Analysis of tar removal in a partial oxidation burner

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Analysis of tar removal in a partial oxidation burner

PROEFSCHRIFT

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Chapter 1

Introduction

Renewable energy will be important in the near future. In the Netherlands, the energy production from renewable sources should be 10% in 2020. From this 10%, 42% should be energy from biomass [78]. Biomass gasification is an interesting option for energy production from biomass. For the introduction of small-scale fixed bed biomass gasifiers however, the production of tars in this process is one of the major problems. Apart from causing environmental hazards, tar is known to create process-related problems in the end use devices, such as fouling, corrosion, erosion and abrasion. Before the gas can be introduced into the gas engine, the tar content has to be reduced to low values. The cleaning systems nowadays are too expensive to be used in small-scale applications [65]. This study focuses on these small-scale applications. A burner geometry in a concept of a gasifier that produces little tar, is evaluated in more detail.

1.1 Background

In literature, various overviews can be found of the existing types of gasifiers and cleaning methods (e.g. [21], [65]). Among the existing types of gasifiers, fixed bed downdraft gasifiers are the most suitable for small-scale processing of biomass [65].

![Figure 1.1: A conventional fixed bed downdraft gasifier](image-url)
A schematic representation of a conventional fixed bed downdraft gasifier is shown in figure 1.1. The four zones -drying, pyrolysis, combustion, and reduction- that are generally involved in the gasification process are shown schematically. A principle advantage of this type of gasifier is that, ideally, the tar produced in the pyrolysis stage will be cracked when it passes through the homogeneous high temperature area of the combustion zone. In practice, however, the tar may slip through relatively cold parts of this zone without conversion. Furthermore the solid feedstock is often not completely pyrolysed upon entering the reduction zone (which is below the combustion zone as shown in figure 1.1). The tar produced are usually not cracked, probably because of a lack of residence time and insufficiently high temperatures. Typical tar contents of synthesis gas from fixed bed downdraft gasifiers are 500-1000 mg/Nm$^3$ (e.g. [4]). It has been shown that the use of an internal pyrolysis recycle loop with a separate internal combustion chamber in a fixed bed gasifier may lead to a synthesis gas with a very low tar content [74]. However, the tar reducing mechanism in this combustion chamber is not clear yet. To examine this process more closely, a concept of a gasifier-configuration is used in which the separate combustion chamber is placed outside the gasifier.

Figure 1.2: The concept of the gasifier-configuration

As shown in figure 1.2 this configuration consists of a gasifier (left side) and an external combustion chamber (right side). An ejector in which pressurised air is used to suck in pyrolysis gas from the gasifier drives the recycle loop. The temperature in the recycle loop is increased to a level at which thermal cracking and partial oxidation occurs by burning a part of the pyrolysis gas. This configuration resembles the Delacott gasifier used for char production [44]. Another comparable concept: a so called ‘two stage’ gasifier, has been developed in Denmark (e.g. [8], [30]), where the adding of air in a second stage is studied. Also the use of a recycle loop is studied in literature, e.g. Gaudemard et al. [28] tested a so called ‘recycle gasifier’, which uses a recycle loop.

This study focuses on the combustion chamber. However, the total concept is held in mind when testing the burner. In this concept, the tar content of the gas obtained from a gasifier, might be reduced by thermal treatment and partial oxidation in the burner. For the thermal treatment, the temperature in this chamber is increased moderately (till about 500 °C) by burning a small amount of the low-calorific pyrolysis gas from the gasifier (the left part of figure 1.2). This small amount of the gas is burned by adding little air.
1.2 Tar components

Tar formed in gasification is a mixture of organic components ranging from low molecular weight components like benzene to heavy polyaromatic hydrocarbons (PAHs) [71]. Several definitions of tars are used in practice, however, two definitions are nowadays most widely accepted. According to the Tar Guideline [56] the definition should be ‘a generic (unspecified) term for the entity of all organic components present in the producer gas excluding gaseous hydrocarbons (C_1 to C_6). Benzene is not included.’. Another widely used and almost similar definition is the one of Milne et al. [55]; tars are here defined as: ‘The organics produced under thermal or partial oxidation regimes (gasification) of any organic material; they are generally assumed to be largely aromatic.’ Although tars may consist of over a hundred different components [1], in most cases only about 20 species are present in significant quantities [46]. Tars form when biomass or any other organic material is heated. The heating causes the molecular bonds to break. The smallest molecules formed in this way are gaseous. The larger molecules are called primary tars. These primary tars -which are always fragments of the original material- can react into secondary tars by further reactions at the same temperature and to tertiary tars at higher temperatures [23]. Evans and Milne [23] show the tar product distribution as a function of temperature and time by using multivariate analysis of product composition (see figure 1.3).

Figure 1.3: Four groups of tar components as a function of temperature at 0.3 s residence time [23]

Four major product classes are identified as a result of gas-phase thermal cracking reactions: 1. primary products 2. secondary products 3. alkyl tertiary products, like toluene and 4. condensed tertiary products like PAHs without substituents: benzene, naphthalene, acenaphthylene, anthracene, phenantrene and pyrene. In the downdraft product spectrum the tertiary aromatic products are predominant.

Quantities and compositions of tars from biomass gasifiers depend on a large number of parameters. Important parameters are the type and properties of the biomass feed (e.g. biochemical and chemical composition, water content and particle size) and
the gasification conditions (pressure, temperature, gas residence time at high temperature). In fact, also the type of gasifier strongly determines the tar content of the produced fuel gas. The reason that the content and composition of tar is largely determined by the gasifier type, is caused by differences in hydrodynamics (flow behaviour) in the gasifier, micro-mixing and local availability of oxygen or a locally high temperature. These parameters can significantly affect the quality of the gas and the composition of the tar. As the concentration of tars from downdraft gasifiers can vary over three orders of magnitude -depending on the design of the gasifier-, it can be expected that also the composition of the downdraft gasifier tars can change accordingly.

1.3 Problem definition

Several methods for tar removal are possible (see for example [73]): tar removal by physical processes (e.g. filters), thermal methods and catalytic methods are the options that are most often used. Until now relatively little attention is paid to partial oxidation as a way to remove tars. Brandt and Henriksen ([11] and [12]) investigated thermal cracking and partial oxidation of pyrolysis gas in a reactor at 800, 900 and 1000 °C. Experiments are performed with an excess air ratio varying from 0 (i.e. thermal cracking) to 0.7. The minimum tar content was measured at 900 °C together with an excess air ratio of 0.5. It was also shown that the temperature in the reactor only had an influence at small excess air ratios in the temperature regions investigated [12]. Also Jenssen et al. [41] studied the reduction of tar in pyrolysis gas. They found that this reduction is a function of temperature and oxygen content. Thermal cracking seems to take place when raising the temperature from 500 to 900 °C. Furthermore, adding oxygen above 700 °C also results in a considerable reduction of the tar content. The amount of tar generated at 500 °C is 12 %. This is reduced to 1.1 % by raising the temperature to 900 °C and adding oxygen. The results indicate also that the tar and not the carbon monoxide is oxidized. This agrees well with earlier observations. Boroson et al. [10] even found that the major tar conversion product during cracking is carbon monoxide. Ranzi et al. [64] concluded that the major product during low temperature combustion of a hydrocarbon n-butane is carbon monoxide. Beenackers et al. [48] saw the same tendency by partial oxidation of naphthalene in artificial biomass producer gas. All these different studies indicate that partial oxidation might be a promising method for the reduction of the tar content; a favorable result also is that this process even might convert the tars to burnable permanent gases.

From the literature cited above, it seems that the use of a separate combustion chamber is an interesting option for tar removal. The evaluation of a burner geometry for this process, is divided into two main parts. The choice of the burner geometry is described in detail in chapter 2, for now however, it is important to know is that the geometry used is based on air injection by several nozzles. These nozzles are supposed to create diffusion flames. Mixing is crucial for these diffusion flames. In the first part, both the mixing of the flows in the burner geometry and the mixing downstream of the burner is studied. In the second part, the influence of the process on the tars is addressed. A short introduction to each of the parts is described below.
1.3.1 Mixing

The mixing in the configuration can be divided in two parts: ‘fuel air mixing’ and ‘burner outlet mixing’. The problem is that both of the mixing processes depend on the same macro-motion of the gases, introduced mainly by the two most important mass-flows: the pyrolysis gases and the air. These two parts are shown in figure 1.4.

As shown in this figure, the first mixing is the mixing of the pyrolysis gases (fuel) and the air. This mixing should result in an easy combustible and stable burning mixture: which is in this study called ‘fuel-air mixing’. The second mixing is the mixing of the burnt and the unburnt gases to create a homogeneous high temperature for the cracking in the chamber: which is here called ‘burner outlet mixing’. These two processes with their aimed effect are summarised in table 1.1.

![Figure 1.4: The mixing: fuel-air mixing and burner outlet mixing](image)

<table>
<thead>
<tr>
<th>Mixing Process</th>
<th>Aimed effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing pyrolysis gases and air</td>
<td>Make an easy combustible and stable burning mixture</td>
</tr>
<tr>
<td><em>Fuel-air mixing</em></td>
<td></td>
</tr>
<tr>
<td>Mixing of burnt and unburnt gases</td>
<td>Create homogeneous high temperature for cracking</td>
</tr>
<tr>
<td><em>Burner outlet mixing</em></td>
<td></td>
</tr>
</tbody>
</table>

For the first mixing process -the fuel-air mixing- the mixing should not be too turbulent and fast, mainly while -compared to the pyrolysis gas- there is little air. The intention is to inject the air by means of several nozzles and to create diffusion flames on the separation layer of the gas and the air jets. To realise a locally stoichiometric mixture of pyrolysis gas and air, well controlled mixing for this process is of crucial importance. The term diffusion flame is generally used to classify any combustion process for which the fuel and oxidiser are separated prior to combustion. Diffusion flames can best be described as a combustion state controlled by mixing phenomena - i.e. the diffusion of fuel into oxidiser or vice versa - until some flammable mixture
Chapter 1

ratio is reached. However, for the second mixing process, turbulent mixing by air jet injection is a possible solution to create a homogeneous mixture directly downstream of the burner. These two solutions do not fully coincide, therefore optimisation of the whole mixing process is difficult.

1.3.2 Tar removal

The temperature and the residence time of the gases are important parameters for the removal of the tar by thermal cracking and partial oxidation. However, as mentioned above, exact knowledge about the influence of process parameters (temperature, residence time, and gas composition) on the reduction of tar is still scarce (e.g., [12], [10], and [48]). When combusting biomass fuel gases in a burner, the tars in the gases can undergo several processes [57]:

1. they are completely combusted;
2. they are only partly combusted;
3. they form higher hydrocarbons and/or soot;
4. they are cracked to lighter components.

The combustion characteristics of a biomass tar strongly depend both on the physical and the chemical state of the tar. For the physical state the situation depends on whether the tar occurs as a gas (i.e. individual tar molecules) or as a liquid. In the liquid case, the tar can be present as tar aerosols and/or as part of particulates, the latter in the form of a composition of both solids (dust, char, soot) and adsorbed liquids (tar). For the chemical state the assumption is often made that tars crack to carbon monoxide, hydrogen and other light gases. This is true for primary product cracking, but the condensed tertiary products are more likely to grow in molecular weight [55].

To study the behaviour of the tars in the burner geometry, two parameters are of special importance in this study: the temperature (and the residence time at that temperature) and the amount of oxygen. In the burner these parameters are coupled: oxygen is needed to realise the burning, which elevates the temperature. Therefore, the effect of temperature alone on the tar removal is studied in another set-up, by heating the gases in an electrically heated tubular reactor.

1.4 Outline

Figure 1.5 shows an overview of the chapters in relation to the burner geometry. Chapter 2 describes experiments in a perspex (methyl methacrylate) set-up using water. These experiments result in an indication of the appropriate volume flow-ratio of the gas and the air flow in the burner. In chapter 3 the burner is tested at various inlet conditions using low calorific -but tar free- gas. These several inlet conditions are: the heating value and power, the inlet gas composition, the primary air, the secondary air and the inlet temperature. Chapter 4 concentrates on the mixing at the burner outlet, i.e. the mixing of the burnt and the unburnt gases. This mixing should create a homogeneous temperature downstream of the burner. Particle Image Velocimetry (PIV)
Figure 1.5: An overview of the chapters of this thesis in relation to the burner geometry

and stereo-Particle Image Velocimetry (stereo-PIV) are used to study the velocity field in detail.

In the second half of the project the tar removal part is elaborated. This part deals with the cracking and polymerisation of the tars present in the biogas. In chapter 5, the influence of temperature and residence time on the tar will be highlighted. For these experiments an existing set-up at the Energy Research Centre of the Netherlands (ECN) is used in which the gases coming from a gasifier are heated electrically. Next, in chapter 6, partial oxidation is examined in the burner geometry studied in this thesis. Again low calorific gases are used in the burner geometry, but now naphthalene is added to the gas-flow to simulate the tars in a biogas. Finally, in chapter 7 the concluding discussion is described.
Chapter 2

Burner design

The focus of this chapter is the mixing of the pyrolysis gases and the air. This mixing should create a stable combustible mixture using little air. First, the air injection is discussed. After that, the design considerations are described, followed by a determination of the effect of flow ratio variations, which are visualised in a perspex set-up using water and dye. Finally, a description of the final burner geometry is given.

2.1 Air injection

As stated in the previous chapter, the injection of the air is crucial for this burner. The problem is that both of the mixing processes depend on the same macro-motion of the gases. Recently, the use of a passive mixing device to enhance the mixing of a jet with the surrounding has been studied extensively (e.g. [6], [84]). Enhancing the mixing by placing for example tabs [6] or lobed jet nozzles [84] appears to be very effective. But placing tabs or lobed nozzles in the pyrolysis gas-stream might cause problems, because tars might stick on these devices. So the tar itself, is also a complicating factor for both of the mixing processes mentioned in chapter 1. Therefore, swirl mixing introduced by the air injection nozzles without tabs or lobed nozzles seems to be the most promising option.

In general, two air injection configurations for combustion applications exist [79]: jets in crossflow and swirl crossflow mixing. The first one, jets in crossflow, is the most basic case. The second one is the same basic case, but with swirl added. Jets in crossflows are flows found for example in primary and secondary combustion systems. Mixing of a single jet in a crossflow has been studied more often ([72]) than multiple jets in a crossflow [36]. Most combustion systems, however, consist of multiple air jets that mix in a crossflow [79]. Generally, the objective is to obtain a homogeneous mixture of the injectant and the mainstream. The degree and rate of mixing are especially important in combustion applications since burning efficiency and exhaust composition depend directly on mass transfer and reaction kinetics. Whereas kinetics are difficult to control, the mixing process is easily affected by a number of parameters.

The injection of air into the crossflow by means of swirling jets is not very common for air design systems. The Babcock and Wilcox Company has currently adopted this type of air introduction system, based on numerical modeling studies. They state that uniform air distribution by swirling jets allows the burner to achieve the lowest
possible emissions \[49\]. The swirling air introduces recirculation zones near the wall, whereas the inner jet provides mixing in the core of the main flow. The system allows thorough mixing in the core of the flow as well as in the near wall zone.

2.2 Design considerations

In the past, experience has played a major role in the determination of the air nozzle geometry. Trial-and-error methods have been employed in developing the mixing quality of individual designs to a satisfactory standard. Experimental investigations into the mixing performance, carried out on actual chambers, have led to useful empirical data. But often it appears to be difficult or impossible to distinguish the separate influences of all variables involved \[37\]. It is now generally accepted that a satisfactory mixing pattern depends on an adequate penetration of the air jets, on the use of the correct number of jets to form sufficient localized mixing regions and on the injection angle. However, the way in which a given total inlet air area is translated into a particular number and a particular size of the nozzles is still a matter of experience.

So quantitative design rules for mixing systems for these requirements are not readily available. In this study the design considerations will be translated in terms of the ratio of the volume flows, the swirl numbers and desired temperatures. This section describes the cold flow mixing experiments that are used to determine the influence of the geometry and flow variations on mixing patterns in this specific configuration. In jet mixing the dominant parameters are \[79\]:

1. \(\alpha\): injector angle in flow direction
2. \(\theta\): injector angle in circumferential direction
3. \(n\): number of injectors
4. \(\dot{V}_{\text{inner}}/\dot{V}_{\text{outer}}\): volume flow ratio.

Figure 2.1 shows these parameters. The definition of these parameters in this study is as follows. The injector diameter is 2 mm, the injector angle \(\alpha\) is 45° (in flow direction, see the left part of figure 2.1) and \(\theta\) (in circumferential direction, see the right part of figure 2.1) also 45°. In preliminary experiments the number of injectors is varied. This variation is performed while the total area of the nozzles is kept constant. The lower the number of injectors, \(n\), the more downstream the mixing starts. The intensity of the mixing remains the same. In these preliminary experiments also the difference between an odd and even number of injectors is studied. The odd numbered situations appear to mix more effectively and more smoothly. Hence, regarding the importance of the contact of the air and the fuel in the burner, the odd numbered situation seems to be more convenient. For the burner geometry of the final set-up, seven injectors are used \((n = 7)\). For a single jet in a crossflow Liscinsky et al. \[51\] have shown that mixing is not affected significantly by the shape of the injection nozzles. Therefore, the shape of the nozzles chosen in this study is circular: holes are drilled in the wall of the inner tube.

By fixing these parameters only two variables are left: the velocity of the fuel flow and the velocity of the air flow. The aim is to use these two parameters to create a
swirling flow -to realize the burner outlet mixing- and, at the same time, to form the jets -to realize the fuel-air mixing-. Because the nozzles inject the air under an angle in flow direction as well as in circumferential direction, a swirling motion is introduced.

General effects of introducing swirl in a jet flow are that with increasing degrees of swirl [52]: 1) the width of the jet increases, 2) the rate of entrainment increases and 3) the rate of decay in the jet increases. The effects of inlet flow swirl on the subsequent flow field are increasingly dramatic as the degree of swirl increases. As swirl velocities decay with downstream distance, a positive axial pressure gradient $\frac{dp}{dy}$ is found on the axis, as a consequence a region of recirculation is formed. However at low degrees of swirl, this pressure gradient is not strong enough to cause this axial recirculation. Figure 2.2 illustrates schematically the flow characteristics of a weak and a strong swirl in the burner geometry. At the left a weak swirling flow is shown: typically without recirculation zones. At the right, the swirl is strong. As shown in the figure, recirculation zones (shown by the dashed lines) are present in this situation.

The degree of swirl in a flow is usually characterized by the swirl number $S$. Gupta et al. [32] define this $S$ for swirling jets as a non-dimensional number representing the moment of the circumferental flux ($G_\theta$) divided by the moment of the axial flux ($G_y$) times the equivalent nozzle radius ($\frac{d}{2}$). That is [32]:

$$ S = \frac{G_\theta}{G_y \left(\frac{d}{2}\right)}. $$

(2.1)

In this equation they define $G_\theta$ as the impuls momentum in the circumferential direction like:

$$ G_\theta = \int_0^{\frac{d}{2}} (v\rho w(2\pi r + \rho w)2\pi r)dr; $$

(2.2)
Figure 2.2: A weakly swirling jet without recirculation zones on the axis at the left; A strongly swirling jet with recirculation zones on the axis at the right [32]

where \(v, u\) and \(w\) are the velocity components in cylindrical polar coordinates \((y, r\) and \(\theta)\). The axial flux of the swirl momentum \((G_y)\) consists of an axial flux of axial momentum -including the \(y\)-direction turbulent normal stress term- and a pressure term:

\[
G_y = \int_0^y (\rho v^2 + \rho u^2 + (p - p_\infty)) r dr. \tag{2.3}
\]

Gupta et al. [32] retain the pressure term in the form of \(-\frac{\rho w^2}{2}\) and assume for both the \(G_\theta\) and the \(G_y\) that the turbulent terms are negligibly small. When solid body rotation plug flow is assumed, the following deduction can be made in terms of the maximum velocities measured at the exit plane: \(v = v_{\text{max}}\) and \(w = w_{\text{max}}(\frac{r}{d/2})\). This implies that the axial velocity \(v\) has a constant flat profile and the swirl velocity \(w\) increases from 0 (at \(r = 0\)) to \(w_{\text{max}}\) (at \(r = \frac{d}{2}\)) at the outer wall. The swirl number \(S\) in this case can be defined as [32]:

\[
S = \frac{G}{1 - (\frac{G}{2})^2}, \tag{2.4}
\]

where \(G\) represents the ratio of the maximum velocities measured at the exit plane: \(G = \frac{w_{\text{max}}}{v_{\text{max}}}\).

From experiments done by Chigier [15], it appeared that the theoretical relation for solid body plug flow realistically describes the actual flow case for values of \(S\) less than 0.4. For higher degrees of swirl, however the axial velocity deviates considerably from plug flow. This maximum value of the swirl number will be held in mind when calculating the \(S\) by equation 2.4 in the next chapters.
2.3 Flow experiments using liquid water

To investigate the mixing in the proposed burner geometry, a perspex (methyl methacrylate) set-up is built. In this set-up, water is used instead of gas. The geometry is scaled by the Reynolds number, so it is possible to compare the water flows with the gas flow situations. In the experiments, the two water flows are both observed in the cold state.

![Perspex experimental set-up](image)

Figure 2.3: The perspex experimental set-up

Figure 2.3 shows this perspex set-up, consisting of two tubes. The flows are visualised with dye. Both inlets of the flows (the inner tube as well as the outer tube) are connected to a water tap. The water flow coming from the set-up is collected in a bucket. By timing the captured volume, the volume flow is determined (from which together with geometry parameters, the velocity is calculated). The volume flow of each of the flows and the accompanying position of the individual valves are determined separately. Several set points are recorded with a digital camera. In both the inner and the outer flow several colors of ecoline are injected. Plastic medical injection pumps are used to inject the ecoline in the flow (therefore the injection is not perfectly homogeneous).

When varying the ratio of both flows three typical flow regimes appear. The criteria that are used to characterise the flow regimes are (1) the kind of mixing and (2) the starting position of the mixing. Using these criteria, a good distinctive classification of typical flow regimes can be made. Flow differences are large, and are thus easily observed. Especially the ratio of the volume flows in the inner tube and the outer tube is a convenient parameter to make a functional separation of these flow regimes.

The three figures in 2.4 display typical images of the flow regimes. Three main flow regimes are observed: the ‘cup’ (a), the ‘typhoon’ (b) and the ‘jet-mixing’ (c) regime. In these images both of the flows are directed upwards. In this case only the flow in the inner tube is visualized with dye. So the dye is in fact a visualisation of the ‘fuel’ used in the burner later on. The black arrows indicate the position of the injection nozzles. The names used for the different regimes are derived from the visual patterns that occur. As shown in figure 2.4(a), the kind of mixing present in this regime resembles...
the shape of some cup-like bowl, like shown at the top side of the figure. This kind of mixing is very turbulent. However, directly downstream of this ‘cup’, the dye is completely dispersed in the surrounding water. As shown in the figure, the colour of the water downstream of the cup is almost colourless. The typhoon-like mixing is even more explosive, figure 2.4(b) shows that the mixing directly starts at the injection nozzles. The velocity in the inner tube is high: during the experiments it is found that the injected plume of dye moves downstream in a short time. The mixing downstream the nozzles, results in a more dark homogeneous coloured flow. The darkest coloured flow, however, is found in the case of the jet mixing regime (as shown in figure 2.4(c)). The ‘jet mixing’ regime is called that way because of the small jets that emerge from the injection nozzles. The mixing in this regime is more moderate than the mixing in the two other regimes, therefore the mixing results not directly in a homogeneous mixture. At a few centimeters downstream of the holes a homogeneous mixing state is reached, as shown in figure 2.4(c).

