 h e \lambda a_2, \quad (3.4) \]

Substituting \( r = 15 \text{ mm}, h = 2 \cdot 10^{-3}, e \lambda = 0.362 \cdot 120 \text{ W/mK} \) the net heat flux is given by

\[ P = 246 \text{ W/mm}^2, a_2, \quad (3.5) \]

where \( a_2 \) is the coefficient from the parabolic temperature distribution in the burner plate. Typically, \(-0.1 < a_2 < 0.1 \text{ K/mm}^2\), which means that the net heat flux to or from the burner plate does not exceed 25 W. This number should be compared with the heat flux “leaking” from the burner head to the unburnt gas flow (heat flux 4 in figure 3.2).

To estimate this heat flux, CFX calculations are carried out in which the burner head, the flow and the heat fluxes are modelled. In figure 3.6, the results are shown for two situations; the bottom one without the thermally isolating ring, the top one with the ring present. Blue indicates low temperature (295 K), red indicates high temperature (380 K).
3.2 Burner head

Figure 3.6: The effects of heat flux from the burner head to the unburnt gas mixture on the temperature, simulated with CFX. Top: with ceramic ring, bottom: without ceramic ring. The contours of the burner are drawn with black lines. Blue color indicates a temperature $T = 295$ K (cold), red $T = 380$ K (hot). The graphs at the right show the temperature profiles of the unburnt gas flow, at the outflow.
It is clear that the isolation has a considerable effect; the lower part of the burner head is kept cool, and this part of the burner wall does not contribute to the heating of the unburnt gas mixture, nor does it leak heat to the construction support, thereby avoiding a large time to relax to a stationary state. For the heating of the gas mixture, it can be seen from the temperature profiles that the difference between the two situations is small at the outflow $r = 15$ mm, but that a temperature rise exists in the region near the burner wall. Therefore, care should be taken when measuring the temperature distribution in the burner plate in this region. Since this outer region is already marked as outside the 1D area of the flame because of the flow pattern, this is no serious additional concern.

### 3.3 Thermocouples

To improve the thermocouple measurements, the following topics are analyzed in detail in the following sections:

- **Thermocouple methods (section 3.3.1):** two different approaches to measure temperature differences across the burner plate are compared, in order to choose the method that is most accurate.

- **Cooling by thermocouple wires (section 3.3.2):** by extracting heat from the burner plate, the thermocouple wires disturb the equilibrium temperature distribution in the burner plate. The order of magnitude of the disturbance is estimated.

- **Attachment of the thermocouple (section 3.3.3):** by using a method that will attach the wires in a reproducible manner, errors caused by random differences in the attachment will be reduced. Instead of mounting the wires (0.1 mm thick) directly into a hole (0.5 mm diameter) of the burner plate, wires are mounted in a specially prepared cylinder which is subsequently attached in the burner plate, reducing errors due to positioning.

- **A simple model to correct the systematic errors in the measured temperatures (section 3.3.5):** After applying the improved attachment method, small errors in the order of a few Kelvin remain. In order to find the source of these systematic deviations, the vertical gradient in the burner plate is analyzed. Based on this analysis, a correction method is proposed to account for these deviations, leading to smoother parabola.

#### 3.3.1 Thermocouples: conventional versus differential

The physical principle behind a thermocouple is the Seebeck effect: when two ends of a wire are at a different temperature, there will be a net voltage between the two ends depending on the temperature difference of the beginning and the end of the wire. The resulting voltage can be seen as an equilibrium of two processes: one process is the “flow” of electrons from one end to the other caused by a change in electronic band population due to temperature. The other process is the flow in the other direction caused by the
potential difference induced by the first process. Generally, the resulting voltage $V_w$ along the wire can be written as

$$V_w = \int_{T_1}^{T_2} \frac{dV_w}{dT} dT = \int_{T_1}^{T_2} e_S dT,$$

where the Seebeck coefficient $e_S$ is defined. The Seebeck coefficient depends on the material of the wire. Since a thermocouple consists of a pair of wires, having Seebeck coefficients with opposite signs, a net voltage can be generated between the two cold ends of the thermocouple. The magnitude of this voltage depends on the temperature difference between the cold ends and the joint of the two materials. As pointed out in detail in appendix A, the Seebeck effect can be used in two ways in the burner head: first the conventional configuration, where two wires of different material are attached to the spot where the temperature is to be measured. Second, the differential configuration, where only one constantan wire is attached to a certain spot in the burner plate and the voltage difference between two such wires is measured. It can be shown easily (appendix A) that the resulting voltage between two constantan wires is a measure for the temperature difference across the two spots with wires attached — in fact, the brass material of the burner plate is used in this case as part of the “thermocouple”. Some advantages of the differential measurement method are:

- The quantity of interest is a temperature difference, which is now measured directly.

- The disturbance of the flow is reduced because the number of wires in the burner head is reduced. Also, the heat drawn from the burner plate into the thermocouple wires is reduced.

There are also disadvantages:

- The Seebeck coefficient of brass is not tabulated in literature; however, experimental data from van Maaren[43] are available. Furthermore, we are interested in the adiabatic state of the flame; an error in the magnitude of the parabolic coefficient $\alpha_2$ will not affect the measurement results for the adiabatic burning velocities.

- Standard thermocouple transmitters apply a so-called cold junction compensation on the measured voltage. However, in the differential case the cold junction is actually moved to one of the plate-wire joints. This means that normal voltage measurement equipment has to be used, and care should be taken that the equipment is suited for the generally very low (order millivolts) voltages.

For the new burner head, it is chosen to use the differential configuration, since the advantages outweigh the disadvantages.
3.3.2 Cooling by thermocouple wires

To determine whether there is significant cooling by thermocouple wires, an estimate is made of the temperature drop over the glued brass constantan interface, due to conduction of heat over the constantan thermocouple wire. Since the conduction coefficient of the glue is two orders of magnitude lower compared with brass, it can be expected that there is a temperature decrease going from the burner plate to the thermocouple wire.

The system burner plate – thermocouple wire

In the “differential” configuration of the thermocouples in the burner plate, only one "conventional" thermocouple (copper/constantan) is present, being the reference thermocouple. The other positions have a constantan wire without the copper counterpart. When measuring the voltage between the constantan wire of the reference couple and a constantan wire at some other position, effectively a brass constantan thermocouple is created with the cold junction at the reference couple. Thus, the measured thermovoltage will represent the temperature difference between the reference point and the single constantan wire. The constantan wires are attached to the burner plate with a special glue advised by the manufacturer of the thermocouple wires. The heat loss is estimated in two extreme situations: in case of complete external isolation of the wire and in case of heat contact with the flow. Then, the order of magnitude of the temperature measurement error can be determined in both cases. Actually, the heat loss problem is coupled to the temperature decrease, but the estimate of uncoupling both is sufficient in this case.

Isolated assumption

First, we assume that the thermocouple wire is thermally perfectly isolated from the gas at the outside. In the next section the unisolated case will be considered.

For a thermally isolated wire, the energy equation can be written simply

\[ \frac{dQ}{dt} = -\lambda_k A \frac{dT_k}{dx} = \text{constant}, \]  

with \( \lambda_k \) the conduction coefficient of the wire, \( A \) the cross section of the wire and \( \frac{dQ}{dt} \) the heat flux through the wire in J/s, which is constant because of the assumption of perfect isolation. The heat flux can be calculated straightforward by substitution:

\[ \frac{dQ}{dt} = -22 \text{ W/(Km)} \cdot \frac{1}{4} \pi (0.1 \cdot 10^{-3} \text{ m})^2 \cdot \frac{373 \text{ K} - 293 \text{ K}}{50 \cdot 10^{-3} \text{ m}} = 2.8 \cdot 10^{-4} \text{ W}, \]  

where it is assumed that the wire is kept at 293 K when it exits the burner head, 50 mm from the attachment to the burner plate.
3.3 Thermocouples

Unisolated assumption

This case is more complicated, as we have to consider the heat transfer from the thermocouple wire to the gas flow. The energy equation now reads (van Maaren [43])

\[ \alpha_k (T_H - T_k) + \frac{1}{4} d_k \lambda_k \frac{d^2 T_k}{dx^2} = 0, \quad (3.9) \]

where \( \alpha_k \) is the heat transfer coefficient, depending on the Nusselt number \( Nu \). \( T_H \) is the temperature of the flow surrounding the thermocouple wire at temperature \( T_k(x) \). The conduction coefficient of the thermocouple wire is given by \( \lambda_k \). The Nusselt number is given by (Bradley [6]) and is valid for a wire that is perpendicular to the flow field, which is not true for our case. However, we use it as a reasonable estimate for the order of magnitude:

\[ Nu = 0.42 Pr^{0.2} + 0.57 Pr^{0.33} Re^{0.5}, \quad (3.10) \]

where the Prandtl number \( Pr \) and the Reynolds number \( Re \) were used. These numbers are given by

\[ Pr = \frac{\mu c_{pg}}{\lambda_g}, \quad (3.11) \]

\[ Re = \frac{\rho_g u d_k}{\mu}, \quad (3.12) \]

with \( \mu \) the viscosity, \( c_{pg} \) the heat capacity, \( \lambda_g \) the heat conductivity, \( \rho_g \) the density and \( u \) the velocity of the gas flow and \( d_k \) the diameter of the thermocouple wire. Now, the heat transfer coefficient \( \alpha_k \) can be calculated by

\[ \alpha_k = \frac{Nu \lambda_g}{d_k}. \quad (3.13) \]

Substitution of \( \mu = 18.6 \cdot 10^{-6} \) Pas, \( \rho_g = 1.161 \text{ kg/m}^3 \), \( c_{pg} = 1007 \text{ J/(kg \text{ K})} \), \( \lambda_g = 26.2 \cdot 10^{-3} \text{ W/(Km)} \), \( u = 30 \text{ cm/s} \) and \( d_k = 0.1 \text{ mm} \) results in

\[ Re = 1.87 \]
\[ Pr = 0.715 \]
\[ Nu = 1.09 \]
\[ \alpha_k = 286 \text{ W/(Km}^2). \]

The heat transfer coefficient \( \alpha_k \) appears to be high for an air flow. This is probably caused by limitations of the Nusselt relationship (3.10). Knowing the heat transfer coefficient, we continue solving the differential equation (3.9) for the wire temperature. The solution is of the form

\[ T_k = T_0 + T_1 \exp (-bx) \quad (3.14) \]

For the boundary conditions we use

\[ T(0) = T_{pl} \quad (3.15) \]
\[ T(\infty) = T_H \quad (3.16) \]
leading to $T_0 = T_f$ and $T_1 = T_{pl} - T_f$. Substitution of (3.14) in (3.9) gives

$$T_k(x) = T_f + (T_{pl} - T_f) \exp \left( -2 \frac{\alpha_k}{d_k \lambda_k} x \right).$$

The heat extracted from the burner plate is given by

$$\frac{dQ}{dt} \bigg|_{x=0} = -\lambda_k \frac{1}{4} \pi d_k^2 \left. \frac{dT_k}{dx} \right|_{x=0} = \frac{\pi}{2} \sqrt{\lambda_k \alpha_k d_k^3} (T_{pl} - T_f).$$

Substitution of $T_{pl} = 373 \text{ K}$, $T_f = 293 \text{ K}$, $\lambda_k = 22 \text{ W/(Km)}$, $\alpha_k = 286 \text{ W/(Km^2)}$ and $d_k = 0.1 \text{ mm}$ gives the heat loss of the burner plate to the unisolated wire:

$$\frac{dQ}{dt} \bigg|_{x=0} = 1.0 \cdot 10^{-2} \text{ W}.$$  

Compared with the isolated case (equation (3.8)), the heat loss is larger by a factor of 36. Apparently, the heat transfer from the wire to the flow is considerable.

**Temperature decrease**

From these heat losses we can predict the order of magnitude of the error in the temperature measurement due to this effect. Let’s consider the hole and thermocouple wire as two concentric cylinders. The inner one, with diameter $d_k$ and temperature $T_k$, is the thermocouple wire, which functions as a heat sink. The heat removed by the wire was calculated in the previous sections, for two special cases. The outer cylinder consists of silver glue, with diameter $d_h$ (the hole diameter) and temperature $T_{pl}$. For the heat flux $dQ/dt$ in the outer cylinder we can write

$$\frac{dQ}{dt} = 2\pi h \lambda_s \frac{dT}{dr},$$

with $h$ the plate thickness and $\lambda_s$ the conduction coefficient of the silver glue. As we are interested in the temperature difference $T_{pl} - T_k$ we integrate from $r = \frac{1}{2} d_k$ to $r = \frac{1}{2} d_h$:

$$\Delta T = T_{pl} - T_k = \int_{\frac{1}{2} d_k}^{\frac{1}{2} d_h} \frac{dQ}{dt} dr = \int_{\frac{1}{2} d_h}^{\frac{1}{2} d_k} \frac{dQ}{dt} dr = \frac{dQ}{dt} \ln \frac{d_h}{d_k}.$$  

Substituting $h = 2.0 \text{ mm}$, $\lambda_s = 1.57 \text{ W/(Km)}$, $d_h = 0.5 \text{ mm}$ and $d_k = 0.1 \text{ mm}$ results in

$$\Delta T = 81.6 \text{ K/W} \cdot \frac{dQ}{dt}. $$
with $dQ/dt$ given by (3.8) or (3.20), depending on the assumption concerning isolation of the wire. So for the temperature decrease we find

$$\text{isolated} : \Delta T = 0.02 \text{ K} \quad (3.24)$$

$$\text{unisolated} : \Delta T = 0.8 \text{ K} \quad (3.25)$$

The difference between an isolated and unisolated wire is about 1 K. These values can be seen as limiting cases; the real temperature difference can be expected to be in between these values. The calculations show that care should be taken when using silver glue for attaching thermocouple wires. Even in the perfectly isolated case, a high Seebeck coefficient for the silver glue could cause an unexpected large contribution to the measured thermovoltage. Unfortunately, the Seebeck coefficient of the silver glue is unknown. To circumvent this problem, a new attachment method for the thermocouple wires is necessary, reducing the amount of silver glue.

### 3.3.3 Attachment of thermocouple wires

In the old burner plates, thermocouple wires were attached in one of the holes in the burner plate. The thermocouple wires have a diameter of 0.1 mm, while the hole has a diameter of 0.5 mm (0.4 mm is in use as well). In both cases, there is quite a gap between the thermocouple and the material of the burner plate, which becomes filled with another material, either solder or a special glue with relative good thermal and electrical conductivity (although they are still very low in comparison with these parameters for brass). Since the Seebeck coefficient for these materials is unknown, it is undesired to have a relatively large amount of it in the space between the wire and the burner plate, as was shown in section 3.3.2. Because of several uncertainties arising from the bridging of the gap by material with unknown properties, and observing rather large deviations of the thermocouple measurements from the parabolic fit, it was concluded that another attachment of the wires should be used, where these uncertainties are reduced. Therefore, the attachment shown in figure 3.7 is used in the next versions of the burner plates; a small brass cylinder is manufactured which has the diameter of a hole where it can be

![Figure 3.7: Improved method of attachment of a thermocouple wire to the burner plate, reducing the amount of unknown material between the wire and the material of the burner plate. Left: Hole in burner plate, middle: the specially manufactured cylinder, right: the thermocouple wire to be attached.](image-url)
mounted in, without a need for soldering or glueing. In this cylinder, a very small hole is drilled which is only slightly larger than the wire(s) it will contain. Also, the hole is drilled with a well-known length, so that all thermocouple wires in the plate are attached in the same way, at the same height, when the wire(s) are put in the hole until they are blocked. To fasten the wires, the silver glue is used again, but now in a much smaller amount. A remark has to be made here: since it is still unknown how the surface contact is between the wire and the cylinder, deviations are still expected to occur. However, they are supposed to be substantially reduced.

### 3.3.4 Pressing ring

As can be seen in figure 3.2, the burner plate is attached to the burner head by a tight fit. Since the burner plate has a different (average) temperature than the burner head, the thermal expansion of the plate is slightly different. This can cause a bad thermal contact between the plate and the head, resulting in distortions of the rotational symmetry. To ensure a good thermal contact under all circumstances, the burner plate is secured into the burner head using a pressing ring, as shown in figure 3.8. The thermal contact is now independent from the difference in thermal expansion. After adding the pressing ring to the burner head, the observed scatter in the thermocouples was reduced significantly.

### 3.3.5 Vertical temperature gradient

Despite the care taken to attach the thermocouple wires in a manner as reproducible as possible, systematic temperature deviations still occur, and a way to explain them has to be found, as well as a way to correct for those errors. The systematic temperature
deviations can be investigated to find any dependency on other parameters. When the energy equation is applied to the burner plate assuming a uniform heat flux to the burner plate, it can be shown that the temperature as a function of radius in the burner plate can be written as a parabolic function

\[ T_p(r) = T_c \left(1 - \frac{1}{4} \alpha^2 r^2 \right), \quad (3.26) \]

where \( T_c \) is the temperature in the center of the burner plate, and \( \alpha \) a constant which can be real or complex. The reason for writing it this way will be convenient later. As shown in chapter 2, equation (3.26) is actually the equation for the temperature averaged over the vertical distance of the plate. Typically, the radial variations in temperature are an order of magnitude larger than the vertical variations.

