Tar formation in a fluidised-bed gasifier

Impact of fuel properties and operating conditions

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Preface

This report describes the results of the ECN contribution to the project "Primary measures to reduce tar formation in fluidised-bed biomass gasification", conducted by order of the Agency for Research in Sustainable Energy (Samenwerkingsverband Duurzame Energie, abbreviated as SDE) under contract number P1999-012. The overall project has been executed by the following group of five partners: ECN Biomass, Eindhoven University of Technology (TUE), KEMA, TNO Environment, Energy and Process Innovation (TNO-MEP), and University of Twente (UT). The project co-ordination was conducted by ECN Biomass and the SDE programme manager was C. Daey Ouwens. Industrial guidance to the project work was provided by A.C. van Dongen (Reliant Energy), H.P. Calis and H.J.P. Haan (Shell Global Solutions).

Abstract

The overall objective of the work described in this report has been to assist designers and operators of fluidised-bed biomass gasification based systems by providing detailed data concerning the impact of fuel properties and gasifier operating conditions on the resulting tar content and composition, and concerning the underlying mechanisms. The tar content and composition have been interpreted in terms of their impact on the performance of downstream equipment using a dedicated tar classification system. In this respect, water solubility and condensation behaviour, expressed in terms of the tar dewpoint, were identified as the most important tar properties. Attention has been paid mostly to atmospheric-pressure, air-blown bubbling-fluidised-bed (BFB) gasification of woody biomass, but circulating-fluidised-bed (CFB) gasification was addressed as well.

The main part of the work consisted of a systematic experimental study using a 1 kg/h lab-scale BFB gasifier. In addition, some experiments were conducted in a 100 kg/h CFB gasifier as well. Much emphasis was given to the determination of the tar *composition* by measuring individual tar compounds using either the Solid Phase Adsorption method or the Guideline method. In the lab-scale BFB gasifier, the impact of three fuel properties (ash content, moisture content and lignocellulose composition) and two operating conditions (gasification temperature and gas residence time) was determined. The results were found to be representative for circulating-fluidised-bed (CFB)-gasification as well, provided that differences in gasification temperature and gas residence time (distribution) are taken into account. The report contains data to account for these differences.

Finally, based on the experimental findings, the potential of tar control by primary measures (i.e., adjustment of fuel properties or gasifier operating conditions) has been discussed.

Keywords

biomass, fluidised-bed gasification, tar, tar formation, tar classification, primary measures, decomposition, cracking, polymerisation

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SUMMARY

Gasification technologies are expected to play a key role in expanding the use of biomass as a major renewable energy source. The conversion of the solid feedstock to a gaseous fuel (producer gas or synthesis gas) significantly increases its potential. The gas can be used for applications such as co-firing in coal- or natural gas-fired power plants, electricity generation in stand-alone conversion devices, and the production of gaseous/liquid fuels or chemicals.

For all these applications, a more or less extensive cleaning of the product gas is required. In particular, proper control of the tar content (or the combination of tar and particulates) to avoid, e.g., fouling due to tar condensation or difficult to handle and hazardous tar-water mixtures, often is a major challenge. Basically, there are two main options for controlling the tar content in gasifier product gas, *viz*.:
- by applying downstream cleaning processes (secondary measures) or,
- by optimising biomass fuel properties and/or gasifier design and operating conditions (primary measures).

Generally, the latter should be considered first, because of their inherent potential of being more cost effective. Therefore, five R&D organisations in the Netherlands headed by ECN teamed to elucidate the possibilities of these primary measures. The project has been focussed on *air-blown, atmospheric-pressure fluidised-bed gasification of woody biomass*, being one of the major gasification technology applications.

In this report, ECN contributions to this overall project are described. These contributions are based on the main conclusions of an inventory study at the start of the project, being:
- In many studies, tar is considered as a lump-sum compound, while in downstream processes only specific tar compounds may be problematic and others may be harmless or even beneficial.
- Many studies focus on tar formation, without paying attention to the impact of the tar concentration and composition on the performance of downstream processes.
- Only a limited number of studies have addressed the relation between tar concentration and/or composition and gasification conditions in a systematic way. The impact of biomass fuel properties on tar formation and downstream problems received even less attention.

From these conclusions, it was decided to dedicate the ECN work (apart from co-ordinating the overall project) to providing detailed data concerning the impact of fuel properties and gasifier operating conditions on the resulting tar content and composition, and concerning the underlying mechanisms. The tar content and composition were to be interpreted in terms of their impact on the performance of downstream equipment. In this respect, water solubility and condensation behaviour, expressed in terms of the tar dewpoint, were identified as the most important tar properties. Attention was to be paid mostly to bubbling-fluidised-bed (BFB) gasification, but circulating-fluidised-bed (CFB) gasification was addressed as well.

To meet these objectives, first, a literature survey was conducted on tar formation in (fixed-bed and) fluidised-bed gasifiers and on the underlying mechanisms. Then, the main part of the work consisted of a systematic experimental study. Most of the experiments were performed in a 1 kg/h lab-scale BFB gasifier, but experiments were conducted in a 100 kg/h CFB gasifier as well. Much emphasis was given to the determination of the tar *composition* by measuring individual tar compounds using either the Solid Phase Adsorption method or the Guideline method[1]. However, to allow a concise presentation of experimental results and obtaining mechanistic insight, the individual tar compounds were grouped into the following five classes based on the behaviour of the tar compounds in downstream processes:

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[1] The Guideline method resulted from a broad international effort co-ordinated by ECN to arrive at a widely-accepted, standard tar measurement method. Details can be found on the dedicated web-site www.tarweb.net.

Class 1: GC-undetectable tars (= tar compounds that cannot be detected with a GC-FID or GC-MS, equipped with a non-polar capillary column).

Class 2: Heterocyclic components (like phenol, pyridine, cresol) with a high water solubility.

Class 3: Aromatic compounds (1-ring; e.g., xylene, styrene, toluene). Light hydrocarbons that are not important in condensation and water solubility issues.