In figure 2.5, the relative position of the start of the mixing is plotted as a function of the ratio of the volume flows. This relative position is expressed in terms of the distance (in cm) to the injection nozzles. A positive sign means that there is downstream mixing, whereas a negative sign indicates that the mixing already starts before the nozzles: upstream mixing. The cases shown in figure 2.5 are grouped by the mixing regimes they are assigned to. The circles give an indication of the areas where the regimes occur. As shown in this figure the starting point of the mixing in the cup regime is in all cases negative: this means that upstream mixing occurs. This upstream mixing is probably caused by pressure effects. The starting position of the typhoon regime
Figure 2.5: The position of the mixing as a function of the ratio of the volume flows

is right at the nozzles (position zero as plotted), whereas in the jet mixing regime the mixing starts somewhat higher (about 2 cm) above the nozzles.

Figure 2.6 shows the Reynolds number in the inner tube \((Re_{\text{inner}})\) as a function of the swirl number \((S)\). Note that for the cases with a swirl number larger than 0.4, the approximation of the swirl number by equation 2.4 is not reliable. This swirl number calculation however, is only used as an indication for the swirl number that is present in the regimes. The circles indicate the area in which the regimes are located. It is found that the swirl numbers of the cup and the typhoon regime are large. Only strong swirling jet flows, which have approximately an \(S \geq 0.6\), possess sufficient radial and axial pressure gradients to cause a central recirculation zone. This zone is not observed in weaker degrees of swirl ([5], [15]). These recirculation effects probably cause the earlier starting of the mixing in the cup regime. As shown, the \(S\) is below 0.6 for the other two regimes: so the swirl in these regimes is weak. For the burner geometry, the mixing of the two flows should not be too turbulent, because the contact area and contact time of the fuel and the air has to be large enough to establish a locally stoichiometric mixture for the burning. Therefore the cup regime is not likely to be suitable for the burner.

Another important goal of this study is to create a flow situation with a lot of fuel and little air. This makes the ratio of the flow in the inner tube (the 'fuel') and the outer tube (the 'air') an interesting parameter. Figure 2.7 shows the Reynolds number in the inner tube \((Re_{\text{inner}})\) as a function of the ratio of the volume flows \((\text{volume flow}_{\text{inner}}/\text{volume flow}_{\text{outer}})\). The three mixing regimes are plotted separately in this figure, again the circles do indicate the areas where the regimes are present. This figure shows that the cup as well as the typhoon regime cover a region with a ratio of the flows beneath 1. This means that there is more air than fuel added. This is obviously the reason for the colour intensity difference observed for the mixing
Figure 2.6: The Reynolds number in the inner tube ($\text{Re}_{\text{inner}}$) as a function of the swirl number ($S$) for the three mixing regimes.

Figure 2.7: The Reynolds number in the inner tube ($\text{Re}_{\text{inner}}$) as a function of the ratio of the volume flows for the three mixing regimes.
regimes. Comparing the intensity of the colour of the dye when the mixing starts in figure 2.4(a) and 2.4(b) to figure 2.4(c), the latter is more intensely coloured. More intensely coloured means that the fuel flow is larger than the air flow. This matches the goal of this study. This result, together with the moderate swirl number present in this regime, makes the jet mixing regime the most promising one.

Table 2.1 summarises the characterisation of the regimes at aspects like the mixing type, the start position and the colour intensity. In the column entirely at the right a schematic small picture of each regime is shown.

<table>
<thead>
<tr>
<th>Regime</th>
<th>Mixing</th>
<th>Start</th>
<th>Downstream Color Int.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cup</td>
<td>turbulent</td>
<td>-1 to -10 cm</td>
<td>low</td>
</tr>
<tr>
<td>Typhoon</td>
<td>turbulent</td>
<td>0 cm</td>
<td>low</td>
</tr>
<tr>
<td>Jet mixing</td>
<td>moderate</td>
<td>+2 cm</td>
<td>high</td>
</tr>
</tbody>
</table>

The flow field type of figure 2.4(c), the jet-mixing regime, is most likely to suit for the intended diffusion flame jets in the burner, because this flow regime meets the two demands of (1) creating a stable combustible mixture (mixes well but not too turbulent) and (2) using little air (the regime is present at large ratios of fuel and air).

2.4 Burner design

From the water experiments presented above the most promising range for the ratio of the volume flows is determined. This ratio is however also restricted by the desired temperature downstream of the burner and the amount of air needed for the burning.

Temperature

Although no real gasifier is used in this study, it is reasonable to make an estimation of the volume flows needed for the desired temperature, based on the output of a theoretical gasifier. Because small scale gasification is the aim of the study, a gasifier with a thermal power of 10 kW\text{th} is taken as a starting point. When assuming complete conversion of wood into gas, the mass flow of pyrolysis/recycle gas is calculated by:

\[
m_{pr} = \frac{\rho \cdot P_{th}}{H_{V_{wood}}},
\]

with \(\rho\) the density of the pyrolysis/recycle gas (about 1 kg/Nm\(^3\), \(P_{th}\) the thermal power of 10 kW\text{th} and \(H_{V_{wood}}\) the heating value of wood: about 18 MJ/Nm\(^3\) [67]. For the mass flow of pyrolysis gas this means a flow of \(5.6 \times 10^{-4}\) kg/s. For the energy released by the burning \((m_{pb} H_{V_p})\) should hold:

\[
m_{pb} H_{V_p} = (m_b + m_u + m_{air}) c_p(T_d - T_{in}),
\]
with \( \dot{m}_b \) the mass flow of the burnt part of the pyrolysis/recycle gas, \( \dot{m}_u \) the mass flow of the unburnt part of the pyrolysis/recycle gas and \( \dot{m}_{\text{air}} \) the mass flow of the air. \( HV_{\text{pr}} \) is the heating value of the pyrolysis/recycle gas, here assumed to be 5 MJ/Nm\(^3\) (see the next section for details of the heating value of biogas). \( c_p \) is the specific heat that is estimated for the whole mixture. \( T_d \) is the desired downstream temperature and \( T_{\text{in}} \) is the inlet temperature of the biogas. The desired temperature is set at 500 \(^\circ\)C and the inlet temperature is in a worst case situation only 20 \(^\circ\)C. For the energy released by the burning should also hold:

\[
\dot{m}_b HV_{\text{pr}} = (\dot{m}_b + \dot{m}_{\text{air}}) c_p (T_d - T_{\text{in}}).
\]

(2.7)

Here is the \( T_{\text{ad}} \) the adiabatic flame temperature of the mixture: for a biogas mixture typically 1654 \(^\circ\)C [17]. Combining equation 2.6 and 2.7 for the conditions mentioned above (a heating value of 5 MJ/Nm\(^3\), an inlet temperature of 20 \(^\circ\)C and temperature at the outlet of 500 \(^\circ\)C), results in an estimated volume flow ratio of about 5.

**Amount of air**

As stated in the previous chapter, another aim for the geometry is to use as little air as possible for the burning (and nevertheless create a homogeneous temperature of about 500 \(^\circ\)C). For burning situations a common measure for the ratio of the air and the fuel used, the air factor \( \lambda \), is defined as the ratio of the air and the fuel in the actual situation divided by the ratio of the air and the fuel in the stoichiometric situation [19]; in brief:

\[
\lambda = \frac{(\text{air/ fuel})_{\text{actual}}}{(\text{air/fuel})_{\text{stoich}}}
\]

(2.8)

The index ‘stoich’ denotes that it concerns a stoichiometric air/ fuel ratio. The required \( \lambda \) in the desired burning situation is low, so when using equation 2.8 this means: the lower the \( \lambda \), the higher the excess of fuel. A situation using a fuel excess is wanted, because the aim of this study is to make a clean gas with a calorific value that is as high as possible. A commonly used \( \lambda \) in gasification situations is 0.2 (a.o. [66]). The ratio of the volume flows as discussed in the previous section is directly coupled to the value of \( \lambda \) in the burning situation: the higher the ratio of the volume flows (as defined in this study), the higher the fuel excess and the lower the \( \lambda \).

Figure 2.8 illustrates the relation between the \( \lambda \) and the ratio of the fuel and the air in the burner geometry. Note that these data only hold for this inlet gas composition: H\(_2\): 15 \%, CO: 15 \%, CH\(_4\): 2 \% and N\(_2\): 58 \%, resulting is a heating value of 4.2 MJ/Nm\(^3\). From the global reactions for methane, hydrogen and carbon monoxide, the stoichiometric amount of oxygen needed, is calculated by multiplying the percentages of CH\(_4\) by 2; and H\(_2\) and CO by 0.5. This figure shows that a \( \lambda \) value of 0.2 is attained for this particular situation, when the ratio of the volume flows is about 5. So, to achieve the required \( \lambda \) of 0.2, the ratio of gas and air required for the partial oxidation will be in the region of the jet-mixing regime and also suits the demand of a downstream temperature of 500 \(^\circ\)C. In this figure four extra cases for the \( \lambda \) is 0.2-situation, are shown. These cases will be used in some of the experiments in the next chapter: their inlet gas composition is different from the trend-line. ‘Pure H\(_2\) LHV 4.2’ means that only hydrogen and nitrogen (39 \% hydrogen together with 61 \% nitrogen) is used for a heating value
The $\dot{V}_{\text{gas}}/\dot{V}_{\text{air}}$ as a function of the $\lambda$; Inlet gas composition: H$_2$: 15 %, CO: 15 %, CH$_4$: 2 % and N$_2$: 58 %; LHV: 4.2 MJ/Nm$^3$; together with four cases which will be used in the next chapter.

of 4.2 MJ/Nm$^3$. Similar holds for the ‘pure CH$_4$ 4.2’-case, that only methane and nitrogen is used: 11.5 % methane with 88.5 % nitrogen. For the ‘pure H$_2$ LHV 10.8’ and the ‘pure CH$_4$ LHV 10.8’-cases, a heating value of 10.8 MJ/Nm$^3$ is used. This means for the pure hydrogen situation that only hydrogen is used, and for the pure methane case a mixture of 30 % methane and 70 % nitrogen. Using the same heating value as the trend-line (4.2 MJ/Nm$^3$), it is shown that the pure hydrogen - nitrogen case coincides with the carbon monoxide containing cases. For the methane - nitrogen case however, a small decrease in the ratio of the flow velocities is found: the ratio for $\lambda$: 0.2 is only 4.2 in this case. For the 10.8 MJ/Nm$^3$ case the difference is larger: for the pure methane case a ratio of 1.6 is calculated, whereas for the pure hydrogen case a ratio of 1.7 is found. This difference might influence the behaviour of the flame. The low values for the 10.8 MJ/Nm$^3$ case should be kept in mind in the next chapter.

The final set-up

After testing the flow situation in this cold-flow-situation using liquid water, a new set-up is built. This set-up will be tested in a burning-situation using gas. The geometry of this new set-up is determined by scaling the perspex water set-up by the Reynolds number. The Reynolds number in the injection nozzles ($\text{Re}_{\text{inj}}$) is kept constant at about 1000. The diameter of the injection nozzles is the same for the water and the gas set-up: $d_{\text{inj}}$ is $\varnothing$ 2 mm. Also the number of nozzles is the same: $n$ is 7. The ratio between the volume flows in the inner tube and in the injection nozzles is around 5.

As shown in figure 2.9(a), the burner consists of two concentric tubes. The gas mixture enters the central inner tube at the bottom of the set-up. The air enters the outer tube at two sides symmetrically and then passes one of the seven injection nozzles into the inner tube. An electrical wire-igniter is used to ignite the flame (not shown in the figure). After the ignition, the igniter is removed from the set-up. The flames stabilise
Figure 2.9: The experimental set-up in 2D and 3D

at the injection nozzles in the inner tube. Downstream, the partly burnt gas mixture enters the diverging part. This diverging outlet decreases the flow rate, which helps to stabilise the flame. Figure 2.9(b) shows a shaded three dimensional view of the burner.
This chapter focuses on the influence of variation in the inlet quantities on the behaviour of the burner. The behaviour is studied by measurement of the outlet temperature and the outlet gas composition. Knowing the effect of variations at the burner inlet is of special importance for biogas, since the composition and the amount of this gas coming from a gasifier is not at all constant. It is possible to test the burner in a wide range of settings. The variables studied in this chapter are:

- **working range of the burner**; to determine the ratio of the volume flows at which the flame is stable. These results are coupled to the water mixing experiments of the previous chapter, furthermore the mixing regime of the stable burning situation is determined;

- **heating value and amount of fuel added**;

- **gas composition of the fuel**; to study the effect of the mole fraction of methane and the mole fraction of hydrogen present in the inlet fuel. Changing the inlet gas composition, alters the kind of radicals present in the flame. In these experiments the heating value and power are kept constant;

- **$\lambda$**, the amount of primary air that is added in relation to the amount of fuel;

- **amount of secondary air**; these experiments are mainly performed to study to which amount the co-flow can be added without participating in the burning;

- **inlet temperature of the fuel**.

First however, some important aspects concerning the burner will be described.

### 3.1 The burner

The set-up is made of stainless steel and placed inside a glass bell to control the air-intake of the burner. In figure 3.1, this burner is shown together with some characteristics of the burner environment. In figure 3.1(a) the burner and the glass bell are shown schematically. The glass bell is about 750 mm in height. As shown, the burner is placed on a small table. The inlets of the fuel and the air are conveyed through this table. The air that is added, is divided in two flows: called the primary air and the secondary
The primary air should be used for the burning. As shown, this air flow is added symmetrically to the burner. The secondary air is added as a co-flow that is not supposed to burn: this flow is necessary for control of the back pressure. The air inlet for the secondary air is shown at the most left side. In almost all experiments presented in this chapter, this flow is set to 1 l/min (which is small compared to the total flow which is about 49 l/min). The flows are adjusted using Mass Flow Controllers (MFCs). These controllers are used to adjust the magnitude of the gas-flows. By changing the magnitude of the gas flows individually, the gas composition of the inlet fuel is altered. In figure 3.1(b) the set-up is shown, without the glass bell. At the front (in the lower right corner), the secondary air inlet is shown. As shown, a little plate is mounted a few centimeters above this inlet. This plate distributes the secondary air more equally. Due to the small amount of secondary air that is added (in almost all experiments) however, the Reynolds number of this flow in the glass bell is only about 10. Therefore the flow will be dispersed slowly and homogeneously in the surroundings of the burner. A groove (in the table) and positioning blocks are shown also: in this way the position of the glass bell is fixed.

![Diagram](image1)

**Figure 3.1:** Schematic view of the burner environment and the burner

As mentioned, two variables are measured: the temperature and the gas composition. The temperature is measured, using type K thermocouples at five points above the burner outlet, as shown in figure 3.2(a). The first point is at 90 mm downstream the burner, the next points each 30 mm above the first thermocouple. Due to the movement of the gas flow downstream of the burner, likely induced by the swirl, it is hard to read out the digital display of the thermocouple read-out instrument: the displayed temperature fluctuates in the order of several degrees during the measurements. The temperature variation between thermocouples 1 and 5 (so over a distance of 120 mm)
is relatively small (about 20 degrees). In most cases discussed in the results, the measured temperature at 120 mm downstream (so the second thermocouple) of the diverging outlet is shown. By choosing the same couple for all experiments, a comparable situation is created. The second thermocouple is chosen while this couple is the one closest to the burner that gives reliable data for all measured cases. The results measured with this couple approach the average temperature of the five couples best. For example, the first couple starts glowing for some specific cases when the flame moves downstream the burner, the temperature measured in that case deviates from the temperature measured by the other couples. Figure 3.2(b) shows an impression of the position of the flames. A side-top view of the burner is shown. The flames are located inside the inner tube of the burner. A closer look shows that 7 flames are located right at the injection nozzles.

![Figure 3.2](image1.png)

(a) Schematic view of the position of the thermocouples and the flames

(b) A side-top view of the burner: right at the nozzles 7 blue flames are located

**Figure 3.2:** Position of the thermocouples and the flames (Inlet gas composition: H$_2$: 32 %, CH$_4$: 2 % and N$_2$: 66 %; LHV: 4.2 MJ/Nm$^3$; $\lambda$: 0.2; P: 2.8 kW) in relation to the burner

The gas composition is measured using a gas chromatograph (GC). The GC used is described in detail in appendix C, where also the used calibration procedure is explained and some aspects of the accuracy are addressed. The samples for the GC are taken directly downstream of the glass bell (as shown in figure 3.1(a)): so at a height of about 500 mm downstream of the diverging part of the burner. In this way the gas composition is measured for the situation that the gases have a residence time of about one second in the glass bell, so the same situation like in the proposed gasifier configuration. During this residence time the gases might still be reacting. Another effect of the choice of the sampling point is that the sampled gases are already at a relative low temperature (about 200 à 300 °C). This will be discussed in detail in appendix C in the section about accuracy. In this appendix also the calibration procedure is described. The GC is calibrated for 6 components: hydrogen (H$_2$), methane (CH$_4$), oxygen (O$_2$), carbon dioxide (CO$_2$), carbon monoxide (CO) and nitrogen (N$_2$). The water is extracted from the sample, so all the mole fractions measured are dry concentrations.

In this chapter, the behaviour of the burner is studied with and without using carbon monoxide. For safety reasons the experiments of the next chapter will be performed without the use of carbon monoxide. In these experiments lasers will be
used. The lab where these experiments are performed is tightly closed because of the laser light. This closed environment can cause problems using a toxic gas like carbon monoxide in such high amounts as used in the burner experiments. Therefore, most of the experiments in this chapter are performed without the use of carbon monoxide. However, to check the influence of this component, some experiments are repeated for a carbon monoxide containing inlet mixture. These experiments will be compared to the equivalent without the use of carbon monoxide in the fuel mixture.

The heating value, or the energy content, of the gas is an important property. Biogas is often categorised by energy content. Low energy biogas is commonly reported as gas with a calorific value of 4-12 MJ/Nm$^3$ (e.g. [66]). For biomass gasification with air holds that this results in gas with a heating value of 4-8 MJ/Nm$^3$ [73]. The energy content of the biogas depends much on the type of gasifier used. Fixed bed gasifiers are generally divided in three gasifier-types: updraft, downdraft and crossdraft. The inlet composition of the gas will be a combination of an updraft and a downdraft gasifier. Table 3.1 shows an example of the gas composition and energy content of the gas of an updraft and a downdraft gasifier.

### Table 3.1: Gas composition (mole %) and energy content (MJ/Nm$^3$) for a downdraft and an updraft fixed bed gasifier [66]

<table>
<thead>
<tr>
<th>Gasifier Gas Analysis</th>
<th>Updraft</th>
<th>Downdraft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H$_2$)</td>
<td>6.9</td>
<td>15.2</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>29.5</td>
<td>22.1</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>2.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Carbon Dioxide (CO$_2$)</td>
<td>6.1</td>
<td>9.7</td>
</tr>
<tr>
<td>Nitrogen (N$_2$)</td>
<td>55.3</td>
<td>50.8</td>
</tr>
<tr>
<td>Lower Heating Value</td>
<td>5.26</td>
<td>5.04</td>
</tr>
</tbody>
</table>

This table shows that the difference in heating value is not very large for these two types of fixed bed gasifiers. A lower heating value of about 5 MJ/Nm$^3$ is a realistic assumption. In this study the fuel mixtures are characterised using their lower heating value (i.e. the heat that evolves by the complete combustion of a unit of volume of gas with air and constant pressure of 101.325 kPa and a constant temperature when the water produced by the combustion remains as a vapour [29]). A mixture of several gases without tar is used in this chapter. In this way resemblance between the biogas and the gases used, is realised. One advantage of using mixtures, is that it is possible to test the influence of the gas composition of the inlet fuel on the outlet temperature, gas composition and stability of the flame. In this study the lower heating value of the mixture is calculated from the heating values of the separate components, so:

$$LHV = \% \text{CH}_4 \cdot LHV_{\text{CH}_4} + \% \text{H}_2 \cdot LHV_{\text{H}_2} + \% \text{CO} \cdot LHV_{\text{CO}}; \quad (3.1)$$

where \% CH$_4$ is the volume fraction of methane, \% H$_2$ is the volume fraction of hydrogen and \% CO is the volume fraction of carbon monoxide; and LHV for the lower heating values: with LHV$_{\text{CH}_4}$ the heating value of methane (35.882 MJ/Nm$^3$), LHV$_{\text{H}_2}$
the heating value of hydrogen (10.779 MJ/Nm$^3$) and LHV$_{CO}$ the heating value of carbon monoxide (12.634 MJ/Nm$^3$) [29].

As shown in the table, biogas contains nitrogen and carbon dioxide. In this study the carbon dioxide is replaced by nitrogen for practical reasons. While both of these gases play the role of an inert dilutent, the influence of this replacement should be minimal. It is important to mention that to a limited degree, the carbon dioxide can become involved in the flame chemistry (for example caused by the water shift reaction which states that CO$_2$ together with H$_2$ converts to CO and H$_2$O). Haniff et al. [34] studied the burning velocities of methane-nitrogen-air mixtures and methane-carbon dioxide-air mixtures. The burning velocities in the carbon dioxide case are systematically higher. Their results show also an increase in this difference when more of these components is used in the fuel. They state that the faster decrease of the burning velocity for carbon dioxide might be due to the larger specific heat of this component. Also the radiation emitted is known to be higher for carbon dioxide compared to nitrogen. This higher radiation might cause a quicker cooling of the gas downstream.

The power used to operate the burner is another important parameter for determination of the working range of the burner. The definition of this parameter in this particular case is however difficult, because only a small part of the gas is actually burned. Considering the set-up from a ‘system’ viewpoint, it is reasonable to define a power based on the amount of pyrolysis gas: $P_{\text{fuel burner}}$. This power is calculated, as if all the gas is burned. From the viewpoint of this burner, however, defining a power based on the amount of the air is more logical: $P_{\text{air burner}}$. Knowing the heating value of the fuel, the fuel burner power can be calculated by multiplying this lower heating value (LHV) by the total volume flow of the fuel $\dot{V}_{\text{inner}}$:

$$P_{\text{fuel burner}} = \text{LHV} \cdot (\dot{V}_{\text{inner}}).$$  \hspace{1cm} (3.2)

The power based on the amount of air, $P_{\text{air burner}}$, equals this value multiplied by $\lambda$:

$$P_{\text{air burner}} = \lambda \cdot \text{LHV} \cdot \dot{V}_{\text{inner}} = \lambda \cdot P_{\text{fuel burner}}.$$  \hspace{1cm} (3.3)

In this study several fuel powers in the range up to 4 kW are tested.