While doing experiments, it turns out that thermocouples measuring the temperature in the burner plate show remaining systematic deviations of a few K, after all the modifications introduced so far, suggesting that these deviations are connected with the vertical temperature difference. Moreover, it appears that these deviations can be modeled quite accurately and consequently can be corrected for. The parameter needed to describe the correction is the parabolic constant \( \frac{1}{4} \alpha^2 \) in equation (3.26). To find the physical background of this correction and to gain insight in the quantities involved, the solution of the 2-dimensional energy equation will be approximated. To be able to solve the 2-dimensional conduction problem, the system in figure 3.9 will be approximated by the situation depicted in figure 3.10. Heat transfer between the unburnt gas and the burner plate inside the plate is neglected, because most heat transfer takes place by conduction from the flame to the top of the burner plate, as has been numerically observed by Rook [38]. Therefore, the plate is considered to be at a constant temperature \( T_0 \) at the edge \( r_0 \), while there is a uniform heat flux \( q_+ \) entering the plate at the top \( x = h \), and
a uniform heat flux $q_-$ leaving the plate at the bottom $x = 0$. The net heat flux from the flame to the plate is given by $q = q_+ - q_-$, resulting in a temperature $T_c$ in the center of the burner plate. The energy equation applied to the burner plate in cylindrical coordinates reads

$$\frac{1}{\epsilon} \frac{\partial^2 T_p(x, r)}{\partial x^2} + \frac{1}{r} \frac{\partial T_p(x, r)}{\partial r} + \frac{\partial^2 T_p(x, r)}{\partial r^2} = 0. \quad (3.27)$$

where $T_p$ is the plate temperature, and $\epsilon$ is defined as

$$\epsilon = \frac{\lambda_{p,x}}{\lambda_{p,r}}. \quad (3.28)$$

in accordance with the definition used by van Maaren [43] to account for the perforation pattern of the burner plate. It is assumed that the thermal conductivities $\lambda_{p,x}$ in the axial direction and $\lambda_{p,r}$ in the radial direction do not depend on temperature and hence they can be assumed constant. To solve equation (3.27) four boundary conditions are needed: $\partial T_p(x, r)/\partial r|_{r=0} = 0$ represents the rotational symmetry of the problem, $\partial T_p(x, r)/\partial x|_{x=0} = q_-$ and $\partial T_p(x, r)/\partial x|_{x=h} = q_+$ to account for the heat gain and loss, respectively. Finally, $T_p(0,0) = T_i$ is used for the temperature in the center of the burner plate. The solution of equation (3.27) and boundary conditions, after some approximations, reads

$$T_p(x, r) = T_c \left[ 1 + c \epsilon \alpha^2 h x \right] \left[ 1 - \frac{1}{4} \alpha^2 r^2 \right], \quad (3.29)$$

with $c$ a constant. Details of the solution of equation (3.27) are given in Appendix B. Compared to the simple one-dimensional case equation (3.26), the 2-dimensional axisymmetric approximation in equation (3.29) of the heat conduction problem is extended by a height-dependent factor. This factor contains the parabolic constant $\alpha^2$ and the height $x$, corresponding to the effective attachment height of the thermocouple. This parameter is fixed for each thermocouple $n$, and will be designated $x_n$, with $1 \leq n \leq 6$, since 6 thermocouples were used for determining the temperature distribution. Consequently, the correction is proportional to the parabolic constant and different for each thermocouple, as observed in the experiment. Also, the effective attachment heights, $x_n$, of each thermocouple can be estimated from a series of experiments using equation (3.29). A final remark is made about the ratio $\epsilon$ of the thermal conductivities occurring in the height correction: when a burner plate is used with a perforation pattern that causes a larger radial gradient (i.e. small $\lambda_{p,r}$), the temperature profile will also show larger deviations due to the vertical gradient.

### 3.4 Typical measurement

The observed deviations in thermocouple temperatures are modeled by a linear function in $\alpha^2$, since equation (3.29) suggests that the correction factor is proportional to $\alpha^2$. Typical examples of the temperature profile are given in figure 3.11, where CH₄/air flames
3.4 Typical measurement

Figure 3.11: Typical temperature profiles in the burner plate when a CH\textsubscript{4}/air flame with $\phi = 1.00$ is stabilized. Velocities range from 30.0 to 37.0 cm/s ($v_{\text{ad}} = 35.7$ cm/s). Horizontal: radial position in mm, vertical: temperature in $^\circ$C. Lines are fitted parabola.

Figure 3.12: The temperature differences of thermocouples 1-6 to the parabolic fit, as a function of $\alpha^2$.

with $\phi = 1.00$ are stabilized, having different velocities around the adiabatic velocity, 35.7 cm/s. Each temperature profile of figure 3.11 can be fitted straightforwardly to a parabolic function, as in equation (3.26). As seen in figure 3.11, the deviations between the measurements and the fit appear to be systematic for each thermocouple.

For each temperature profile, the fit yields two parameters: the temperature in the center of the burner plate $T_c$ and the parabolic coefficient $\frac{1}{\alpha^2}$. The next step is to determine the temperature deviation $\Delta T$ per thermocouple, as a function of $\alpha^2$. In figure 3.12, the
residuals $\Delta T_i$ are shown using the same measurements as in figure 3.11. The residual temperatures appear to be a reasonable linear function of $\alpha^2$, supporting the hypothesis that these systematic errors are (at least partially) caused by a different effective height $x_m$ per thermocouple. The result does not completely comply with equation (3.29), since an offset is needed in the correction to accurately compensate the observations. However, this offset is rather small ($< 1 \text{ K}$), and it is assumed that this is due to effects not included in the model – for example the possibility that some of the glue used to attach the thermocouple wires remains at the bottom of the burner plate, or cooling of the spot by the gas flow due to this amount of extra material.

To find the correction parameters, a fit was made through the residuals of several flames ($\phi = 0.80$, $\phi = 1.00$ and $\phi = 1.20$), as well as the temperature profiles found when only a cold flow (without a flame) was present. The resulting parameters were used to make the corrections in the temperature measurements. In figure 3.13, a corrected measurement is shown; compared to figure 3.11, the scatter of the individual thermocouple measurements is reduced. To estimate the error in the burning velocity due to the remaining scatter in the thermocouples after the correction has been applied, the sensitivity $s$ is defined as

$$ s = \left. \frac{d\alpha^2}{dS} \right|_{\alpha^2=0}, \quad (3.30) $$

indicating the variation of the parabolic parameter $\alpha^2$ when the velocity is changed. This quantity can be determined during the interpolation procedure. Assuming the typical remaining thermocouple scatter to be $\sigma_{tc}$, this leads to an uncertainty in the parabolic parameter of

$$ \sigma_{\alpha^2} = \frac{2\sigma_{tc}}{r_b^2}, \quad (3.31) $$
3.4 Typical measurement

![Figure 3.14](image)

Figure 3.14: Error estimate of parabolic parameter due to scatter $\sigma_c$ in thermocouple measurements. The thermocouple with radial position $r_b$ is the outermost thermocouple. The line indicates the parabola that would still be acceptable when the thermocouples read equal temperatures.

![Figure 3.15](image)

Figure 3.15: The resulting uncertainty in $S_L$ due to remaining scatter in the thermocouple measurements. The method has the smallest error when the heat release of the flame is maximal, around $\phi = 1.05$.

where $r_b$ is the radial position of the outermost thermocouple used to measure the temperature profile in the burner plate, as illustrated in figure 3.14.

The resulting uncertainty in the burning velocity is given by combining equations (3.30) and (3.31):

$$\sigma_{S_L} = \frac{1}{s} \frac{2\sigma_c}{r_b^2}. \quad (3.32)$$

In our case, $\sigma_c = 0.5$ K (after correction) and $r_b = 10.5$ mm, resulting in figure 3.15, where the sensitivity function $s$ was determined by fitting the sensitivities, found from the interpolation results, to a third-order polynomial. The resulting curve reflects the fact that the heat flux method is most accurate where the flame produces most heat, i.e. at $\sim \phi = 1.05$.

The parabolic parameters $\alpha^2$ from each measurement shown in figure 3.13 are plotted as a function of gas velocity in figure 3.16. As is obvious, the adiabatic burning velocity can
Improvements of the heat flux method

Figure 3.16: Interpolation to the adiabatic burning velocity by plotting the parabolic parameter $\alpha^2$ as a function of gas velocity ($\phi = 1.0$, methane/air, $T_u = 300$ K, $p_u = 1.0$ bar).

be found easily by interpolating the curve and determining the intersection with $\alpha^2 = 0$. This procedure was repeated for a range of equivalence ratios of interest, giving finally a plot of burning velocities against equivalence ratios. It can be seen in figure 3.16 that the results at high gas velocities do not fit the other measurements. The cause for this is that at these velocities the flame has such a large stand-off distance from the burner plate that increasing the velocity does not change the heat flux much. In fact, these flames are, at least partially, blown off, which can often be seen in the experiment, because they are not flat anymore over the entire burner plate. These points are therefore not taken into account when making a fit through the results to obtain the adiabatic burning velocity. All the measurements, including those with lower heat transfer, were checked that they contain at least one data point with a positive $\alpha^2$, and that these data points were not in the region where the flame partially blows off.

3.5 Conclusions

Based on experiments with the heat flux setup at the start of this research, a detailed analysis has been carried out to find possible sources of systematic errors and uncertainties. Analysis of the heat fluxes present in the burner head has lead to an improved burner head, with separated hot and cold water circuits. Thermocouple measurements are improved by attaching them in a well reproducible manner. The addition of a pressing ring provides a better thermal contact between the burner plate and the heating circuit. After all improvements, some scatter in the order of a few Kelvin is still seen in the temperature measurements. Using a simple model for the vertical temperature gradient in the burner plate, it is shown that the scatter can be understood and corrected for, leading to an improved accuracy. The typical uncertainty, due to the thermocouples, in the de-
termination of the adiabatic burning velocity for a stoichiometric methane/air flame is \( \pm 0.5 \) cm/s.

The improved heat flux setup will be used to perform burning velocity measurements for mixtures of lower alkanes with air in chapter 5. Also, the setup is used as a base for extending the method to lower pressures, which will be presented in chapter 6.
Chapter 4

CARS validation

4.1 Introduction

In this chapter, an experimental validation of the heat flux method is carried out, in addition to those already performed by van Maaren [44] with LDV, which were focused on the flatness of the flow field. An excellent test for the adiabatic state of the flame is to measure the temperature profile in the flame, since the adiabatic temperature can be calculated very accurately (within a few K) using equilibrium assumptions. In a practical situation, radiation losses will occur, which results in a lower temperature in the flame. To account for this effect, calculations are performed which use a simple gas radiation model, implemented in Chem1D [40] using a GRI 2.11 [5] reaction mechanism. Measured vertical temperature profiles are compared with the calculated profiles as well as the equilibrium temperatures.

The temperature in a methane/air flame is typically 2000 K. In this region, thermocouples are difficult to apply because two effects need to be corrected for: the cooling of the thermocouple by radiation and the local heating of the gas mixture because of catalytic effects of the thermocouple material on the oxidation process. CARS, a laser technique based on the probing of quantum states of the N₂ molecule in the flame [14], has been developed in recent years to a well established level of measuring temperatures with an accuracy much better than what can be achieved with other experimental methods in the temperature range of interest. Typically, the uncertainty achieved by averaging multiple single measurements (“shots”) is 20 K to 30 K, corresponding to 1 % of the temperature. Therefore, a comparison of CARS measurements with calculated adiabatic temperatures will provide a solid basis to draw conclusions on the performance of the present burner to stabilize adiabatic flames.

This chapter is based on “The heat flux method to produce burner stabilized adiabatic flames: a validation with CARS thermometry” [3]. A more detailed analysis of the CARS process is given in appendix C. Because the CARS validation was carried out as an early part in the research, the burner used for the CARS measurements did not yet contain
any of the improvements discussed in chapter 3. Although the values for the adiabatic burning velocities used in this chapter are slightly different from the final results in this thesis, both values are consistent within their respective uncertainties.

In section 4.2, the flame conditions used in this chapter are presented, and the locations in the flames to be measured with CARS. Section 4.3 shortly describes the CARS technique used for determining temperatures. Practical problems that are specific for this study are analyzed. In section 4.4, the numerical models which are used to obtain the temperatures for comparison with the CARS experiments in atmospheric CH$_4$/air flames are shortly described. The results are presented and discussed in section 4.5.

The support of the Delft University of Technology, where the CARS measurements were performed, is gratefully acknowledged.

### 4.2 The flames

Four flat adiabatic methane/air flames at atmospheric pressure are investigated in this work. We have chosen for the equivalence ratios $\phi = 0.80$, $\phi = 0.90$, $\phi = 1.00$ and $\phi = 1.10$. In table 4.1, the experimental settings at adiabatic conditions are given. It should be noted that the burning velocities listed in table 4.1 originate from [43], and therefore are slightly different from results shown in this thesis using the improved heat flux setup. However, the values in table 4.1 are consistent with the present data in appendix D when the respective uncertainties are considered. In previous work [46] it has been shown that adiabatic burning velocities agree very well with results of the counterflow method [29] when the results of Law et al. are corrected for stretch with a non-linear correction model.

The uncertainties in table 4.1 are estimated from mass flow controller accuracies and calibrations. The adiabatic condition of the flame can be checked by the thermocouples all yielding the same temperature, indicating no net heat flux through the burner plate. In one of the flames ($\phi = 0.80$), a horizontal CARS temperature profile is measured to check in which area the flame is one-dimensional. Furthermore, vertical temperature profiles are determined in all flames. As the laser beam hits the burner plate when measuring very close to it, care is taken not to hit the thermocouples. Consequently, the position of the vertical profile is not exactly in the middle of the flame, but typically at a distance of 1 mm from the central axis. However, it will turn out that this is well within the 1D area. The lowest measurement point is 0.3 mm above the burner plate. In steps of 0.1 mm, the CARS measurement volume is moved up. When the measurement

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$S_L$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80 ± 0.04</td>
<td>24.0 ± 0.7</td>
</tr>
<tr>
<td>0.90 ± 0.03</td>
<td>32.0 ± 0.8</td>
</tr>
<tr>
<td>1.00 ± 0.03</td>
<td>36.5 ± 0.9</td>
</tr>
<tr>
<td>1.10 ± 0.03</td>
<td>38.0 ± 0.9</td>
</tr>
</tbody>
</table>

Table 4.1: Conditions of the premixed adiabatic methane/air flames measured with CARS
volume has reached a position well above the flame front, where the gradient is not so high anymore, larger steps are taken up to a height of 35 mm.

4.3 CARS

Coherent Anti-Stokes Raman Scattering (CARS) is based on the probing of quantum states of certain molecules. In this work, the \( \text{N}_2 \) molecule is probed, as this molecule is present in sufficient quantity in air-fed flames. We used the folded BOXCARS configuration, where two pump beams and one Stokes beam are focused in the measurement volume. All rotational and vibrational levels of the molecules present in the measurement volume are probed at the same time by using a broadband Stokes beam, causing the CARS signal to contain a temperature and density dependent spectrum. This spectrum depends on the temperature, due to the Boltzmann distribution of the energy level population density. By comparing a measured spectrum with theoretical spectra by a least squares fit, the temperature belonging to the measured spectrum is determined. The computer code used to fit the measured spectra is DACAPO (Brüggeman [7]), extended with custom written front-ends.

To generate the pump beams and the Stokes beam, two lasers are used; a frequency-doubled Nd:YAG laser (Continuum YG-680) and a dye laser (Continuum TDL-60) operated with Rhodamine 101. The Nd:YAG laser provides pulses with a wavelength of 532 nm at a pulse frequency of 10 Hz. The beam is split in three parts; two beams are used as pump beams in the CARS process. The third beam is used for pumping the dye laser which delivers the broadband Stokes beam, having a bandwidth of 150 cm\(^{-1}\) FWHM and a central wavelength tuned to 607 nm. The CARS signal is spectrally dispersed in a spectrometer (SPEX-1404 0.85-m) and recorded on a back-illuminated CCD camera (Princeton Instruments TE/CCD-1100P) with 1100x330 pixels. The vertical direction of the CCD (330 pixels) is binned to obtain an array of 1100 pixels, which are digitized and stored in a PC.

The effects of stimulated Raman pumping are investigated by varying the laser beam power while keeping the flame, and thus the temperature in the probe volume, constant. It turns out that the resulting CARS spectra and the fitted temperatures do not depend on the laser beam power[24], from which it is concluded that stimulated Raman pumping can be neglected in the temperature results in this work. Also, nonlinear effects in the CCD are unlikely to occur.