Class 4: Light polyaromatic hydrocarbons (2-3 ring PAH compounds; e.g., naphtalene, fluorene, phenanthrene). These components condense at relatively high concentrations and intermediate temperatures.

Class 5: Heavy polyaromatic hydrocarbons (4-7 ring PAH compounds; e.g., fluoranthene, pyrene, up to coronene). These compounds condense at relatively high temperature at low concentrations.

In the experimental programme, the impact of three fuel properties (ash content, moisture content and lignocellulose composition) and two gasifier operating conditions (gasification temperature and gas residence time) was determined. In general, these parameters were varied independently, i.e. while keeping the others constant. Also the equivalence ratio ER was mostly kept constant, which was made possible by the trace heating on the wall of the lab-scale gasifier. All experiments were conducted with feeding the air as primary air through the bottom plate of the bubbling fluidised bed only. Although it was realised that air staging, feeding part of the air as secondary air in the freeboard may have a large impact on tar formation, this was beyond the scope of the present study.

Variation of the **ash content** in the bed, simulated by co-feeding high-ash char (approx. 40 wt% ash), had a negligible impact up to a maximum tested char/biomass ratio of 17 wt%.

An increase in **moisture content** from 10 to 45 wt%, simulated by mixing dry biomass off-line with water, led to a decrease in total tar content from 14 to 8 g/m_n^3. Also all the individual tar classes showed a clear decrease. However, the highly water-soluble heterocyclic compounds (class 2 tars) could not be eliminated completely at the given gasification temperature of 800-825°C and approx. 4 s gas residence time, and the tar dewpoint only showed a slight decrease. Fuel with high moisture content needs extra energy for the evaporation of water and heating of the water vapour. In a large-scale gasifier, the extra heat can/will be generated by increasing the ER in the gasifier. This will lead to even lower tar concentrations. However, this may result also in a decrease in cold gas efficiency, and a drop in energy efficiency. Also the gas volume flow will increase due to both the increasing fuel moisture content and the increasing ER. This results in an increase in the size of unit operations downstream the gasifier. For many applications, the loss in energy efficiency and the increasing size of unit operations will probably outweigh the advantage of lower class 2 and class 5 tar concentrations. However, this might not be the case for indirect biomass co-combustion (see below).

The **lignocellulose composition** seems to have some effect on the total tar concentration, while having no significant effect on the tar composition. Experiments with a fuel prepared from pure cellulose gave lower tar concentrations than experiments with willow and beech. Despite the lower tar concentrations, the tar dewpoint remained nearly the same. This means that fouling due to tar condensation will happen at similar process conditions. However, due to the lower tar concentrations, the amount of condensed tar species will be substantially lower for the cellulose case.

Increasing the **gasification temperature** from 750 to 900°C at constant ER appeared to have a large impact on tar formation, in particular on the tar composition. The class 2 tars were decomposed almost completely at 850°C and higher. On the other hand, the 2-3 ring PolyAromatic Hydrocarbon (PAH) compounds (class 4) and the 4-7 ring PAH compounds (class 5) concentration continuously increased with increasing temperature, leading to a continuous and substantial increase in tar dewpoint. The class 3 light aromatic compounds went through a maximum at 780-800°C, just as the total tar concentration.

Since it was realised that in an actual, industrial-scale gasifier, there is a coupling between the gasification temperature and the equivalence ration ER, additional experiments were conducted with a simultaneous, coupled variation of the gasification temperature and ER (higher ER to get higher temperature). These experiments gave a strong decrease in total tar over the temperature range of 750-950°C. However, here again the tar dewpoint showed an increase due to an increase in heavy PAH compounds (class 5 tar). A more detailed analysis, focussing on the heavy tar fraction in particular, revealed that the heavy PAH compounds are formed by dimerisation reactions of two PAH compounds or by cyclisation or polymerisation reactions of unsaturated C2-C4 hydrocarbons like acetylene and ethylene. These latter compounds are produced in the decomposition of aromatic as well as linear hydrocarbons.

Finally, increasing the **gas residence time** (in the freeboard of a bubbling-fluidised-bed gasifier) was found to have a similar, but much smaller, effect than increasing the gasification temperature.

The reported results of lab-scale bubbling-fluidised-bed (BFB)-gasification were found to be representative for circulating-fluidised-bed (CFB)-gasification as well, provided that differences in gasification temperature and gas residence time (distribution) are taken into account. The report contains data to account for these differences.

Primary measures
Based on the findings concerning the impact of fuel properties and gasifier operating conditions on tar content and composition, conclusions may be drawn concerning the possibilities of tar control by primary measures. To this purpose, a distinction should be made between firing the product gas in a coal-fired boiler (indirect co-firing) or in a stand-alone boiler on the one hand, and more advanced applications of the product gas on the other hand.

In indirect co-firing, generally, the product gas temperature is kept as high as possible to prevent tar-induced problems. In that case, the gas will not be cooled to temperatures below the water dewpoint and tars with a high water solubility (class 2) do not pose a problem. However, the gas cooling will require in most cases a mild control of the heavy PAH content in the product gas to avoid tar-induced fouling problems. Generally, to this purpose primary measures in the form of a proper selection of fuel properties and gasifier design and/or operating conditions seem to offer enough possibilities. The same holds for the case, where the product gas is kept at high temperature and then fired in a stand-alone boiler.

More advanced applications, such as firing the product gas in a gas engine or a gas turbine, or using the product gas for the production of gaseous or liquid fuels, generally require a much cleaner product gas and often require the product gas to be cooled down to (near-)ambient temperature. In these cases, generally, primary measures will not suffice to meet the requirements concerning tar content and composition, and secondary tar removal will be necessary. However, primary measures may be applied then to optimise the tar composition for these secondary removal processes or for gas cooling and cleaning processes in general. For example, if water scrubbing is applied, primary measures may be used to fully decompose the highly water-soluble class 2 tars, leading to a considerable reduction in wastewater treatment cost.

Recommendation
Given the important role of the class 1 tar fraction and its complex composition, it is recommended to put more effort in the determination of the composition of this tar class in future work.