The temperature that can be reached by the burning of the gas, can be estimated theoretically. When the $P_{\text{air burner}}$ as defined in equation 3.3, is theoretically assumed to be used for an increase of the outlet temperature only, the theoretical temperature increase can be calculated using:

$$P_{\text{air burner}} = \dot{m} \cdot c_p \cdot \delta T;$$  \hspace{1cm} (3.4)

where $\dot{m}$ is the total mass flow that should be heated; and the temperature change of interest is $\delta T$. The specific heat ($c_p$) is a crucial factor in this calculation, but not at all a known one. The $c_p$ is calculated as a combination of the several individual components; using 2.21 kJ/kgK for methane, 14.3 kJ/kgK for hydrogen, 1.05 kJ/kgK for carbon monoxide, 1.04 kJ/kgK for nitrogen and 1 kJ/kgK for air. So, combining the expressions for $P_{\text{air burner}}$ (equations 3.3 and 3.4), results in a theoretically expected temperature.
3.2 Flame stability range

The working range of the burner is tested in a wide range of ratios of the volume flows and swirl numbers. Two arbitrary cases for the gas situation are studied: one case using a heating value (LHV) of 4.2 MJ/Nm$^3$ and a power of 2.8 kW and the other case using a heating value of 5.4 MJ/Nm$^3$ and a power of 2.1 kW. These cases are shown separately in the figure 3.3. This figure shows the Reynolds number in the inner tube ($Re_{\text{inner}}$) as a function of the ratio of the volume flows ($\text{Volume flow}_{\text{inner}}/\text{Volume flow}_{\text{outer}}$). Only the stable burning cases are plotted in this figure. This figure is a combination of the results of the water flow experiments shown in figure 2.7 and the burning results. It is found that a range of volume flows from 2 to 8 results in a stable flame situation. As shown in this figure all the stable cases do coincide with the jet-mixing area as defined in the previous chapter.

![Figure 3.3: Re\text{inner} as a function of $\dot{V}_{\text{gas}}/\dot{V}_{\text{air}}$. Inlet gas composition burning cases: H$_2$: 15 and 20 %, CO: 15 and 20 %, CH$_4$: 2 % for both and N$_2$ 48 and 58 %; LHV: 4.2 MJ/Nm$^3$ and LHV: 5.4 MJ/Nm$^3$; P: 2.8 and 2.1 kW](image)

Interesting are also the values of $S$ in these cases. As stated before the swirl number $S$ is used to characterise the swirl intensity in the flow, where the value of 0.6 separates high and low swirl cases. Figure 3.4 shows the same data as figure 3.3, however now the Reynolds number in the inner tube ($Re_{\text{inner}}$) is shown as a function of the swirl number $S$. In this figure, it is shown that the swirl numbers in the stable burning situations are low. As shown, the stable cases all coincide with the area in which the jet mixing regime is defined. The case denoted with the ‘star’ symbol represents the values of the mixture that is used in most of the experiments in this chapter. While the swirl numbers in the burning cases will all be below the critical value of 0.4, the derivation of $S$ (equation 2.4) is valid. This means that the approximation for the swirl number $S$ is suitable. Another conclusion is that the swirl situation in the burner is typically a low swirl case, since the swirl number is below 0.6.
In this section, the effect of variation in heating value on the outlet temperature is studied. To determine this effect other variables have to be constant, like the burner (fuel) power and \( \lambda \). Changing the heating value is done by altering the hydrogen and the carbon monoxide fractions in the fuel. The nitrogen concentrations change accordingly: all this alters the heating value. To keep the burner power \textit{and} the lambda at the same level in all set-points, the value of the total volume flow of the fuel added has to be decreased. Figure 3.5 shows the temperature as a function of the heating value of the inlet fuel. In this figure corrected measured values are shown together with theoretical values. The calculation of the theoretical temperatures is described in section 3.1. The measured values are corrected for radiation losses. This correction is described in detail in appendix A. The burner power is 2.8 kW in all cases. \( \lambda \) is kept constant at 0.2.

This figure shows that the measured temperature increases when the heating value increases. In other words, delivering more energy per cubic metre (i.e a higher heating value) results in a higher temperature. It is found the burner operates well using a mixture of hydrogen, carbon monoxide, methane and nitrogen. These experiments show that it is possible to operate the burner in a stable way with a diffusion flame, at calorific values down to 3 MJ/Nm\(^3\). This value is low enough for the purpose of this study: burning low calorific pyrolysis gas coming from a downdraft/updraft gasifier which has values (see table 3.1) ranging from 5.5 - 5.8 MJ/Nm\(^3\).

It is also shown that the measured values differ from the theoretical ones. The higher temperature in the measurements might be due to the chosen location of the thermocouples. The temperature is measured only at the center axis of the burner, so...
probably the secondary air is not heated yet, when the gases pass the thermocouples. The assumption made in the calculation is that both of the flows, the fuel as well as both air flows, are immediately heated by the burning. For higher heating values the difference in temperature between the theory and the measured values decreases. When considering that the heating value is lowered by adding more nitrogen to the fuel (at a constant volume flow of the fuel). Adding more nitrogen means that there is more inert volume that should be heated by the flame. This might cause the increase in difference for the lower heating values.

The effect of variation in the burner (fuel) power is also studied. The temperature is measured in several cases, when using different powers. The differences in temperature however are minimal. The accuracy of the thermocouples is not high enough to determine a possible trend. When tackling this problem theoretically, it can be shown that the theoretically expected increase in temperature is similar for the different powers. From this observation two conclusions can be drawn: the losses are apparently negligibly small and also the combustion is independent of the absolute velocity of the flows (which means that the combustion is thus independent of the flow regime is laminar or turbulent).

### 3.4 Inlet gas composition

In this section, the influence of the inlet gas composition of the fuel is studied. The effects on the temperature and the gas composition are investigated, while the mole fractions of methane and hydrogen in the inlet fuel is varied. Various set points are tested. Like in some preliminary experiments, it is not possible to operate the burner using a pure methane-nitrogen mixture at the heating value of 4.2 MJ/Nm³ (P: 2.8 kW and \( \lambda \): 0.2). The experiments presented in this section use a heating value of 10.8
MJ/Nm³, while for this situation the whole range of hydrogen fractions is covered. In these experiments, no nitrogen is added in the 'pure hydrogen flame situation'. This means that then the ratio of the fuel and the air volume flows is different from the other ratios studied in this thesis. In the other cases, always a value of about 5 is realised. For the 'pure hydrogen'-situation a ratio of the volume flows of only 1.7 is needed to realise the required 0.2-value for $\lambda$ and a fuel power of 2.8 kW (also shown in figure 2.8 in chapter 2). This means that now, compared to the fuel flow a relatively large volume of air flow is added.

Figure 3.6 shows the temperature 120 mm downstream of the burner as a function of hydrogen molar fraction in the inlet fuel, using a heating value of 10.8 MJ/Nm³. As shown in this figure, the temperature for the cases where methane and hydrogen are both present is almost constant. A small increase (730 to 780 °C) is found when adding more hydrogen. Several parameters influence the temperature downstream of the burner when adding more hydrogen, for example the specific heat ($c_p$), the density ($\rho$) or geometry related features. One remarkable aspect is that a small shift in flame position is found when adding more hydrogen. The pure hydrogen flame is observed to move more downstream in the burner. The distance from the flame to the thermocouple is shortened in this way. So the elevation in temperature is not necessarily a result of more heat produced by the flame. On the other hand, the shift is small and the distance to the burner (120 mm) should probably be large enough to level out this effect. This position might also be the first opportunity for the fuel to get in contact with the secondary air: probably a second flame forms at this position. The measurements of the gas composition might give more insight in the mechanism that increases the temperature in the cases that contain more hydrogen.

Not shown in a figure but worth mentioning, is that comparing the temperatures found in the 4.2 MJ/Nm³ and the 10.8 MJ/Nm³ situation, shows that the temperature is systematically higher in the latter case. This is an expected result, because in the
case of a higher heating value there is more energy available. This result resembles the effect of the heating value as found in the previous section.

In figure 3.7 the molar composition at the outlet is plotted as a function of the hydrogen fraction at the inlet. The gas chromatograph measures six components in the gases at outlet of the burner: carbon dioxide, hydrogen, oxygen, nitrogen, methane and carbon monoxide. These components are the only ones the GC is calibrated for. Because the columns are not suited for the separation of water, the water in the outgoing gases is extracted from the sample, so no water will be found in the gases: dry concentrations are measured.

![Graph showing molar composition at the outlet as a function of hydrogen molar fraction at the inlet.](image)

Figure 3.7: Composition at the outlet as a function of hydrogen molar fraction at the inlet; Inlet gas composition: a variable composition of H$_2$, CH$_4$ and N$_2$; LHV: 10.8 MJ/Nm$^3$; $\lambda$: 0.2; $P$: 2.8 kW

As shown, the burnable carbon containing molecules (CO and CH$_4$) decrease when increasing the hydrogen fraction. Stated in a more clear way: the carbon containing molecules decrease when the amount of methane in the input decreases: according to the carbon balance this is a logical occurrence. Figure 3.7 shows that the methane is the first component to decrease with increasing hydrogen fraction. The carbon monoxide decreases also, but the methane appears to be consumed first. The amount of carbon dioxide decreases slowly; only in the pure hydrogen case, this value drops to zero. It is also shown that the hydrogen is increasing with an increasing mole fraction of hydrogen.

The oxygen fraction is plotted in a special way. The measured oxygen fraction is diminished by the mole fraction of secondary air present at the inlet. When only the primary air is consumed by the flame and the secondary air is only a supporting flow, then the amount of oxygen left in the outlet gas is approximately equal to the amount of oxygen feeded by means of the secondary air. Note however that this is only true when the volume stays about constant. Whether the total volume at the inlet is equal to the volume at the outlet, can be checked by comparison of the mole fractions of the nitrogen at the inlet and the outlet. It is found that these two quantities resemble each other quite well in all cases. When the fraction of the `oxygen in the outlet minus
the oxygen fed by the secondary air’ equals zero, presumably only the primary air is used by the flames. As shown in figure 3.7 this quantity is only small positive (about 0.2 %) in almost all cases. Only in the cases approaching the pure hydrogen flame negative values are found. In this case the mixture consumes probably also a part of the secondary air (the co-flow) that is added to the surroundings of the burner: so in fact these flames burn at a higher $\lambda$ than 0.2. This might also cause the increase of the temperature found in figure 3.6. In the other situations, the results indicate that the co-flow acts only as a supporting flow.

The balances of all components are checked: carbon, hydrogen, oxygen and nitrogen. Like mentioned before, some components are not measured: water, C$_3$ components and nitrogen oxides. Taking into consideration that these fractions are the dry values, the amount of water formed can be roughly estimated by the fraction of hydrogen atoms missing (divided by a factor two). This fraction varies from 0 - 2 %. In the same way an estimation of the amount of water formed can be estimated by the missing fraction of oxygen atoms: the same order of fractions is found in this way.

![Figure 3.8](image_url)

**Figure 3.8:** The relative heating value as a function of hydrogen molar fraction at the inlet: the measured data together with the corrected data (which reflect only the effect of the burning); Inlet gas composition: a variable composition of H$_2$, CH$_4$ and N$_2$; LHV: 10.8 MJ/Nm$^3$; P: 2.8 kW; $\lambda$: 0.2

The heating value of the outlet gas is calculated from the data of the measured gas composition. Figure 3.8 shows the ratio of the outlet heating value of the gases and the initial (lower) heating value of the incoming gases (the relative heating value) as a function of hydrogen fraction in the inlet fuel for the measured data in corrected and uncorrected state. A correction for the dilution by the primary air flow is applied to gain more insight in the effect of the burning process only. As mentioned in the previous chapter, the ratio of the volume flows desired for a 10.8 MJ/Nm$^3$ mixture (and a $\lambda$ of 0.2), is 1.7. For the 4.2 MJ/Nm$^3$ cases however, a value of about 5 is needed. This means that for the 10.8 MJ/Nm$^3$ case more primary air is needed. Because the primary air used will cause dilution, it is interesting to take a closer look at the ‘burning data’. These data are corrected for dilution by the primary air and display therefore
the effect of the burning only. As shown in this figure the real heating value of the
gas downstream of the burner is about 60 % of the inlet heating value; however, when
only considering the effect of the burning on the heating value of the outlet, this value
is much higher: about 87 % in almost all cases. The outlet heating value stays rather
constant. The changes of the methane and carbon monoxide fraction seem to level out
the changes in hydrogen fraction with regard to the heating value of the gas. The pure
hydrogen situation seems to be a special case. This is the only case in the figure that
shows the same trend as found in the previous section: an increase in temperature
coinciding with a decrease in heating value. As shown in the gas composition in this
case, more oxygen is consumed. The secondary air might be used in this flame. So, the
assumption of elevating the temperature by increased reduction of the heating value
might hold for this situation. Summarising, we can state that the results support the
statement that for a mixture of hydrogen and methane the exact mole fraction of these
components is not a critical factor.

3.5 Primary air

To investigate the effects of the amount of the primary air used, again two variables
are measured: temperature and gas composition. In this experiment the fuel flow is
kept constant. So, when adding more air to this flow, $\lambda$ is increased. The effect of
adding more primary air on the temperature is shown in figure 3.9. In this figure the
output of only one of the thermocouples is shown: the one 120 mm downstream of the
burner. The heating value is 4.2 MJ/Nm$^3$ for all cases, using an inlet composition of
32 % hydrogen, 2 % methane and 66 % nitrogen. The amount of primary air is varied
during the experiment. As shown, increasing of the amount of primary air leads to an
increase of temperature.

![Figure 3.9: Temperature 120 mm downstream of the burner as a function of primary air flow l/min; Inlet gas composition: H$_2$: 32 %, CH$_4$: 2 % and N$_2$: 66 %; LHV: 4.2 MJ/Nm$^3$; P: 2.8 kW](image-url)
In figure 3.10 the same temperature data as in figure 3.9 are shown, however in this case the air flow is converted to the quantity $\lambda$. As shown in this figure, the temperature rises, when $\lambda$ increases. The higher temperature is probably created while more of the fuel is consumed in the flames. In other words, more of the energy content and more of the power present in the fuel is used by the flames. To check this theory, it is interesting to examine the power used by the flames: the $P_{\text{air burner}}$. In figure 3.10 this air power is plotted as a function of $\lambda$. This is the amount of the burner power that is used when burning all the primary air that is added to the burner (as defined in equation 3.3). The amount of air power increases when $\lambda$ increases, so the increase in measured downstream temperature is a logical occurrence.

![Graph showing temperature and power as a function of $\lambda$.](image)

**Figure 3.10:** Temperature (120 mm downstream of the burner) and the actual used power (theoretically) as a function of $\lambda$; Inlet gas composition: $H_2$: 32 %, $CH_4$: 2 % and $N_2$: 66 %; LHV: 4.2 MJ/Nm$^3$; $P$: 2.8 kW

Also the effect of carbon monoxide on the temperature is studied. To check the influence of this component, the outlet temperature will be studied in three different cases. One of these cases is the experiment shown above.

**Table 3.2:** Used fuel mixtures (mole %) together with the lower heating value (LHV) (MJ/Nm$^3$) and the density $\rho$ (kg/m$^3$)

<table>
<thead>
<tr>
<th>CH$_4$ (%)</th>
<th>H$_2$ (%)</th>
<th>CO (%)</th>
<th>N$_2$ (%)</th>
<th>LHV (MJ/Nm$^3$)</th>
<th>$\rho$ (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>15</td>
<td>15</td>
<td>68</td>
<td>4.2</td>
<td>1.07</td>
</tr>
<tr>
<td>5</td>
<td>22.4</td>
<td>0</td>
<td>72.6</td>
<td>4.2</td>
<td>0.97</td>
</tr>
<tr>
<td>2</td>
<td>32</td>
<td>0</td>
<td>66</td>
<td>4.2</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Table 3.2 shows the three different compositions used, with their heating values and densities. As shown, the amount of carbon monoxide is replaced by an increase
in the hydrogen or in the hydrogen and the methane concentration. The fifth column displays that the heating value for these fuel mixtures is kept constant. For the burning, it is also important that the densities of the mixtures are quite similar. As shown in this table, the densities of the two first mixtures resemble each other the most.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
</tr>
<tr>
<td>520</td>
</tr>
<tr>
<td>540</td>
</tr>
<tr>
<td>560</td>
</tr>
<tr>
<td>580</td>
</tr>
<tr>
<td>600</td>
</tr>
<tr>
<td>620</td>
</tr>
<tr>
<td>640</td>
</tr>
<tr>
<td>660</td>
</tr>
<tr>
<td>680</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>λ</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% CH₄; 32% H₂; 0% CO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% CH₄; 22.4% H₂; 0% CO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% CH₄; 15% H₂; 15% CO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.11**: Temperatures (120 mm downstream of the burner) as a function of $\lambda$ for three different compositions as shown in table 3.2; LHV: 4.2 MJ/Nm³; P: 2.8 kW

Figure 3.11 shows the temperature at 120 mm downstream of the burner for these three situations. The temperature is lowest for the situation containing carbon monoxide. There is a difference of only 20 °C between the carbon monoxide containing mixture and the 5% methane mixture without carbon monoxide. Between the experiments with and without carbon monoxide (using 2% methane in both cases), a difference is found of about 80 °C. The difference between the two mixtures without carbon monoxide is a little smaller: about 60 °C. This might be an effect of the differences in density. As shown in table 3.2 the density of the mixture using more methane resembles the biogas-like case (the one using carbon monoxide) most. As shown in the figure, the temperatures of those two mixtures are closer to each other than the temperature measured for the 2% methane situation without carbon monoxide. For the burner outlet experiments of the next chapter, where the temperature is important, this 5% methane composition will be used.

It is interesting to study the effect on the individual components in the outlet when more primary air is added. For the composition using 2% methane without carbon monoxide, figure 3.12 shows the composition at the outlet as a function of $\lambda$. Two effects play a role in this situation: on one hand there is the effect of the burning of the fuel; while on the other hand the primary air dilutes the composition measured at the outlet. To decouple these two effects the data are shown twice: the pure data as well as the data corrected for dilution by the primary air are shown. Note that these corrected data are not a physical result; they serve only as a help for the understanding
Various components [Mole %]

\[ \text{[CO}_2\text{]} \]
\[ \text{[CO]}^{*20} \]
\[ \text{[CH}_4\text{]}^{*20} \]
\[ \text{[H}_2\text{]}/ \text{5} \]
\[ \text{[O}_2\text{]} - \text{O}^{\text{sec}} \]

Figure 3.12: Composition at the outlet as a function of \(\lambda\): the measured data together with the corrected data (which reflect only the effect of the burning); Inlet gas composition: \(\text{H}_2\): 32 %, \(\text{CH}_4\): 2 % and \(\text{N}_2\): 66 %; LHV: 4.2 MJ/Nm\(^3\); P: 2.8 kW

of the process. The methane is the first component that disappears with an increasing \(\lambda\): at a \(\lambda\) of \(\geq 0.4\) no methane is left in the outlet gas. The carbon monoxide decreases also, but more slowly than the methane. The corrected data show a lower decrease as the measured ones, this means that the decrease of carbon monoxide caused by the burning is in fact even slower than found in the measurements. For carbon dioxide, an interesting difference is found between the measured data and the corrected ones. From the measurements the carbon dioxide level appears to stay almost at the same level; when correcting for dilution however, it is found that this fraction doubles in the measured \(\lambda\)-range.

Another interesting effect is found for the hydrogen: the measured data show a decrease when increasing \(\lambda\). When correcting for dilution however, the amount of hydrogen stays at a constant level. This could indicate that the hydrogen does not participate more in the burning when \(\lambda\) is increased. However, this effect might be a combination of two processes. Based on the results found for the burning of methane, might be concluded that the primary air added in the burner give a preference to burn methane and (to a lesser extend) carbon monoxide instead of hydrogen. This results in two effects:

1. only little hydrogen is burned, because of this preference
2. hydrogen might form from the process of burning methane in a situation where little air is present

The second effect is easily explained by examination of the possible global reactions for methane burning. Because there is little oxygen present, the reaction where hydrogen
is formed might be dominant:

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2 \]  \hspace{1cm} (3.5)

instead of (using 2 \text{O}_2) and giving \text{CO}_2 and 2 \text{H}_2\text{O}. Apparently, first the partial reaction of burning methane to carbon monoxide and hydrogen takes place, followed by the oxidation of the formed carbon monoxide. When there would be enough air, after this methane and carbon monoxide burning reactions, the hydrogen would burn while forming water. For this last step apparently no oxygen and probably activation energy, is left.

The oxygen is again plotted as the "measured oxygen fraction diminished by the mole fraction of secondary air used at the inlet" (after again first comparing the nitrogen fractions at the inlet and the outlet). This value increases when \( \lambda \) increases (as shown in figure 3.12). When correcting this value for the dilution by the primary air however, it is found that the effect of burning only is minimal: the corrected value stays at about 0.4. This means that not all the air is used in the burning. This value being not below zero, might indicate that the secondary air is only a supporting flow in these experiments. In the next section however, the influence of the secondary air will be studied in detail.

From these composition data the conclusion can be drawn that when more air is added to the burner, the amount of air that is burned stays about the same. This might also cause the minimal effect on the temperature.

The trends of the measured results shown in figure 3.12 resemble globally the results found in literature about gasification of wood (e.g. [20] and [66]). For example, Desrosiers [20] shows outlet compositions of experiments that are performed in a gasifier fed with air at atmospheric conditions as a function of the air equivalence ratio. This equivalence ratio is comparable to \( \lambda \) as defined in this study. Figure 3.13 shows his results. Of course the situation is different because wood and air is used, instead of only gas (in a composition like coming from wood) like used in this study.

![Figure 3.13: Composition at the outlet as a function of the equivalence ratio (ER) [20]](image-url)
When comparing the results of Desrosiers with the results of the outlet gas composition found in this study, in general the same trends are shown. In both situations, the methane is the component that decreases first. A decrease in the amounts of hydrogen and carbon monoxide is found in both of the situations. Although, for the experiments using the burner geometry the carbon monoxide decreases faster than the hydrogen. This is opposite to the decrease of these components in the results of Desrosiers. This remarkable difference might be due to the characteristics of the processes used.

The carbon dioxide however shows a different tendency: instead of a decreasing-increasing curve shown by Desrosiers, the amount of carbon dioxide in this study stays about the same. This might be a result of the inlet gas composition that is chosen. Real biogas from wood contains about 8% carbon dioxide and 15% carbon monoxide [66]. However, in the inlet gas used in the experiments of figure 3.12 no carbon dioxide or carbon monoxide is used.

Wang and Frenklach [81] studied the kinetics in premixed flames. They also report that increasing the air flow leads to a decrease in hydrogen and carbon monoxide concentrations. Pan et al. [61] studied the injection of secondary air by the gasification of residual biomass and coal. They found that increasing the amount of air added, results in a decrease of the hydrogen and carbon monoxide concentrations in the gas composition. Moreover, they saw that adding more air reduces the heating value of the outgoing gases, caused by a decrease in the concentrations of carbon monoxide and hydrogen.