Because of the application of a broadband Stokes beam, it is possible to obtain the temperature from a single laser pulse. As the laminar flames in this work are stationary, it is possible to improve the signal to noise ratio by averaging subsequent laser pulses. One way to do this is to determine the temperature belonging to each spectrum and to average the temperatures determined from this spectra; at flame temperature, we find a normal distribution with a standard deviation \( \sigma \) of 80 K. Similar values were found by Eckbreth [14] and Kröll [26]. When averaging temperatures this way, the (statistical) uncertainty of the average temperature is estimated to be \( \sigma / \sqrt{N} \). With typically 100 laser pulses in our case, the uncertainty is 8 K. Instead of determining the temperature from every
single pulse spectrum, the single pulse spectra can be added to obtain one spectrum, from which the temperature can be calculated. This temperature is always within 5 K of the average of the single pulse temperatures. The fluctuations leading to the normal distribution with $\sigma = 80$ K are mainly attributed to pulse to pulse fluctuations in the dye laser profile. The dye profile is investigated by measuring the non-resonant spectrum in methane. It appears that not only shot to shot fluctuations are present, but also a drifting of the profile on a larger time scale, typically in the order of minutes. This drifting is caused by effects of temperature and dye concentration in the dye laser, which turn out to be difficult to stabilize. Therefore, the dye profile, averaged over typically 100 pulses, is determined before and after a series of measurements. By comparison of temperatures calculated with both dye profiles, it turns out that these temperatures can differ up to 40 K, depending on the stability of the dye-laser system. It is assumed that this temperature difference $\delta T$ can be considered as a 100 % confidence interval, with a distribution as shown in figure 4.1. Since it is more convenient to express uncertainties in terms of a standard deviation $\sigma$, referring to a normal distribution, the 100 % interval is converted to a standard deviation $\sigma$ by applying the usual definition for the standard deviation to this particular case

$$\sigma_{\text{drift}}^2 = \int_{-\delta T}^{\delta T} x^2 \cdot \frac{1}{2\delta T} dx = \frac{\delta T^2}{3}. \quad (4.1)$$

where $\delta T$ denotes the observed temperature difference before and after a series of measurements and $\sigma_{\text{drift}}$ is the resulting standard deviation (68 %) assigned to the long term drifting effect. The final uncertainty in the CARS temperature measurement is obtained by statistically adding both uncertainties

$$\sigma_{\text{tot}}^2 = \sigma_{\text{dip}}^2 + \sigma_{\text{drift}}^2. \quad (4.2)$$

The uncertainty $2\sigma_{\text{tot}}$ (95 % confidence interval) will be used further on in this work for the error bars assigned to the temperature measurements.

The diameter of the measurement volume is approximately $2/\pi \cdot w$, where $w$ is the waist diameter of the laser beam, according to[14]. In our setup, this leads to a diameter of 50 $\mu$m, while the length is estimated to be a few millimeters. As the length is larger...

![Figure 4.1: A 100 % confidence interval (left) and the normal distribution (right) with uncertainty intervals $\sigma$ (68 %) and $2\sigma$ (95 %).](image)
than the width, it is important to arrange the experiment in such a way that the long axis of the measurement volume is perpendicular to the gradient in the flame. If this is not the case, the presence of hot as well as cold regions in the measurement volume results in an averaged temperature measurement. Since cold spectra have much higher intensities than hot spectra, the resulting temperature would be much lower than the spatially weighted temperature [50]. This effect is inevitable in the flame front, where a very steep temperature gradient $dT/dh$ exists, in the order of a few $1000 \text{ K/mm}$; with a measurement volume of $50 \mu\text{m}$ width and $3 \text{ mm}$ length, accounting for a possible misalignment of the flame and measurement volume of $1^\circ$, we find $e = 100 \mu\text{m}$ for the resulting effective width. The temperature difference $\Delta T_{\text{vol}}$ across the measurement volume can be estimated by

$$\Delta T_{\text{vol}} = e \cdot \frac{dT}{dh}.$$  \hspace{1cm} (4.3)

It can be expected that the observed temperatures in the flame front will differ not more than $\Delta T_{\text{vol}}$ from the real temperatures. As it will turn out that gradients in our case have a magnitude up to $4000 \text{ K/mm}$, the upper limit for the error is $400 \text{ K}$. A more thorough study of the effect of a temperature gradient in the measurement volume was performed by Zhu [50]. Applying those results to our case, an error of $100 \text{ K}$ can be expected.

Finally, care is taken to account for the background radiation that is collected by the CCD as well. Especially for the measurements that were close to the burner plate, reflections of the laser beams on the plate result in a large background signal. For these measurements, the background is determined for each height separately by blocking the Stokes beam so that no resonant signal occurs. This background is subtracted from the CARS spectra.

From this analysis it can be concluded that the most important uncertainty in the temperature measurements is caused by the long-term dye profile drifting. Depending on the stability of the dye-laser and the time between the dye-profile measurements, this uncertainty can be as large as $40 \text{ K}$ (based on 100 pulses). This uncertainty is different for each measurement run and therefore determined separately each time. It is lumped with the observed pulse to pulse fluctuation error of $8 \text{ K}$ (also based on 100 pulses) in order to finally obtain a confidence interval of $95 \%$ for the resulting CARS temperature measurements. However, in the flame front where a large gradient exists, an additional (systematic) error is present which can be estimated by considering the magnitude of the gradient.

### 4.4 Calculations

Two types of calculations are performed to compare the CARS results with theory; adiabatic temperatures are calculated using the EQUIL code from Sandia National Laboratories [23]. This code determines the equilibrium concentrations and temperature and is known to be accurate within a few K.

Secondly the model Chem1D, developed at the Eindhoven University of Technology [40], is used to calculate the vertical temperature profiles, using the GRI reaction mechanism version 2.11 [5]. A simple radiation model is implemented to account for radiation losses.
of the flame. This model, proposed by Liu and Rogg [33], accounts for radiation of H$_2$O and CO$_2$ by assigning a Planck absorption coefficient $k_p$. The absorption coefficient depends on the local H$_2$O and CO$_2$ concentrations in the flame. In figure 4.2, $k_p$ is shown for the case $\phi = 0.80$. Also, the H$_2$O and CO$_2$ molar fractions and the temperature are shown. It is seen that $k_p$ varies between 0.60 and 0.66 above the flame front. For other equivalence ratios, the graphs show similar trends, although $k_p$ takes another value; In table 4.2 the lower and upper values of $k_p$ are given as a function of equivalence ratio, in the region above the flame front where an almost linear increase of $k_p$ is found. The influence at lower heights is negligible because the temperature is still low there.

![Figure 4.2: The Planck absorption coefficient $k_p$ as a function of the height in a one dimensional flame; H$_2$O and CO$_2$ molar fractions and the temperature are shown, on which $k_p$ depends.](image)

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>lower $k_p$</th>
<th>upper $k_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.60</td>
<td>0.66</td>
</tr>
<tr>
<td>0.90</td>
<td>0.57</td>
<td>0.62</td>
</tr>
<tr>
<td>1.00</td>
<td>0.54</td>
<td>0.58</td>
</tr>
<tr>
<td>1.10</td>
<td>0.50</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Table 4.2: Lower and upper values of the absorption coefficient $k_p$.

It was checked that the 1D model, without radiative losses, gives the same final temperatures within a few K as the equilibrium calculations. It should be noted that the agreement between the 1D model and the equilibrium often occurred at a height of typically 100 mm, which is much higher than the maximum height, 35 mm, in the present
4.5 Results

In this section, the results of the CARS measurements are presented and a comparison with calculations is made. One horizontal profile is shown first. The vertical profiles will be considered afterwards.

In figure 4.3, a horizontal profile through the flame with $\phi = 0.80$ is shown, at 3 mm above the burner plate. This height is located above the flame front, which is stabilized typically at a few tenths of a millimeter above the burner. However, at 3 mm the maximum temperature in the flame is not reached yet. All temperatures in this figure are determined by calculating the temperature belonging to a CARS-spectrum formed by the addition of 100 laser pulses. At the boundaries, a large gradient can be observed. Within a radius of 10 mm from the center of the burner, the temperature is almost constant. This is the 1D-area of the flame. For the temperatures in the 1D-area an average is found of 1942 K, with a standard deviation of 10 K. As explained in section 4.3, this uncertainty arises from pulse to pulse fluctuations of the dye-laser. The long-term drifting of the dye-profile, however, leads to an uncertainty of 26 K in this case.

Concerning the vertical profiles, we first consider the most interesting part which contains the steep temperature gradient in the flame front. In figure 4.4 the results are shown for $\phi = 0.80$ to $\phi = 1.10$. The height $h = 0$ corresponds to the upper surface of

![Figure 4.3: Horizontal temperature profile in an adiabatic flame with $\phi = 0.80$, 3 mm above the burner. Line: equilibrium temperature calculated with EQUIL (1982 K)]
Figure 4.4: Vertical temperature profiles in adiabatic flames, up to a height of 2.0 mm. Markers: measurements. Solid lines: calculations. Dashed lines: calculations 0.03 or 0.04 off (plus or minus) the nominal equivalence ratio. Dotted lines: equilibrium temperatures (EQUIL). The uncertainty in vertical positioning is indicated in graph (a).
the burner plate, where it is assumed that the gas temperature has a value of 353 K, equal to the temperature of the burner plate. The uncertainty in the experimental reference height \( h = 0 \) is 0.1 mm, arising from the uncertainty in the vertical alignment of the burner plate and the laser beams.

In figure 4.4 it can be seen that all measurements in the steep gradient, from 0 to 0.5 mm, are below the calculated profile. Partly, this is caused by the gradient that is present within the CARS measurement volume. Another important source of error is the uncertainty in the height, indicated in the figure. This uncertainty is systematic for all measurement data within one profile, since it originates from the alignment error at the beginning of the experiment. In table 4.3, the data relevant to the initial temperature rise are summarized; the CARS gradient is determined by the slope of the linear fit that can be made through the first four measurement points, which are all between 0.15 mm and 0.5 mm height. To compare the experimental slopes with numerical ones, a linear fit is also made in the modelled slopes, on the same interval [0.15 mm, 0.50 mm] that is used for the measurement data. The result of this operation for \( \phi = 0.90 \) can be seen in figure 4.5. The temperature difference \( \Delta T_{\text{diff}} \) between the model and the measurement is determined in the middle of the steep slope region, and presented in table 4.3. The observed

![Figure 4.5: The preheating zone containing four measurement points; line: Chem1D model, dashed: linear fits through the measurements resp. the model. The difference between both linear fits is taken as the deviation \( \Delta T_{\text{diff}} \).](image)

and modelled slopes in this table agree well; the deviation \( \Delta T_{\text{diff}} \) can be well explained considering both the error due to the temperature gradient (100 K) and the vertical alignment error (±0.1 mm). Since the temperature gradients, like in figure 4.5, do not vary very much as a function of height in the given interval, it is assumed that the errors due to the gradient are equal for all four measurement points in this zone. Therefore, the temperature gradients can be compared directly with the modelled gradients.
Table 4.3: Observed temperature gradients, modelled temperature gradients and differences between the observed and modelled temperature in the middle of the steep slope region.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>CARS</th>
<th>ChemID</th>
<th>$\Delta T_{\text{diff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>$2.6 \cdot 10^3$ K/mm</td>
<td>$2.9 \cdot 10^3$ K/mm</td>
<td>$9 \cdot 10^1$ K</td>
</tr>
<tr>
<td>0.90</td>
<td>$3.6 \cdot 10^3$</td>
<td>$3.4 \cdot 10^3$</td>
<td>$8 \cdot 10^1$</td>
</tr>
<tr>
<td>1.00</td>
<td>$3.8 \cdot 10^3$</td>
<td>$3.6 \cdot 10^3$</td>
<td>$2 \cdot 10^2$</td>
</tr>
<tr>
<td>1.10</td>
<td>$4.0 \cdot 10^3$</td>
<td>$3.7 \cdot 10^3$</td>
<td>$3 \cdot 10^2$</td>
</tr>
</tbody>
</table>

In the region above the flame front in figure 4.4, the error is determined largely by the uncertainty due to the dye profile instability. Since the dye profile stability differs from one measurement to another, the resulting errors are not the same for every equivalence ratio.

The solid lines in the figures denote the numerical calculations at the corresponding equivalence ratio. The dashed lines denote calculations at equivalence ratios $0.03$ or $0.04$ (for $\phi = 0.80$) off the nominal value, to demonstrate the effect of the experimental uncertainties (listed in table 4.1) on the flame temperature.

The overall agreement of measurements and calculations is very good; mostly, they are consistent, although there is a tendency that the measured temperatures exceed the calculated ones in the region after the steep gradient, typically from $0.7$ mm on. Especially at $\phi = 1.10$, the measured temperatures are higher ($50$ K) than the calculation.

In figure 4.6 the complete measurement domain is presented, i.e. up to a height of $35.0$ mm. The equilibrium temperatures are shown as dotted horizontal lines. Because of radiation losses, the measurements as well as the calculations do not reach this temperature, but they show a slight decrease after some maximum temperature. The agreement between measurements and calculations is generally good. Only for $\phi = 1.10$, the measurement data is situated above the calculated profile. The slopes due to radiation losses appear to be consistent.

When using these flames as reference flames in other techniques, it is interesting to know how the maximum temperatures deviate from the calculated equilibrium temperatures and ChemID model temperatures. To make this comparison, the maximum temperature in the measured vertical profile is determined by interpolation of a third-order polynomial function fitted through the part of the measured profile in which the maximum is located. In table 4.4, the results are given. For the model as well as for the measurements, the height where the maximum temperature occurs is given. It appears that the maximum observed CARS temperatures are only $10$ K lower than the equilibrium temperatures. This is presented in figure 4.7, showing an excellent agreement between the CARS measurements and the equilibrium calculations. The height where the maximum occurs appears to be very well predicted by the model. Since the ChemID model (without radiation loss correction) approaches the equilibrium temperatures within $1$ K typically at a height of $10$ cm, which is far above the height investigated here, the relatively large differences between the equilibrium temperatures and the maxi-
Figure 4.6: Vertical temperature profiles in adiabatic flames, up to a height of 35.0 mm. Markers: measurements. Solid lines: calculations. Dashed lines: calculations or off (plus or minus) the nominal equivalence ratio. Dotted lines: equilibrium temperatures (EQUIL).

Minimum Chem1D temperatures can be explained, which are not only due to radiation losses. Comparing Chem1D with CARS, a larger discrepancy is found than comparing EQUIL with Chem1D, especially when $\phi > 1$. Either the CARS measurements are too high, or
Table 4.4: The equilibrium temperatures, Chem1D model maximum temperatures and measured maximum temperatures in adiabatic flames. The heights where the maximum temperatures occur are specified for the model and for the measurements.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>equilibrium model</th>
<th>height (mm)</th>
<th>CARS height (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>1982</td>
<td>1957</td>
<td>1972 ± 28</td>
</tr>
<tr>
<td>0.90</td>
<td>2141</td>
<td>2083</td>
<td>2131 ± 28</td>
</tr>
<tr>
<td>1.00</td>
<td>2231</td>
<td>2159</td>
<td>2211 ± 49</td>
</tr>
<tr>
<td>1.10</td>
<td>2216</td>
<td>2150</td>
<td>2208 ± 20</td>
</tr>
</tbody>
</table>

Figure 4.7: The temperature as a function of fuel/air mixture ratio for an adiabatic flat flame. Line: equilibrium calculations, markers: CARS measurements. Error bars denote the experimental uncertainties.

the Chem1D model predicts too low values. Since the slopes in the post burning zone for CARS and Chem1D agree very well, a too low Chem1D prediction should not be caused by the radiation model, but by certain reactions performing too slowly, which is very unlikely. Therefore we conclude that the CARS measurements tend to be slightly too high, especially at higher $\phi$. In the literature, Mokhov[35] states that CARS thermometry measurements tend to be too high by typically 30 K, based on the observation that the measured temperature in a flame that is very near the blow-off condition (and thus adiabatic) is always higher than the corresponding adiabatic temperature. A thorough investigation is not given, but a hypothesis[30] is that the presence of a CO resonance influences the non-resonant background. Therefore, this effect increases with $\phi$, since flames with higher equivalence ratio contain more CO. This tendency is also seen in the present work. Therefore, we conclude that the present measurements, when this uncertainty is additionally taken into account, are in good agreement with the Chem1D calculations.
4.6 Conclusions

CARS has been applied successfully to flat, stretchless adiabatic methane/air flames at atmospheric pressure. The accuracy is determined mainly by the instability of the dye laser system, leading to typical errors of a few tens degrees Kelvin, estimated by measuring the dye profile before and after a measurement series. In the preheating zone a larger error (up to 300 K) occurs due to the presence of a temperature gradient in the measurement volume as well as the vertical positioning uncertainty of the burner. However, the resolution in the measurements is sufficient to resolve the temperature gradient in the flame front for comparison with theory.

The measurement of the horizontal profile through the flame confirms that the flame is flat within the 1D area, as expected by previous calculations and measurements. Vertical temperature profiles are measured in adiabatic flames at equivalence ratios of 0.80, 0.90, 1.00 and 1.10 respectively. There is good agreement between these profiles and the corresponding calculated ones.