1. INTRODUCTION

Gasification technologies are expected to play a key role in expanding the use of biomass as a major renewable energy source. The conversion of the solid feedstock to a gaseous fuel (producer gas or synthesis gas) significantly increases its potential. The gas can be used for applications such as:
- Co-firing in coal- or natural gas-fired power plants,
- Electricity generation in stand-alone conversion devices (gas engines, gas turbines, fuel cells),
- Production of gaseous/liquid fuels or chemicals.

For all these applications, however, a more or less extensive cleaning of the product gas is required. And, although gasification of solid fuels is already an old technology and the specific volumes of gas to be treated are much smaller than after combustion, product gas cleaning appears to be a (and often *the*) major area of concern. This can be specified further in saying that, in particular, the reduction of the tar content (or the combination of tar and particulates) often is the major challenge. In many applications, the tar content in the product gas has to be controlled to prevent a range of possible problems in downstream equipment (see also Figure 1.1), such as:
- Fouling and plugging due to tar condensation and soot formation,
- Difficulties in handling tar-water mixtures,
- Contamination of waste streams.

Figure 1.1   *Tar related problems of fouling (left) and wastewater production (right) in a biomass gasification process.*

Basically, there are two main options for controlling the tar content in gasifier product gas, *viz.*:
- by applying downstream cleaning processes (secondary measures) or,
- by optimising biomass fuel properties and/or gasifier design and operating conditions (primary measures).

Generally, the latter should be considered first, because of their inherent potential of being more cost effective. Therefore, five organisations in the Netherlands teamed in a project, funded by the Agency for Research in Sustainable Energy (Samenwerkingsverband Duurzame Energie, abbreviated as SDE), to elucidate the possibilities of these primary measures. The five organisations are: ECN (project co-ordinator), Eindhoven University of Technology (TUE), KEMA, TNO-MEP and University of Twente (UT). The project has been focussed on *air-blown, atmospheric-pressure fluidised-bed gasification*, being one of the major gasification technologies for biomass [1].

In this report, ECN contributions to the overall project are described. These contributions are based on the main conclusions of an inventory study at the start of the project [2], being:

- In many studies, tar is considered as a lump-sum compound, while in downstream processes only specific tar compounds may be problematic and others may be beneficial.
- Many studies focus on tar formation, without paying attention to the impact of the tar concentration and composition on the performance of downstream processes. The grouping or classification of tar compounds is mostly based on the formation mechanisms and not on their impact in downstream processes (see, e.g., Evans and Milne [3]).
- Only a limited number of studies have addressed the relation between tar concentration and/or composition and gasification conditions in a systematic way. The impact of biomass fuel properties on tar formation and downstream problems received even less attention.

Furthermore, it was found that many different tar definitions are applied, and even worse, in many publications tar is not clearly defined at all. This leads to much confusion and makes it often difficult or even impossible to compare results obtained and reported by different researchers.

Objectives

From these conclusions, it was decided to dedicate the ECN work (apart from co-ordinating the overall project) to assisting designers and gasifier operators by providing detailed data concerning the impact of fuel properties and gasifier operating conditions on the resulting tar content and composition, and concerning the underlying mechanisms. In addition, the tar content and composition were to be interpreted in terms of their impact on the performance of downstream equipment. This should then enable a first assessment of the practical and economic feasibility of identified, most promising primary measures.

Being a practical and meaningful definition for biomass gasification, tar has been defined as "all organic compounds with a molecular weight larger than benzene (excluding soot and char)".

Approach

To meet these objectives, first, a literature survey has been conducted on tar formation in (fixed-bed and) fluidised-bed gasifiers and on the underlying mechanisms. Results of this survey are described in Chapter 2 and 3 respectively. Then, the main part of the work consisted of a systematic experimental study to determine the impact of fuel properties and gasifier operating conditions on tar formation and on the performance of downstream processes. Most of the experimental work has been conducted in a 1 kg/h lab-scale bubbling-fluidised-bed gasifier, but the relation between tar formation in a bubbling-fluidised-bed and a circulating-fluidised-bed gasifier has been addressed as well.

In the experimental work, much emphasis was given to the determination of the tar *composition* by measuring individual tar compounds. This was based on the notion, that only specific tar compounds may be problematic and others may be beneficial in downstream processes. However, given the large amount of tar compounds in the product gas, it was realised that a concise presentation of experimental results and obtaining mechanistic insight would highly benefit from a grouping or classification of these tar compounds. Clearly, this tar classification should then be based on the behaviour of the tar compounds in downstream processes. In this respect, two major properties of tar compounds were identified to be of crucial importance, *viz.*, condensation behaviour and water solubility. Condensation behaviour is important, e.g., with respect to fouling in gas cooling or gas cleaning equipment. On the other hand, oxygenated or heterocyclic tar compounds containing O and/or N atoms like phenol are highly water soluble due to their high polarity. They may lead to hazardous wastewater, resulting in high disposal/processing cost for low-temperature gas cleaning systems. Based on these considerations, in the overall SDE-project a tar classification system containing five different tar classes was derived, as presented in Table 1.1 [1].

Table 1.1 *Tar classification system with a focus on the physical properties water solubility and condensation.*

	Description
Class 1	GC-undetectable tars. This class includes the heaviest tars that condense at high temperature even at very low concentrations.
Class 2	Heterocyclic components (like phenol, pyridine, cresol). These are compounds that generally exhibit high water solubility, due to their polarity.
Class 3	Aromatic compounds. Light hydrocarbons that are not important in condensation and water solubility issues.
Class 4	Light polyaromatic hydrocarbons (2-3 ring PAH compounds). These compounds condense at relatively high concentrations and intermediate temperatures.
Class 5	Heavy polyaromatic hydrocarbons (4-7 ring PAH compounds). These compounds condense at relatively high temperature at low concentrations.

GC-undetectable tars = tar compounds that cannot be detected with a GC-FID or GC-MS, equipped with a non-polar capillary column like the one prescribed in the Guideline (see Section 4.3.2).

The experimental work is described in Chapter 4 and 5, and finally, the main conclusions of the ECN work are given in Chapter 6.