![Figure 3.14: The relative heating value as a function of λ: the relative LHV is based on the measured data and the corrected data (which reflect only the effect of the burning); Inlet gas composition: H₂: 32 %, CH₄: 2 % and N₂: 66 %; LHV: 4.2 MJ/Nm³; P: 2.8 kW](image)

So, since a higher λ results in lower hydrogen and carbon monoxide concentrations in the gas, the heating value of the product gas will change. Based on the data of the several individual components the heating value of the outlet gas can be determined. Figure 3.14 shows the ratio of the outlet heating value of the gases and the initial heating value of the incoming gases as a function of λ; both the measured data and the
data which are corrected for dilution by the primary air are shown. A decrease of the relative heating value is shown. It is shown that the decrease of the heating value for the measured data, which include both the dilution and the burning effect, is 73 \% for \( \lambda \) is 0.2 and 47 \% for \( \lambda \) is 0.75. The effect of the burning only, ranges from 87 to 82 \%: this means that there is indeed an increase of the consumption of the fuel by the flames: resulting in an increase of temperature and an increase of the air power (as shown in figure 3.10). These results support the theoretical calculation of the \( P_{\text{air\_burner}} \) because this relative decrease in heating value is only possible when a higher amount of this power is used. In the air power calculation, all the primary air is assumed to be used in the flame. This means that the secondary air is assumed to act only as an inert co-flow.

### 3.6 Secondary air

The influence of the secondary air flow on the burner behaviour is an important aspect. The secondary air is added as a co-flow and is meant to control the environmental pressure of the burner, so it is important that this flow does not participate in the burning process. Therefore it is interesting to investigate whether this air participates in the flame or not and also to which amount the co-flow can be added without starting to participate in the burning. As shown in the experiments of the previous section, when adding a small amount of secondary air (about 1 l/min) this air is apparently not participating in the combustion process. This is checked by the calculation of the 'oxygen minus secondary air' plot in figures 3.7 and 3.12: this quantity is zero in most of the cases. Again two variables are measured: the temperature and gas composition.

![Figure 3.15](image_url)

**Figure 3.15:** Temperature 120 mm downstream of the burner as a function of the co-flow; Inlet gas composition: \( \text{H}_2: 32 \%, \text{CH}_4: 2 \%, \text{N}_2: 66 \% \); and \( \text{H}_2: 15 \%, \text{CH}_4: 2 \%, \text{CO:} 15 \% \) and \( \text{N}_2: 68 \% \)

Figure 3.15 shows the temperature at 120 mm downstream the burner as a function of the secondary air flow for two cases: one set of experiments using carbon monoxide and one without. Both compositions have a heating value of 4.2 MJ/Nm\(^3\). The tem-
temperature for the cases that contain carbon monoxide shows a lower value compared to the other cases. Increasing the amount of secondary air results in a decrease of temperature: for both situations a cooling effect is observed. This cooling effect also indicates that the secondary air acts indeed only as a co-flow. As found in the section 3.4 only in the pure hydrogen situation the co-flow burns in the combustion process. It is found here that in the more biogas-like cases (using a combination of hydrogen and methane), the temperature will decrease when adding more co-flow.

![Graph showing the relationship between CO\textsubscript{2}, CO, CH\textsubscript{4}, H\textsubscript{2}, and O\textsubscript{2} concentrations and co-flow rate.]

**Figure 3.16:** Composition at the outlet (the data are corrected for dilution by the co-flow) as a function of the co-flow; Inlet gas composition: H\textsubscript{2}: 32 %, CH\textsubscript{4}: 2 % and N\textsubscript{2}: 66 %; LHV: 4.2 MJ/Nm\textsuperscript{3}; P: 2.8 kW

To see what happens in detail, the outlet gas composition is measured for the situation without carbon monoxide in the fuel. In figure 3.16 the molar fraction of several components is plotted as a function of the co-flow rate. By adding more secondary air to the flow, the concentration of the components in the outlet gas is diluted by the amount of air added. The data plotted in this figure are corrected for this dilution effect. The measured gas composition stays the same for the corrected situation. Again the oxygen fraction is plotted as the measured oxygen fraction minus the mole fraction of secondary air used. As shown in this figure this value is again zero; this is also a proof that the secondary air is not reacting when added in a range from 1 to 8 l/min. So these results indicate that the co-flow is only supporting the flow.

Figure 3.17 shows the ratio of the outlet heating value of the gases and the initial heating value of the inlet gases as a function of the secondary air added. The ‘ratio’-data are based on the outlet gas composition data that are corrected for dilution. This figure shows that the decrease of the heating value of the fuel gas for the corrected value is minimal: about 73.5 % of the initial heating value remains. As mentioned before, in the experiments in all sections of this chapter -except the current one- a co-flow of 1 l/min is used. As shown the effect of dilution by this amount of co-flow is only about 2 %.
Figure 3.17: The relative heating value as a function of the co-flow: based on the measured data and the corrected data (for which a correction for dilution by the co-flow is applied); Inlet gas composition: \( \text{H}_2: 32\% \), \( \text{CH}_4: 2\% \) and \( \text{N}_2: 66\% \); LHV: \( 4.2 \text{ MJ/Nm}^3 \); P: 2.8 kW

3.7 Inlet temperature

When using the burner in the gasifier concept described in chapter 1, the gases coming from the gasifier will be recycled through the combustion chamber: the gases at the inlet of the burner will have an increased temperature. Therefore, it is interesting to study the effect of the inlet temperature on both the downstream temperature and the gas composition. In all the experiments discussed in the previous sections in this chapter, the inlet temperature was about 20 °C (293 K). In this section some of these 20 °C-experiments are performed again, now preheating the inlet fuel to 200 °C (473 K); so the difference in temperature is 180 °C. In the first subsection, this higher inlet temperature is studied while varying the inlet gas composition. In the second subsection, the primary air experiments are repeated using this higher inlet temperature.

Inlet gas composition

The influence of the inlet temperature on the outlet gas temperature and the composition is studied while varying the inlet composition of the fuel. As mentioned before, in the 20 °C case, it was not possible to study the pure methane-nitrogen flame at a heating value of \( 4.2 \text{ MJ/Nm}^3 \), therefore these experiments were performed at a heating value of \( 10.8 \text{ MJ/Nm}^3 \). For the 200 °C case however, it is no problem to stabilise the flame for all the different inlet compositions at \( 4.2 \text{ MJ/Nm}^3 \).

Figure 3.18 shows the temperature 120 mm downstream of the diverging burner outlet at the centreline of the burner in all cases: an inlet temperature of 20 °C and 200 °C for the \( 10.8 \text{ MJ/Nm}^3 \) case and an inlet temperature of 200 °C for the \( 4.2 \text{ MJ/Nm}^3 \) case. This temperature is plotted as a function of the hydrogen fraction and corrected
for radiation losses like described in appendix A. Note that in the ‘pure hydrogen’ case for the 4.2 MJ/Nm$^3$ situation only 39 % hydrogen is present in the fuel. The remaining part of the inlet fuel is nitrogen to lower the heating value of the mixture to 4.2 MJ/Nm$^3$. The conditions for the 10.8 MJ/Nm$^3$ case are similar to the conditions presented in section 3.4. For these two 10.8 MJ/Nm$^3$ conditions, the inlet temperature is the only variable that is changed and thus the effect found is caused by the elevation of this inlet temperature. The outlet temperature in the 200 °C case is systematically higher: about 140 à 150 degrees. The temperature for the 4.2 MJ/Nm$^3$ case is lower than for the 200 °C inlet temperature situation in the 10.8 MJ/Nm$^3$ case. This means that an increase of temperature is found when increasing the heating value of the fuel: the same result as found in the experiments focusing on the effect of variation in heating value of section 3.3. Note that this 4.2 MJ/Nm$^3$ temperature profile is important for the measurements in chapter 6, where the same conditions (200 °C inlet temperature and 4.2 MJ/Nm$^3$ heating value) are used for the treatment of the tars.

In literature, only a few studies concentrate on inlet temperature effects in a burning situation with regard to the outlet temperature and composition. A similar result as found in this study, is observed by Lin et al. [50]: an increase in the burnt gas temperature is shown when increasing the inlet temperature. Most of the studies about inlet temperature effects however, focus on other parameters than studied here. Knystautas et al. [47] state that reaction zone lengths decrease slightly, when increasing the initial temperature. Gu et al. [31] describe an increase in burning velocity when increasing the inlet temperature. This might cause the stabilisation of the pure methane flame for the 4.2 MJ/Nm$^3$ mixture. All these parameters might influence the gas composition. So interesting now, is to study the effect of this elevation in temperature on the outlet composition of the gases.
The effect on the gas composition for the two 10.8 MJ/Nm$^3$ situations, is shown in figure 3.19. In this figure, both the 20 ºC case and the 200 ºC case are plotted. (Note that the methane concentration is multiplied by a factor 5 and the hydrogen is divided by a factor 5). The effect of the inlet temperature on the gas composition is minimal. For the hydrogen concentration the largest difference is found: this value is a few percent higher for the 200 ºC mixture. Due to the higher inlet temperature of the gas, the reactivity is likely to be higher. Also the $c_p$ is somewhat higher. The amount of air added to the fuel however and also the oxygen concentration found in the outlet composition, is the same for the 20 and the 200 ºC cases. So, probably the same amount of fuel is burned using a similar quantity of the air added. Another explanation might be that this finding indicates that the temperature at which the sample is taken is already that low: the composition might be frozen. The residence time of the outlet composition in the glass bell is about 1 s. The temperature during this traject will be below 500 ºC. The effect of low temperatures is checked numerically with Chemkin - Perfectly Stirred Reactor (PSR) ([45]) using a GRI 3.0 mechanism. For 800 K (about 500 ºC) the composition is calculated numerically for several residence times. The compositions found are quite similar for various residence times. This is likely to be the main reason for the found similarity of the gas compositions for the different inlet temperatures.

The gas composition for the inlet temperature of 200 ºC using a 4.2 MJ/Nm$^3$ mixture, is shown in figure 3.20. This figure shows the same trend when increasing the hydrogen fraction as found in the 10.8 MJ/Nm$^3$ situations. However, due to the difference in heating value are the fractions of the gases of course lower. An increase of hydrogen fraction in the inlet results again in a decrease of the carbon containing components and an increase of the outlet fraction of hydrogen.
Figure 3.20: Gas composition as a function of hydrogen molar fraction at the inlet for an inlet temperature of 200 °C; Inlet gas composition: a variable composition of H₂, CH₄ and N₂; LHV: 4.2 MJ/Nm³; λ: 0.2; P: 2.8 kW

Figure 3.21: The relative heating value as a function of hydrogen molar fraction at the inlet for inlet temperatures: 20 °C (solid line) and 200 °C (dashed line); Inlet gas composition: a variable composition of H₂, CH₄ and N₂; LHV: 10.8 MJ/Nm³; λ: 0.2; P: 2.8 kW
According to the minimal effect on the gas composition, the effect of the elevation in the inlet temperature on the heating value in the output will be also minimal. Figure 3.21 shows this relative heating value as a function of the hydrogen fraction for the two 10.8 MJ/Nm³ situations. The heating value in the output in the 200 °C case is slightly elevated compared to the 20 °C case. Like the heating values for the 10.8 MJ/Nm³ cases, the heating value for the 200 °C 4.2 MJ/Nm³-situation stays also at about the same value for all different gas compositions. However the relative heating value left after the burning, is somewhat higher: about 73 %.

**Primary air**

For a heating value of 4.2 MJ/Nm³, measurements are performed to study the effect of λ at an inlet temperature of 20 °C and 200 °C. Figure 3.22 shows the outlet temperature as a function of λ. For both cases, the temperatures shown in this figure are measured at 120 mm downstream of the diverging burner outlet and corrected for radiation losses. Again, like in the experiments varying the hydrogen content of the inlet gas, the temperature at the outlet is elevated (about 150 °C) by the increased inlet temperature. The difference in increase of the outlet temperature however, diminishes slightly when increasing λ. This might be the result of the increased amount of (cold) air that is added in the higher λ cases.

![Figure 3.22](image)

*Figure 3.22:* Temperature 120 mm downstream of the burner as a function of λ; Inlet gas composition: H₂: 32 %, CH₄: 2 % and N₂: 66 %; LHV: 4.2 MJ/Nm³; P: 2.8 kW

Figure 3.23 shows the gas composition as a function of λ. Note that in this figure the carbon monoxide and the methane are multiplied by 10, and the hydrogen is divided by 10. Both the inlet temperatures show the same trend. However, again the influence is minimal. The difference for higher λ’s is even less: this is most clear found for the hydrogen, where for example for λ is 0.75 the values of the 20 and 200 °C case coincide.

Figure 3.24 shows the relative heating value as a function of λ. For lower values of λ the heating value in the output in the 200 °C case is slightly elevated. Increasing λ however, results in a decrease of this difference. As shown, at a λ-value of 0.75
the relative heating value is the same for the two different inlet temperatures. So the temperature increasing effect of the elevated inlet temperature decreases, when \( \lambda \) is increased.

To understand these results, more information is needed. As mentioned earlier, the relation between the inlet temperature and the gas composition is not often studied. Pitts [62] found relatively constant carbon monoxide concentrations for several inlet temperatures for high values of \( \phi \) (\( \phi > 1.3 \)). Because \( \phi \) equals \( 1/\lambda \), this means that he observed carbon monoxide concentration for values of lambda smaller than 0.8 to be independent of the inlet temperature. This coincides with the \( \lambda \)-range studied in this chapter. He performed a study on fuel rich diffusion flames in general, studying both the output of carbon monoxide and hydrogen. For carbon monoxide, he states that because of the lack of oxygen in rich flames (i.e. using a low \( \lambda \)) carbon monoxide is formed more than carbon dioxide.

For hydrogen, Pitts concludes that the formation of hydrogen is inlet temperature dependent. However this dependency is only found for temperatures higher than 1100 K (827 °C). As shown in figure 3.22, the temperature reached in the results shown here, is smaller than this value. However, the local temperatures in the flame are likely to be higher than measured at the centreline at a height of 120 mm above the outlet. These local temperatures could result in the increase of hydrogen of a few percent in the 200 °C case. These observations of Pitts, both for the hydrogen and the carbon monoxide, support the similarity of the results found in the 20 °C case and the 200 °C case.
Figure 3.24: The relative heating value as a function of $\lambda$ for inlet temperatures: 20 °C (solid line) and 200 °C (dashed line)

3.8 Conclusion

For gases coming from a gasifier, there is considerable uncertainty concerning the heating value, the temperature and the gas composition. Therefore, it is of special importance that the burner geometry can cope with various situations when using a $\lambda$ of 0.2. The results in this chapter show that a stable flame is attained for heating values down to 3 MJ/Nm$^3$, which is even less than the desired value of about 5 MJ/Nm$^3$. For several mixtures -containing methane, hydrogen or carbon monoxide and nitrogen- is found that the exact mole fraction of these components is not a critical factor. Methane is the first component that is consumed in the flame. Hydrogen however, seems to stabilise the flame at low heating values. The co-flow is not participating in the burning. For variations in inlet temperature, almost no change in gas composition is found. For higher inlet temperatures however, the burning is more stable. An important aspect of course is to produce a gas that is still burnable. The heating value downstream of the burner is quite high: still 73 % of the inlet heating value. Under all these conditions, the desired temperature of about 500 °C downstream of the burner, is realised.
Chapter 4

Burner outlet mixing

The temperature and the residence time of the gases are important parameters for the removal of the tar. Therefore, it is of special interest to study the velocity field and the temperature field downstream of the burner. In this chapter the second part of the mixing is studied: the mixing of the burnt and the unburnt gases. To examine this mixing in detail, several experiments are performed. Particle Image Velocimetry (PIV) is used to study the flow field directly downstream of the diverging burner outlet in detail: 2-dimensional as well as 3-dimensional. Also the temperature profile downstream the outlet is studied.

First, the flow is visualised using a high-speed camera. After that, the temperature profile is described. In the third section, the velocity profile in the flow and some related features are studied. The last section couples the temperature and the velocity: resulting in calculated residence times at a certain temperatures in the flow field. Of special interest is the distance downstream at which the temperature distribution becomes more homogeneous.

4.1 Flow visualisation

Preliminary measurements using a high-speed camera are performed to visualise the flow downstream of the burner. In this way more insight is gained in the mixing process. Preliminary PIV results show a lot of variation: two sequential images show a totally different flow field. The frequency of recording of the two PIV recordings is 15 Hz. To determine what happens in the mean time between the PIV image pairs, high-speed images are recorded.

The high-speed camera experiments are performed at a rate of 2250 Hz with a camera type Kodak Ektra Pro HS 4540. The flow in the inner tube is seeded with aluminum oxide (Al$_2$O$_3$) particles (φ about 1 μm) to visualise the flow field. An Argon continuous laser is used to illuminate the particles. The intensity of the light scattered by the particles is an indication for the mixing pattern of both flows: as one flow is seeded, a high intensity of light means a high intensity of seeding and thus a presence of the seeded flow at that place. The images are recorded both with and without ignition of the mixture.

Two typical high-speed camera images of the flow field in the cold state are shown in figure 4.1. The value of the volume flows is the same as for the burning situation
Figure 4.1: Typical high-speed camera image of the flow field in the cold state; Inner flow: 40 l/min; Outer flow: 8 l/min; Seeding: Al$_2$O$_3$

(a) Typical high-speed camera image of the flow field in the cold state at time: $t: 0\ s$
(b) Typical high-speed camera image of the flow field in the cold state at time: $t: 0.44\ s$

presented later on. Figure 4.1(a) shows the image at time $t = 0\ s$; whereas the second image (figure 4.1(b) is recorded 1000 images later, at $t = 0.44\ s$). A quiet, relatively low velocity flow, is shown. When examining the recordings, it is found that the seeding at the outer-sides of the flow moves even downwards; this might be caused by the relatively low flow velocity. The height of these images is about 135 mm. At the bottom of this figure a lighter coloured ellipse is shown: this is the top of the divergent part of the burner (about 90 mm in diameter). The dark band slightly above the burner exit, is caused by refraction of laser-light. As mentioned before, there is a glass bell placed on top of the burner to control the air intake. To avoid reflection and scattering of the laser light in the spherical glass wall, the wall is flattened at the two positions where the laser light passes through the glass. At these positions two windows are glued to the glass bell. The dark band is caused by an overlap between the glass bell and the glass window.

When igniting the mixture however, the structures found are larger and the velocity is higher. A typical image of the development of the mixing of the flows in the warm state, is shown in figure 4.2. The image is displayed twice. Figure 4.2(a) shows the image in pure state; whereas in figure 4.2(b) arrows are shown, which indicate the flow pattern. Also some dimensions are shown. The high-speed camera images show that the flow can be characterised as a turbulent and quickly fluctuating flow, with compact vortices. Another remarkable feature is the quick flutter of the flame, found in horizontal direction.

When comparing the mixing pattern of the cold flow situation with the situation with flame, the most striking difference is the velocity difference of the flows. When following a vortex in time, the time before a vortex collapses is shortened by eleva-
Burner outlet mixing

(a) Warm state

(b) Again warm state: the arrows roughly indicate the flow pattern, the dimensions are given in mm

Figure 4.2: Typical high-speed camera image of the flow field in warm state; Inlet gas composition: H\textsubscript{2}: 22.4 %, CH\textsubscript{4}: 5 % and N\textsubscript{2}: 72.6 %; Seeding: Al\textsubscript{2}O\textsubscript{3}; LHV: 4.2 MJ/Nm\textsuperscript{3}; \(\lambda\): 0.2; P: 2.8 kW; Inlet temperature: 20 °C

tion of the temperature. The flow velocity appears to double for the warm situation. Estimating this difference theoretically, the velocity in the warm situation should be a factor 2.6 larger (regarding the estimated temperature difference between the two situations: about 500 °C compared to 20 °C). Another difference between the cold and the ignited situation is the light intensity found in the image: due to the light that is emitted by the flame, the intensity of the light emitted by the seeding is different.

These preliminary high-speed camera images give a good first impression of the flow and serve as a basis for further study in this chapter, when using more complex measurement techniques. The remainder of the experiments described in this chapter are all performed under burning conditions, so in warm state.

4.2 Temperature

Temperatures are measured at 56 positions downstream of the burner using type K thermocouples (bead: \(\varnothing\) 1 mm). These couples are mounted in a line of seven points in the horizontal direction (spaced 15 mm from each other). To obtain data over the whole domain of interest, a guided track is constructed to move the seven couples easily to eight different positions in the vertical direction (also spaced 15 mm).

Figure 4.3 shows the interpolated average temperature profile in the flow, which is corrected for radiation, conductive and convective losses of the thermocouples as described in appendix A. The zero x position (on the horizontal axis) is located at the centerline of the burner. The zero y position (on the vertical axis) is at the upper
edge of the burner, at the end of the diverging part. So the (0,0) position is set at the burner outlet. In this figure 4.3 it is shown that already about 30 \text{ à} 40 \text{ mm} downstream of the diverging outlet of the burner the temperature is already quite homogeneous. Furthermore, it is shown that at 100 \text{ mm} and beyond the temperature in the flow is well mixed: the temperature profile at this height shows a homogeneous temperature of about 500 \textdegree C.

Worth mentioning is that this temperature profile indicates that there is indeed no flame existing at the outlet of the burner. This agrees well with the findings of the previous chapter 3. The temperature profile shows a high temperature core at the centerline of the burner. This indicates that the diffusion flames are located in the inner tube of the set-up and are formed at the height of the air-injection holes in there. However, for diffusion flames with weak swirl Beer and Chigier [5] state that there is a relatively cold, high velocity core over almost the whole length of the diffusion flame, with the main reaction zone present at the surface of the cold central core and the surrounding air. In figure 4.3 it can be shown that the core of this flow is instead of relatively cold, relatively warm. So the mixing studied in this chapter is the mixing of two flows: the burnt and the unburnt gases at the outlet of the burner.

4.3 Velocity

4.3.1 Particle Image Velocimetry technique

Technique

Particle Image Velocimetry (PIV) is used to study the flow field downstream of the burner outlet. 2-dimensional as well as 3-dimensional (stereo-PIV) measurements are
performed. The PIV technique is a laser optical measuring principle for fast and non-intrusive measuring of whole flow fields. A thin pulsed sheet of laser light is generated in the flow that is investigated. This flow is seeded with particles. Two images of the illuminated tracer particles are recorded with a digital camera. The displacement of the particles in between the two laser pulses is proportional to the flow velocity. The flow velocity in small interrogation areas is calculated by determining the displacement of the particles using the known scaling of the observed region. In general, the velocities are derived using either auto correlation or cross correlation of the images. When using cross correlation the direction of the movement is unambiguous determined. The direction of the movement in this turbulent 3D flow is not trivial, so in this study cross-correlation is used. The PIV algorithm is based on standard 2D FFT's, facilitated with a Gaussian subpixel-interpolation and a correction for in-plane particle loss [3].

PIV is performed using a (Kodak, 10 bit, 1008 x 1018) CCD camera.