The CARS measurements demonstrate that the present burner provides a well defined flame, which can be set to an adiabatic state by relatively simple means. Such flames can be very useful to serve as a reference flame in other laser based techniques.
Chapter 5

Results for lower alkanes

5.1 Introduction

The heat flux method as described in chapter 2 and improved in chapter 3 is used to determine the adiabatic burning velocities of the lower alkanes methane, ethane, propane, \textit{n}-butane and iso-butane at atmospheric pressure. The equivalence ratio is varied from typically 0.7 to 1.4, while the temperature is (295 ± 3) K. For methane, a set of measurements is performed with the inlet temperature varying from 295 K to 370 K for fixed equivalence ratios $\phi = 0.80$, $\phi = 1.0$ and $\phi = 1.2$. Measurements are compared with other data available in literature, either numerical or experimental. All measured data are tabulated in appendix D. As pointed out in chapter 2, the error bars throughout this chapter represent a 95% uncertainty interval. The vertical bars arise from the added uncertainties of velocity (MFC’s, temperature and pressure) and thermocouples, while the horizontal bars have their origin in the equivalence ratio due to the uncertainties in the MFC’s, as described in section 2.3.2.

5.2 Measurement sensitivity

As explained in section 3.4, the resulting uncertainty in the burning velocity is determined mainly by the remaining scatter in the thermocouple measurements (after the vertical gradient correction has been applied) and secondly by the uncertainties in the MFC’s controlling the unburnt gas flow. The latter has a typical value of ±0.2 cm/s and is constant over the entire range of equivalence ratio and velocity. This uncertainty is determined during the calibration procedure, which is described in appendix G.

The uncertainty due to the thermocouple scatter turned out to be determined by the sensitivity $\alpha$, equation (3.30). The sensitivities for all fuels are shown in figure 5.1. The sensitivity is a function of the heat release by the flame and has therefore a maximum around $\phi = 1.0$. Since the heat release depends on the fuel/air mixture being burnt,
the sensitivity function is different for each fuel/air mixture. However, for the lower alkanes used in this work, the order of magnitude is the same, so the uncertainty function previously shown for methane (figure 3.15, section 3.4) also holds roughly for the other alkanes, which means that the typical thermocouple uncertainty around $\phi = 1.0$ is $\pm 0.5 \text{ cm/s}$. For the calculation of the uncertainties in this chapter, the slight dependency is taken into account by using a different sensitivity function for each fuel, based either on a second or third order polynomial fit, whatever fits best to the experimental data.

### 5.3 Methane

For mixtures of methane with air, many experimental data are available. Therefore, the comparison between the heat flux measurements and other data is made in several steps. First, a comparison with a lot of available data around 295 K is presented, followed by a comparison with recent experiments where proper care was taken to either circumvent or correct flame stretch issues. Also, a comparison with Chem1D [40] calculations, based on several often used mechanisms (GRI 2.11, GRI 3.0 and Warnatz) is presented. Finally, the measurements with elevated initial temperature are compared to data from literature and known correlations.

In figure 5.2, a large amount of literature data is compared to the heat flux results. The heat flux data present values within the broad scatter of available data. The uncertainties in the heat flux experiments appear to be smaller than the scatter in the data. However, it is reasonable to assume that the more recent measurements represent a more accurate reference for the adiabatic burning velocity, because in these experiments care has been taken to correct for stretch effects with recent insights. A comparison with reasonably recent (1989 and later) data sets is shown in figure 5.3, where the data set of Vagelopou-
Los [42] is included. The results by Vagelopoulos are obtained from a so-called ultralow strain-rate flame, where the strain-rate in counterflow flames was varied from positive to negative, so that effectively the burning velocity is found by interpolation, as opposed to the traditional counterflow techniques where it is found by extrapolation, bearing uncertainties associated with the model used for extrapolation. The typical strain-rate in these counterflow flames is in the order of 100 s\(^{-1}\), which is considered small. For comparison, van Maaren [45] showed that this quantity is two orders of magnitude smaller (1 s\(^{-1}\)) for the flat flame used in this work. Also included in figure 5.3 are the experiments by Gu [18], based on closed vessel experiments and corrected for stretch effects. The measurements by van Maaren [44] using the original heat flux setup are consistent with the
present work. Not shown in figure 5.3 are the error bars for these measurements, which are typically ±1.0 cm/s around φ = 1.0, twice as large as for the present heat flux results. An example of the “classical” counterflow technique as applied by Law [29] yielded a relatively high value for the burning velocity of a stoichiometric methane/air mixture: 40.5 cm/s. It has been shown by van Maaren [46] that correction of the data by Law with an appropriate (non-linear) stretch model leads to consistency with the heat flux results and other recent measurements by various authors using corrections for stretch. Table 5.1 shows an overview of the burning velocities as found by several workers, all for stoichiometric mixtures, in chronological order. It can be concluded that recent experiments converge towards a value around $S_L = 36$ cm/s for a stoichiometric mixture.

In figure 5.4, results are shown from calculations using the Chem1D [40] software, implementing several often used mechanisms: the Smooke reduced mechanism, GRI 2.11, GRI 3.0 and the Warnatz scheme. The Smooke mechanism contains only a limited set of chemical species (16) and reactions, and calculations can therefore be performed in less time than with the other more complex mechanisms. The GRI mechanisms are tuned for use with methane and contain considerably more species (50) and reactions. The Warnatz mechanism contains a C4 mechanism and can therefore be used for hydrocarbons containing up to 4 C-atoms. Since this mechanism is fitted to older measurements with
5.3 Methane

### Table 5.1: Overview of burning velocity measurements (for $\phi = 1.0$) in literature with the technique used, in chronological order.

<table>
<thead>
<tr>
<th>year</th>
<th>author</th>
<th>reference</th>
<th>technique</th>
<th>$S_L$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1961</td>
<td>Karpov</td>
<td>[21]</td>
<td>closed vessel</td>
<td>35.1</td>
</tr>
<tr>
<td>1968</td>
<td>Lindow</td>
<td>[32]</td>
<td>nozzle burner</td>
<td>42.1</td>
</tr>
<tr>
<td>1970</td>
<td>Edmondson</td>
<td>[16]</td>
<td>flat flame, heat extraction</td>
<td>35.7</td>
</tr>
<tr>
<td>1971</td>
<td>Reed</td>
<td>[37]</td>
<td>nozzle burner</td>
<td>39.7</td>
</tr>
<tr>
<td>1972</td>
<td>Andrews</td>
<td>[1]</td>
<td>closed vessel</td>
<td>42.6</td>
</tr>
<tr>
<td>1972</td>
<td>Günther</td>
<td>[19]</td>
<td>flat flame</td>
<td>41.5</td>
</tr>
<tr>
<td>1984</td>
<td>Wu &amp; Law</td>
<td>[49]</td>
<td>stagnation/bunsen flame</td>
<td>39.2</td>
</tr>
<tr>
<td>1986</td>
<td>Iijima</td>
<td>[20]</td>
<td></td>
<td>34.9</td>
</tr>
<tr>
<td>1988</td>
<td>Kawakami</td>
<td>[22]</td>
<td>closed vessel, zero gravity</td>
<td>34.5</td>
</tr>
<tr>
<td>1989</td>
<td>Egolfopoulos</td>
<td>[17]</td>
<td>counterflow</td>
<td>40.0</td>
</tr>
<tr>
<td>1993</td>
<td>Law</td>
<td>[29]</td>
<td>counterflow</td>
<td>40.5</td>
</tr>
<tr>
<td>1994</td>
<td>van Maaren</td>
<td>[47]</td>
<td>flat flame, heat flux</td>
<td>37.0</td>
</tr>
<tr>
<td>1995</td>
<td>Clarke</td>
<td>[9]</td>
<td>closed vessel</td>
<td>36.8</td>
</tr>
<tr>
<td>1997</td>
<td>Chao</td>
<td>[8]</td>
<td>counterflow, stretch corrected</td>
<td>34.9</td>
</tr>
<tr>
<td>1998</td>
<td>Vagelopoulos</td>
<td>[42]</td>
<td>counterflow, ultralow strain</td>
<td>36.7</td>
</tr>
<tr>
<td>2000</td>
<td>Gu</td>
<td>[18]</td>
<td>closed vessel</td>
<td>36.8</td>
</tr>
<tr>
<td>2002</td>
<td>This work</td>
<td></td>
<td>flat flame, heat flux</td>
<td>35.7</td>
</tr>
</tbody>
</table>

Table 5.2: Overview of calculation results using Chem1D for the burning velocity $S_L$ at $\phi = 1.0$ with several mechanisms.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>$S_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smooke</td>
<td>37.3</td>
</tr>
<tr>
<td>GRI 2.11</td>
<td>37.8</td>
</tr>
<tr>
<td>GRI 3.0</td>
<td>36.8</td>
</tr>
<tr>
<td>Warnatz</td>
<td>38.2</td>
</tr>
</tbody>
</table>

higher $S_L$ values, it results in burning velocities that are higher than what typical recent experiments suggest. Table 5.2 contains an overview of calculation results at $\phi = 1.0$ for convenient comparison.

5.3.1 Temperature dependence

The dependence of burning velocity on the initial mixture temperature is determined for methane/air mixtures at three equivalence ratios in a range up to 353 K. This is a rather limited range compared to available data in literature (up to 750 K), restricted by the present design of the heat flux equipment; the unburnt gas mixture is led through a heat exchanger immersed in the same water that is used to keep the plenum chamber at
constant temperature. Using this water circuit as a heating medium limits the maximum inlet temperature to 373 K, and in practice even lower due to losses in ducts and pipes. Furthermore, for the application of the heat flux method as described in this thesis, using interpolation, it is necessary that the water jacket keeps the edge of the burner plate at a higher temperature than the unburnt gas temperature. It turned out that an inlet temperature of 353 K is the maximum achievable with the present setup. When doing future experiments with higher temperatures, not only the water needs to be exchanged as a heating medium, but also the construction materials need to be adapted to withstand temperatures up to 700 K.

Figure 5.5 shows the measured temperature dependence of the methane/air burning velocity at equivalence ratios of 0.80, 1.00 and 1.20 respectively. Also included are correlations by Metghalchi and Keck [34], of the following form:

\[ S_L = S_{L,0} \left( \frac{T_w}{T_0} \right)^{\alpha_T} \left( \frac{p_w}{p_0} \right)^{\beta_P}. \]  

(5.1)

Here, \( S_{L,0} \) is the unstretched laminar burning velocity at the reference temperature and pressure \( T_0 = 293 \) K and \( P_0 = 1000 \) mbar. The parameters \( \alpha_T \) and \( \beta_P \), which depend on \( \phi \), are determined by fitting to experimental data. The values for these parameters are taken over from Gu [18], so the lines actually represent the best fits through the measure-
5.4 Ethane

Measurements of the burning velocity of ethane/air mixtures are not so numerous in literature as methane. Data by Warnatz [48] are available, and Egolfopoulos [17] provides another more recent data set. Konnov [25] performed a set of ethane measurements on a copy of the present heat flux equipment.

Figure 5.7 shows the measurement data as well as a calculation by Warnatz. Since the chemical mechanism used in this calculation is based on early measurements, also shown in the same figure, it results in a rather high value for the burning velocity when compared to the heat flux results. Considering the convergence of the methane mea-
measurements towards a value within a small range, it can be concluded that the heat flux results represent a more accurate value for the unstretched burning velocity than the older measurements.

The good agreement of the measurements with the data by Konnov [25] show that it is possible to reproduce the results not only in the same setup, but also in a newly built copy of the setup, indicating that all major factors contributing to systematic errors are understood and accounted for.

The present measurements also coincide with data by Egolfopoulos [17], which appears somewhat strange since this measurement set by Egolfopoulos shows higher values for methane and propane, as compared to the heat flux results (figures 5.2 and 5.8). In section 5.7, a comparison of the data set as a whole is made. Table 5.3 shows the values for $\phi = 1.0$ for the ethane data shown in figure 5.7.

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Figure 5.6: Temperature dependence of methane/air burning velocity in the range 290–380 K for a stoichiometric mixture, comparison with other experiments. Line: correlation by Metghalchi and Keck [34], with parameters by Gu [18].
5.5 Propane

Because propane is an often used fuel in for example engines, more data are available than for ethane. An overview using a lot of data is shown in figure 5.8. As is the case with the methane measurements, a considerable amount of scatter exists due to the neglect of stretch effects in the past. In table 5.4, values for stoichiometric mixtures are given as found by the various authors. Again, the tendency is that the heat flux method gives a value that is lower than most of the older measurements.
74 Results for lower alkanes

Figure 5.8: Adiabatic burning velocity of propane.

<table>
<thead>
<tr>
<th>year</th>
<th>author</th>
<th>reference</th>
<th>technique</th>
<th>$S_L$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1952</td>
<td>Singer</td>
<td>[39]</td>
<td>Burner</td>
<td>47.1</td>
</tr>
<tr>
<td>1959</td>
<td>Gibbs</td>
<td></td>
<td></td>
<td>46.1</td>
</tr>
<tr>
<td>~1960</td>
<td>Warnatz</td>
<td>[48]</td>
<td></td>
<td>47.4</td>
</tr>
<tr>
<td>1963</td>
<td>Kuehl</td>
<td>[27]</td>
<td></td>
<td>38.1</td>
</tr>
<tr>
<td></td>
<td>Lavoie</td>
<td>[28]</td>
<td></td>
<td>38.1</td>
</tr>
<tr>
<td>1989</td>
<td>Egolfopoulos</td>
<td>[17]</td>
<td>counterflow</td>
<td>43.6</td>
</tr>
<tr>
<td>1993</td>
<td>Law</td>
<td>[29]</td>
<td>counterflow</td>
<td>44.1</td>
</tr>
<tr>
<td>2002</td>
<td>This work</td>
<td></td>
<td>heat flux</td>
<td>39.5</td>
</tr>
</tbody>
</table>

Table 5.4: Overview of burning velocity measurements for $\phi = 1.0$ for propane/air mixtures

5.6 $n$-butane and iso-butane

For butane, a comparison can be made with the fairly recent data set by Davis[11], who measured burning velocities for both $n$-butane and iso-butane. Also Warnatz presented some data, as well as calculations based on these data, for $n$-butane. The results and
An interesting comparison with literature would be the ratio of the burning velocities of the lower alkanes. However, this is difficult because the differences in the burning velocities are of the same order of magnitude as the differences that are found by using several techniques. Therefore, to make such a comparison, the best way is to find a set of measurements, all performed using the same technique, and compare the results by considering the ratios $S_{L, \text{literature}} / S_{L, \text{heatflux}}$ for each alkane, at the reference equivalence ratio $\phi = 1.0$. This comparison is presented in table 5.5, where data by Warnatz [48] and Egolfopoulos [17] are used. As already shown previously in this chapter, the results by Warnatz are systematically higher than the heat flux results. However, the ratio of both methods is consistent within reasonable margins. The comparison with data by
Egolfopoulos [17] shows that the ratios for methane and propane are the same, but significantly different for ethane. Considering the consistency in the order of the heat flux data with the Warnatz data, it seems plausible to assume that a systematic error exists in the ethane part of the Egolfopoulos measurement set.

### Table 5.5: Comparison of $S_L$ ($\phi = 1.0$) with data by Warnatz [48] and Egolfopoulos [17].

<table>
<thead>
<tr>
<th>fuel</th>
<th>heat flux</th>
<th>Warnatz ratio</th>
<th>Egolfopoulos ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>35.7 ± 0.5</td>
<td>41.8</td>
<td>40.0</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>40.7 ± 0.5</td>
<td>51.0</td>
<td>40.2</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>39.5 ± 0.5</td>
<td>47.4</td>
<td>43.6</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>37.1 ± 0.5</td>
<td>44.0</td>
<td>1.19</td>
</tr>
<tr>
<td>iso-C$<em>4$H$</em>{10}$</td>
<td>33.4 ± 0.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.8 Conclusions

The heat flux method has been successfully applied to a set of lower alkanes as a function of equivalence ratio. The initial temperature of the fuel/air mixtures is 295 K, except for methane where also measurements up to 353 K were performed, at equivalence ratios 0.80, 1.00 and 1.20. The typical uncertainty in the determination of the adiabatic burning velocity $S_L$ is ±0.5 cm/s for measurements around $\phi = 1.0$, and increases up to 1.0 cm/s for flames where the heat release is smaller (i.e. $\phi < 0.7$ and $\phi > 1.3$). Because the burning velocities and heat releases are similar for all fuels investigated, this typical uncertainty holds for all of them.

Comparison with available literature data shows that the heat flux results are consistent with results by other techniques such as the counterflow or the closed vessel technique, provided that a proper correction is made in those experiments to account for stretch effects, which is the case with the more recent measurements (Vagelopoulos [42]).