2. TAR FORMATION IN A BIOMASS GASIFIER

Several types of gasifiers have been developed or are still under development for the thermal conversion of biomass. Tar formation and reduction is one of the important topics in the gasifier development. Generally, the various gasifiers can be grouped in three main classes, *viz.*: fixed-bed, fluidised-bed and entrained-flow gasifiers. Entrained-flow gasifiers are normally operated at high temperature (typically 1300-1500°C), and because of this high temperature level do not produce significant amounts of tar. Fixed-bed and fluidised-bed gasifiers, on the other hand, are normally operated at substantially lower temperature levels and do produce significant amounts of tar.

Not only large differences occur in the amount of tar produced, but also in the tar composition. For example, the element composition of tar is strongly dependent on the conditions of formation. Pyrolysis tars are formed at low temperature and consist mostly of aromatic compounds with a high percentage of O and N atoms. On the other hand, tar compounds that are formed at high temperature are also aromatic, but hardly contain hetero O and N elements.

Evans and Milne proposed a tar classification system to characterise tar from different types of biomass gasifiers (and pyrolysis units) [3-5]. They identified four major tar classes:
1. Primary tars;
2. Secondary tars,
3. Alkyl tertiary tars and
4. Condensed tertiary tars.
Primary tars are characterised by cellulose-, hemicellulose- and lignin-derived products, i.e. products from the main components of the biomass. Secondary tars are characterised by phenolics and olefins and are products from the conversion of primary tars. The alkyl tertiary products are characterised by methyl derivates of aromatics (styrene, xylene, and styrene) and, finally, the condensed tertiary tars are polyaromatic hydrocarbons (PAH) without substituents. In Chapters 2 and 3, these tar classes will be used to describe tar formation in (fixed-bed and) fluidised-bed gasifiers and the underlying mechanisms.

2.1 Operation of fixed-bed and fluidised-bed biomass gasifiers

A fixed-bed gasifier contains a moving bed of biomass. The gasification process in a fixed-bed gasifier can be separated in 4 distinct zones:
1. drying
2. pyrolysis
3. combustion
4. gasification (reduction)
The gas flow direction relative to the biomass flow direction strongly influences the tar content and composition in the product gas of a fixed-bed gasifier.

In an updraft (fixed-bed) gasifier, the incoming air flows from the bottom to the top, in counter-current with the moving biomass/char bed. At the bottom of the gasifier, the incoming air reacts with the char that is produced in the pyrolysis and gasification zones. When the hot combustion gas flows to the top of the reactor, the gas cools down and passes the gasification, pyrolysis and drying zone respectively. The tar concentration in the product gas at the outlet of the gasifier is relatively high and the elemental tar composition is close to the composition of pyrolysis tar. I.e., the gasifier product gas contains mainly primary and secondary tars as defined by Milne and Evans.

In a downdraft gasifier, the incoming air flows from the top/middle to the bottom, in co-current with the moving biomass/char bed. Near the air inlet, the pyrolysis products from the pyrolysis zone are partly combusted in the combustion zone. The heat generated in the combustion zone is transferred to the pyrolysis and drying zone respectively above the combustion zone. The combustion products CO_2 and H_2O react with the pyrolysis char at the bottom of the gasifier. Due to the endothermic heterogeneous reactions with char the gas cools down, while it flows down to the outlet at the bottom of the gasifier. Tars that are not converted in the combustion zone can further react in the char bed. Generally, a downdraft gasifier produces a gas with a low tar content. Tars from a downdraft gasifier have a relatively low concentration of oxygenated hydrocarbons in comparison with pyrolysis tars and are classified by Milne and Evans as secondary and tertiary tar compounds.

A fluidised-bed biomass gasifier comprises a fluidised bed of hot (often sand) particles which are not consumed during gasifier operation. Biomass is fed directly into or on top of the sand bed. Air is used as the fluidisation medium and as gasification medium. Generally, the four steps for the conversion of the biomass (drying, pyrolysis, combustion and gasification) cannot be clearly separated as in a fixed-bed gasifier. A fluidised-bed biomass gasifier produces a gas with a tar concentration of typically 10 g/m_n^3 [5]. The tars consist mainly of secondary and tertiary tars, although at lower temperatures also some primary tars may still be present.

2.2 Tar production in a fluidised-bed biomass gasifier

A fluidised-bed biomass gasifier can be operated in different regimes. The regimes are determined by the gas flow rate, gas properties and solids (sand) properties. When particles are fluidised with a gas flow that is considerably below the terminal velocity of the particles, the bed can be considered as a bubbling fluidised bed (BFB). A BFB normally has a freeboard above the bed to prevent entrainment of solids. While increasing the gas velocity above the terminal velocity of the particles, entrainment becomes appreciable and particles should be returned to the bed to maintain a certain bed height. The bed can then be considered as a circulating fluidised bed (CFB).

In a fluidised-bed biomass gasifier, biomass particles are fed directly into or on top of a bed of sand. The high heat transfer rate (approx. 400 $W/m^2/K$) from the hot fluidised-bed particles to a biomass particle ensures rapid heating. The biomass particle will go through a drying and pyrolysis process. These processes are accompanied by gas production inside the particle. The processes yield permanent gases, primary + secondary tars and char as the main products (Figure 2.1). Gases from outside hardly penetrate into the particle [6]. Thus, the drying and pyrolysis process inside the particle is hardly influenced by the gas composition surrounding the particle. The composition of the pyrolysis products leaving the biomass particle is mainly dependent on particle heating rate, biomass composition, ash content and composition, moisture content and particle size.