In ‘normal’ PIV, a source of errors is the presence of an out-of-plane component of the velocity. When this component of velocity is significant, this will lead to loss of particles. As soon as the particle leaves the illuminated sheet the trace is ended. In the same way, particles entering the light sheet can cause mismatches. These two error sources are called the perspective error. When applying the stereo-PIV technique this ‘error’ is used to resolve the third velocity component. The light sheet used is thicker than the sheet used for ‘normal’ PIV. In this study a thickness of about 8 mm is used. In this way a stronger perspective effect is introduced for each camera. Since the perspective effect is different for each camera, the third velocity component can be resolved. This technique is a 2C/3D technique: a 3 dimensional (3D) field is determined using 2 component (2C) measurements.

Set-up

An overview of the whole set-up is given in figure 4.4(a). Stereo-PIV is performed using two CCD cameras (Kodak, 10 bit, 1008 x 1018) recording the same area at the same time (camera 1 and 2 in figure 4.4(a)). A third CCD camera (camera 3 in the figure, also Kodak, 10 bit, 1008 x 1018) is used for the 2D recordings.

The sheet of light is created by an Nd-YAG laser (f= 15 Hz, \( \lambda = 352 \text{ nm} \) and a pulse of 200 mJ). For the stereo-PIV measurements the laser sheet is about 8 mm in width. Narrow-band bandpass filters are used to filter the light: only the frequency of the light emitted by the laser is recorded by the cameras. PIV uses particles as tracers. The gas flow is seeded with \( \text{Al}_2\text{O}_3 \) particles of about 1 \( \mu \text{m} \). For accuracy and non-intrusivity reasons the particles should be chosen carefully. For example, it is important that the particles follow the flow, so the density of the particles and the flow should ideally be the same. Therefore the particles have to be small and mono-disperse. They also have to be spherical for the light scattering properties. It is also important that the distribution of particles in the flow is homogeneous. A seeding device is designed to dispense the particles in the flow. This is done using a capillary-like tube in a conical outlet box. For combustion holds that the particles should not be consumed by the combustion process. In practice, \( \text{Al}_2\text{O}_3 \)-particles of 1 \( \mu \text{m} \) in diameter are best suited for combustion processes. The melting point of 2300 K is high enough to survive most fuel-air combustion and the production is relatively cheap at the required diameter [70].

As shown in figure 4.4(a), the laser is positioned on the left side of the set-up,
whereas the two stereo-PIV cameras are positioned on the opposite side. By positioning the cameras in this way, both cameras record forward scattering. The positioning angle used for these cameras is 45°. Calibration is done by placing a calibration grid at eight different positions (each spaced at 0.5 mm) in the width direction of the laser sheet. In appendix B the grid itself, the calculations used for the calibration and the accuracy of the calibration are described.

A photograph of only the two stereo-PIV cameras and the burner is shown in figure 4.4(b). As shown in this photograph the two cameras are mounted on a rail, especially suited for the mounting and exact placement of these cameras. Scheimpflug mounts are used to position the cameras. As shown at the left of the figure, the burner and the calibration grid are placed under a glass bell. Preliminary ‘normal’ PIV and stereo-PIV experiments are done both with a cold mixture as well as with an ignited mixture. From these results together with the mixing results obtained with the high-speed camera and the data of the temperature profile, the area of interest for the velocity measurements is determined within the possibilities of the equipment.
The measurements are performed in a plane segment of 50 mm in height. The position of the measuring area in relation to the burner is shown in figure 4.5. The measuring area starts 10 mm above the diverging outlet and ends 50 mm above that (so 60 mm above the diverging outlet). A PIV image contains 30 x 30 data points. The center of the diverging outlet of the burner is at position (0,0) for the $x$ and $y$ direction. The width of this outlet is 90 mm.

The mixture used in the experiments is again a low caloric (but tar free) gas. The used gas mixture consists of hydrogen (22.4 %), methane (5.0 %) and nitrogen (72.6 %). So the heating value (LHV) is again 4.2 MJ/Nm$^3$. The burner fuel power used is 2.8 kW and $\lambda$ is 0.2 (i.e. $V_{\text{inner}}/V_{\text{outer}}$ is about 5).

### 4.3.2 Velocity field

PIV as well as stereo-PIV are used to study the velocity field downstream of the burner set-up. The averaged 2D velocity field of 300 PIV image-pairs is shown in figure 4.6. This field is calculated from the recordings of camera ‘3’ in figure 4.4(a). In this 2D picture the plotted arrows display the velocity $u$ in the $x$ direction and the velocity $v$ in the $y$ direction. The arrows that display these velocities are multiplied by a factor 10. The background color in this figure also quantifies the vertical velocity component ($v$). As shown in this figure the 2D velocity field is mainly directed straight upwards. The velocity component $v$ (in the $y$ direction) is larger than the $u$ component (in the $x$ direction); O($u$) ~ 0.01 m/s and O($v$) ~ 0.3 m/s.

Comparing the vertical velocities shown in this figure 4.6 with the temperature field of figure 4.3, a relation between the temperature and the vertical velocity is found. The region in the center of the bottom of the figures is one with a higher temperature and also with a higher velocity ($v$). At about 30 mm downstream of the burner, the vertical velocity is distributed more homogeneously. It is interesting that the temperature simultaneously spreads to a more homogeneous distribution.

In figure 4.7, again the averaged $u$-$v$ field is plotted in arrows, this field is now calculated from the images recorded with the two cameras ‘1’ and ‘2’ shown in figure 4.4(a). At the background the averaged third velocity component $w$ in the $z$ direction is plotted. This figure shows that it is indeed possible to determine the velocity-component in the direction perpendicular to the laser sheet. The velocity component $w$ (in $z$ direction) is of the same order as the velocity component $v$ in the $y$ direction: O($v$) ~ 0.3 m/s and O($w$) ~ 0.1 m/s. These results give a good indication for the swirl in the flow.

So, the arrows in both figure 4.6 and figure 4.7 represent the 2D field of the flow. The 2D flow field of figure 4.6 is however generated by the single camera, whereas the 2D flow field of 4.7 is generated by the two stereo-PIV cameras together. As shown, the field generated by the two stereo-PIV cameras and the 2D flow field recorded by the single camera are quite similar. However, more detailed analysis of the horizontal velocity component ($u$) shows that this component has a small systematic deviation in one direction in the 3D recordings. This is likely caused by the positions of the cameras. This effect is probably enhanced by the relatively small size of the displacement in the $x$ direction compared to the size of the other displacements.

Knowing the velocity field in three directions now, other interesting parameters like the swirl number, the turbulent kinetic energy and the residence times can be derived from these data. The next sections address these parameters.
Figure 4.6: Averaged 2D flow field, based on 300 image pairs; Inlet gas composition: H$_2$: 22.4 %, CH$_4$: 5 % and N$_2$: 72.6 %; LHV: 4.2 MJ/Nm$^3$; $\lambda$: 0.2; P: 2.8 kW; Inlet temperature: 20 $^\circ$C

Figure 4.7: Averaged 3D flow field, based on 300 image pairs; Inlet gas composition: H$_2$: 22.4 %, CH$_4$: 5 % and N$_2$: 72.6 %; LHV: 4.2 MJ/Nm$^3$; $\lambda$: 0.2; P: 2.8 kW; Inlet temperature: 20 $^\circ$C
4.3.3 Swirl number

As mentioned before, the degree of swirl in a flow is usually characterised by the swirl number $S$. According to the results of the 3D velocity field presented in the previous section, this flow can be characterised as a weak swirling flow: $S_{\text{max}} \approx 0.2$. Only strong swirling jet flows, which have an $S$ larger than 0.6, possess sufficient radial and axial pressure gradients to cause a central recirculation zone. This zone is not observed in weaker degrees of swirl [5]. In figure 4.7 indeed no recirculation zone is shown, this matches with the estimation of the swirl number of 0.2 in this flow.

![Swirl number as a function of $y$](image(a))

![Spreading angle as a function of $x$](image(b))

**Figure 4.8:** Some characteristics of the flow

An estimation of the decay of the swirl number in the vertical ($y$) direction is shown in figure 4.8(a). This number is determined by equation 2.4, where for $G$ the ratio of the maximal measured values of the $v$ and the $w$ are used which are obtained from the PIV data. First a slight increase is shown; this is probably an effect of the presence of the higher vertical velocity $v$ in that area (like shown in figure 4.6). As mentioned before, this higher velocity is likely to be a result of the higher temperature that is present there (like shown in figure 4.3). A strong decrease is shown from about 20 to 30 mm downstream of the burner outlet, likely caused by the decrease of the tangential velocity $w$ (like shown in figure 4.7). This decrease coincides with the height at which the temperature becomes more homogeneous. More downstream than 40 mm, the $S$ is approximately constant.

Of special interest is the spreading of the flow downstream of the diverging outlet. By estimating the spreading angle, more insight is gained in this phenomena. This spreading angle as a function of the $x$ direction is, shown in figure 4.8(b). This angle is calculated from the velocity field, based on the Kelvin theorem. This theorem assumes a constant circulation for a free vortex: i.e. $\Gamma = \oint \vec{w} \cdot r' ds$ is constant. Figure 4.9 shows the situation. For a certain value of $R_0$, $w$ is measured. The angular velocity $\Omega$ equals this measured velocity $w$ divided by $r$. For several values of $i$, the Kelvin theorem for this case states that $(\Omega R_0)_i = \text{constant}$. So for several heights $y$, the radii $r_x$ and $r_{y+i}$ are determined by the decay of the velocity $w$. From these calculated values for $r_x$ and $r_{y+i}$, the angle $\alpha$ is determined for various $R_0$’s. In figure 4.8(b), a clear separation is found between an inner and an outer space. The angles shown in the center of this
figure \((-10 \leq x \leq 10)\) might be influenced by the presence of the flame and the higher temperature, and are therefore not representative for the total spreading angle. The direction of the flow in this area is quite straight ahead. For the positions beside the center, an angle of about \(40^\circ\) is shown. Further from the center the angle is steadily increasing. Remarkable is that the angle is larger than the angle of the diverging outlet of the burner, which is \(30^\circ\).

### 4.3.4 Turbulent kinetic energy

The Reynolds number of the flow varies from about 2447 in the cold gas-flow in the burner to about 291 in the hot flow 60 mm downstream the outlet in the glass bell. The estimated Reynolds numbers for three different positions related to the burner are shown in figure 4.10.

![Figure 4.10: The Reynolds number as a function of the position for the warm case; Inlet gas composition: H\(_2\): 22.4 %, CH\(_4\): 5 % and N\(_2\): 72.6 %; LHV: 4.2 MJ/Nm\(^3\); \(\lambda\): 0.2; P: 2.8 kW; Inlet temperature: 20 °C](image-url)
An indication of the turbulent kinetic energy in this flow is given by parameter $k$. In this case $k$ is defined as:

$$k = \frac{1}{2} \sqrt{\overline{u'^2} + \overline{v'^2} + \overline{w'^2}}$$

(4.1)

where $\overline{u'^2}$ is the mean value of the squared fluctuation in $x$-direction, $\overline{v'^2}$ in $y$ direction and $\overline{w'^2}$ in $z$-direction.

Figure 4.11 shows the $k$ as a function of position. As shown in this figure the fluctuations are statistically quite inaccurate. The figure is, like the velocity field figures, an average of 300 PIV image pairs.

![Figure 4.11: Kinetic energy $k$ as a function of position, based on 300 image pairs](image)

The figure shows that high local values are present. The larger the size of the sample, the better the estimation will be. For the estimated fluctuations, $\sigma_{\text{fluc}}$, holds:

$$\sigma_{\text{fluc}} = \frac{s}{\sqrt{n_{\text{sample}}}}$$

(4.2)

with $s$ the real fluctuations of the population and $n_{\text{sample}}$ the sampling size. The sampling size in this case is only 300. Enhancing this number will improve the estimation. In spite of the number of images being quite low, some features can be mentioned. First, the influence of the flame, on the increase of turbulence is found at the bottom of this figure, mainly caused by fluctuations in the velocity in vertical direction ($v$). This agrees well with the measurements of e.g. Chigier et al. [15] on swirling flows under flame and no-flame conditions. They found substantial increases in turbulent kinetic energy and velocity fluctuations downstream as a consequence of combustion.
Another increase of turbulent kinetic energy is observed at the centerline of the flow. A similar fluctuation pattern is found in other studies for weak swirling flows with a swirl number of comparable size (a.o. [63]), and with this swirl number in case of combustion (a.o. [16]). These fluctuations are mainly caused by fluctuations in the velocity in the swirling direction \( w \): fluctuations in the center of the swirling flow. Almost no effect is observed of the fluctuations in the horizontal direction \( u \): these fluctuations are small compared to the other two directions (order (0.003 m/s) compared to order (0.015 m/s) in the other directions).

**4.4 Residence time**

Combining the velocity field information and the temperature data in the area directly downstream the burner, as presented in this chapter, the residence time of particles at a certain temperature can be calculated. In this way, more insight is gained in the time needed to reach a homogeneous temperature distribution for individual particles. A set of particles is released in a random way (numerically) in the 2D velocity field (calculated from the PIV experiments). The path the particles follow is shown in figure 4.12(a). In this figure 50 particles are released in the flow. The background shows the temperature profile the particles encounter during their path. Note that the velocity field used is only the 2D field, so the third velocity component is not included. Also the effect of fluctuations is levelled out by the averaging of the velocity field. In figure 4.12(b) the residence time of 1000 particles is shown as a function of the temperature. It is found that the residence time of the particles at the higher temperature is short. The whole PIV field only gives flow field information for 50 mm in height. So for a velocity of about 0.3 m/s in upward direction, like shown in figure 4.6, the residence time in the measured area is small. A peak is found for a residence time of 10 ms and 650 \( ^\circ \text{C} \), which is experienced by about half of the particles. Note however,
that this peak will spread more evenly in reality, because when for example the 3D velocity field or the fluctuations will be included in these calculations, more dispersion in the residence times will be found. As shown, the residence times downstream of the burner will be in the order of a few 10 ms. In the temperature plot, in spite of these short residence times the temperature distributes quite homogeneously, at already 30 à 40 mm downstream of the burner.

It is interesting to compare these results with the residence times inside the burner. Because of the solid walls of the burner, it was not possible to perform measurements inside of the inner tube. To give an indication of the residence times in the burner, the residence time of the gas in the inner tube of the burner can be derived theoretically. Based on the volume flows added to the burner (LHV: 4.2 MJ/Nm$^3$ and P: 2.8 kW) the ‘cold’ velocity in the inner tube can be calculated: this will be 1.2 m/s. From this velocity, the velocity directly above the flames can be estimated. Based on the temperature difference, an increase of the velocity of a factor 3 is plausible. This estimated velocity together with the distance of 35 mm that is present in the tube above the air injection nozzles, results in a residence time of about 10 ms for the gases inside the inner tube of the burner. This time is of the same order as the residence times found in the measuring area directly downstream of the diverging outlet.

4.5 Conclusion

Stereo-PIV measurements show that it is indeed possible to determine the velocity in the direction perpendicular to the laser-sheet. These stereo-PIV results give a good indication for the swirl in the flow. The swirl number is about 0.2, which matches with the fact that no recirculation zone is observed in the stereo-PIV results. A small increase is observed in the center of the burner, this is probably an effect of the flame. A small increase is observed as an effect of the flame in the center of the burner. A spreading angle of about 40° is derived. Also some preliminary results regarding the influence of the flame on the increase of turbulence are obtained. Mainly due to the fluctuations in the velocity in vertical direction ($v$), the kinetic energy close to the burner is increased. Fluctuations on the centerline of the flow are mainly caused by fluctuations in the velocity in the swirling direction ($w$). Almost no effect is found of the fluctuations in the horizontal direction ($u$): these fluctuations are small compared to the other two directions. Combining the temperature field and the velocity field, residence times of the particles at the temperatures can be determined. The residence times are small: order of 10 ms. The same order of residence times is found theoretically for the gases inside the inner tube of the burner. In these short residence times however, the temperature field is distributed quite homogeneously.
Chapter 5

Tar and temperature

In the partial oxidation burner two effects occur: (1) the effect of the oxidation itself and (2) the effect of thermal treatment caused by the heat that is released by the oxidation. These two effects might both contribute to the removal of the tars. In this section only the thermal treatment part is considered: the influence of the temperature and the residence time of the gases on the tars is studied without adding air. The combination of an elevated temperature together with the adding of air will be highlighted in the chapter 6. Due to the welding used for the construction of the burner, it is practically not possible to perform the thermal treatment experiments in the burner geometry. Therefore another set-up is used, available at the Energy Research Centre of the Netherlands (ECN). The experiments are performed in an electrically heated tubular reactor using biogas coming from a gasifier. Although the temperature and the residence times are higher than in the experiments using the burner geometry (see chapter 6), these experiments will give basic insight in the effect of the thermal treatment on the tars for various process conditions.

5.1 Experimental set-up

An experimental set-up at ECN was available to determine the effect of two parameters: temperature and residence time. The set-up is shown in figure 5.1. During the experiment 500 g/h wood (willow) is gasied an air-blown bubbling-fluidized-bed gasifier at a temperature of 825 °C. The gas coming from the gasifier has a temperature of about 450 °C. A sample (0.015 Nm³/h to 0.6 Nm³/h) is taken from this flow. This sample is first led through a heated quartz filter, which removes the dust, soot and other particles from the gas. This filter is mainly applied for stability and reproducibility reasons, and is also important for this study, as the gases are completely soot free when entering the test-section. In this way the soot captured in the filter behind the test-section, is per definition equal to the soot formed in the test-section.

The entire set-up is heated at a constant temperature of 400 °C to prevent condensation of the tars. Downstream of the quartz filter, the gas enters the test section. This is an electrically heated tubular reactor, where the thermal treatment of the gas and the tars is performed. This reactor is shown at the bottom of figure 5.1. An electrical tunnel oven surrounding the quartz tube is used for the heating. With this oven, it is possible to heat up the tube homogeneously to 1150 °C. The oven is 700 mm in length
Figure 5.1: Experimental set-up for the thermal treatment of the gas using a electrically heated tubular reactor

and 75 mm in diameter. Because of the length needed to increase the temperature of the gas in the oven to the desired temperature, an inlet length is defined. Thermocouples are mounted in the reactor to determine this length. The difference between the total length and the inlet length is defined as the effective length. This turns out to be 475 mm. The thermocouples measure the temperature on the centerline of the tubular reactor. For the determination of the effective length the temperature is assumed to be constant in the radial direction. However, in practice the temperature of the gases near the heated walls is of course higher. The gas flow through the reactor determines the residence time. This flow is realised by the pump at the end of the circuit. While the capacity of the pump is a fixed quantity, the diameter of the reactor has to be chosen carefully. The optimal diameter, based on the effective length and the desired residence time variation is 30 mm.

Downstream of the reactor the gases are led again through a heated (450 °C) filter. The collected amount of soot in this filter is measured gravimetrically. The weight of the filter is measured before and after one experiment run. The weighing afterwards, while the temperature is 450 °C, is of course a measurement without any water present in the gas. To make sure that the weighing before the experiment is also without water, the filter is heated to 120 °C. Finally, the gas is led through a volume flow meter. This meter is used to determine the set point of the pump. To protect the flow meter and the pump from the tars, the gases are carefully cleaned by the backup absorber bath (shown at the right of figure 5.1). This bath is a column held at 5 °C, so all the tars condense in the column.

Experiments on the cracking of tar are performed in a temperature range of 900 to 1150 °C and residence times of 1 to 12 s. This range is chosen while below 900 °C and below 1 s no effects are expected. Type K thermocouples are used to measure the temperatures. The residence time is adjusted by changing the flow through the set-up. This flow is changed by a pump at the end of the circuit. To analyze the tar content before and after the cracking, Solid Phase Absorption (SPA) is used. In this method an aminophase absorbs all the organic components. Afterwards, this aminophase is ana-
lysed by a specialised laboratory using a gas chromatograph combined with a mass spectrometer (a GC/MS). The smaller components (like benzene, toluene, and xylene) and the permanent gas composition (carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), nitrogen (N₂) and methane (CH₄)) are on-line analyzed by a micro gas chromatograph (micro GC). Because of the constant column temperature of the micro-GC (max 110 °C), it is only possible to measure the lighter tar CₓHᵧ components like benzene, toluene and xylene (BTX). A Flame Ionisation Detector is used. In this chapter, tar is defined as the hydrocarbon components that can be measured by the SPA method. Benzene however, is excluded from the definition. More details about the procedures and methods can be found in the masters work of Verschuur [80].

5.2 Total tar concentration

To study the overall effect of the temperature and the residence time, experiments using a temperature range of 900 to 1150 °C and residence times between 1 and 12 s are carried out. The tar concentration was measured by the SPA method. Figure 5.2 shows the total tar concentration as a function of the residence time at four different temperatures. This concentration is determined by summation of all tar components found.

![Figure 5.2: Tar concentration as a function of residence time](image)

The figure displays also the mean value of the total tar concentration before the cracking (at 0 s): i.e., about 8 g/Nm³ (standard deviation of 0.85). Raising the temperature as well as the residence time results clearly in a decline in tar concentration. For example, in figure 5.2 is shown that a temperature of 1150 °C requires a residence time of about 4 seconds to diminish the tar concentration to 0.2 g/Nm³. In literature this value of 0.2 g/Nm³ is often used as a practical conditions that is at least required when using the biogas in a gas motor [35].

Remarkable is that there seems to be a difference in the results of these experiments and the results of other studies (e.g., [10], [43] and [41]). In these studies a strong decrease in the tar concentration between 500 and 900 °C is observed. At 900 °C there is
-according to their figures- hardly any tar left. In the present study, however, the decrease only seems to start at temperatures around 900 °C. The difference can probably be explained by considering the amount and the kind of tar. At lower temperatures, in general there is a large amount of oxygen-rich tar present. This tar is easy to decompose and is at higher temperatures (say above 800 °C) partly converted to a much smaller amount of tar in which hardly any oxygen is left; it is mainly composed of benzene and higher ring components. This kind of tar is more difficult to decompose. So, probably 900 °C is needed in this study, because the gasifier produces no oxygen-rich tars.

5.3 Outlet gas composition

To determine the effect of the thermal treatment on the product gas, several components in the gas are measured. Figure 5.3 shows the development of the gas composition versus the residence time at 1150 °C. Only the 1150 °C situation is shown, because the effect on the gas composition is most visible in this case (at this temperature also most of the tar is converted as shown in figure 5.2): the other cases show the same tendency.

The gas composition shows an increase in carbon monoxide and hydrogen concentrations, while the carbon dioxide and methane concentrations drop. This was also observed by Brandt and Henriksen [13]. It supports one of the research goals: creating a synthesis gas with a high amount of carbon monoxide and hydrogen.

5.4 Individual tar concentration

To study the cracking in more detail, the tar is classified into several groups of components: 1-ring, 2-ring, 3-ring, 4-ring and ≥ 5-ring. This classification is shown in
Benzene is excluded from the 1-ring subgroup. Despite the fact that benzene is an aromatic hydrocarbon component consisting of 1 ring, it is often excluded from the tar definition (like stated in chapter 1).