For methane, where most data are available, it can be seen clearly that the scatter is reduced when comparing only recent measurements. The results converge towards a value around 36 cm/s, which is lower than most of the older measurements.
Chapter 6

Extension of the heat flux method to low pressures

6.1 Introduction

As shown in chapter 5, the heat flux method with the introduced improvements provides a well defined adiabatic flame and yields consistent results for the adiabatic burning velocity for lower hydrocarbons. These measurements were all performed at atmospheric pressure, for which the burner was originally developed by van Maaren. However, there is an interest to extend the working range of the heat flux method, both to high pressure and low pressure. High pressures are of practical interest because of the application of combustion in numerous practical appliances, for example engines and gas turbines. On the other hand, low pressures are more of scientific interest. Application of laser diagnostic experiments, for example the quantification of LIF and Cavity Ring Down Spectroscopy are attempts to gain a more thorough understanding of the details of combustion kinetics. Both techniques can be developed better in low pressure flames. First, in the case of LIF, the collisional quenching vanishes at low pressure, the most difficult phenomenon to account for when interpreting LIF in a quantitative way. Second, the flame front widens at low pressure: instead of a flame front of typically 0.5 mm at atmospheric pressure, in which the interesting processes take place, the flame front broadens to a few millimeters, which can be considered as a more convenient way to investigate this area. Furthermore, reaction mechanisms that are used as the basis for calculations are often based on fits to low pressure measurements, but experiments with the heat flux method were never performed in this region. Certainly, it is interesting to compare measurements with the heat flux method to results from other techniques in lower pressure flames. To this end, adaptations to the setup need to be introduced to be able to yield the adiabatic burning velocity with sufficient accuracy, and to be aware of possible sources of systematic errors connected to the extended range of operation.

In this chapter, first the region of interesting pressures is defined and the new setup
is described in section 6.2. Following up to the sensitivity analysis in chapter 3, the necessary modifications to the burner plate are discussed for a sufficient accuracy to be reached in section 6.3. The problem of fuel diffusion at low pressures, leading to systematical errors, is discussed in section 6.4, followed by some typical measurements in section 6.5. To show the influence of the burner heads, both measurements with a brass burner head and a steel burner head are shown and compared in section 6.6, especially regarding their sensitivity, as defined earlier in section 3.4. In section 6.7 the results are compared with other measurements as well as calculations.

6.2 Setup

Many experimentally fitted correlations exist for the pressure dependence of the burning velocity \( S_L \). As a first-order estimate, the following is generally assumed for stoichiometric methane/air flames [1]:

\[
S_L \sim p^{-1/2},
\]  

(6.1)

which states that the burning velocity \( S_L \) increases when the pressure is reduced. For the low pressure setup, where the range of interest is focused on 100–1000 mbar, this means that the MFC dimensions should be adapted to be able to maintain a reasonable accuracy; the mass flow rate scales with the pressure, and accounting for equation (6.1) results in smaller mass flows \( \sim p^{1/2} \), and thus smaller dimensioned MFC’s. The setup previously described in chapter 3 was adapted for low pressure by building the burner into a low pressure vessel and making the necessary adaptations for burning under low pressure circumstances. The setup is shown schematically in figure 6.1, where some parts that are identical to the atmospheric version shown previously are omitted: the thermostat controllers, the mixing panel with MFC’s and the interface to a PC.

The low pressure vessel is based on rectangular aluminium plates with a thickness of 30 mm, which has the advantage that it can be made in-house. The disadvantage of having many seals, all of which suffer from leaking, is acceptable because the pressure range where the vessel is operated does not require a very tight vacuum — in fact, the pressure range to 100 mbar is generally not even considered a vacuum.

Ignition of the gas mixture is achieved by a Tantalum wire heated by an electrical current of typically 20 A. The igniter wire can be rotated so it will not disturb the flame once it is ignited. A spark igniter was avoided, because the power supplies can cause strong induction currents which could disturb delicate electronic circuits such as those used in MFC’s.

The pressure is stabilized by the combination of a pressure gauge, excess pumping of burnt gases and an additional MFC for air to compensate for the pressure loss due to excess pumping. The MFC and pressure gauge are part of a control circuit where the setpoint of the pressure gauge is kept constant while varying the flow through the MFC (max. 2 L\(_L\)/min). To be successful, the excess pumping needs to be roughly set by adjusting a needle valve between the vessel outlet and the pump. This pressure control can be operated in the range 10 to 200 mbar.
Three windows (10 mm thickness quartz) are built into the vessel walls to observe the flame. The length of the windows is 100 mm, corresponding to the maximum variation in height that can be achieved with the vertical translation stage to which the burner is attached.

Several connections are made in the bottom of the vessel for water (hot and cold), gases (one for the mixture, one for the controlling air flow) and thermocouple wires (one for all wires). The burnt gases are fed through a heat exchanger before entering the pump. The heat exchanger is kept at a temperature of around 50°C, to avoid condensation of water on the vessel walls.

Because the pressure at the downstream side of the MFC’s is lowered, several calibra-
tions with the flow piston prover setup (appendix G) are carried out varying the pressure difference over the MFC to study the effect of large pressure drops on the performance. The downstream pressure was necessarily kept at atmospheric pressure, but since the mass flow primarily depends on the pressure difference, this is not considered a problem. Variation of the inlet pressure from 2 to 8 bar showed that the flow is only weakly affected (typically 1 % in this range). These experiments are described in more detail in appendix G.

Another concern at low pressure is the fact that the heat flux from the flame to the burner plate is lower than at atmospheric conditions. This means that the sensitivity of the heat flux method decreases with a larger uncertainty as a result. To circumvent this, a new burner plate is made for low pressure experiments. By choosing steel, with a lower heat conductivity, and making the plate thinner, the sensitivity is increased.

6.3 The burner plate

Because of the use of stainless steel, some limitations exist compared to the brass burner plate: the steel plate is thinner (to reach a reasonable manufacturing time) and cannot be used as a part of a thermocouple such as in the brass case. Therefore, only the conventional configuration for thermocouple measurements, as explained in section 3.3.1 is available. Furthermore, due to the thickness of only 1 mm, the small cylinders as described in section 3.3.3 cannot be used. Therefore, a relatively large scatter is to be expected for measurements using a steel burner plate. The pressing ring, as described in section 3.3.4 was not used in the steel version of the burner head as the fit of the burner plate in the head appeared to be very tight.

6.3.1 Cold flow measurements

As an initial test of the performance with the steel burner plate, the temperature distribution is determined for a range of air flows, at atmospheric pressure, without a flame. Results of these experiments are shown in figure 6.2. As compared to the equivalent measurements for brass, the temperatures are lower than with brass, as expected due to the lower heat conduction coefficient of steel. For high velocities, the temperature in the center of the burner plate even approaches the inlet temperature (23 °C). Because the temperature difference is much smaller here, the heat transfer from the plate to the air flow decreases, and the assumption of a constant heat flux $q$ over the entire burner plate is not valid. This can be seen in figure 6.2, where the measured temperatures at higher inlet velocity do not nicely fit a parabola anymore, but are flattened out in the center region. This becomes even better visible when plotting the parabolic coefficients from the fits to the measurements, as shown in figure 6.3. For velocities above 12 cm/s, the parabolic coefficient in the steel burner plate does not increase anymore. Since the parabolic fit is not applicable in these circumstances, the procedure of fitting is actually meaningless here. To compare the sensitivities of both burner plates, the slopes of both lines in figure 6.3 are determined. In the case of the steel burner plate, only the data for velocities lower
6.3 The burner plate

Figure 6.2: Temperature distribution with only a cold flow present. Symbols: measurements, lines: parabolic fits. Note the distortion of the parabola for higher inlet velocities.

Figure 6.3: Comparison of parabolic coefficients in a cold flow as a function of inlet velocity, for a brass and a steel burner plate.

than 12 cm/s are taken into account. The ratio of the slopes is 9.4; this number reflects the ratio of sensitivities and can be estimated easily, since the dependence on relevant quantities of the parabolic coefficient $a_2$ is given by

$$a_2 \propto q/((he \lambda)) \propto h \cdot f(v)/(he \lambda) = f(v)/(e \lambda), \quad (6.2)$$

where $q$ is the heat transfer from the gas to the plate, $h$ the plate thickness, $\lambda$ the heat conductivity of the plate material and $e$ the ratio of horizontal and vertical conductivity, as defined earlier in chapter 3. In the case of a cold flow, the heat transfer $q$ is proportional to the plate thickness $h$, and it depends on the velocity with a function $f(v)$, which is
assumed to be the same for both burner plates. Note that \( h \) cancels in equation (6.2): for a cold flow, the parabolic coefficient \( \alpha_2 \) does not depend on the plate thickness. For the ratio of sensitivities, it follows that it is proportional to the heat conductivity only, since both \( f(v) \) and \( \epsilon \) are identical for the two investigated burner plates. For 300 K, the heat conductivities for brass and steel are 125 W/(mK) and 13 W/(mK), respectively. The ratio is 9.6, close to the value found by comparing the slopes in figure 6.3. For a cold flow, it can be concluded that the difference in sensitivities of the burner plates is according to the expectation. Note that when a flame is present, most of the heat transfer will be around the downstream side of the burner plate (Rook [38]). Therefore, the plate thickness \( h \) will not cancel from equation (6.2), and \( \alpha_2 \sim 1/(h\lambda e) \).

6.3.2 Thermocouple behaviour

In chapter 3, it was analyzed how the deviations of the thermocouple measurements from the fitted parabola (the residuals) can be explained and used for correction: the residual is a linear function of the parabolic coefficient \( \alpha_2 \). This was checked in a range of equivalence ratios. By using the results of these measurements, a linear correction function for each separate thermocouple is determined, which is used to reduce the scattering around the fit. Although this does not change the measured burning velocity significantly, the uncertainty associated with the measurement is reduced. Since the correction method only depends on the parabolic coefficient, the correction is expected to be the same at lower pressures. This is checked for both the brass and steel burner plate. Typical residuals are shown in figures 6.4 and 6.5 for brass and steel, respectively. The data originate from experiments in the range 80–200 mbar. The residuals in the brass burner plate are

![Figure 6.4: Typical thermocouple residual for the brass burner plate in the pressure range 80–200 mbar.](image)

of the same type as at atmospheric pressure: roughly linear with the parabolic coefficient \( \alpha_2 \), such as was shown in figure 3.12. The coefficients describing the residuals in the steel plate are an order of magnitude larger than for the brass plate. The primary reason is the
lower heat conductivity of steel, causing a larger vertical gradient. A second reason is that the thermocouples are not attached using the method with small cylinders described in section 3.3.3. Therefore, the upper surface of the thermocouples, consisting of the silver containing glue, is rough and can be different for each thermocouple, resulting in a locally different effective heat transfer coefficient from the plate to the thermocouple. This becomes more important when the temperature gradient just above the burner plate is larger, thus when the flame standoff distance decreases, which is the case when the pressure increases. Therefore, it is observed that the scatter around the fit becomes larger in the range 160–200 mbar. When the flame is effectively blown off, the scatter is considerably less, because there is no large temperature gradient above the burner plate as is the case with a stabilized flame with large heat loss.

Despite the relatively large scatter, the correction method of section 3.3.5 will be applied when analyzing the measurements with the steel burner plate, as it reduces the scatter considerably.

6.4 Fuel diffusion

At low pressure, the flames observed are not always perfectly flat. Typically, it is seen that the flame has a higher standoff distance at the edges as shown in figure 6.6a. When the unburnt gas velocity is increased, the flame becomes (at least visually) flat. The thermocouple measurements show that in this case the flame is superadiabatic \((u > S_L)\). Increasing the velocity further does not immediately lead to blow-off, as in the atmospheric case, but results in a curved flame (figure 6.6). In fact, the flow is adapted to create a flame with a larger surface, and therefore the burning velocity in the flame is lower than the average flow velocity just above the burner plate. The increased standoff distance \(\delta\)
extension of the heat flux method to low pressures

Figure 6.6: Typical flame shapes above the burner plate at a pressure of 100 mbar. Upper left: stabilized \((u < S_L)\), lower left: visually flat but superadiabatic \((u > S_L)\), lower right: blown off \((u >> S_L)\).

At low pressure leads to a concern for the radius of the 1D area, because with increasing distance of fuel diffusion into the surrounding, the 1D area will decrease. A rough estimate can be made of this effect by considering the one-dimensional fuel concentration \(C\) in a diffusion process with initial concentration \(C(\xi, t)\) given by

\[
C(\xi, 0) = \begin{cases} 
0 & \xi < 0 \\
C_0 & \xi > 0 
\end{cases}
\]  

(6.3)

where \(\xi\) is the coordinate from the edge to the center of the burner plate. At the edge of the burner plate, \(\xi = 0\). Since an effect near the edge of the burner plate is considered, the diffusion equation is considered in cartesian coordinates, neglecting the cylindrical symmetry. As boundary condition, \(C(0, t) = 1/2C_0\) is assumed. The solution of the diffusion equation is then given by the error function

\[
\frac{C(\xi, t)}{C_0} = \frac{1}{2} + \frac{1}{2} \text{erf} \left( \frac{\xi}{2 \sqrt{D t}} \right),
\]  

(6.4)

with \(D\) the diffusion coefficient. By good approximation, assuming ideal gas behaviour, \(pD\) is constant, with \(p\) the pressure. A typical value is \(pD = 1.5\) Pa m²/s. Substituting \(t = \delta/v\), with \(v\) the unburnt gas velocity, and an estimate for the standoff distance \(\delta = D/v\), equation (6.4) can be rewritten as

\[
\frac{C(\xi, t)}{C_0} = \text{erf} \left( \frac{\xi}{2 \sqrt{1.5\delta}} \right) = \text{erf} \left( \frac{\xi \nu \rho}{3} \right),
\]  

(6.5)

from which it can be concluded that the critical diffusion width \(\xi_0\) scales with \(\sim 1/\sqrt{p}\), if \(\nu = S_L \sim p^{-1/2}\) is used. In figure 6.7, the concentration is shown for atmospheric pressure and for 100 mbar. At lower pressure, the fuel concentration drop near the edge of the flow is considerably larger than at atmospheric pressure, caused by a higher diffusion coefficient \(D\) and the larger standoff distance \(\delta\). Since the 1D area is starting at
6.4 Fuel diffusion

\( \xi = 5 \text{ mm}, \) the concentration drop due to diffusion becomes a serious concern at low pressure.

When significant fuel diffusion occurs, the flame is effectively blown off near the edge of the burner plate. This causes a distortion of the net heat flux distribution to the burner plate for a flame near the adiabatic state. Near the edge the heat flux is negative: the unburnt gas mixture is heated by the burner plate but due to the blown-off state of the flame in this region there is no heat gain from the flame. In the inner region of the burner plate the flame is stabilized and the net heat flux is positive. Since one of the basic assumptions of the heat flux method is that the net heat flux \( q \) is uniform over the burner plate, a systematic error in the measurements can be expected.

To estimate this error, a situation is considered where the net heat flux \( q \) is not a constant over the entire burner plate, but a function of radius \( r \):

\[
q(r) = \begin{cases} 
q_i & r < r_d \\
q_e & r_d < r < R 
\end{cases}
\]

(6.6)

Here, \( q_i \) is the heat flux in the “inner” area and \( q_e \) is the heat flux in the area near the edge of the burner plate. \( R \) is the radius of the burner plate and \( r_d \) is the radius where the heat flux is assumed to change. This radius can be estimated using equation 6.5. For example, figure 6.7 shows that \( r_d \approx 10 \text{ mm} \) for 100 mbar. Since the flame is blown off at the edge and stabilized in the inner area, \( q_e < 0 \) while \( q_i > 0 \). This approximation is rather rough, but adequate for the purpose of determining the order of magnitude of the error expected in the low pressure measurements. The temperature distribution in the burner plate can now be written as

\[
T(r) = \begin{cases} 
T_i - q_i / (4\varepsilon \lambda h) \cdot r^2 & r < r_d \\
T_e - q_e / (4\varepsilon \lambda h) \cdot r^2 + c \ln(r/r_0) & r_d < r < R 
\end{cases}
\]

(6.7)
consisting of a parabolic function according to equation (2.5) in the inner area, and a solution to equation (2.4) near the edge. Because the symmetry condition is not required for \( r_d < r < R \), a logarithmic term occurs. The constants \( T_i, T_e \) and \( c \) are chosen such that both the temperature and the temperature gradient are continuous in \( r = r_d \), and that the edge temperature \( T(R) \) equals the prescribed temperature. In the heat flux method, the flame is considered adiabatic when the net heat flux is zero. In the case of fuel diffusion, this condition is found when

\[
\int_0^{r_d} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) dr = - \int_{r_d}^{R} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) dr, \tag{6.8}
\]

or

\[
r_d^2 q_i = -q_e (R^2 - r_d^2). \tag{6.9}
\]

Therefore, the heat flux in the stabilized flame area can be expressed as

\[
q_i = -q_e \left( 1 - \frac{R^2}{r_d^2} \right). \tag{6.10}
\]

The heat gain \( q_e \) in the edge region can be estimated using the cold flow measurements in section 6.3.1

\[
q_e = 4e \lambda h a_e, \tag{6.11}
\]

with \( a_e \) the parabolic coefficient corresponding to the unburnt mixture velocity in a cold flow. Combination of eqs. 6.10 and 6.11 gives for the parabolic coefficient \( a_i \) in the inner region

\[
a_i = \frac{q_i}{4e \lambda h} = a_e \left( 1 - \frac{R^2}{r_d^2} \right). \tag{6.12}
\]

Using the sensitivity \( s \), as defined by (3.30), an error estimate for the burning velocity is given by

\[
\Delta S_L = \frac{a_i}{s} = \frac{a_e}{s} \left( 1 - \frac{R^2}{r_d^2} \right). \tag{6.13}
\]

Substituting typical values for a \( 100 \text{ mbar} \) measurement into equation 6.13, \( R = 15 \text{ mm} \), \( r_d = 10 \text{ mm} \), \( a_e = 0.1 \text{ K/mm}^2 \) and \( s = 0.02 \text{ K mm}^{-2} \text{sm}^{-1} \), the result is \( \Delta S_L = -6 \text{ cm/s} \). This means that the measurement result will be around \( 6 \text{ cm/s} \) lower than the actual adiabatic burning velocity, which is unacceptably high for an accurate measurement.