Outside the particle, the pyrolysis products are partly combusted with oxygen. After combustion, the remaining char may be further gasified, and several gas phase reactions, like water gas shift (WGS), reforming, polymerisation and cracking reactions, change the gas composition continuously inside the gasifier. In general, the gas phase reactions are influenced by the gas composition, gasification temperature, equivalence ratio, type of bed material and the gas residence time inside the gasifier. Also, remaining char or ash can influence/catalyse the gas phase reactions. The tar concentration and composition in the product gas at the outlet of a fluidised-bed gasifier is the result of the drying/pyrolysis and the consecutive combustion and gas phase reactions. Therefore, all parameters that influence one of these processes logically do influence the final tar concentration and composition at the outlet of the gasifier.
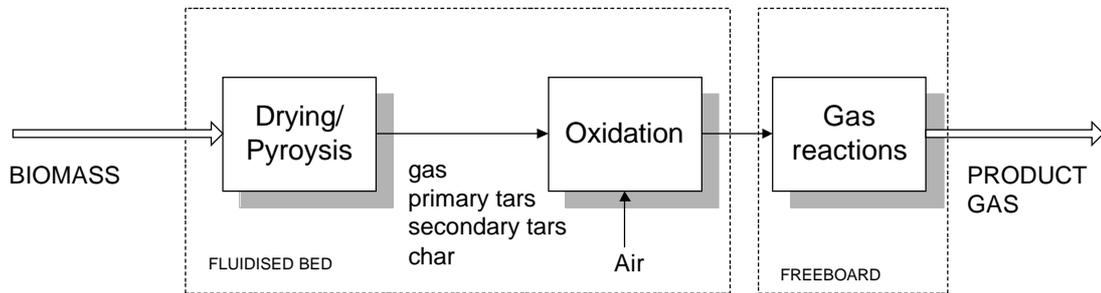
Figure 2.1 *Schematic representation of the four processes of drying, pyrolysis, oxidation and gas (phase) reactions in a bubbling-fluidised-bed biomass gasification process.*

The location of the steps is given for a bubbling fluidised-bed gasifier with a dense bed of sand and an empty freeboard. Air is used as the gasification as well as fluidisation medium. Actually, the gas (phase) reactions occur in the sand bed as well, but the gas residence time in the sand bed is only limited compared to in the freeboard.

Beside the process parameters and biomass composition, also the type of gasifier may influence the tar content and composition in the product gas. In a BFB gasifier, the biomass particles stay in the bed and thus the drying and pyrolysis process as well as the oxidation mainly take place in the bed at the bottom of the gasifier. Gas escaping the bed remains several seconds in the freeboard before exiting the gasifier, allowing gas phase reactions to change the tar concentration and composition. In a CFB gasifier the bed is circulating. Generally, the gasifier has been designed in such a way that, theoretically, the large biomass particles remain in the bottom section of the gasifier, in order to avoid the presence of pyrolysis products in the product gas. In practice, however, part of the biomass particles may be carried over the top. Therefore, the pyrolysis process might practically proceed over the total height of the gasifier. Thus, the tar composition in the product gas of a CFB gasifier might be different from the composition in a BFB gasifier, even when the gas residence time and gasification temperature are similar.

The wide range of fuel parameters, gasifier design parameters and operating conditions that influences the pyrolysis and/or gas phase reactions [7-11], makes the prediction of a tar concentration based on a general biomass composition, air flow rate and type of gasifier very challenging, but a too ambitious goal for the current work. As a first firm start, the work described in this report has been aimed at a detailed investigation of the impact of various fuel properties and gasifier operating conditions on tar formation.

2.3   Thermodynamic gas composition

Thermodynamics determine the driving force for a reaction to occur. When a gas is in thermodynamic equilibrium, the global gas composition will not change when a catalyst is applied or the gas residence time is increased. A fluidised-bed biomass gasifier normally operates at a temperature of typically 750-950°C. At this temperature, reactions are fast enough for a high conversion of the biomass into gas. Most inorganic compounds in the biomass remain solid and leave the gasifier with the ash in the product gas. Although reactions are fast enough for the conversion of the biomass into combustible gases, this does not ensure that the product gas is at thermodynamic equilibrium. Kinetics might be rate determining.

Figure 2.2 shows the product gas composition at thermodynamic equilibrium for an atmospheric, air-blown fluidised-bed gasifier fuelled with beech and operated at a

temperature of 700 to 950°C and an equivalence ratio (ER) of 0.25. The thermodynamic calculations were performed using the process simulation programme Aspen Plus.
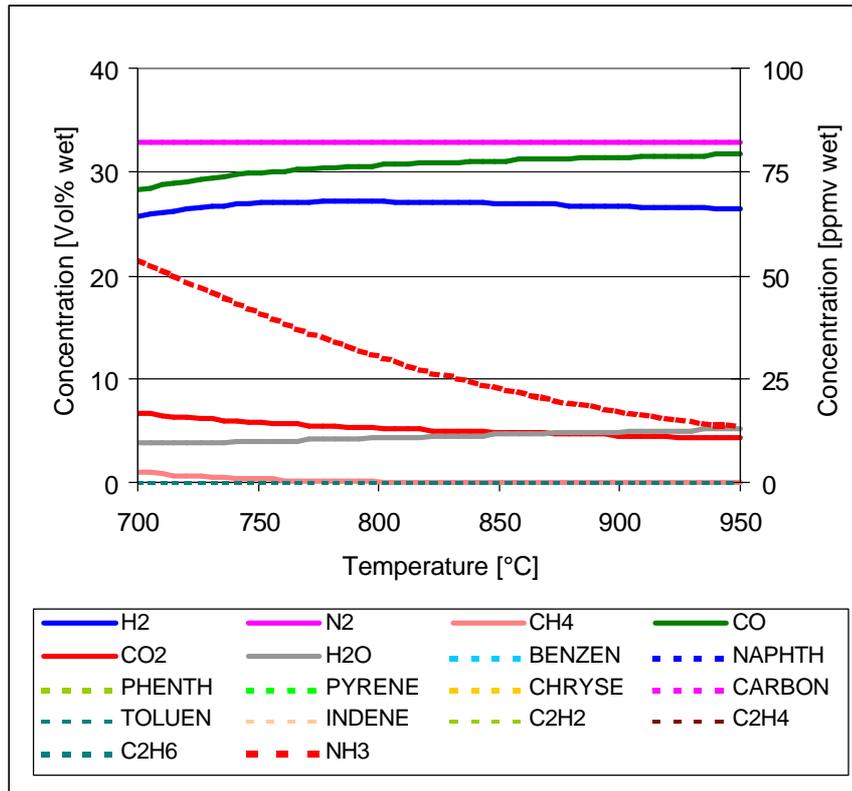
Figure 2.2   *Product gas composition at thermodynamic equilibrium vs. gasification temperature for a fluidised-bed gasifier fuelled with beech at an ER of 0.25.*

The solid lines represent concentrations in vol.%, while the dotted lines represent concentrations in ppmv . The concentrations are given on wet basis.