**Table 5.1:** Classification of the tar components in several groups, based on their number of rings

<table>
<thead>
<tr>
<th>Name</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-ring</td>
<td>Toluene, Xylene, Styrene, Phenol and O-cresol</td>
</tr>
<tr>
<td>Two-ring</td>
<td>Indene, M/p-cresol, naphthalene, Quinoline, Iso-Quinoline, 2-Methyl-naphthalene, 1-Methyl naphthalene, Biphenyl and Ethyl-naphthalene</td>
</tr>
<tr>
<td>Three-ring</td>
<td>Acenaphtylene, Acenaphthene, Fluorene, Phenantrene and Anthracene</td>
</tr>
<tr>
<td>Four-ring</td>
<td>Fluoranthen, Pyrene, Benzo(a)-anthracene, Chrysene and Benzo(b)fluoranthen</td>
</tr>
<tr>
<td>Five-ring and more</td>
<td>Benzo(k)fluoranthen, Benzo(a)pyrene, Perylene, Indeno(123-cd)perylene, Dibenz(a,h) anthracene and Benzo(ghi)perylene</td>
</tr>
</tbody>
</table>

**Figure 5.4:** Several grouped tar component concentrations as a function of residence time at 1075 °C; benzene is excluded from the 1 ring group

It is possible to determine the development of the cracking process in more detail by studying these separate classes in time. In figure 5.4, for example, the concentration of the several tar components is shown as a function of the residence time at 1075 °C. This figure shows a decrease of the one- and two-ring components when increasing the residence time. As shown, the three-ring component stays for two seconds at the same level, but after those two seconds also this component decreases at larger residence times. The four- and five-ring components however, increase in the first two seconds.
As shown in the figure, these components also decrease after those two seconds. A possible conclusion from this observation is that a polymerisation process occurs when heating the biogas at a constant temperature. To check this hypothesis, carbon balances of all situations are made.

### 5.5 Carbon balance

The assumption of polymerisation can be studied by balancing the carbon components at the inlet and the outlet of the reactor. The balances are made for all the studied cases. The balance of the carbon in the 1075 °C situation is shown in table 5.2. The ‘soot’ is measured by weighing the amount of carbon stuck in the filter downstream the tubular reactor.

**Table 5.2:** The carbon balance at a temperature of 1075 °C and a residence time of 3.29 s

<table>
<thead>
<tr>
<th>Input of C g/h</th>
<th>Output of C g/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>69</td>
</tr>
<tr>
<td>CO₂</td>
<td>87</td>
</tr>
<tr>
<td>CH₄</td>
<td>20</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>15</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>1</td>
</tr>
<tr>
<td>Benzene (C₆H₆)</td>
<td>11</td>
</tr>
<tr>
<td>Toluene (C₇H₈)</td>
<td>3</td>
</tr>
<tr>
<td>Xylene (C₈H₁₀)</td>
<td>–</td>
</tr>
<tr>
<td>Tar</td>
<td>5</td>
</tr>
<tr>
<td>Soot</td>
<td>–</td>
</tr>
<tr>
<td>HCN</td>
<td>–</td>
</tr>
<tr>
<td>Total</td>
<td>212</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Output of C g/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
</tr>
<tr>
<td>CO₂</td>
</tr>
<tr>
<td>CH₄</td>
</tr>
<tr>
<td>C₂H₄</td>
</tr>
<tr>
<td>C₂H₆</td>
</tr>
<tr>
<td>Benzene (C₆H₆)</td>
</tr>
<tr>
<td>Toluene (C₇H₈)</td>
</tr>
<tr>
<td>Xylene (C₈H₁₀)</td>
</tr>
<tr>
<td>Tar</td>
</tr>
<tr>
<td>Soot</td>
</tr>
<tr>
<td>HCN</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

| 91              |
| 82              |
| 17              |
| 1               |
| –               |
| 7               |
| –               |
| –               |
| 2               |
| 11              |
| –               |
| –               |
| 211             |

Table 5.2 shows that the ‘total’ input and output agree well; 99.5 % of the carbon in the input is also found in the output. The amount of carbon in the C₁ and C₂ components (CO, CO₂, CH₄, C₂H₄, and C₂H₆) in the output almost equals the amount in the input. The carbon balance also shows that a large part of the tar and smaller CₓHᵧ components are converted into soot probably by polymerisation. The amount of carbon from soot, tar and benzene in the output comes very close to the amount of carbon from tar, benzene and toluene in the input.

Combining all the results, a plausible explanation for the high amounts of soot formed in our experiment is that soot is not only formed from the polymerisation of tar, but also from polymerisation of one-ring aromatics. The whole process can be summarized as follows: smaller C-containing components convert step by step into soot: small ring components (e.g. benzene) are converted step by step into higher ring components. The longer the residence time and/or the higher the temperature, more of the high ring components are converted into soot.
5.6 Comparison with literature

In literature, soot formation is a problem that is often mentioned in relation to cracking or combustion of tar-containing hydrocarbons. The mechanisms of formation of polycyclic aromatic hydrocarbons and their possible growth to soot in the pyrolysis and combustion of hydrocarbons have been studied extensively (a.o. [2], [9], [26], [27], [40], [42], [54], [59] and [68]). Although many important details of polycyclic aromatic hydrocarbons and soot formation remain poorly understood, there is considerable agreement on the general features of the processes involved. The pathway for soot formation in homogeneous mixtures according to Bockhorn [9] is shown schematically in figure 5.5.

![Figure 5.5: Example of a pathway for soot formation [9]](image)

This figure shows a growth process in time: soot forms from smaller components. In numerical studies, models in general start with pyrolysis, followed by the formation of polycyclic aromatic hydrocarbons, their ‘planar’ growth and coagulation into spherical particles, and finally surface growth and oxidation of the particles [27]. This is likely the mechanism that also causes the behaviour of the tars during the thermal treatment as described in this chapter.

Based on experimental study Homann and Wagner [38] suggested pathways leading to carbon formation. Based on a comparison between acetylene and benzene flames, they conclude that from the difference some processes can be explained. They concluded that the formation of greater amounts of carbon in benzene flames is due to the fact that more efficient hydrocarbon “building bricks” for soot particles are available in the zone of maximum hydrocarbon radical concentration. The importance of cyclisation reactions and the ease of carbon formation in benzene flames (found by e.g. [24]) prompted Palmer et al. [60] to suggest that, at least under certain conditions, benzene formed may be an important intermediate in soot formation. Although there is considerable evidence that PAH are key reactants in soot formation and that PAH growth is through free radical intermediates, historically other species have also been considered to be key soot formation reactants and some of these are still of interest [14]. For example ionic pathways to soot formation might be important under some kind of...
In the biomass literature, Olsen [59] showed that thermal cracking at 1100 °C converts tar into gas and soot, and he found that because of this soot formation the gas is not perfectly clean even at this high temperature. Jess [42] studied the thermal reactions of aromatic hydrocarbons and the influence of the presence of hydrogen and steam. He states that soot formation is strongly inhibited by hydrogen. He concludes that especially for naphthalene, hydrogen inhibits soot formation. A simplified reaction scheme for the thermal conversion of aromatic hydrocarbons in the presence of hydrogen and steam is shown in figure 5.6.

![Simplified reaction scheme of thermal conversion of aromatic hydrocarbons in the presence of hydrogen and steam](image)

This figure summarises the numerous primary and consecutive reactions in the following main reaction paths: (I) cracking reactions lead to hydrocarbons with smaller carbon numbers than in naphthalene; (II) condensation reactions lead to soot (plus soot precursors / condensed products) (III) carbon monoxide occurs by consecutive reaction of soot and organic cracking products (all above methane) with water (H₂O).

### 5.7 Conclusion

It is shown that the tar concentration, as a function of time, decreases starting at about 900 °C. At 1150 °C the concentration drops after 4 s below a value of 0.2 g/Nm³. At temperatures below 1100 °C and at short residence times, some components (3-ring, 4-ring, and 5-ring) increase, only higher temperatures and longer residence times phase out this effect. Moreover the concentrations of carbon monoxide and hydrogen increase with increasing residence time, whereas the concentrations of carbon dioxide and methane decrease. As shown in the example of the carbon balance, the total input and output agree well. It is clear that the amount of soot increases with increasing residence times. Probably the process can be described as follows: smaller C-containing ring components convert step by step to soot: the longer the residence time, the higher the amount converted into soot. The process is accelerated as the temperature increases.
Chapter 6

Tar and partial oxidation

In the previous chapter, it is shown that heating the gas (in a range of 900 - 1150 °C) results in polymerisation of small tar components. This polymerisation finally leads to the formation of soot. In practice, this soot can be removed by means of a filter, but it is more desirable to avoid this soot formation in the first place. The present chapter focuses on the behaviour of tar in an oxidizing environment. In the experiments in this chapter naphthalene is used as a model component. The experiments concentrate on the main question: when using little air ($\lambda = 0.2$), will the tars polymerise or will they crack into lighter components like carbon monoxide and hydrogen. The thermal treatment experiments of the previous chapter are performed in a $\lambda = 0$ situation. Although, the experiments presented in the previous chapter are performed in a different set-up using different inlet gas compositions and residence times; it is interesting to compare this situation with the $\lambda (\neq 0)$ experiments presented in this chapter.

6.1 Experimental set-up

To study the influence of partial oxidation on the reduction of the tar concentration in the gas in the burner geometry, a set-up is built. Because of the possible carcinogenicity of the released combustion products, the experiments are performed in a closed environment. Therefore, a safety construction is built around the set-up. This safety construction is made of 6 mm thick aluminum sheet material. Also a special extractor fan is used to remove and clean the outlet gases.

Also for safety reasons, the component chosen as a model tar component is naphthalene. This component is denoted as relatively harmless, compared with a more carcinogeneous component like benzene. For higher ring components compared to naphthalene, holds that the processing is difficult because of their condensation behaviour: the whole set-up should be heated to even higher temperatures, and also inserting the component in the gas flow would be more difficult. Another aspect is that naphthalene resembles the tars coming from a downdraft gasifier. As mentioned in chapter 1, tertiary aromatics are predominant in the downdraft product spectrum. Naphthalene is a tertiary component and therefore useful as a model component. Furthermore, another reason for using of naphthalene refers to the aim of these experiments. The aim is to determine whether the tar components will polymerise or crack into lighter particles. As mentioned before, naphthalene is a 2-ring aromatic hydrocarbon. Therefore it is
possible to translate the effect of the burner geometry on this tar component in terms of the detection of smaller aromatics or components than naphthalene (indicating a cracking trend) or larger aromatics (indicating a polymerisation trend).

Of special importance for the design of the set-up is the condensation behaviour of the tar components, because the tar components could clog the tubing or, even worse, the burner or the measuring system. The temperature at which the tars condense depends strongly on the concentration of the tars in the gas. The partial pressures of the polycyclic aromatic hydrocarbons (PAHs) in a group (i.e. 2-ring, 3-ring, 4-ring, 5- and higher ring) are in the same order of magnitude [57]. The amount of naphthalene added is low in the experiments described in this chapter, so the partial pressure is low: therefore condensation is not likely to occur. Nevertheless, the tubing in the set-up is heated to about 200 °C. In figure 6.1 a schematic overview of the whole set-up is shown.

![Figure 6.1: A schematic overview of the set-up](image)

A saturator is used to saturate a small nitrogen flow with naphthalene. The boiling point of naphthalene (C\textsubscript{10}H\textsubscript{8}) is 217 °C. A heat exchanger using hot air, heats the nitrogen and the naphthalene. As shown in this figure 6.1, little solid naphthalene balls are placed inside the saturator. In the wall of the saturator hot air is injected by means of a blower. The power and the temperature of the blower can be adjusted. The set point that leads to a steady state of 200 °C for the nitrogen and the naphthalene, is determined before starting of the experiments. Downstream the saturator, the small naphthalene-nitrogen flow is heated by the hot air from the blowers. The cold gases coming from the bottles and this small flow are mixed in the mixing unit, shown in figure 6.1 in the center of the figure. The gas is controlled by mass flow controllers (MFC’s). This flow is first led through a copper wire that is wrapped around the hot vessel (depicted as the black left to right line around the vessel). The unit is heated with hot air coming from a second air blower. A photograph of the saturator and the mixing vessel is shown in figure 6.2. The saturator is the unit at the left of the figure, the mixer is the small unit at the right. The saturator and the mixing unit are insulated using special heat resistant insulation material (based on glass). The top layer consists
of aluminum tape. Close to the saturator and the mixing unit, at the bottom of the figure, the two air blowers are shown.

Figure 6.2: The saturator (left) and the mixing unit

Electrically traced tubing (heated at 200 °C) is used to transport the mixture of the gases and the naphthalene to the burner. Also for the transport of the gas-sample to the GC heated tubing is used (heated also at 210 °C). The inside diameter of this tubing is 1/8 inch, which is small for traced tubing, therefore the tubing used is especially made for this application. For this sampling, two tubes are used: one for the sample taken before the burning and one for the sample taken downstream of the burner. To measure the amount of naphthalene added, samples are also taken from the sampling point downstream of the burner without igniting the flame. As shown in the figure at the left side of the burner at the bottom of the glass bell, secondary air is added. In the experiments performed in this chapter this secondary air flow is 1 l/min.

A special gas chromatograph is used to analyse the gases: an ultrafast-GC. For the analysis of the hydrocarbons a capillary column is placed in a separate compartment of the GC: a programmable oven. This programming shortens the analysis time of the polyaromatic hydrocarbons (PAHs) and the benzene, toluene and xylene (BTX) from about half an hour to three minutes. In the appendix C the GC is described in detail; in this appendix also the calibration procedure is described. The chromatograph measures the concentrations in parts per million (ppm). This quantity is converted to grams per cubic metre by using the mole masses: for one-ring 78 g/mol, two-ring 128 g/mol, three-ring 178 g/mol, four-ring 228 g/mol and five-ring 278 g/mol.

Similar experiments as shown in chapter 3 are performed using the same mixture compositions of hydrogen, methane and nitrogen. The total set-up is heated at about 200 °C: so the inlet temperature is the same as in the experiments in the last section of chapter 3. The only difference between those experiments and here, is that naphthalene is added to the gas-mixture, and in that way used as a model component. The amount
of naphthalene is too small to cause significant differences in the outlet gas composition and temperature.

Two sets of experiments are described here. In the first set, the $\lambda$ is varied in a range from 0.2 to 0.75 to determine the effect of partial oxidation on the tars. In the second set of experiments, the behaviour of the tars will be studied as a function of the mole fraction of hydrogen, because in this way the effect of the radicals present on the naphthalene can be determined.

### 6.2 Primary air

In this section the effect of the amount of primary air on this naphthalene concentration is studied. Figure 6.3 shows the total tar concentration as a function of the $\lambda$. Increasing $\lambda$ results in an increase of the total tar concentration for the $\lambda$ range 0.2 to 0.65. This figure shows also the total tar concentration at the inlet: in all cases this value is 2.6 mg/Nm$^3$ (see the solid line in figure 6.3). So a difference is found between the total amount of tar at the inlet and the amount at the outlet. This means that not all the naphthalene components are converted to measurable tar components in the outlet gases.

![Figure 6.3: Total tar concentration as a function of $\lambda$ and the total inlet concentration Inlet gas composition: H$_2$: 32 %, CH$_4$: 2 % and N$_2$: 66 %; C$_{10}$H$_8$: 2.6 mg/Nm$^3$; LHV: 4.2 MJ/Nm$^3$; P: 2.8 kW; Inlet temperature: 200 °C.](image)

The increase of the tar concentration when increasing the $\lambda$, is also found in literature ([43], [46], [61] and [83]), but only for specific situations. These studies state that there is an optimum in the addition of oxygen with regard to the reduction of the tar concentration: no oxygen added leads to the formation of polyaromatic hydrocarbons and soot, but ‘too much’ oxygen does the same. In between, there is an optimum for the tar removal. This optimum is also present in the results presented in this thesis. In the previous chapter, it is shown that heating only leads to polymerisation and soot.
Whereas a $\lambda$ of 0.2 minimises the tar concentration. Adding more air results in an increase of the total tar concentration.

![Graph showing tar components as a function of $\lambda$.](image)

**Figure 6.4:** Several grouped tar components as a function of $\lambda$. Inlet gas composition: $H_2$: 32%, $CH_4$: 2% and $N_2$: 66% $C_{10}H_8$: 2.6 mg/Nm$^3$; LHV: 4.2 MJ/Nm$^3$; P 2.8 kW; Inlet temperature: 200 °C

It is interesting to see what happens to the naphthalene in detail. Figure 6.4 shows the tar components classified in separate subgroups, classified by the number of rings. Increasing $\lambda$ leads to the formation of higher ring aromatic components. Because benzene ($C_6H_6$) is in general not defined as a tar component, the amount of benzene is plotted as a separate component, and excluded from the one-ring group. As shown here, the benzene follows the same trend as the small tar components: when higher ring components evolve the benzene disappears. This indicates that the soot formed at the higher $\lambda$'s is a polymerisation process. So a similar process as found in the previous chapter seems to occur also at high $\lambda$'s. For the desired $\lambda$ situation (0.2) however, the tar concentration is low: only 7.5 % of the initial value. Another indication for the soot formation, is the flame colour present in the higher $\lambda$-situations. When increasing the $\lambda$ a red/yellow flame appears, which in general indicates that there is soot formation in the flame.

Wang and Kinoshita [83] studied the behaviour of tar components for different gasification conditions. One of the situations studied is the increase of the equivalence ratio (ER); which is similar to the $\lambda$ as used in this thesis. Their results show that increasing the ER leads to a decrease of the 1-ring components, while the other multi-ring components increase with an increasing ER. Also Jönsson [43] shows that the tar concentration decreases when adding some oxygen and increases again when the amount of oxygen is increased more. Tregrossi et al. [77] studied rich premixed flames burning at atmospheric pressures at different C/O ratios. Overall, they found that the C/O ratio does not affect the distribution of PAHs, but the main effect on the aromatic species is that the maxima of the concentration of species shifts more downstream in the flame. The division of products between the gaseous and condensed phases was not affected by an increase of the C/O ratio (and thus a decrease of the $\lambda$). Wang et al. [82] give
indications of a competition between the soot formation and oxidation; the soot ‘wins’ for the higher temperatures and higher oxygen addition situations. So, this same trend is found in the results presented in this section.

### 6.3 Inlet gas composition

To gain more insight in the fundamentals underlying the tar conversion process, the hydrogen-methane content of the fuel is varied.

![Graph showing total tar concentration as a function of hydrogen fraction and the total inlet concentration.](image)

**Figure 6.5:** Total tar concentration as a function of hydrogen fraction and the total inlet concentration; Inlet gas composition: a variable composition of H\(_2\), CH\(_4\) and N\(_2\); C\(_{10}\)H\(_8\): 2.6 mg/Nm\(^3\); LHV: 4.2 MJ/Nm\(^3\); \(\lambda\): 0.2; P: 2.8 kW; Inlet temperature: 200 °C

In figure 6.5 the total tar concentration is shown as a function of the hydrogen fraction in the inlet fuel. The concentration of naphthalene at the inlet is plotted in the same figure: the total amount of tars at the inlet is about 2.6 mg/Nm\(^3\). This figure shows a decrease in the tar concentration as the concentration of hydrogen in the fuel increases. Again, a difference is found between the total amount of tar at the inlet and the outlet, so in all situations the naphthalene converts to unmeasurable components. This amount of unmeasurable components however, strongly increases for situations with a hydrogen fraction larger than 25 %. To see what happens in detail, in figure 6.6 several grouped tar components are shown as a function of the hydrogen fraction in the inlet fuel.

This figure shows that the higher ring components decrease when increasing the hydrogen fraction. At high hydrogen fractions almost all the naphthalene is converted to smaller components: so likely there is a cracking trend. In the pure methane situation and situations with a relatively high amount of methane, higher ring components are observed. Apparently, a sooting tendency is present in these situations.

As mentioned before (shown in figure 6.5), in all situations the naphthalene converts to unmeasurable components. In the pure methane case however, these unmeasurable components are likely to be soot particles, whereas in the pure hydrogen case
Figure 6.6: Several grouped tar components as a function of hydrogen fraction; Benzene is excluded from the 1-ring group; Inlet gas composition: a variable composition of H₂, CH₄ and N₂; C₁₀H₈: 2.6 mg/Nm³; LHV: 4.2 MJ/Nm³; λ: 0.2; P: 2.8 kW; Inlet temperature: 200 °C

these components are more likely to be small components like benzene and permanent gases. Benzene increases while the other aromatic components all decrease.

In literature this effect is often reported ([42], [69], [75], [76]). Du et al. [22] conclude that hydrogen, with its large diffusivity, can be quite effective at suppressing soot inception, despite a corresponding increase in flame temperature. Also is known that when soot formation is once started, there is an acceleration in the soot particle growth at low hydrocarbon concentrations [75]. This acceleration is according to Tesner [76] caused by destruction of hydrocarbon radicals on the growing surface. The separate influence of the two burnable components in the fuel will be discussed below. The results of the extremes of the hydrogen-methane range will be used to gain more insight in the process of the partial oxidation.

Hydrogen

The hydrogen flame is of special interest, because the naphthalene that is added is the only carbon source in this flame. Therefore, it is possible to determine what happens to the naphthalene in detail. Figure 6.7 shows the distribution of the carbon containing components in the hydrogen-naphthalene-nitrogen flame. Methane is the component that is most formed in the flame. A logical result, while due to the fact that the flame is typically a fuel rich flame there is a lot of hydrogen and little oxygen present. The 2-ring components are really low and even the 3-, 4- and 5-ring components (not shown) are all zero.

It is interesting to make a carbon balance for this situation. In this way probably more insight in the underlying mechanism for this almost tarless flame situation will be gained. Table 6.1 shows this carbon balance. The permanent gases (shown in the first three rows of the table) are measured using the thermal conductivity detector (TCD)
in the gas chromatograph. The remaining components are measured using a flame ionisation detector (FID). The methane output is measured twice: using both the TCD and the FID. Therefore two ‘total amounts’ are shown: one for the methane measured with the TCD and one for the methane measured with the FID. As shown in this table, both of the balanced total amounts at the outlet agree well with the amount measured at the inlet. So the naphthalene added at the inlet is converted to smaller components in the outlet gas.

**Table 6.1:** The carbon balance in the hydrogen - nitrogen - naphthalene flame situation

<table>
<thead>
<tr>
<th>Input of C mg/h</th>
<th>Output of C mg/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>CO</td>
</tr>
<tr>
<td>CO₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>CH₄</td>
<td>CH₄ TCD</td>
</tr>
<tr>
<td>CH₄</td>
<td>CH₄ FID</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>C₂H₆</td>
</tr>
<tr>
<td>Benzene (C₆H₆)</td>
<td>Benzene (C₆H₆)</td>
</tr>
<tr>
<td>Toluene (C₇H₈)</td>
<td>Toluene (C₇H₈)</td>
</tr>
<tr>
<td>Xylene (C₈H₁₀)</td>
<td>Xylene (C₈H₁₀)</td>
</tr>
<tr>
<td>Naphthalene (C₁₀H₈)</td>
<td>Naphthalene (C₁₀H₈)</td>
</tr>
<tr>
<td>3-ring</td>
<td>3-ring</td>
</tr>
<tr>
<td>4-ring</td>
<td>4-ring</td>
</tr>
<tr>
<td>5-ring</td>
<td>5-ring</td>
</tr>
<tr>
<td>Total</td>
<td>Total (TCD)</td>
</tr>
<tr>
<td></td>
<td>Total (FID)</td>
</tr>
</tbody>
</table>
Methane

When the methane content of the gas is increased, larger polyaromatic hydrocarbons are formed. For these situations a sooting tendency is found. It is interesting that for the experiments without naphthalene (described in section 3.4) the pure methane flame is hardly producing any tars or soot. This resembles the results of Roesler et al. [69], they suggest that methane is not an actual soot promoter in flame situations; however, it does interact synergistically with the fuels to produce more polyaromatic hydrocarbons and soot than would otherwise have been expected.