### 6.5 Typical measurements

Both the brass version and the steel version of the burner plate were used to perform low pressure measurements. With the brass burner plate, measurements from 1 bar down to \( 100 \text{ mbar} \) were carried out. The range of the steel burner plate was limited to a range from 100 to \( 200 \text{ mbar} \); because of the low heat conductivity of steel, the burner plate would risk to overheat and bend at pressures higher than \( 200 \text{ mbar} \).
Typical measurements for both the brass and steel plate are shown in figures 6.8 and 6.9, for a comparable set of unburnt gas velocities, both at a pressure of 100 mbar. The measurement in the steel burner plate is corrected for the vertical gradient. Two differences are clear immediately: first, the temperature variations with velocity are much higher with the steel burner plate, i.e. the sensitivity is larger, as expected. Second, the temperature at the edge of the burner plate is constant for steel, while it varies in the case of the brass burner plate. This is because of the pressing ring, described in chapter 3, that was present on the brass burner, but not on the steel version. However, it does not influence the parabolic coefficients that are used to determine the adiabatic burning velocity.
To gain insight in the behaviour of the flame at low pressure, a series of measurements is performed at 100 mbar while varying the unburnt gas velocity from 30 cm/s to 120 cm/s, a range that is far larger than necessary for determining the burning velocity. The parabolic coefficient of the temperature profiles in the burner plate is shown in figure 6.10 for a flame at 100 mbar. Compared to the atmospheric case (figure 3.16), it can be seen that the “blow-off” state lasts much longer, due to the surface increase of the flame as shown in figure 6.6a. Due to the high velocity here (v >> S_L), the flame is not stabilized on the burner anymore. The temperature distribution in the burner plate in this region is caused mainly by the unburnt gas mixture passing. The behavior of the parabolic coefficient a_2 as a function of v is approximately linear in this region. The visually flat flame (figure 6.6b) is observed when the flame is superadiabatic, typically around v = 60 cm/s. In the region of interest for measuring burning velocities, 40–55 cm/s, the flame is curved towards the burner plate, as shown in figure 6.6a. As explained earlier, this is attributed to the diffusion of fuel into the surrounding, reducing the 1D area.

6.6 Sensitivity

As shown in section 3.3.5, the sensitivity is an important quantity in determining the uncertainty of the measurement. In figure 6.11, the sensitivity coefficient s, as defined in section 3.3.5, is plotted for the brass burner plate in the entire pressure range from 100 to 1000 mbar. From atmospheric pressure to 100 mbar, the sensitivity is reduced more than an order of magnitude. This implies that the uncertainty associated with the adiabatic burning velocity measurements is increased by an order of magnitude. Since the typical uncertainty at 1000 mbar (around φ = 1.0) is 0.5 cm/s, the expected uncertainty at 100 mbar is around 5 cm/s for brass. For the low pressure range 80–200 mbar, the sensitivity is shown for both the brass and steel burner plate in figure 6.12. The sensi-
6.7 Results

In Figure 6.13, the burning velocity measurements are shown for both the brass and steel burner plate, in the whole pressure range 80–1000 mbar, as well as a Chem1D calculation.
using the GRI 2.11 mechanism. The first thing that is obvious from these results is the sharp decrease of the measurement results for $S_L$ below a pressure of 200 mbar. This decrease is not present in the GRI calculation results, and it is therefore attributed to the fuel diffusion described previously in section 6.4. The order of magnitude of 6 cm/s that the heat flux method would underestimate according to that analysis seems consistent with the observed fall-off of the data below 200 mbar. Therefore, it would be necessary to work around this effect in the future if more accurate measurements are performed in this pressure range. For the pressure range $> 200$ mbar however, the agreement between the measurement data and the calculations is very well, apart from a slight overprediction by the calculations at pressures near 1000 mbar.

![Graph showing burning velocity $S_L$ at low pressure determined with the heat flux method for a stoichiometric methane/air flame. Line: GRI 2.11 based measurements.](image)

6.8 Conclusions

The heat flux method has been operated in the pressure range 80–1000 mbar. It is shown that the sensitivity of the method decreases rapidly with pressure and therefore another burner plate material (steel) is necessary to keep the uncertainties in an acceptable range. The diffusion of fuel into the surrounding, together with the increased stand-off distance at low pressure, causes a reduction of the 1D area and therefore visible disturbances in the flame shape. This is the main reason that the measurements fall off dramatically at pressures below 200 mbar. Applying the heat flux method in this pressure range would
require a circumvention of the problem, for example by increasing the burner radius or preventing the fuel diffusion to take place.
Extension of the heat flux method to low pressures
Nomenclature

\( \alpha_2 \) \hspace{1em} \text{parabolic coefficient} \hspace{1em} \text{K/m}^2
\( A \) \hspace{1em} \text{area} \hspace{1em} \text{m}^2
\( c \) \hspace{1em} \text{heat capacity} \hspace{1em} \text{J/(kg K)}
\( C \) \hspace{1em} \text{concentration} \hspace{1em} \text{m}^{-3}
\( d_h \) \hspace{1em} \text{hole diameter} \hspace{1em} \text{m}
\( d_k \) \hspace{1em} \text{wire diameter} \hspace{1em} \text{m}
\( D \) \hspace{1em} \text{diffusion coefficient} \hspace{1em} \text{m}^2 / \text{s}
\( e_S \) \hspace{1em} \text{Seebeck coefficient} \hspace{1em} \text{V/K}
\( E \) \hspace{1em} \text{energy} \hspace{1em} \text{J}
\( f_{x_2} \) \hspace{1em} \text{air factor} \hspace{1em} \text{1}
\( h \) \hspace{1em} \text{burner plate thickness} \hspace{1em} \text{m}
\( h \) \hspace{1em} \text{distance} \hspace{1em} \text{m}
\( k_p \) \hspace{1em} \text{Planck absorption coefficient} \hspace{1em} \text{1}
\( M \) \hspace{1em} \text{molar mass} \hspace{1em} \text{kg/mol}
\( N_u \) \hspace{1em} \text{Nusselt number} \hspace{1em} \text{1}
\( p \) \hspace{1em} \text{pressure} \hspace{1em} \text{Pa}
\( P \) \hspace{1em} \text{heat flux} \hspace{1em} \text{W}
\( Pr \) \hspace{1em} \text{Prandtl number} \hspace{1em} \text{1}
\( q \) \hspace{1em} \text{mass flow} \hspace{1em} \text{kg/s}
\( Q \) \hspace{1em} \text{mass flow} \hspace{1em} \text{L}_m / \text{min}
\( Q \) \hspace{1em} \text{heat} \hspace{1em} \text{J}
\( r \) \hspace{1em} \text{radius} \hspace{1em} \text{m}
\( R \) \hspace{1em} \text{radius} \hspace{1em} \text{m}
\( R_0 \) \hspace{1em} \text{gas constant} \hspace{1em} \text{J/(kg mol)}
\( Re \) \hspace{1em} \text{Reynolds number} \hspace{1em} \text{1}
\( s \) \hspace{1em} \text{stoichiometric factor} \hspace{1em} \text{1}
\( s \) \hspace{1em} \text{sensitivity} \hspace{1em} \text{K/m}^2 (\text{m/s})^{-1}
\( S_{\text{MFC}} \) \hspace{1em} \text{MFC setpoint} \hspace{1em} \text{1}
\( S_L \) \hspace{1em} \text{laminar burning velocity} \hspace{1em} \text{m/s}
\( t \) \hspace{1em} \text{time} \hspace{1em} \text{s}
\( T \) \hspace{1em} \text{temperature} \hspace{1em} \text{K or °C}
\( u \) \hspace{1em} \text{velocity} \hspace{1em} \text{m/s}
\( v \) \hspace{1em} \text{velocity} \hspace{1em} \text{m/s}
\( V \) \hspace{1em} \text{voltage} \hspace{1em} \text{V}
$X$  molar fraction  1

Greek symbols

$\alpha$  heat transfer coefficient  $\text{W}/(\text{Km}^2)$
$\alpha$  volumetric heat transfer coefficient  $\text{W}/(\text{Km}^3)$
$\alpha^2$  parabolic coefficient  $\text{K}/\text{m}^2$
$\delta$  standoff distance  m
$\epsilon$  geometric factor  1
$\epsilon$  emissivity  1
$\epsilon$  width of CARS measurement volume  m
$\lambda_y$  heat conduction coefficient  $\text{W}/(\text{Km})$
$\mu$  viscosity  Pas
$\rho$  density  $\text{kg/m}^3$
$\rho_0$  density at 273 K, 101325 Pa  $\text{kg/m}^3$
$\sigma$  uncertainty
$\sigma_{SL}$  uncertainty laminar burning velocity  m/s
$\sigma_{UC}$  uncertainty thermocouple temperature  K
$\phi$  equivalence ratio  1
$\Phi$  heat flux  W
Appendix A

Thermocouples

The “trick” used in a thermocouple is to combine two materials having Seebeck coefficients with opposite signs, causing the voltages created in both wires to add up and make a measurable voltage (in the order of millivolts).

So, considering a thermocouple means applying the basic equation (3.6) twice. Let’s go from ambient temperature $T_a$, the temperature of the measuring device (e.g. a voltmeter or special device), to the temperature $T_{hot}$ to be measured and back through the second wire to $T_a$:

$$V_{tc} = \frac{T_{hot}}{T_a} \int_{T_a}^{T_{hot}} e_A dT + \int_{T_{hot}}^{T_a} e_B dT. \quad (A.1)$$

The two materials are denoted by $A$ and $B$ respectively, and the corresponding Seebeck coefficients are chosen so that $e_A$ and $e_B$ have opposite signs. The voltage generated and measured is $V_{tc}$. Unfortunately, equation (A.1) contains a lot of unknown quantities: of course the temperature $T_{hot}$, but also the ambient temperature $T_a$ and the Seebeck coefficients $e_A$ and $e_B$. These coefficients are not tabulated in literature. Instead, the following relationship can be found, either as a table or as a (polynomial) formula:

$$V_{tc,0}(T_{hot}) = \int_{T_{hot}}^{T_0} e_A dT + \int_{T_0}^{T_{hot}} e_B dT. \quad (A.2)$$

The thermocouple voltage is given as a function of the hot temperature $T_{hot}$, or vice versa, with $e_A$ and $e_B$ as a couple and the temperature $T_0$ as a reference voltage, being $0\,^\circ\mathrm{C}$. The fact that a standard couple of materials is tabulated poses no problem in the case of copper and constantan. However, the reference voltage at $0\,^\circ\mathrm{C}$ makes it necessary to manipulate a bit with (A.1) to get $T_0$ into the equation in order to be able to use the given relationship (A.2). As we will see, this will give rise to the so called cold junction.
compensation. Starting to rewrite (A.1) into

\[
V_{tc} = - \frac{T_a}{T_0} \int_{T_0}^{T_a} e_B dT + \frac{T_{ini}}{T_0} \int_{T_0}^{T_{ini}} e_A dT - \int_{T_a}^{T_{ini}} e_B dT + \int_{T_{ini}}^{T_0} e_A dT, \tag{A.3}
\]

we introduced the reference temperature \( T_0 \) as required for inserting a relationship from literature. Necessarily, to keep the same expression as (A.1), extra terms are introduced to cancel the extension of the integral limits from \( T_a \) to \( T_0 \). Applying (A.2) twice to (A.3), with \( T = T_{hot} \) and \( T = T_a \) leads to

\[
V_{tc} = -V_{tc,0}(T_a) + V_{tc,0}(T_{hot}) = -V_{cj}(T_a) + V_{cj}(T_{hot}). \tag{A.4}
\]

The term \( V_{cj}(T_a) = V_{tc,0}(T_a) \) is called the cold junction compensation. It accounts for the fact that the measurement temperatures in the experiment \( (T_a) \) and in literature \( (T_0 = 0 \degree C) \) are different.

**The conventional configuration**

In the "conventional" configuration of the thermocouples in the burner, five thermocouples are used in the usual straightforward way. The thermovoltage \( V_{tc} \) is determined by a conditioner. In the conditioner, the voltage \( V_{cj}(T_a) \) is added to the measured voltage \( V_{tc} \), giving \( V_{tc,0}(T_{hot}) \), as follows from (A.4):

\[
V_{tc,0}(T_{hot}) = V_{tc} + V_{cj}(T_a) \tag{A.5}
\]

The cold junction compensation \( V_{cj}(T_a) \) is determined electronically in the conditioner itself by measuring the voltage over a temperature dependent diode. The temperature dependence of the diode is known, so with correctly chosen resistors, the cold junction compensation is established. Of course, this compensation only works well for the particular thermocouple type it was designed for. In this case, the user of the conditioner reads a voltage as if the measurement device would be at the reference temperature \( T_0 = 0 \degree C \).

As thermovoltages are rather small (order millivolts) and therefore are easily disturbed, the conditioner converts the voltage \( V_{tc,0}(T_{hot}) \) into a current \((4-20 \text{ mA})\) that can be "transported" to the AD converter of the Multilab interface, a device that connects the experiment with a PC. In the computer program reading the interface, the current is transformed back into the original voltage \( V_{tc,0}(T_{hot}) \). The relationship between voltage and current is set by potentiometers on the conditioner print.

**The differential configuration**

The conventional thermocouple configuration has a disadvantage for the purpose we want to use it; i.e., the determination of temperature differences across a burner plate, as the temperature gradient determines the heat flux through the plate. In the conventional setup, temperature differences are determined by subtracting two temperatures...
both measured by a copper constantan thermocouple. As the difference is rather small in comparison to the absolute temperature, typically 5 to 10 K compared to 300 K, a relatively large error can be expected. Therefore, it is more accurate to measure the differences directly, also because a thermocouple actually is a device for measuring temperature differences.

In the “differential” configuration, one thermocouple is used as described in the previous section: a normal copper constantan thermocouple, called the reference thermocouple. The other couples, however, are formed by a constantan wire connected to the burner plate, made out of brass. Now, the temperature difference with the reference thermocouple can be determined by measuring the voltage over the following “path”: constantan wire of reference couple — brass plate — constantan wire at position to be measured. One disadvantage is that there is in fact a brass constantan thermocouple. This combination of materials is not tabulated in literature and we have to rely on the experiments of van Maaren [44]. Now let’s write down the expression for the generated voltage of the mentioned path:

\[ V_{ic} = \int_{T_a}^{T_{ref}} e_{c,d}dT + \int_{T_{ref}}^{T_0} e_{br}dT + \int_{T_0}^{T_{hot}} e_{c,d}dT. \]  

(A.6)

The Seebeck coefficients \(e_{c,d}\) and \(e_{br}\) are for constantan and brass respectively. \(T_a\) is again the ambient temperature, \(T_{ref}\) the reference temperature at the copper constantan thermocouple and \(T_{hot}\) is the temperature at the brass constantan junction. Again, we have to rewrite equation (A.6) to an expression where we can substitute known relationships, meaning that the integral limits have to start or end with \(T_0\):

\[ V_{ic} = \begin{cases} 
\frac{T_0}{T_a} \left( \int_{T_a}^{T_{ref}} e_{c,d}dT + \int_{T_{ref}}^{T_0} e_{c,d}dT \right) + \frac{T_{ref}}{T_0} \left( \int_{T_0}^{T_{hot}} e_{br}dT \right) - \frac{T_0}{T_a} \left( \int_{T_a}^{T_{ref}} e_{br}dT + \int_{T_{ref}}^{T_0} e_{br}dT \right) - \frac{T_0}{T_{hot}} \left( \int_{T_0}^{T_{hot}} e_{c,d}dT \right). 
\end{cases} \]  

(A.7)

The first and the fifth term in (A.7) cancel. Rewriting to tabulated relationships by combining the second and third terms as well as the fourth and sixth terms yields

\[ V_{ic} = -V_{ic,br,0}(T_{ref}) + V_{ic,br,0}(T_{hot}), \]  

(A.8)

where the index \(br\) denotes brass constantan, 0 means with \(T_0 = 0 \text{°C}\) as reference temperature. \(V_{ic,br,0}(T_{hot})\) is the quantity of interest, and \(V_{ic,br,0}(T_{ref})\) can be calculated when \(T_{ref}\) is known from the reference copper constantan thermocouple. So \(V_{ic}\) remains to be measured.
Thermocouples
Appendix B

Solution of the energy equation

To find an approximation of the solution of equation (3.27), the temperature \( T_p(x, r) \) is written as

\[
T_p(x, r) = Y(x) S(r), \tag{B.1}
\]

separating the temperature into two functions, which only depend on one variable. Substituting (B.1) into the differential equation (3.27) and subsequent separation yields

\[
r^2 \frac{d^2 S(x)}{dr^2} + r \frac{dS(x)}{dr} + \alpha^2 r^2 S(x) = 0 \tag{B.2}
\]

\[
\frac{d^2 Y(x)}{dx^2} = \epsilon \alpha^2 Y(x), \tag{B.3}
\]

where the constant \( \alpha^2 \) is introduced. Equation (B.2) is a special form of the Bessel equation, and its general solution is

\[
S(r) = c_1 J_0(\alpha r) + c_2 Y_0(\alpha r), \tag{B.4}
\]

consisting of the zero order Bessel functions of the first kind \( J_0 \) and of the second kind \( Y_0 \). Because of the symmetric boundary condition, it can be concluded that \( c_2 = 0 \).