It appears from Figure 2.2, that the concentration of the main gas compounds CO, CO_2, H_2, and N_2 hardly changes with increasing temperature. Above a temperature of 800°C, light hydrocarbons like CH_4, C_2H_2, and, C_2H_4 are not present in the product gas anymore. The light tar compounds naphthalene, toluene and indene, as well as the heavy tar compounds phenanthrene, pyrene and chrysene are neither present in this temperature window. The NH_3 concentration is decreasing with increasing temperature.

In practice, the concentration of the light as well as heavy tar compounds sum up to a total concentration of typically 1500 ppmv. The naphthalene concentration can be as high as 2 g/m_n^3 and the toluene concentration can be 3 g/m_n^3. Also the CH_4 concentration is with 3-5 vol.% normally higher than the concentration of methane in the product gas at thermodynamic equilibrium. The N_2 concentration is typically 45 vol.% (in comparison with approx. 33 vol.% in Figure 2.2), which can be explained from the presence of unconverted hydrocarbons.

Apparently, the reactions in a fluidised-bed biomass gasifier are too slow to reach thermodynamic equilibrium. This means that there is a driving force for tar reduction by changing process conditions or using additives.

3. CHEMISTRY OF BIOMASS CONVERSION

The thermal conversion of biomass in a gasifier is accompanied by complex chemistry. In general, the conversion comprises four different processes: drying, pyrolysis, combustion and gasification. In a fluidised-bed gasifier, these four processes are not clearly separated in distinct zones like in a fixed-bed gasifier; the products of all four processes will mix and interact. With respect to tar formation, gas phase reactions continuously change the tar contant and composition.

Different transformation stages can be distinguished, when a biomass particle is heated from ambient temperature to the gasifier temperature (see Figure 3.1). At low temperature, structural de-polymerisation of the building blocks cellulose, hemicellulose and lignin of the biomass and further cracking and oligomerisation reactions of the pyrolysis gases yield solid char, permanent gases, and tar. At high temperature, the char is converted into CO and H_2 and the inorganic ash is left as solid. Although each gasifier aims at complete carbon conversion, the ash contains normally a certain amount of carbon, resulting in black ash instead of yellow/grey ash.

| Biomass: beech | Char: from willow | C-containing ash | Ash |
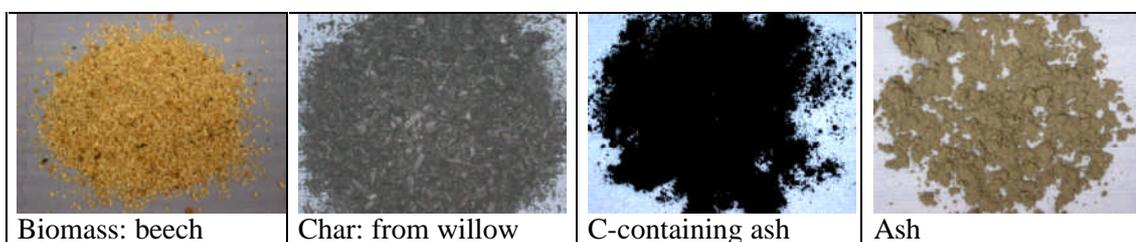
Figure 3.1 *Transformation of solid biomass (left) to grey ash (right) in a fluidised-bed gasifier.*

As described in Chapter 2, the escaping gases from a biomass particle in the fluidised-bed contain primary and secondary tars, which are partly combusted with gasification air outside the particle. After combustion, several gas phase reactions, like water gas shift (WGS), reforming, polymerisation and cracking reactions, lead to a decrease in the concentration of primary and secondary tar compounds with increasing residence time. With the decomposition of these tars, other (secondary and tertiary) tar compounds are formed as well as lighter compounds, like CH_4, CO, H_2, CH_4 and unsaturated C2-C4 hydrocarbons. Although the total tar concentration in the product gas decreases with increasing gasifier temperature and residence time, the tar composition changes from mainly light tar compounds to a mixture of heavy and light tars. The heavy tar compounds are mainly polyaromatic hydrocarbon (PAH) compounds that can be produced by dimerisation reactions of two PAH compounds or by cyclisation or polymerisation reactions of unsaturated C2-C4 hydrocarbons like acetylene. At a temperature of 700-850°C, the PAH growth is most likely due to dimerisation of two PAH compounds in a radical-radical or radical-molecule reaction. Above a temperature of 850-900°C, the PAH growth can be a result of both dimerisation of two PAH compounds or the polymerisation of unsaturated C2-C4 hydrocarbons like acetylene and ethylene. These compounds are produced in the decomposition of aromatic as well as linear hydrocarbons.

The influence of gasification temperature on tar conversion is illustrated in Figure 3.2. In this figure, derived from various data reported in literature [12-20], conversion-temperature diagrams for primary tar mixtures and secondary and tertiary tar compounds are given. Updraft tar and pyrolysis oil can be considered representative for the conversion of primary tars. The conversion of updraft tar and pyrolysis oil starts at 500°C and is completed at 700°C. Phenol and cresol are secondary tar compounds that are produced from primary tars. These heterocyclic tars are converted between a temperature of 750°C and 850°C. The tertiary tar compounds naphthalene, phenanthrene, and anthracene are thermally stable and are converted at relatively