Roesler et al. [69] studied the role of methane on the growth of aromatic hydrocarbons and soot in several fundamental combustion processes. They conclude that the effect of the methane content on the formation of polyaromatic hydrocarbons and soot production in a non-aromatic fuel mixture differs significantly with the combustion system used. For a diffusion flame containing a small amount of aromatic hydrocarbons, it holds that increasing the methane fraction of the fuel, results in a conversion of carbon into soot via a synergistic chemical mechanism. They state that the synergy of methane with other hydrocarbons to produce polyaromatic hydrocarbons is attributable to the ability of methane to produce methyl radicals, that will then promote the production of aromatics that rely on odd-carbon numbered species. According to Roesler et al. benzene, naphthalene and pyrene show the strongest sensitivity to the presence of methane: this synergy trickles down to soot via enhanced inception and surface growth. They observed these results strongest under the fuel rich environments using a diffusion flame. These conditions do resemble the conditions used in the experiments described in this chapter.

6.4 Conclusion

The effect of partial oxidation on tar is studied in the burner geometry. Naphthalene is used as a model component in these experiments. When adding some primary air ($\lambda = 0.2$), the total tar concentration is low (only 7.5% of the inlet mg/Nm$^3$). It is interesting that when more air ($\lambda > 0.4$) is added to the burner, the same sooting tendency is found as in the case of thermal treatment only. By changing the amount of hydrogen in the inlet gas, the tar concentration in the outlet is considerably affected. Hydrogen seems to be an inhibitor for soot formation: only a small amount of hydrogen present in the inlet gas transforms the sooting/polymerisation process into cracking. Therefore, the process created by the burner geometry might be a promising method for the application of small-scale biomass gasifiers.

6.5 Discussion

In biomass literature, little is known of the effect of hydrogen on thermal cracking and partial oxidation. From hydropyrolysis and gasification of coal however, there is literature available. From these dehydrogenation studies, it appears that methane might be formed by hydrogenation of one of the double bonds of an aromatic ring (e.g. [39] and [58]). This is probably the process that takes place in the cases when the fuel is
hydrogen rich. For the results presented, this methane forming process is evident for the pure hydrogen-nitrogen flame situation.

However, for hydrogen fractions lower than 20 % (and methane is larger than 24 %, which never occurs in biogas situations) a strong increase in the total tar concentration is found. When examining the composition of the tars as presented above, it is shown that higher ring compounds are formed. Note that because of the constant heating value, the amount of methane and nitrogen is increased when decreasing the hydrogen. Therefore, the effect of methane and naphthalene might be dominant in this situation. The hypothesis for these situations is that the combination of methane and a little naphthalene results in a sooting tendency. For example, Roesler et al. [69] suggest that for diffusion flames, methane together with a small amount of naphthalene interact synergistically to produce polyaromatic hydrocarbons and soot.

Frenklach [25] has proposed a H-abstraction/C\textsubscript{2}H\textsubscript{2}-addition reaction mechanism for polycyclic aromatic hydrocarbon (PAH) growth. This mechanism will be discussed in more detail later on. Recent literature shows that other radicals than acetylene can play an important role also. For example, D’Anna et al. [18] show that for non-premixed flames, propargyl addition to benzyl radicals is one of the key components in the formation of naphthalene, and not the HACA mechanism. Also Roesler et al. [69] state the recombination of cyclopentadienyl radicals and the addition of benzyl and propargyl is the mechanism that leads to soot in methane-air diffusion flames doped with a small amount of hydrocarbons. They conclude that the HACA mechanism is less important for this flame type. Summarised can be concluded that all these theories agree on the idea that radical processes are likely to be the driving force behind soot formation observed in some flames, the mechanism causing the formation depends however strongly on the situation.

It is interesting to take a closer look on the H-abstraction/C\textsubscript{2}H\textsubscript{2}-addition reaction mechanism (HACA mechanism) like proposed by Frenklach [25]. For the HACA mechanism three regimes exist, in which hydrogen plays different roles:

1. A high temperature regime where \([\text{H}_2] \cong \text{[C}_2\text{H}_2]\);
2. A low temperature regime where \([\text{C}_2\text{H}_2] \gg \text{[H}_2]\);
3. A low temperature regime where \([\text{C}_2\text{H}_2] \ll \text{[H}_2]\).

Because of the hydrogen variations performed in this chapter, these regimes are of special interest for the explanation of the results found. Frenklach argues that different parameters control the growth of PAH for these three different conditions. The two low temperature regimes are of interest for the current study: roughly, regime (II) resembles the situations with a hydrogen fraction lower than 20 % and regime (III) resembles the situations higher than 20 % hydrogen in this study. Figure 6.8 indicates the position of the regimes in the figure of the total tar concentrations as presented in figure 6.5. For regime (II), he states that the growth of aromatics to higher molecular compounds is explained by a mechanism consisting of two reaction pathways: (1) direct combination of intact aromatic rings, e.g. the combination of two benzene rings leads to biphenyl, which reacts further towards PAH compounds; and (2) a sequence of H-abstraction/C\textsubscript{2}H\textsubscript{2} addition (HACA). This HACA mechanism states that aromatic rings grow by H abstraction, which activates the aromatic molecules, and acetylene addition, which propagates molecular growth by cyclisation.
Figure 6.8: Indication of the position of the regimes depicted in the figure concerning the total tar concentration as a function of hydrogen fraction

For regime (III) however, the growth rates of PAH vary with \([H]/[H_2]\), where the inverse dependence on \([H_2]\) is due to the reverse reaction \(A_i + H \rightleftharpoons A_{i-} + H_2\). Here \(A_i\) denotes an aromatic molecule containing \(i\) aromatic rings and \(A_{i-}\) denotes an aromatic radical. In this way, chemical suppression of soot in diffusion flames due to addition of hydrogen to the fuel seems likely. Frenklach [25] states for this situation that the PAH growth rate is controlled by the thermodynamics of the H-abstraction and the kinetics of the acetylene addition to aromatic radicals, and the concentrations of H, \(H_2\) and \(C_2H_2\).

So, the idea of radical pathways as a mechanism for the formation of soot like found in literature is consistent with the results presented in this chapter.
Chapter 7

Concluding discussion

7.1 Conclusions

In this thesis a partial oxidation burner for the removal of tar from biogas is evaluated. Tar in synthesis gas from biomass gasifiers is presently the main difficulty for the introduction of this gas for power generation. Especially for small-scale applications, it is important that the tar can be removed without the use of -often expensive-cleaning equipment. Tar will impose serious limitations on the use of the gas due to fouling of downstream process equipment and high maintenance costs. Before the gas can be introduced into the gas engine, the tar content has to be reduced to low values (e.g., 0.2 g/Nm$^3$ is often used for gas motors). A partial oxidation burner is evaluated in this thesis. This burner should remove tars by burning a small amount of the (to be cleaned) fuel. Processes like partial oxidation and thermal cracking of the tars will occur. In this thesis, a specific partial oxidation burner geometry is studied. In this geometry a small amount of fuel is burned while using diffusion flames. These flames are created by injecting little air through several nozzles. The evaluation is performed in several steps. First, the mixing in the geometry is visualised in a perspex set-up using water and dye to determine the range of volume flow ratios at which the burner is likely to burn stable. Secondly, the burner is tested in a wide range of settings on its stability, outlet temperatures and outlet gas compositions. After that the velocity field and the temperature distribution of the burnt and the unburnt gases downstream of the burner are studied. Finally, the effect of thermal treatment and partial oxidation on the tar composition is determined. These experiments are divided in two parts: first, the effect of thermal treatment only is studied in an electrically heated tubular oven. After that experiments on the effect of partial oxidation are performed in the burner geometry.

In chapter 2, the behaviour of the volume flows in the burner geometry is studied in a perspex set-up using water. Several ratios of volume flows and several swirl numbers are tested. Three regimes are identified: the ‘cup’, the ‘typhoon’ and the ‘jet-mixing’ regime. The criteria that are used to characterise the flow regimes are (1) the kind of mixing and (2) the starting position of the mixing. The regime that is called the jet-mixing regime, turns out to be the most promising, because this flow regime meets the two demands of (1) creating a stable combustible mixture and (2) using little air. Scaling this set-up by the Reynolds number, the final set-up is build in stainless steel.

In chapter 3, the stability of the burner geometry, the outlet temperature and the
outlet composition of the burner is studied in various biogas-resembling compositions. However, no tar is added yet. The composition and temperature of the gases coming from a gasifier differ a lot. The burner should be able to cope with the variations at the inlet, even while using an air factor ($\lambda$) of 0.2. First, the range of ratios of the volume flows at which the combustion is stable is determined. The burning is stable for the cases that coincide with the ‘jet-mixing’ regime as identified in chapter 2. The burner meets the demands of burning low calorific gas ($\text{LHV} = 5 \text{ MJ/Nm}^3$) in a stable way using little air ($\lambda = 0.2$). The outlet temperature and gas composition are measured for several variables: the heating value and power, the inlet gas composition, the primary air, the secondary air and the inlet temperature. Even for heating values of the fuel down to 3 MJ/Nm$^3$, for various inlet compositions of methane, hydrogen, carbon monoxide and nitrogen and for two different inlet temperatures, a stable flame is attained. It is also important that the gas is still combustable downstream of the burner. For the biogas-like conditions, the downstream heating value is still 73 % of the inlet heating value. Under all these conditions, the desired temperature of about 500 °C is attained.

Next, the flow field and the temperature distribution downstream of the burner is studied in chapter 4. Particle Image Velocimetry (PIV) and stereo-Particle Image Velocimetry (stereo-PIV) are used to determine the average velocity field. The stereo-PIV results give a good indication for the swirl in the flow: the swirl number is about 0.2, which indicates that there is a weak swirl. At about 30 mm above the burner, the vertical velocity as well as the swirl velocity shift to a more homogeneous distribution. The temperature spreads simultaneously to a more homogeneous situation. It is interesting that this homogeneous distribution is reached despite of the small residence times downstream of the burner: which is in the order of milliseconds.

The effect of thermal treatment on the tars is studied in chapter 5. For this thermal treatment an existing experimental set-up at the Energy Research Centre of the Netherlands (ECN) is used. The outlet compositions of the gas are measured in experiments which are performed in a temperature range of 900 to 1150 °C and at residence times in the range of 1 to 12 s. The inlet gas is coming from an air-blown bubbling-fluidized-bed gasifier. It is shown that the decrease of the tar concentration, as a function of time, starts at about 900 °C. Moreover, the concentrations of carbon monoxide and hydrogen increase with increasing residence time, whereas the concentrations of carbon dioxide and methane decrease. The amount of soot increases with increasing residence times. Probably, the thermal process can be described as follows: smaller carbon-containing ring compounds convert step by step to soot: the longer the residence time, the higher the amount converted into soot. The sooting process is accelerated when the temperature increases.

Finally, in chapter 6 the effect of partial oxidation on the tars is studied in the burner geometry designed in this thesis. Again low calorific fuel mixtures are used, but now naphthalene is added as a model component. To determine the effect of partial oxidation on the tars, experiments are performed in a $\lambda$-range of 0.2 to 0.75. Furthermore, for a $\lambda$ of 0.2, experiments are performed to determine the effect of the hydrogen/methane concentration at the inlet on the tars. For a fuel composition that resembles biogas, a decline in total tar concentration is found for a $\lambda$ of 0.2. Increasing $\lambda$ however ($\lambda \geq 0.4$), shows a polymerisation trend. When increasing the hydrogen concentration in the fuel, the total tar concentration decreases. For these situations a cracking trend
is found. However, for situations with a relatively low amount of hydrogen (which automatically means a high amount of methane) higher ring compounds are present: probably sooting occurs in these situations. For the situation when using a biogas-like mixture and a \( \lambda \) of 0.2, the composition of the total tar decreases to only 7.5% of the inlet tar concentration. This makes this burner geometry a promising option for the cleaning of biogas from small-scale biomass gasifiers.

7.2 Discussion

The question is still what happens in detail during the processes described in this thesis. Based on the results obtained, it is clear that the behaviour of polyaromatic hydrocarbons is not determined by a single parameter: several parameters influence the process to different degrees. In the partial oxidation process, a distinction in two parts can be made: a thermal part and an oxidation part. The processes in the thermal part convert the tar components into soot as shown in chapter 5 of this thesis. However, partial oxidation (which is in fact a combination of the thermal and the burning part), may lead to a decrease of the tar concentration to lighter components (like shown in chapter 6).

For the situation containing 32% of hydrogen, the effect of the amount of oxygen is studied. Here an increase of the tar concentration at the outlet is found, when adding more oxygen. A possible explanation is that the amount and the kind of radicals is changed by the presence of the oxygen. The oxygen seems to consume the radicals that prevent the soot formation. In literature, for the adding of oxygen, the same processes are reported, however almost no explanations are presented. Marinov et al. [53] state that the removal of phenyl and naphtyl by oxygen leads to precursors of polyaromatic hydrocarbons. From the results of this study, it might be concluded that the radicals that prevent the soot formation are removed when \( \lambda \geq 0.4 \). Another support of this hypothesis is found in chapter 5 where soot is formed in a thermal treatment situation (when \( \lambda \) equals zero). While no combustion takes place, only a small amount of radicals will be formed by the thermal process. Again, the formation of soot seems to be promoted by the absence of radicals.

By varying the amount of hydrogen versus methane in the fuel, the amount and kind of radicals present in the burner geometry is changed. When the fuel contains more than about 20% of hydrogen (a fraction that is reasonable for biogas) the total tar concentration is diminished to less than 11% of the inlet tar concentration. Note however, that in this study for the low hydrogen concentrations, compared to real biogas, a large amount of methane is present in the inlet gas: 20% hydrogen means that 24% of methane is present. Diminishing of the total tar concentration however, is found in literature for comparable studies, like shown in the discussion of chapter 6. Summarised, the effect of hydrogen might be a result of the following features: (1) there is little carbon present to create soot, (2) the hydrogen radicals might stop the polymerisation process by neutralising the aromatic radicals by adding of a hydrogen radical, and (3) hydrogen radicals might break the bonds of the aromatics and in this way forming e.g. carbon monoxide and methane.
7.3 Recommendations

Recommendations can be formulated from several viewpoints: from burner viewpoint concerning the gases and the tar, from a system point of view when considering the gasifier concept and of course from a more fundamental point of view to gain insight in the basic processes.

In general, biogas contains carbon monoxide and carbon dioxide. In most experiments in this thesis however, the carbon monoxide is replaced by hydrogen and methane. Similarly holds that the carbon dioxide is replaced by nitrogen. So, from the viewpoint of the burner, it is important to study the effect of these two components in the inlet fuel on the burner behaviour and the tars. In this study naphthalene is used as a representative of tar components. As shown in this thesis, the composition of the components in the inlet fuel is crucial for the behaviour of the tars downstream. Therefore, the effect of the kind of the tars in the inlet fuel is an interesting aspect. Another important aspect is the amount of tars. In the present study, the effect of only 2.6 mg/Nm$^3$ naphthalene in the gas is studied. Interesting now is to study the behaviour of naphthalene in the burner geometry when using a higher concentration at the inlet. Finally, of course, real biogas should be tested in the burner geometry. The disadvantage of using real biogas is that the controllability at the inlet is low. Therefore the proposed systematic experiments described above, should be done first to determine the separate effects. Another aspect is to study the burner behaviour when adding for example nitrogen as a co-flow. The co-flow should compensate for possible underpressuring of the surroundings of the burner. As shown in this thesis, the co-flow is presumably not participating in the burning for the situations of interest. When using nitrogen, it is also for example not possible for the pure hydrogen - nitrogen flame to use the secondary air.

When using the input of a real gasifier, several aspects concerning the system of the burner and the gasifier can be studied. Interesting aspects are for example: a study of the effects of recycling on the gas composition and the temperature of the gasifier gases; an examination of the best way to cause the transport of the pyrolysis gas from the gasifier to the burner; a study of the location where the air should be added to the gasifier or the burner. The last aspect of location of air injection is interesting because ideally all the air used in the gasifier should be added in the burner geometry. The question whether it is possible to operate a gasifier by adding all the air in a separate combustion chamber is an important one.

Another, more fundamental, question for this geometry is the study of thermal cracking for the same geometry and the same conditions. For example by heating the complete geometry electrically. In this way the effect of the thermal cracking and partial oxidation can be compared. This might also give more insight in the basic mechanism. Also a study of the flame behaviour in detail is interesting. Using an optical accessible set-up, could give information about the flame itself. Even optical techniques can be used to determine the positions of various radicals in the flame. In this way, it is for example possible to gain information about the local concentrations. This brings up another interesting fundamental aspect: the kinetics of the process.
References


Appendix A

Thermocouple correction

In this thesis, thermocouples are used for the temperature measurements. Temperatures are measured both for several heights ($y$) and for several radial positions. The situation for the radial positions is described in detail in this appendix. The corrections for the thermocouple measurements in the height are performed in a similar way. The situation used for the temperatures measurements in chapter 4 for which the correction is described here, is shown in figure A.1.

![Figure A.1: Mounting of the thermocouples for the radial temperature measurements downstream of the burner; the frame is placed at several heights in the flow: 7 by 7 measurement points are used.](image)

At steady state, the energy balance for a thermocouple is found from the following equation:

$$0 = -hA(T_{th} - T_{real}) - \sigma \varepsilon A(T_{th}^4 - T_{env}^4) - q_{cond}. \tag{A.1}$$

The first term on the righthand-side is the convective heat transfer where $h$ is the heat transfer coefficient between the surrounding air and the thermocouple bead, $T_{th}$ is the thermocouple temperature and $T_{real}$ is the temperature of the surrounding gas direct around the thermocouple. The next term accounts for the radiative exchange between the thermocouple and the radiative environment at $T_{env}$ (here: room temperature); $\sigma$ is the Stefan Boltzmann constant ($\sigma = 5.67 \times 10^{-8}$ W/m$^2$K$^4$); and $\varepsilon$ is the emissivity of the thermocouple, $\varepsilon \approx 0.2 \ [7]$. The last term represents the heat loss due to thermal conduction along the leads of the thermocouple. For most cases in chapter 3 the temperature
is quite homogeneous in radial direction, therefore the losses due to thermal conduction are negligibly small compared to the radiation and convection losses. In chapter 4 however, the thermal conductivity is estimated and inserted in the correction. The error due to radiation losses, the temperature error $T_{\text{real}} - T_{\text{th}}$, is then as follows,

$$T_{\text{real}} - T_{\text{th}} = \frac{\sigma \epsilon}{h} (T_{\text{th}}^4 - T_{\text{env}}^4). \quad (A.2)$$

The heat transfer coefficient can be derived from a theory based on external forced convection around arrays of beads in a cross-flow [7]. Figure A.2 shows the specific situation for these temperature measurements. As shown in this figure only one row is present, consisting of 7 circles (the seven thermocouples used).

Figure A.2: Cylinders (thermocouples) in cross-flow; at the bottom of the figure the burner outlet is shown

The overall Nusselt number formula is:

$$\Nu_d = \frac{h D}{k}. \quad (A.3)$$

where $h$ is the heat transfer coefficient averaged over all the cylindrical surfaces in the array. In this case the $\Re_D$ is defined as $\frac{v_{\text{max}} D}{\nu}$, with $v_{\text{max}}$ the maximum averaged horizontal velocity through the narrowest cross section formed by the array. The value for the $\nu$ is calculated at the temperature present in the cross section. $\Re_D$ is about 30 in the cases addressed in this thesis. For an aligned arrays of cylinders, with a $\Re_D$ between 1 and 100, the following equation for the array-averaged Nusselt number $\Nu_d$ can be used,

$$\Nu_d = 0.9 \cdot C_n \cdot \Re_D^{0.4} \cdot \Pr^{0.36} \left( \frac{\Pr}{\Pr_{\text{th}}} \right)^{\frac{1}{2}}; \quad (A.4)$$

where $C_n$ is a function of the total numbers in the array; for a one-array aligned array holds that this is 0.7 [7]. All the physical properties, except $\Pr_{\text{th}}$, are evaluated at the mean temperature of the gas that flows through the spaces formed by the cylinders. Knowing this $\Nu_d$, the $h$ is calculated using formula A.3. Finally, formula A.2, with $h = \bar{h}$ is used to calculate the radiation correction.
Appendix B

Stereo PIV calibration

**Procedure:** Calibration for the stereo-particle image velocimetry is performed by placing a calibration grid at eight different positions, each spaced at 0.5 mm, in the width direction in the laser sheet. The grid consists of dots printed on a transparent overhead slide. Transparent dots are printed in a black field. The dots are spaced 3 mm from each other. A few bigger dots are printed in the center. These dots are used as a reference for the images from the two cameras. Figure B.1 shows a photograph of the calibration grid. The calibration grid is mounted by a positioning table to a framework. The grid is shifted by the small positioning screw shown at the top of the grid, this is done without moving or removing the glass bell. A stiff small tubing is connected to the positioning screw. This tube is guided through a hole in the glass bell. In this way the table is moved without moving the glass bell. The positioning table is mounted above the grid because of the desired location of the measuring area. When mounted underneath the grid, a quite large area directly downstream of the burner would not be calibrated.

![Figure B.1: Calibration grid: positioned above the burner in a frame; for the displacement needed for the calibration recordings the positioning table above the grid is used](image)
The calibration recordings couple the physical coordinates \((x, y, z)\) to the recorded pixel coordinates \((i, j)\). The set of equations reflecting this coupling is:

\[
\partial I_1 = \partial x \frac{\partial i}{\partial x} |_1 + \partial y \frac{\partial i}{\partial y} |_1 + \partial z \frac{\partial i}{\partial z} |_1 \\
\partial J_1 = \partial x \frac{\partial j}{\partial x} |_1 + \partial y \frac{\partial j}{\partial y} |_1 + \partial z \frac{\partial j}{\partial z} |_1 \\
\partial I_2 = \partial x \frac{\partial i}{\partial x} |_2 + \partial y \frac{\partial i}{\partial y} |_2 + \partial z \frac{\partial i}{\partial z} |_2 \\
\partial J_2 = \partial x \frac{\partial j}{\partial x} |_2 + \partial y \frac{\partial j}{\partial y} |_2 + \partial z \frac{\partial j}{\partial z} |_2
\]

where indices 1 and 2 indicate to camera 1 and camera 2. In these equations \(\partial x, \partial y\) and \(\partial z\) are the displacements of the seeding particles in \(x, y,\) and \(z\)-direction in reality. These unknown displacements are calculated at fixed points known for both cameras. These equations are used to determine the calibration-factors. In the equations the calibration-factors are \(\frac{\partial i}{\partial x}, \frac{\partial i}{\partial y}, \frac{\partial i}{\partial z}\) and \(\frac{\partial j}{\partial x}, \frac{\partial j}{\partial y}, \frac{\partial j}{\partial z}\). These factors are calculated from the calibration recordings of the calibration grid. \(\frac{\partial i}{\partial x}\) is the relative displacement between pixel displacements and real displacements in \(i\)-direction in the camera. \(\partial I\) is the measured pixel-displacement of seeding particles in the \(i\)-direction in the camera; and so is \(\partial J\) in the \(j\)-direction. This set of four equations and three unknowns is solved by the least squares method.