The general solution of the differential equation (B.3) for the axial part is

\[
Y(x) = d_1 e^{\sqrt{\alpha} x} + d_2 e^{-\sqrt{\alpha} x}, \tag{B.5}
\]

where the constants \( d_1 \) and \( d_2 \) remain to be determined from the boundary conditions. Applying \( T_p(0, 0) = T_c \) to find \( c_1 \) and using power series expansions for the exponential functions yields

\[
T_p(x, r) = T_c J_0(\alpha r) \left( 1 + \epsilon \alpha^2 h x \right), \tag{B.6}
\]

with \( \epsilon = q_-/q \), assumed to be constant. To find \( \alpha \), the Bessel function is written as

\[
J_0(\alpha r) \approx 1 - \frac{1}{2} (\alpha r)^2, \tag{B.6}
\]

assuming that \( \alpha \) is small (it will turn out later that this is indeed the case). Substitution of this approximation gives

\[
\alpha^2 = \frac{4}{r_0^2} \left[ 1 - \frac{T_0}{T_c} \right]. \tag{B.7}
\]
The final approximation for the temperature distribution can be written as:

\[ T_p(x, r) = T_c \left[ 1 + \alpha \alpha^2 h x \right] \left[ 1 - \frac{1}{4} \alpha^2 r^2 \right]. \]  \hspace{1cm} (B.8)

Substituting typical values into equation (B.7), a typical value for \( \alpha \) can be calculated. With \( r_0 = 15 \text{ mm}, T_0 = 380 \text{ K} \) and \( T_c = 420 \text{ K} \) the result is \( \alpha^2 = 1.7 \times 10^{-3} \text{ mm}^{-2} \). This shows that the earlier assumption that \( \alpha \) is small is justified (\( \alpha = 0.041 \text{ mm}^{-1} \)) and that the approximations by power series are expected to be accurate.
Appendix C

CARS thermometry

CARS, Coherent Anti-Stokes Raman Scattering, is based on the probing of rotational quantum states of the \( \text{N}_2 \) molecule. It will be briefly explained here how the scattering processes lead to a spectrum that contains temperature information.

C.1 Energy of rotation and vibration

C.1.1 Rotational energy

The \( \text{N}_2 \) molecule is a diatomic molecule and can therefore rotate. In standard textbooks on quantum physics, the following expression can be found as a result of solving Schrödinger’s equation for a rigid rotator:

\[
E_r = \hbar c B (J + 1)
\]

\( E_r \) is the rotational energy, \( \hbar \) Planck’s constant, \( c \) the speed of light, \( J \) is the rotational quantum number and \( B \) is the rotational constant, given by

\[
B = \frac{\hbar}{8\pi^2 c I}
\]

where \( I \) is the moment of inertia of the rotator. This relationship is idealized in the sense that a strictly rigid rotator does not exist. Therefore, the following expression is used for dealing with a “physical” rotator, introducing the centrifugal distortion constant \( D \) [14]:

\[
E_r = \hbar c \left[ B (J + 1) - D J^2 (J + 1)^2 \right]
\]

As the second term is a correction term, \( D \) is always much smaller than \( B \).
C.1.2 Vibrational energy

A quantum physical expression can be found for the vibrational energy $E_v$ assuming a harmonic potential:

$$E_v = h\nu(v + \frac{1}{2})$$  \hspace{1cm} (C.4)

where $v$ is the vibrational quantum number and $\nu$ the frequency of the oscillation. As in the rotational case, this expression is corrected by additional (small) terms to account for physical effects that are neglected by the simple harmonic approximation. This leads to the following expression for the vibrational energy \cite{14}:

$$E_v = \hbar\nu \left[ \omega_r(v + \frac{1}{2}) - \omega_r x_r(v + \frac{1}{2})^2 + \omega_r y_r(v + \frac{1}{2})^3 + \ldots \right]$$  \hspace{1cm} (C.5)

where $\omega_r = \nu/c$, usually expressed in cm$^{-1}$ and $x_r$ and $y_r$ are the correction factors.

C.1.3 Rotation-vibration interaction

As a molecule simultaneously rotates and vibrates, the vibration will influence the rotation; a vibration will change the moment of inertia of the molecule and this leads to a change in rotational energy storage. To account for this effect, the rotational constants $B$ and $D$ from equation (C.3) are changed:

$$B = B_e - \alpha_e(v + \frac{1}{2})$$  \hspace{1cm} (C.6)

$$D = D_e + \beta_e(v + \frac{1}{2})$$  \hspace{1cm} (C.7)

where $B_e$ and $D_e$ denote the equilibrium values and $\alpha_e$ and $\beta_e$ are the correction factors, as usually small in comparison with the equilibrium values. Due to this correction terms, the rotational energy of the molecule does not only depend on the rotational quantum number, but also on the vibrational quantum number. Therefore, $\alpha_e$ is called the vibration-rotation interaction constant. It will turn out that this interaction is essential for the application of CARS.

C.2 The scattering processes

CARS is based on several molecule-photon interactions. In this section, the overall energy balance is considered in order to understand the CARS spectra found in experiments.

In figure C.1, the scattering processes are depicted schematically. First, a molecule is brought to a so-called virtual state, after which it falls back to a real state. For the first transition, the molecule absorbs a photon with frequency $\omega_1$. The second transition is stimulated in the experiment by a laser beam matching the frequency $\omega_2$, corresponding
C.2 The scattering processes

Virtual states

\( v = 0 \)

\( v = 1 \)

\( \omega_2 \)

\( \omega_1 \)

\( \omega_3 \)

Figure C.1: The energy level diagram of the scattering processes involved in CARS.

to the energy of the second transition. The second transition brings the molecules to a real state. In CARS, the effective selection rule for both transitions is \( \Delta \nu = +1 \) and \( \Delta J = 0 \). Thus the excited state 2 has, compared to the first state, the same rotational quantum number \( J \) and a vibrational quantum number \( v \) incremented by one. The molecule absorbs again a photon of frequency \( \omega_1 \) and then falls back to the state before the first absorption, emitting a photon of frequency \( \omega_3 \). These photons are collected in the experiment and contain the spectral information of interest.

C.2.1 The energy balance in CARS

Now, we will write down the energy of the emitted photon using the expressions for rotational and vibrational energy mentioned in the previous section. As is conventional in spectroscopy, the energy is expressed in terms of the wavenumber \( 1/\lambda \) (cm\(^{-1}\)). The relationship with the physical energy is rather simple:

\[
1/\lambda = \frac{E}{\hbar c} = F
\]  \hspace{1cm} (C.8)

where the “normalized” energy \( F \) is defined to avoid writing down \( \hbar c \) all the time.
As the molecule returns to its original state, conservation of energy reads

\[ F_3 = F_1 + \Delta F_v + \Delta F_r \]  \hspace{1cm} (C.9)

\( \Delta F_v \) and \( \Delta F_r \) are the energy increases due to the change of vibrational and rotational quantum number, respectively. Although the rotational quantum number \( J \) does not change during the transition, there is a change in rotational energy because the rotational constant \( B \) depends on the vibration quantum number (see equations (C.3) and (C.6)). Using the formula for the vibrational energy (C.5) twice, \( \Delta F_v \) is expressed in the vibrational quantum number \( v \) of the first state:

\[
\Delta F_v = F_{v+1} - F_v \\
= \omega_v(v + \frac{3}{2}) - \omega_v x_v (v + 1)^2 - \omega_v(v + \frac{1}{2}) + \omega_v x_v (v + \frac{1}{2})^2 \\
= \omega_v - 2\omega_v x_v (v + 1) \hspace{1cm} (C.10)
\]

Doing similar for the rotational energy \( F_r \) using (C.3) and taking into account the vibration dependency of \( B \) (C.6) yields

\[
\Delta F_r = F_{v+1,J} - F_{v,J} \\
= \left[ B_v - \alpha_v (v + \frac{3}{2}) \right] J(J + 1) - \left[ B_v - \alpha_v (v + \frac{1}{2}) \right] J(J + 1) \\
= -\alpha_v J(J + 1) \hspace{1cm} (C.11)
\]

For simplicity, the centrifugal distortion correction \( D \) is left out here. Substituting (C.10) and (C.11) in (C.9) leads to

\[ F_3 = F_1 + \omega_v - 2\omega_v x_v (v + 1) - \alpha_v J(J + 1) \]  \hspace{1cm} (C.12)

Obviously, the energy \( F_3 \) of the emitted photon depends on the initial vibration state as well as on the initial rotation state; in the observed spectrum the rotational dependency is seen by the equally spaced peaks, whereas the vibrational dependency can be seen at temperatures above 1000 K: a “hotband” appears at the left hand side of the spectrum, due to the transition \( v = 1 \to v = 2 \).
Appendix D

Tabulated $S_L$ results

Atmospheric measurements

$p_u = 1.0$ bar, $T_u = 295$ K

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$S_L$ (cm/s)</th>
<th>$\phi$</th>
<th>$S_L$ (cm/s)</th>
<th>$\phi$</th>
<th>$S_L$ (cm/s)</th>
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106 Tabulated $S_L$ results

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**Temperature measurements**

$p_u = 1.0$ bar

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Low pressure measurements

Note that for pressures lower than 300 mbar, a large systematic error exists due to fuel diffusion (see section 6.4).

\[ T_u = 295 \text{ K} \]

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Tabulated $S_L$ results
Appendix E

Properties of Materials and Gases

Air ($T = 300$ K) (Handbook of Chemistry and Physics [31]):

\[
\begin{align*}
\text{density } \rho_g &= 1.161 \, \text{kg/m}^3 \\
\text{viscosity } \mu &= 18.6 \cdot 10^{-6} \, \text{Pas} \\
\text{conduction coefficient } \lambda_g &= 26.2 \cdot 10^{-3} \, \text{W/(Km)} \\
\text{heat capacity } c_p &= 1007 \, \text{J/(kgK)}
\end{align*}
\]

Heat conduction coefficients of solid materials:

- **constantan [31]** $\lambda_k = 22 \, \text{W/(Km)}$
- **silver glue [36]** $\lambda_s = 1.57 \, \text{W/(Km)}$
- **brass** $\lambda = 125 \, \text{W/(Km)}$ (average in temperature range)
- **maccor** $\lambda_m = 1.46 \, \text{W/(Km)}$

Properties of water:

\[
\begin{align*}
\text{heat capacity } c &= 4200 \, \text{J/(kgK)} \\
\text{density } \rho &= 1000 \, \text{kg/m}^3
\end{align*}
\]

Properties of fuels (molar mass $M$, normal density $\rho_0$, stoichiometric factor $s_{\text{molar}}$):

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<th>$\rho_0$ [kg/m$^3$]</th>
<th>$s_{\text{molar}}$</th>
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Appendix F

The perforated plate burner

F.1 The burner head

The main dimensions of the improved burner head are shown in figures F.1 and F.2, featuring two separate water jackets. The hot and cold part are isolated using a ceramic ring made of Macor.

Figure F.1: Side view of the burner head
Figure F.2: Top view of the burner head
Appendix G

Mass Flow Controllers

Mass Flow Controllers (MFC’s) are used throughout this work to provide the necessary air and fuel flows to the burner. The devices need to be calibrated on a regular basis (according to the manufacturer every 3 months) to provide an accurate gas mixture. The calibration procedure is described briefly, with typical results. Because low pressure experiments were carried out, the pressure dependence of the MFC’s is investigated.

G.1 Calibration setup

The calibration setup is built around a Flow Piston Prover (FPP, figure G.1) setup from Bronkhorst Hi-Tec, consisting of a quartz tube with a mercury sealed piston. The valve at the outlet is normally open, but during a calibration the valve closes and the flow causes the piston to move upwards. The mercury seal ensures that there is no leakage while the piston can move (almost) frictionless. At the inlet of the tube, pressure and temperature sensors are mounted. The piston movement is timed by five sensors positioned along the tube. The result of a measurement is a volume flow, from which the mass flow follows using the measured actual pressure and temperature. The setup is fully automated using the Bronkhorst Flowbus protocol, with RS232 communication to a PC using DDE (Dynamic Data Exchange) server software. The setup consists of two FPPs, one for small flows up to $1 \, \text{L}_n/\text{min}$ and a larger one for flows up to $10 \, \text{L}_n/\text{min}$. A typical MFC calibration is carried out by the following procedure:

1. A large series of calibrations (typically 30) at constant setpoint, to ensure that the MFC delivers a constant flow (within the specification). This is not the case when the MFC has not been powered on for at least half an hour. Also, leakage in piping as well as contamination within the MFC can cause drifting in the order of several percents.

2. Once it is sure that the MFC is fully stabilized, 10 calibrations are carried out at equidistant setpoints. First going up from 10 % to 90 %, then going down from
100 % to 20 %: if the MFC would suffer from hysteresis effects or some other oversighted quantity would change, it becomes visible during data analysis. Each setpoint is calibrated twice and it is checked that both results are within an acceptable range.

3. The calibration data are fitted to a third order polynomial curve. A typical example is shown in figure G.2. Because the data are very close to the curve, the residuals are plotted (figure G.3) to spot any suspicious points, if present. Also, the residual plot is used to determine the uncertainty estimation for the MFC. In this particular case, the uncertainty is ±0.4 % (absolute) over the whole range.
G.2 Pressure dependence

During the low pressure experiments, the pressure on the MFC outlets is reduced and roughly equal to the pressure in the vessel. However, the inlet pressure is constant, which means that the pressure difference $\Delta p$ varies with the vessel pressure. Typically, 2 bar $< \Delta p < 2.9$ bar, while at atmospheric experiments $\Delta p = 2$ bar. Therefore, the calibration setup is used to perform a set of calibrations with $1 \text{ bar} < \Delta p < 7$ bar to be able to estimate the influence of a variable pressure difference. The result is shown in figure G.4, where a 0.9 L/min MFC (with setpoint 50%) is calibrated as a function of the pressure difference.
of pressure difference $\Delta p$. When increasing the pressure difference by 6 bar, the flow changes less than 0.5%. Considering that the pressure difference during the low pressure experiments does not vary more than 1 bar, the variation on the flow will be less than 0.08%, which is well within the scatter of a typical calibration such as shown in figure G.3. Therefore, it is concluded that the influence of the pressure difference $\Delta p$ on the calibration curve can safely be neglected during the low pressure experiments.

### G.3 Dimensions

As explained in section 2.3.2, the dimensions of the MFC’s need to be properly chosen for the particular experiment to avoid excessive uncertainties. Some rules of thumb, based on the analysis in section 2.3.2 and above calibration results, can be written down:

- The setpoints should be as high as possible, and never drop below 10%.
- When changing the equivalence ratio $\phi$ with an increment of interest, for example 0.05, the fuel MFC setpoint should change at least 1% at constant velocity.
- When changing the unburnt gas velocity with an increment of interest, for example 1 cm/s, the air MFC setpoint should change at least 1% at constant $\phi$. 