high temperature between 850-1100°C. Benzene is a thermally stable compound and is only converted between 1000°C and 1300°C at reasonable residence time.
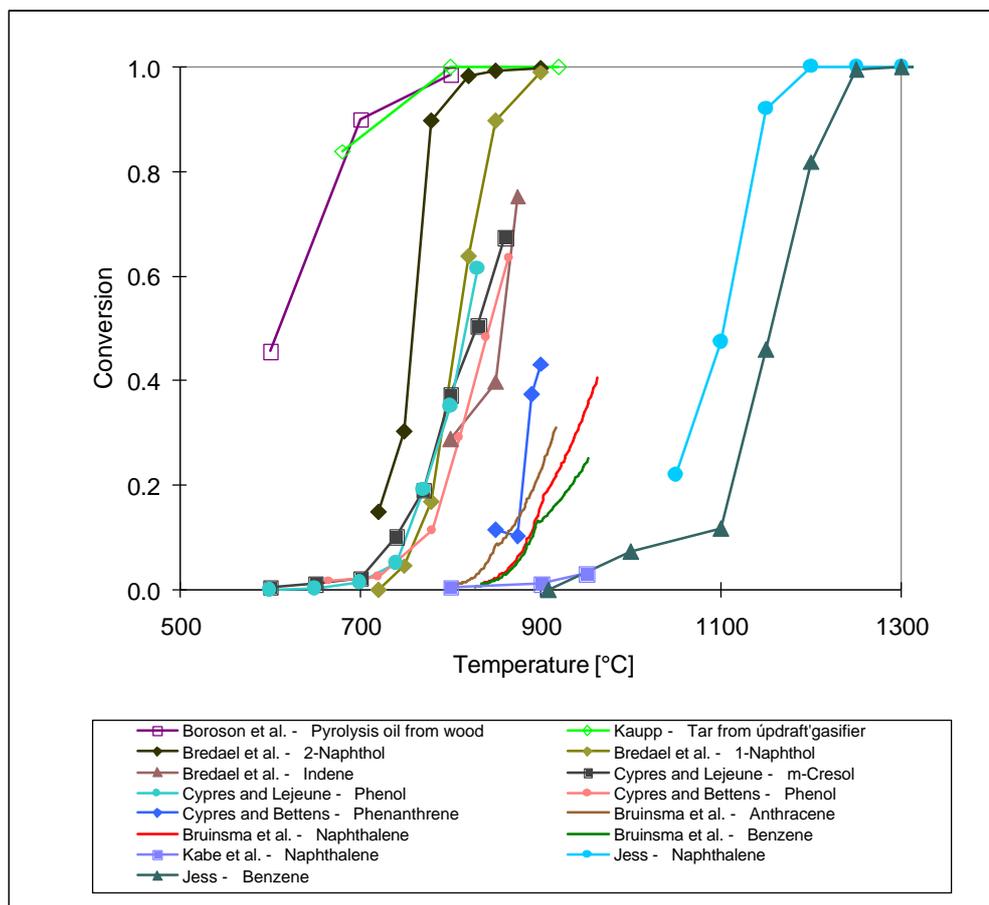
Figure 3.2   *Conversion-temperature diagram of important tar compounds.*

> *The diagram has been obtained from literature data [12-20] by translating these data to a fixed residence time of 2 s.*

The growth in PAH compounds results in heavy compounds that condense out at relatively high temperature and thus increase the risk of fouling in the gas cooler or gas cleaning equipment. Fouling can result in increased maintenance costs and forced outages. The oxygenated tar compounds like phenol have, due to their high polarity, a high water solubility, and cause hazardous wastewater, resulting in high waste disposal costs. Therefore, the gasification temperature and gas residence time in the gasifier must be selected carefully to control the formation of heavy PAH compounds and of tar compounds with a high water solubility.

4. EXPERIMENTAL

The experimental programme at ECN has been focussed on determining the impact of various fuel properties and gasifier operating conditions on tar formation and the resulting consequences for the performance of downstream processes. Emphasis was put on the gasification of woody biomass (see Section 4.1). Most of the experimental work was conducted in a 1 kg/h lab-scale bubbling-fluidised-bed gasifier (see Section 4.2), but the relation between tar formation in a bubbling-fluidised-bed and a circulating-fluidised-bed gasifier was addressed as well.

Based on the results of the literature survey, described in Chapters 2 and 3, the fuel/biomass properties and gasifier operating conditions considered are the following:

Biomass properties
- *Ash content*: Ash in biomass contains a considerable amount of alkali metals. In literature, these metals are reported to be catalytically active in the decomposition of the structural elements of biomass, and thus influence tar formation. Besides alkali metals, biomass ash contains a wide spectrum of other elements that can be active in tar conversion.
- *Moisture content*: Water or steam can be reactive with carbon at high temperature and is applied as a gasification agent in several gasifiers, like the Güssing and Battelle gasifier.
- *Lignocellulose composition*: Also the lignocellulose composition of woody biomass can influence the tar concentration and composition in the producer gas at the outlet of the gasifier. The molecular structure of the biomass compound cellulose is comparable to hemicellulose, but the molecular structure of lignin is completely different. Since de-polymerisation is the first step in tar formation, the lignin content in the biomass seems an important parameter for tar formation.

Gasifier operating conditions
- *Gasification temperature*: The gasification temperature influences the conversion rate of tar, and influences the selectivity towards the formation of tar compounds.
- *Gas residence time*: The gas residence time determines the time for a reaction to occur and proceed. Since tar formation is a multi-step process comprising several consecutive reactions, the gas residence time will certainly influence tar content and composition.

The impact of the type of bed material or the use of bed additives has not been addressed in the present work. However, this item has been covered in the overall SDE-project by TUE [1, 21-23]. All experiments were conducted with feeding the air as primary air through the bottom plate of the bubbling fluidised bed only. Although it was realised that air staging, feeding part of the air as secondary air in the freeboard may have a large impact on tar formation as well, this was beyond the scope of the present study.

4.1   Fuel preparation and composition

Three types of fuel were selected for the experiments: willow, beech, and cellulose/sand granulates. The willow was crushed and sieved to bring the fuel on specification with particle dimensions ranging from 0.7-2.0 mm. Beech with a particle size of 0.75-2.0 mm was bought from J. Rettenmaier & Söhne (Räuchergold HBK 750/2000) and could be used without further preparation. The cellulose was prepared from a super-refined (acid-washed) powder with an alfa-cellulose content of >95%, supplied by Merck. Other properties of this cellulose powder are: maximum fibre length 20-150 μm, ether extract 0.25 %, 4 ppmw iron, 1 ppmw copper. In order to obtain a cellulose fuel with comparable dimensions as beech and willow, the cellulose powder was granulated with silica sand (approx. 14.7 wt%), identical to the bed material. Table 4.1 gives the ultimate and proximate analysis data of the fuels. For willow and beech, more details including the bulk ash composition are given in Appendix 1.