**Accuracy:** The stochastic error sources like out-of-plane particle movement and mismatching of particles, which are encountered during ‘normal’ PIV, hold also for the stereo-PIV situation. Stereo-PIV as applied in this study, is a combination of two pairs of ‘normal’ PIV recordings. So when one of the ‘normal’ PIV calculations contains an error vector for a certain position, the total vector at that position is useless. Therefore, the probability that an error occurs, is larger for stereo-PIV than for ‘normal’ PIV.

For the systematic errors of the measurements, the calibration of the PIV recordings is crucial for the accuracy. The accuracy of the calibration is checked by calculating PIV images of the calibration image pairs. The movement in \(x, y,\) and \(z\) direction is known in this situation, namely the \(x\) and the \(y\) should be zero whereas the \(z\) movement should be 0.5 mm. The histograms of the movements in \(x, y,\) and \(z\) direction are shown in figure B.2. It is found that the movement in the \(x\) direction is indeed 0 (mean = 1.49 e-4 mm). The movement in the \(y\) direction is also 0 (mean = -0.0079 mm). The movement in the \(z\) direction is 0.5 (mean = 0.508 mm). Also interesting is the standard deviation of the measured movements. This indicates the accuracy in the measurement in the directions of the measurement situation. The \(x\) and \(z\) direction movements are coupled quantities in the recorded images in the cameras. These movements are resolved from the two recorded images together. The standard deviation of these two directions is of the same order (std \(x = 0.094\) mm and std \(z = 0.091\) mm). Also a resemblance in histogram shape is clearly found for the \(x\) and \(z\) direction movements. The \(y\) movement is a directly determined one. Both cameras do record this movement independently. The standard deviation of this movement is therefore smaller (std \(y = 0.004\) mm).
Figure B.2: Histograms of the movement calculated from the eight PIV calibration images for which the movement is ideally 0.5 mm in $z$-direction.
Appendix C

The gas chromatograph

The analysis of the outlet gases is split into two different paths. These paths use different detectors and different columns. Figure C.1 shows these two paths schematically.

As shown in the figure, the left side is calibrated for the permanent gases: carbon dioxide, hydrogen, oxygen, nitrogen, methane and carbon monoxide using a thermal conductivity detector (TCD, or hot wire detector). This TCD uses a Wheatstone bridge to produce a signal depending on the thermal conductivity of the gases. In the other side (at the right: the gas-liquid side) the hydrocarbons are analysed using a flame ionisation detector (FID). The permanent gas side at the left, is heated at a constant temperature (65 °C). For the right side, the column is placed in an oven. This oven is programmed. The initial temperature is 40 °C, from then on the oven is heated up with a speed of 180 °C/min. The final temperature of 330 °C is reached after 1.6 min. The oven stays for 0.4 min at this temperature: the analysis for the FID is now finished. The oven is now programmed to cool down, at such a rate that the oven is again at 40 °C when the permanent gas side is ready analysing the permanent gases. After about 6 min the gas chromatograph is ready to take another sample.

In figure C.2 a photograph of the gas chromatograph (on the right) and the computer is shown. The chromatograph is coupled to the computer. It is possible to operate the chromatograph either via the computer or manually by using the control panel. The control panel is positioned at the right upper corner of the gas chromatograph.
Figure C.2: The Gas Chromatograph system: the computer on the left, the Gas Chromatograph on the right.

(like shown in the figure). The gas side and the gas-liquid side are positioned in the chromatograph like shown in the scheme of figure C.1.

Figure C.3 shows a global scheme of the sample loops, the valves, the columns and the detectors used. The line in the centre of the figure separates the two parts: again left the permanent gas and right the hydrocarbon side.

![Diagram showing Gas Chromatograph system](image)

Figure C.3: Overview of columns and valves

As shown at the top side of the scheme two sample loops are used: 250 \( \mu l \) for the permanent gas side and 100 \( \mu l \) for the hydrocarbon side. These sample loops are filled using the two valves drawn right beneath of the sample loops. Another valve is placed in the gas compartment. In this figure the valves are drawn in stand-by position. The switch valves are heated to 300 °C, and they are switched pneumatically
with pressurized air. Three columns are placed in the chromatograph: two are used for the permanent gas analysis, one for the hydrocarbons. The carrier gas used for both paths is helium. At the bottom of figure C.3 the two detectors are shown. The switching of the valves is controlled by a manually inserted so called ‘run table’. Table C.1 shows the run table of the Gas Chromatograph.

Table C.1: Run table for the switching of the valves and the pump (in min)

<table>
<thead>
<tr>
<th>Time</th>
<th>External event</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>number 4 on</td>
<td>Vacuum pump on</td>
</tr>
<tr>
<td>0.80</td>
<td>number 4 off</td>
<td>Vacuum pump off and wait</td>
</tr>
<tr>
<td>1.00</td>
<td>number 3 on</td>
<td>Fills sample loop for FID</td>
</tr>
<tr>
<td>1.00</td>
<td>number 1 on</td>
<td>Fills sample loop for TCD</td>
</tr>
<tr>
<td>1.20</td>
<td>number 1 off</td>
<td>Stops fill sample loop</td>
</tr>
<tr>
<td>1.20</td>
<td>number 3 off</td>
<td>Stops fill sample loop</td>
</tr>
<tr>
<td>2.65</td>
<td>number 2 on</td>
<td>Injects light permanent gas on RT-M sieve</td>
</tr>
<tr>
<td>3.80</td>
<td>number 2 off</td>
<td>Injects heavier permanent gas on by-pass</td>
</tr>
</tbody>
</table>

First, the vacuum pump is activated for 0.8 min as shown in the table. This is to ensure that traces of the previous sample are erased. After that a short period of rest of 0.2 min is programmed to make sure that the gases are in equilibrium when injected on the sample loops. At 1.00 min, the valves E1 and E3 are switched and the filling of the loops starts. After 0.2 min the filling stops: the valves E1 and E3 are switched. This stops the filling and opens the path for the samples to the columns. So in less than 80 seconds, the gas is transported from the sampling point to the columns. At 2.65 min valve E2 is switched. Figure C.4 shows this valve and two of the columns in detail.

![Diagram of the gas chromatograph](image)

**Figure C.4:** The permanent gas side; two columns and valve E2 are shown

The RT-Q plot column separates only the carbon dioxide, ethane and ethene. The hydrogen, oxygen, nitrogen and methane are analysed on a molsieve column (RT-M sieve). A valves is switched such, that the entrance to the molsieve column is blocked...
when the heavier components eluate from the RT-Q plot column. The timing of switching valve E2 is thus crucial. Another important detail is that a pre-separation column is used to back-flush the C₃ components and water. The C₃ components are back-flushed because their eluation time is longer and these compounds are not expected to form in large quantities in the outlet gases. The water is back-flushed because the columns used are not suitable for water.

The data-points are recorded with a rate of 200 points per second, this is needed for the ultra fast side. Because of the high temperature in the oven, the components eluate in a short time interval, so a lot of data-points are necessary to monitor the progress. When combining the chromatograms the program needs the same number of sample points for each detector. The number of sample points for the permanent gas side is therefore also 200. The data are analysed with Chromcard (version 2.1).

Calibration

The calibration for the permanent gas side is performed separate from the calibration of the gas-liquid (hydrocarbon) side. For both sides however, the same global definitions hold for the component identification and the determination of the concentration. The retention time is used to identify a component. This is the time needed for a component to eluate from the column. One important criterion for the choice of a column is that the eluation time for each component that should be analysed, is specific for that component.

To determine the concentration, a so called response factor $RF$ is calculated. This $RF$ is defined as:

$$RF = \frac{\text{Peak area}}{\text{Concentration}}$$  \hspace{1cm} (C.1)

So, a response factor couples the concentration in the gas sample to the peak area measured by the gas chromatograph.

**Permanent gases:** For the permanent gas side, calibration gas from a gas bottle is used. The gas bottle contains 10 % hydrogen, 2 % methane, 1 % oxygen, 10 % carbon dioxide, 15 % carbon monoxide and the remainder (62 %) is nitrogen. For the TCD detector the $RF$s are determined by the Chromcard program. Chromcard derives these factors from the chromatograms made when the calibration mixture is inserted, together with the data of the calibration mixture that are entered in the component table.

**Hydrocarbons:** The hydrocarbons are all analysed in the Ultra Fast Module oven (UFM). The Flame Ionisation Detector (FID) analyses only the hydrocarbon containing compounds. The retention times of benzene, toluene, xylene, naphthalene, phenanthrene and chrysene are determined by manual injection of each single one of these components in the split split-less injector (SSL injector).

The calibration of the (gas-phase) tar-components is performed by injecting fluid standards manually in the SSL injector. A ‘bridge’ component between the gas and the fluids is necessary. The bridge component used is $nC_4$. For this calibration a mixture of $nC_4$ gas and nitrogen is used. First, the response factor of this known concentration of $nC_4$ gas is determined. In this way the actual response factor for $nC_4$ on this column with a Flame Ionisation Detector (FID) can be found. The coupling between this gas
phase component and the fluid components is made by use of theoretical response factors. Theoretical response factors for the compounds using the FID are found in literature (e.g. [33]). When the theoretical and the actual response factor for \(nC_4\) are known, together with the theoretical response factors of several hydrocarbons, the actual response factors for the hydrocarbons can be calculated. These factors display the calibrated relation between the peak area and the concentration of the sampled component, and are entered manually in the program.

Literature (e.g. [33]) shows that the theoretical response factors of the several hydrocarbons are almost the same. Using the gas chromatograph, this relative relation is checked. A diluted mixture of several tar components is injected manually to determine the relative response factors of these components. This injection shows that the response factors of the several hydrocarbons are indeed the same.

When analysing the components downstream of the burner also some components, which are not calibrated, appear. Their peaks however are closely located near the calibrated components. For example, the components that are called the 2-ring group are derived from a summation of all the peak areas around the naphthalene peak. For some small peaks, the standard peak detection parameters that are set in the Chromcard program are not specific enough. In these cases, the detection parameters are entered manually.

**Accuracy:** When estimating the accuracy of the GC measurements, it is reasonable to make a distinction in systematic and stochastic errors. The stochastic errors can be determined by checking the reproducibility of the measurements using a calibration mixture. The reproducibility is quite good: when repeating a measurement both of the detectors measure the same values within 0.05% ± 0.1% for the TCD, and within 1 ppm ± 1% for the FID. The accuracy of the FID is checked for the measurement of methane present in the gas. The calibration mixture is in the order of volume percents, so the amount of methane is far too high for the real ppm range that is addressed in this study. The accuracy of the FID is therefore also checked by adding a methane-nitrogen mixture with only a small amount of methane present in this mixture. The reproducability accuracy found for these settings is 0.01 ppm ± 0.1%.

The systematic accuracy depends of course on the accuracy of the injected calibration components. The calibration gases for the permanent gases as well as the gases (\(nC_4\)) used for the hydrocarbon calibration are bottled with a reliability of 95%.

A systematic error might occur, when the gas sample taken would still have been reacting during the transport from the set-up to the columns in the GC. For the experiments in chapter 3, the gas is sampled using a 1/16” tube which is at room temperature. When taking the gas sample, the gas is cooled quickly by the cold surroundings: this is intended to freeze the gas composition. For the experiments where tars are used, the 1/16” sampling tube is heated to 200°C, to make sure that the tar components will not condense in the tubing. It is interesting to examine whether this sampling temperature is low enough to freeze the composition of the permanent gases. The effect of temperature is checked numerically with Chemkin - Perfectly Stirred Reactor (PSR) ([45]) using a GRI 3.0 mechanism. For 800 K (527°C) the effect of the residence time on the composition is studied. At this temperature, the mixture measured by the GC is calculated for several residence times. This temperature is chosen as a 'worst case' temperature: for lower temperature even longer residence times will be needed to change the gas composition. Figure C.5 shows the concentration that is measured by the GC as a function
of residence time at 800 K. The difference are small for residence times ranging from 4 to 15 s: only for the oxygen and carbon monoxide concentrations small decrease is found. Even for much larger residence times, like shown in the figure for example for 90 and 900 s, the concentrations are quite constant. Again only a decrease is found for the oxygen and the carbon monoxide concentrations: the oxygen even decreases to nearly zero. As mentioned before, the residence time of the sample in the sampling tube and the sample loop together is 1.2 min (i.e. 72 s). So, even for this temperature of 500 °C instead of the 200 °C used for the sampling, the concentrations are quite similar.

![Graph showing concentration measurements over residence time](image)

**Figure C.5:** Numerical calculation of the concentration measured by the GC, as function of the residence time for several components at 800 K

For the systematic error made for the hydrocarbon measurements, another remark should be made about the use of a $nC_4$ gas as a bridge component. In general, the bridge component should preferably resemble the measured components. In this case however, there is an essential difference: the calibration component is an alkene while the measured components are aromatic. This is likely to introduce an error. However in this study, the goal is to determine whether the model compound (naphthalene) will be cracked or polymerised by the burner. This calibration method is good enough to detect that difference, while the systematic error for each of the aromatics is likely to be equal.
Summary

Biomass gasification is an interesting option for renewable energy production. However, for the introduction of small-scale gasifiers using biomass, the tar produced in this process is one of the major problems. Apart from causing environmental hazards, tar is known to create process-related problems in the end use devices, such as fouling, corrosion, erosion and abrasion. Before the gas can be introduced into the gas engine, the tar content has to be reduced to low values. A promising concept for small-scale applications, is to remove the tars by burning a small part of the gas. This partial burning will remove the tars; supposingly both by thermal cracking and partial oxidation.

To investigate the removal processes, a burner geometry is evaluated and modified. The geometry should meet various demands: low caloric gas (5-12 MJ/Nm$^3$) should be burned in a stable way using little air, creating a homogeneous temperature for the thermal treatment of the burnt and unburnt gas downstream of the burner. In this process the mixing is crucial: on one hand the mixing should not be too turbulent, because locally a stoichiometric mixture should create diffusion flames; on the other hand however, the mixing should be turbulent enough to make the temperature homogeneous downstream of the burner.

First, the burner geometry is tested in a perspex (polymethyl metacrylate) set-up using water. By scaling this set-up by the Reynolds number, information was gained about the mixing process in the burner geometry and an optimal value for the ratio of the volume flows is found. The final set-up is built in stainless steel. In this set-up several gas mixtures in various compositions resembling biogas are used, without using tar. It is possible to operate the burner in a stable way using little air at low caloric values (down to 3 MJ/Nm$^3$). So the burner meets the demands for the burning part of the process. The outlet temperature and gas composition are measured at several heating values, powers, fuel inlet compositions and air factors ($\lambda$). For the gas compositions used, it is seen that methane is converted to carbon monoxide and hydrogen.

For the part of the process downstream of the burner, normal and stereo particle image velocimetry (PIV) are used to study the flow field. Also temperature measurements are performed. The temperature measurements downstream of the burner show that at a distance of about two times the diameter of the burner, a homogeneous mixture is attained. The stereo PIV measurements point out that the flow is weakly swirling ($S \approx 0.2$). A strong decay of the swirling motion is seen at the same height where the temperature becomes homogeneous.

The effect of thermal treatment ($\lambda = 0$) on the tars is studied using an experimental set-up at the Energy Research Centre of the Netherlands (ECN). A sooting trend is seen in these experiments: smaller carbon-containing ring compounds seem to convert step by step to soot. The longer the residence times the higher the amount converted into soot, and also an acceleration of the sooting process is seen with an increase of the
Finally, the effect of partial oxidation on tar is studied in the burner geometry. Naphthalene is used as a model compound in these experiments. When adding some primary air ($\lambda = 0.2$), the total tar concentration is low. Interesting is, that when more air ($\lambda \geq 0.4$) is added to the burner, the same sooting tendency is found as in the case of thermal treatment only. By changing the inlet gas composition by adding more hydrogen, the tar concentration in the outlet is considerably affected. Hydrogen seems to be an inhibitor for soot formation: only a small amount of hydrogen present in the inlet gas transforms the sooting/polymerisation process into cracking. When considering the inlet gas compositions that resemble biogas and a $\lambda$ of 0.2 as preferred, little tar is found downstream of the burner: only 7.5 % of the inlet mg/Nm$^3$. Therefore, the process created by the burner geometry might be a promising method for the application to small-scale biomass gasifiers.
Samenvatting

Biomassavergassing is een veelbelovende optie voor duurzame energieproductie. Bij het introduceren van vergassers die geschikt zijn voor kleine schaal, vormt de teer die ontstaat tijdens het vergassingsproces een bron van zorg. Behalve dat het slecht is voor het milieu en de gezondheid, veroorzaakt teer ook problemen in de nageschakelde processen, vooral doordat ze condenseren. Voordat het gas in een gasmotor gebruikt kan worden, moet het teergehalte in het gas verlaagd worden tot acceptabele waarden. Een veelbelovend concept voor kleinschalige applicaties, verwijdert de teer door het verbranden van een deel van de gassen. Dit partiële verbranden zal de teer verwijderen: deels door de thermische behandeling en deels door de partiële oxidatie.

Om dit teerverwijder-principe in detail te kunnen bestuderen, is een brandergeometrie geëvalueerd en aangepast. Deze geometrie moet aan een aantal eisen voldoen. De brander moet laag calorisch gas (5-12 MJ/Nm$^3$) op een stabiele manier kunnen verbranden; terwijl slechts weinig lucht gebruikt wordt, omdat het resterende gas het liefst zo hoog calorisch mogelijk moet zijn. Dit proces moet leiden tot een mengsel van verbrande en onverbrande gassen met een homogene temperatuur, zodat de thermische teerverwijdering een kans krijgen. Het mengproces is in dit geval cruciaal: aan de ene kant moet het mengproces niet te turbulent zijn, zodat de gassen en de lucht de kans krijgen een stoichiometrisch mengsel te vormen een deel van het gas kan verbranden. Aan de andere kant moet het uitmengen na de vlam snel genoeg gaan om de temperatuur homogeen te maken.

De brandergeometrie is eerst bekeken in een met het Reynoldsgetal geschaalde perspex-opstelling. In deze opstelling is met water en kleurstoffen het stromingsgedrag bepaald bij verschillende verhoudingen van volumestromen. Op deze manier is inzicht verkregen in het effect van deze parameter op het mengproces. De uiteindelijke opstelling is gemaakt van Nikkelvrij RVS. De brander is in eerste instantie getest met verschillende gasmengsels met een samenstelling die vergelijkbaar is met biogas, hoewel in dit geval geen teer is gebruikt. De vlam brandt stabiel voor brandstofmengsels met een calorische waarde tot aan 3 MJ/Nm$^3$, terwijl weinig lucht toegevoerd wordt. Aan de eisen gesteld aan het brander/deel van de opstelling is dus voldaan. De temperatuur en de gassamenstelling aan de uitlaat zijn gemeten voor verschillende verbrandingswaarden, vermogens, brandstof (ingangs) composities, lucht-factors ($\lambda$) en ingangstemperaturen. Voor de gebruikte composities geldt dat de methaan lijkt te worden omgezet in waterstof en koolmonoxide. De gewenste temperatuur van 500 $^\circ$C wordt voor alle situaties bereikt.

Het snelheidsveld na de brander is bestudeerd met Particle Image Velocimetry; waarbij zowel gewone PIV als stereo-PIV is gebruikt. Daarbij is ook het temperatuurveld gemeten. Een homogene temperatuurverdeling is waargenomen op een afstand stroomafwaarts van de brander gelijk aan twee keer de diameter van de brander.
De stereo-PIV metingen laten zien dat de stroming een zwakke swirlbeweging maakt ($S \approx 0.2$). Het verval van deze swirlbeweging zet in op dezelfde afstand van de brander als waar ook de temperatuur homogeen begint te worden.

Het effect van thermische behandeling ($\lambda = 0$) op teer is onderzocht in een bestaande opstelling bij het Energie onderzoeks Centrum Nederland (ECN). Deze experimenten laten een conversie van teer naar roet zien. Kleinere koolstofhoudende ring-componennten lijken stap voor stap te omgezet te worden naar roet. Hoe langer de verblijftijd is, hoe meer roet gevormd wordt. Ook blijkt verhoging van temperatuur een versnelling van het roetingsproces met zich mee te brengen.

Het effect van partiële oxidatie is onderzocht in de brandergeometrie, waarbij naf-taleen is gebruikt als model component voor teer. Het blijkt dat het toevangen van een kleine hoeveelheid lucht ($\lambda = 0.2$), resulteert in een lage teerconcentratie. Echter, bij het toevangen van meer lucht ($\lambda \geq 0.4$) ontstaat roet. De hoeveelheid waterstof in de brandstof is van invloed op de teerconcentratie. De resultaten laten zien dat waterstof roetvorming verhindert. Voor de brandergeometrie geldt dat het gebruik van een gascompositie die lijkt op biogas, een productgas lever met weinig teer: slechts 7.5% van de hoeveelheid aan de ingang (mg/Nm$^3$) is over. De omstandigheden gecreëerd door de brandergeometrie zijn dus veelbelovend voor de reiniging van gassen van vastbed-vergassers op kleine schaal.
Dankwoord

Mijn onderzoek is bij uitstek een onderzoek dat verschillende terreinen bestrijkt. Daarmee doel ik op het feit dat naast stromingskundige kennis ook kennis van verbranding en organische scheikunde nodig is. Echter, in mijn ogen is er nog een kant, namelijk de praktische kant: het bouwen van de experimentele opstellingen, expertise in de meettechnieken en natuurlijk ook sterke-mannen-werkjes zoals het losdraaien van schroeven en dergelijke. De heldere kijk van experts met een andere achtergrond dan de mijne is dus onontbeerlijk. Naast de steun van deze experts, heb ik tijdens mijn onderzoek steun gehad van velen. Ik wil hieronder graag een aantal van hen speciaal noemen.


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Marja Houben
Eindhoven, 16th December 2003
Curriculum vitae


In september werd zij voor 4 jaar aangesteld als promovendus bij de faculteit Werktuigbouwkunde binnen de sectie Energy Technology aan de Technische Universiteit Eindhoven. Het in dit proefschrift beschreven onderzoek werd uitgevoerd onder begeleiding van prof.dr.ir. A.A. van Steenhoven, prof.dr. L.P.H. de Goey en dr.ir. H.C. de Lange.