![Figure G.4: Influence of the pressure difference $\Delta p$ between inlet and outlet on the mass flow delivered by an MFC.](image)
Appendix H

Fitting parabola

Fitting experimental data to a parabolic function can be done straightforwardly using a least squares analysis. Consider $N$ data points $(r_i, T_i), 1 < i < N$ which have to be fitted through the parabolic function $f(r) = ar^2 + b$. The linear term is set to zero because of the rotational symmetry of the temperature distribution in the burner plate, as shown in equation (2.5). The sum $S(a, b)$ of the squared residuals to the fit function $f(r)$ is

$$S(a, b) = \sum_{i=1}^{N} (T_i - ar_i^2 - b)^2.$$  \hspace{1cm} (H.1)

For an optimal least squares fit, the sum $S(a, b)$ should be minimized with respect to $a$ and $b$, which requires

$$\frac{\partial S}{\partial a} = 0$$ \hspace{1cm} (H.2)

$$\frac{\partial S}{\partial b} = 0.$$ \hspace{1cm} (H.3)

Substitution of equation (H.1) into eqs. (H.2) and (H.3) and solving the resulting set of equations gives

$$a = \frac{1}{D} \left[ N \sum_{i=1}^{N} r_i^2 T_i - \sum_{i=1}^{N} T_i \sum_{i=1}^{N} r_i^2 \right]$$ \hspace{1cm} (H.4)

$$b = \frac{1}{D} \left[ \sum_{i=1}^{N} T_i \sum_{i=1}^{N} r_i^4 - \sum_{i=1}^{N} r_i^2 T_i \sum_{i=1}^{N} r_i^2 \right],$$ \hspace{1cm} (H.5)

where $D$ is defined by

$$D = N \sum_{i=1}^{N} r_i^4 - \left[ \sum_{i=1}^{N} r_i^2 \right]^2.$$ \hspace{1cm} (H.6)
To estimate the influence of a deviation $\Delta T_j$ on position $r_j$, with $\Delta T_j$ small compared to $T_j$, a disturbed data point $(r_j, T_j + \Delta T_j)$ is substituted in equation (H.4). The following expression is obtained for the disturbed parabolic coefficient $a'$:

$$a' = a + \frac{\Delta T_j}{D} \left[ x_j^2 - \sum_{i=1}^{N} x_i^2 \right],$$  \hspace{1cm} (H.7)

where $a$ is the coefficient without deviation. In the particular case of the temperature measurements in the burner plate, a deviation of data points to the fit is observed where $\Delta T_j \sim a$. Using this in equation (H.7), it can be seen that in the case of $a = 0$, corresponding to the adiabatic state of the flame, also $a' = 0$: these deviations do not alter the result of the burning velocity measurement.
Bibliography


Summary

The adiabatic burning velocity $S_L$ of a gaseous fuel/oxidizer mixture is a key parameter governing many properties of combustion, such as the shape and stabilization of a flame. To determine the burning velocity, several experimental methods exist. Often, these methods are based on producing a flame that does not interact with a burner to prevent heat exchange. Common examples are the counter flow method, based on two opposing jets, and the closed vessel method, where a mixture is ignited in a combustion chamber. These methods have the disadvantage that the flames are stretched; to find the unstretched burning velocity, it is necessary to apply a correction model for stretch. This is a complicated method and sensitive to large errors.

Because the heat flux method produces a flat flame, flame stretch correction is not needed. Instead, the heat exchange with the burner is considered; by measuring the temperature distribution of a burner plate, the net heat flux of the flame to the burner can be determined. The burner plate is heated, and by tuning the unburnt gas velocity until there is no net heat flux, the adiabatic burning velocity is found by interpolation. It can be shown that this flame corresponds very closely to a theoretical free flame, and therefore it is very well suited to serve as a reference flame.

In this PhD work, the heat flux method is analyzed in detail, based on the earlier work by van Maaren. The research results in a better understanding of several aspects of the technique, and an improved burner design. The most important improvements as compared to the old setup are:

- A thermal isolation ring between the hot and cold parts of the burner head, reducing the time for the system to reach a stationary state and permitting a smaller flow in the water jackets.
- A new attachment method for thermocouple wires, resulting in a better temperature measurement.
- A pressing ring to ensure a rotationally symmetric heat conduction from the burner plate to the burner head.
- A simple model to account and correct for the vertical temperature gradient in the burner plate, leading to smaller uncertainties in the measurements.
• A new calibration setup for the mass flow controllers, reducing the uncertainties in the unburnt gas velocity as well as the equivalence ratio \( \phi \). The method is also suitable for hydrocarbons that were problematic to use in the old calibration setup.

• Design of a low pressure chamber with pressure control to perform measurements in the pressure range 100–1000 mbar. Since the heat flux from the flame to the burner plate reduces with pressure, leading to a larger uncertainty, a new burner head is developed. Using a steel burner plate, instead of brass, the measurement sensitivity is increased to compensate for the low pressure effect.

Due to the improvements, the accuracy of the measurements is enhanced: the result for a stoichiometric methane/air flame by van Maaren was \((37.0 \pm 1.0)\) cm/s, while the improved setup gives \((35.7 \pm 0.5)\) cm/s.

Coherent Anti-Stokes Raman Spectroscopy (CARS) thermometry measurements are carried out to investigate whether the temperature profiles of the flames correspond to the calculated profiles of free flames. It turns out that the flames produced by the burner agree well with the calculations, in which a simple radiation model is included in the calculations to account for the temperature decrease due to radiation losses. The order of magnitude of the temperature decrease is 1 K/mm, while the typical temperature in the flame is 2000 K. The uncertainty in the CARS measurements is typically 20 to 30 K. From the CARS measurements it is concluded that the burner produces flames that are very well suited as a reference flames, which can be useful for the development of laser-based diagnostic techniques, such as quantitative LIF (Laser Induced Fluorescence) and CRDS (Cavity Ring Down Spectroscopy).

The improved heat flux setup is used to measure burning velocities of methane, ethane, propane, \( n \)-butane and iso-butane mixtures with air at atmospheric pressure and temperature \( T = 295 \) K, for equivalence ratios in the range \( 0.6 < \phi < 1.5 \). For methane, a set of measurements is performed with unburnt gas temperatures in the range 295–370 K, for three fixed equivalence ratios \( \phi = 0.80, \phi = 1.00 \) and \( \phi = 1.20 \). Low pressure measurements are performed in the pressure range 100–1000 mbar, for a stoichiometric methane/air mixture at temperature \( T = 295 \) K.

The heat flux results are compared with other experimental data as well as with results from calculations based on several reaction mechanisms (GRI, Smooke and Warnatz). For the atmospheric measurements, the heat flux measurements tend to give lower values for the burning velocity \( S_L \) than used to be reported in literature. However, when compared to recent measurements where care was taken to account for stretch effects properly, the heat flux results agree well with data by other authors using various techniques. For stoichiometric mixtures at inlet temperature \( T = 295 \) K, the following adiabatic burning velocities are found: \((35.7 \pm 0.5)\) cm/s for methane, \((40.7 \pm 0.5)\) cm/s for ethane, \((39.5 \pm 0.5)\) cm/s for propane, \((37.1 \pm 0.5)\) cm/s for \( n \)-butane and \((33.4 \pm 0.4)\) cm/s for iso-butane.

Down to \(~ 300\) mbar, the low pressure measurements for a stoichiometric methane/air mixture show a pressure dependence for the burning velocity \( S_L \) that is consistent with calculations based on the GRI 2.11 reaction mechanism, predicting an increase in burning velocity roughly corresponding to the often quoted relation \( S_L \sim p^{-1/2} \). However,
for pressures below 300 mbar, the heat flux measurements give results that are lower than the calculations, suggesting that a systematic error occurs in this pressure range. An estimation of the diffusion of fuel out of the unburnt gas mixture into the surrounding shows that this effect becomes significant for low pressures, leading to a systematical error in the same order of those observed.
De adiabatische verbrandingssnelheid $S_L$ van een gasvormig brandstof/lucht mengsel is een belangrijke parameter die veel eigenschappen beïnvloedt in een verbrandingsproces, zoals de vorm en stabilisatie van een vlam. Deze verbrandingssnelheid kan gemeten worden met diverse experimentele technieken. Vaak zijn deze technieken gebaseerd op het produceren van een vlam die geen interactie heeft met een brander om warmte-uitwisseling te voorkomen. Bekende voorbeelden zijn de tegenstroom techniek, bestaande uit twee tegen elkaar instromende vrije stralen, en de gesloten vat techniek, waarbij een gas/lucht mengsel wordt aangestoken in het midden van een verbrandingskamer. Een nadeel van deze methodes is dat de vlammen niet vlak zijn; om de vlakke verbrandingssnelheid te vinden is het noodzakelijk om een correctie aan te brengen voor de kromming. Dit kan gecompliceerd zijn, en is gevoelig voor relatief grote fouten.

Omdat de warmte flux methode een vlakke vlam produceert is een correctie voor vlamkromming niet nodig. In plaats daarvan wordt de warmte-uitwisseling met de brander beschouwd; door de temperatuurverdeling in de branderplaat te meten, kan de netto warmte flux van de vlam naar de brander bepaald worden. Omdat de branderplaat warm wordt is het mogelijk om de snelheid van het onverbrande gasmengsel zodanig te variëren dat er geen netto warmte flux is. De adiabatische verbrandingssnelheid kan zo bepaald worden door interpolatie. Het kan aangetoond worden dat de resulterende vlam zeer nauw overeen komt met een theoretische vrije vlam. Hierdoor is deze vlam zeer geschikt als referentievlam.

In deze dissertatie wordt de warmte flux methode in detail geanalyseerd, uitgaande van het eerdere werk van van Maaren. Het onderzoek mondt uit in een beter begrip van diverse aspecten van de methode en een verbeterd branderontwerp. De belangrijkste verbeteringen ten opzichte van het oude ontwerp zijn:

- Een thermische isolerende keramische ring tussen het hete en koude gedeelte van de branderkop. Dit verkort de tijd die het gehele systeem nodig heeft om een stationaire toestand te bereiken. Ook kan volstaan worden met kleinere waterstromen in de koelkanalen.
- Een nieuwe techniek om thermokoppeldraden te bevestigen, met een betere temperatuurmeting als resultaat.
- Een aandrukring om een rotatiesymmetrische warmtegeleiding te waarborgen van
de branderplaat naar de branderkop.

- Een eenvoudig model om voor de vertikale temperatuurradiënt in de branderplaat te corrigeren. Hiermee wordt de onzekerheid in de metingen verkleind.

- Een nieuwe calibratie opstelling voor de massastrom regelaars verkleint de onzekerheid in zowel de onverbrande mengselsnelheid als de equivalentieverhouding $\phi$. De methode is ook bruikbaar voor koolwaterstoffen die problemen opleverden met de oude calibratie opstelling.

- Het ontwerp van een lage-druk vat met drukregeling om metingen uit te voeren in het drukbereik van 100 tot 1000 mbar. Omdat de warmte flux van de vlam naar de branderplaat afneemt met de druk, met als gevolg een grotere onzekerheid, is een nieuwe branderkop gebouwd. Met een branderplaat van staal, in plaats van messing, wordt de gevoeligheid vergroot om de lage druk effecten te compenseren.

De verbeteringen leiden tot een hogere nauwkeurigheid: het resultaat voor een stoichiometrische methaan/lucht vlam zoals door van Maaren gevonden was \((37.0 \pm 1.0) \text{ cm/s}\), terwijl de verbeterde opstelling \((35.7 \pm 0.5) \text{ cm/s}\) geeft.

Coherente Anti-Stokes Raman Spectroscopie (CARS) temperatuurmetingen zijn uitgevoerd om te onderzoeken of de temperatuurprofielen van de vlammen overeenkomen met de berekende profielen van vrije vlammen. Uit de metingen blijkt dat de vlammen goed overeenkomen met de berekeningen, waarbij een eenvoudig model is gebruikt om de temperatuurdaling als gevolg van straling te voorspellen. De ordegrootte van de temperatuurdaling is 1 K/mm, bij een typische vlamtemperatuur van 2000 K. De onzekerheid in de CARS metingen bedraagt typisch 20 tot 30 K. Uit de CARS metingen wordt geconcludeerd dat de brander vlammen produceert die zeer geschikt zijn als referentie-vlam. Dit kan nuttig zijn voor de ontwikkeling van laser-diagnostische technieken, zoals quantitatieve LIF (Laser Induced Fluorescence) en CRDS (Cavity Ring Down Spectroscopy).

Met de verbeterde warmte flux opstelling zijn metingen uitgevoerd aan de verbrandingsnelheid van methaan, ethaan, propaan, n-butaan en iso-butaan, allen gemengd met lucht bij atmosferische druk en een temperatuur van $T = 295$ K, bij equivalentieverhoudingen $0.6 < \phi < 1.5$. Met methaan zijn metingen verricht waarbij de onverbrande gastemperatuur variëerde tussen 295 en 370 K, bij drie equivalentieverhoudingen $\phi = 0.80$, $\phi = 1.00$ en $\phi = 1.20$. Een stoichiometrisch methaan/lucht mengsel is doorgemeten bij drukken van 100 tot 1000 mbar, met een begintemperatuur $T = 295$ K.

De warmte flux resultaten worden vergeleken met zowel gegevens uit de literatuur als berekeningen gebaseerd op diverse reactie mechanismes (GRI, Smooke en Warnatz). De atmosferische warmte flux metingen geven doorgaans lagere resultaten voor de verbrandingsnelheid $S_T$, dan de oudere gegevens uit de literatuur. De metingen komen echter goed overeen met recentere experimenten waarbij effecten van vlamkromming netjes verdisonceerden zijn bij de verwerking van de meetdata van gekromde vlammen. Voor stoichiometrische mengsels bij een inlaat-temperatuur van 295 K zijn de volgende adiabatische verbrandingsnelheden gevonden: \((35.7 \pm 0.5) \text{ cm/s}\) voor methaan, \((40.7 \pm 0.5) \text{ cm/s}\) voor ethaan, \((39.5 \pm 0.5) \text{ cm/s}\) voor propaan, \((37.1 \pm 0.5) \text{ cm/s}\) voor n-butaan en \((33.4 \pm 0.4) \text{ cm/s}\) voor iso-butaan.
In het bereik van 1000 tot 300 mbar voor een stoichiometrisch methaan/lucht mengsel wordt met de warmte flux metingen een drukverloop waargenomen voor de verbrandingssnelheid $S_L$ dat overeenkomt met berekeningen gebaseerd op het GRI 2.11 reactie mechanisme, dat een verhoging van de verbrandingssnelheid voorspelt volgens $S_L \sim p^{-1/2}$, dat vaak als vuistregel gehanteerd wordt. Voor drukken onder 300 mbar echter vallen de warmte flux resultaten veel lager uit dan de berekeningen. Dit lijkt te wijzen op een drukafhankelijke systematische fout in dit gebied. Een schatting van diffusie van brandstof uit het onverbrande gasmengsel laat zien dat diffusie een belangrijk effect wordt bij lage druk, en dat systematische fouten kunnen ontstaan van dezelfde ordegrootte als waargenomen in het experiment.
Dankwoord

Een proefschrift komt tot stand dankzij de hulp van velen, zowel collega’s als vrienden die ik op deze plaats hartelijk wil bedanken. Een aantal wil ik met name noemen:


Gert en Koen voor de uurtjes Magic kaarten, in de lunchpauze en in het weekend tot soms later dan aanvankelijk gepland.

Mijn vrienden voor de gezellige uren tijdens weekends, in de mensa, AOR, Effenaar of gewoon onder het genot van een biertje: André, Matthijs, Wim, Jeffrey, Paul, Peter, Hubert en Nico.

Ook buiten Eindhoven is het via email prima mogelijk om regelmatig contact te houden, bijvoorbeeld voor een potje e-schaak met Leo.

Outside the Netherlands, I’d like to thank Silvia and Thomas for their support and friendship.

Verschillende generaties BEST droegen ook bij tot de noodzakelijke ontspanning. De oude generatie uit mijn eigen bestuursjaren door weekends in de Ardennen en de nieuwe generatie door met hen zo nu en dan te borrelen.

Tenslotte wil ik mijn ouders bedanken waar ik altijd terecht kan voor een bezoek.

Mensen, allen heel hartelijk bedankt!

Karel Joop.
Stellingen

behorende bij het proefschrift

Analysis of the Heat Flux Method for Measuring Burning Velocities

van

K.J. Bosschaart

1. De heat flux methode voor het meten van verbrandingsnauwkeurigheid heeft, in tegenstelling tot andere vaak gebruikte methoden, geen correctie nodig voor oprekking van de vlam. Door vergelijking van resultaten kan de heat flux methode bijdragen aan het inzicht en de modellering van vlam-rek.

2. De vlakke vlam die gestabiliseerd is op de heat flux brander, en die ontstaat onder de conditie dat de netto heat flux gelijk aan nul wordt, is de best mogelijke experimentele benadering van een adiabatische 1-dimensionale vlam.

3. Als de heat flux methode, zoals beschreven in dit proefschrift, gebruikt wordt bij een druk onder 300 mbar zijn maatregelen vereist om de invloed van de grens laag op de vlam te verkleinen. Dit kan bijvoorbeeld door de diameter van de branderplaat te vergroten.

4. De elektrische spanning over een thermokoppelaars als gevolg van het Seebeck effect is altijd identiek aan nul, onafhankelijk van de temperatuur.

5. Rommel diffundeert naar het bureau dat het best is opgeruimd. Opruimen van een bureau dat tussen andere bureau's staat leidt dus tot niets.

6. Microsoft staat tot “advanced computing” als McDonald’s tot de Franse keuken.

7. Het is wrang dat World Wide Web pagina's, aanvankelijk bij CERN bedacht om communicatie tussen verschillende computersystemen mogelijk te maken, tegenwoordig door veel “webdesigners” niet voor alle gebruikers geschikt gemaakt worden.
8. Een factor die vaak wordt vergeten in de nauwkeurigheid van experimentele resultaten is de invloed van de experimentator zelf.


10. Een probleem van de wetenschapsquiz is dat het wetenschap probeert te benaderen met een middelbare school instelling.

11. In de huidige vorm van projectaanvragen weegt het te verwachten resultaat mee in de honorering. Een typisch kenmerk van de wetenschap is echter dat de beste resultaten onverwacht zijn; door het toch uitvoeren van afgewezen projecten zouden meer wetenschappelijk interessante resultaten behaald kunnen worden.