Table 4.1   *Ultimate and proximate fuel analysis.*

	Willow	Beech	Cellulose
Ash (db, 550°C)	2.2	1.0	14.7
Moisture (ar)	8.0	10.2	ND
Volatile matter (db)	82.8	83.0	ND
C (daf)	49.4	48.8	44.4
H (daf)	6	6.0	6.2
O (daf)	39	44.5	49.4
N (daf)	0.87	0.14	ND
S (daf)	0.05	0.017	ND
Cl (daf)	0.015	0.005	ND

Composition in wt%; daf = on dry and ash free basis; db = on dry basis; ar = as received; ND = not determined.

4.2   Experimental set-up

The gasification experiments were conducted in the 1 kg/h bubbling-fluidised-bed biomass gasifier WOB[2] at ECN. The gasifier is electrically heated and has an internal diameter of 74 mm (bottom section), increasing to 108 mm (freeboard) at a height of 500 mm. The total length is 1100 mm from the metal distributor plate to the fuel gas outlet. Bed temperatures are measured at four points in the bed. The applied bed material is 0.27 mm dia. silica sand. Typically, the total amount of bed material is 1 kg.

The gasifier is shown schematically in Figure 4.1. Gas samples can be taken at four places in the freeboard, equally distributed over the height. The fifth sampling point is located after the cyclone. The corresponding gas residence times are indicated in Figure 4.1.
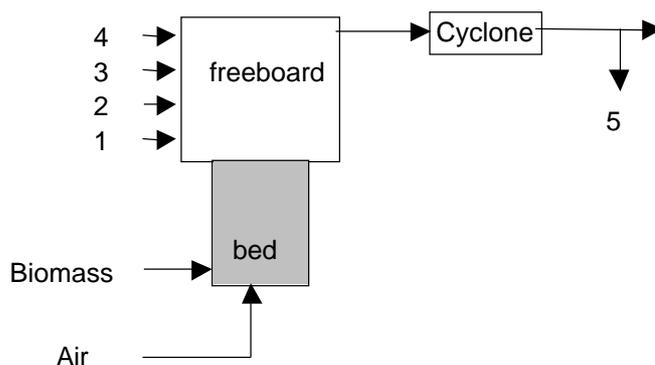
Figure 4.1   *Schematic of the 1 kg/h bubbling-fluidised-bed gasifier (WOB) at ECN.*

> *For standard conditions, i.e. a biomass feeding rate of 1 kg/h, an air flow rate of 16 l_n/min and a gasifier temperature of 850°C, the corresponding gas residence times for the five sampling points are: point 1 - 1.3 s, point 2 - 2.0 s, point 3 - 2.8 s, point 4 -3.6 s, point 5 - 4.0 s.*

4.3   Gas analysis

The gas analysis comprises the measurement of permanent gases as well as tar compounds. The concentration of CO, CO_2, CH_4, H_2, C_2H_4, C_2H_6, benzene and toluene is measured on-line every

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[2] See http://www.ecn.nl/biomass/wob/index.html

minute with gas monitors and/or a micro-GC. The concentration of tar compounds has been determined with the SPA or the Guideline method. These methods will be explained below.

4.3.1   SPA method

The SPA method has been developed by KTH in Sweden [24] to measure tar compounds ranging from benzene up to coronene. The heavy tar fraction cannot be measured.

According to this method, tars are sampled by collection on a column with a small amount of amino-phase sorbent. For each sample, 100 ml of gas is withdrawn from a sampling line using a syringe through a septum. The sampling line is kept at 350°C to prevent/minimise tar condensation. Subsequently, the column is extracted using dichloromethane (DCM) and the solution is then analysed by a gas chromatograph (GC-FID). A non-polar capillary column was applied, focussing on the analysis of, mostly non-polar, fluidised-bed tars. The method is considered to be fast, simple and reliable for the measurement of class 2-5 tars, i.e. from xylenes up to tar compounds with a molecular weight of 300 kg/kmol (up to coronene).

4.3.2   Guideline method

The Guideline method resulted from a broad international effort co-ordinated by ECN to arrive at a widely-accepted, standard tar measurement method [25]. It allows for the sampling and analysis of tars (and particles) in biomass gasification gases. The tar and particle sampling system consists of a heated probe, a heated particle filter, a condenser and a series of impinger bottles containing isopropanol to dissolve the tars. The solvent containing bottles are placed in a warm (bottles 1-4) and a cold bath (bottles 5 and 6), so that the sampled gas is cooled in two steps, first to 20°C and finally to -20°C. The sampling train is shown schematically in Figure 4.2. The post-sampling involves Soxhlet extraction of the tars on the particle filter and the collection of all tars in one bulk solution. Finally, from analysing this bulk solution, two types of tar concentrations can be obtained, *viz.* the concentration of gravimetric tar and concentrations of individual organic compounds. **Gravimetric tar** is defined as the evaporation residue at given and standard conditions (temperature, pressure, duration). Concentrations of **individual organic compounds** are determined by GC-analysis of the bulk solution. The full version of the Guideline as well as a description of the further development into a CEN standard can be found on the dedicated web-site www.tarweb.net.

The gravimetric tars include GC-detectable as well as GC-undetectable (class 1) tar compounds. Therefore the gravimetric tars partly overlap with the GC-detectable tar classes 2-5. The GC-undetectable or class 1 tar concentration can be obtained by the determination of the GC-detectable fraction in the gravimetric tar sample (after redissolution) and subtracting this from the gravimetric tar concentration. Furthermore, HPLC analysis of the gravimetric tars allows the analysis of individual heavy hydrocarbons with a molecular mass higher than coronene.

The range of tar compounds covered by the different tar analysis methods is shown schematically in Figure 4.3.
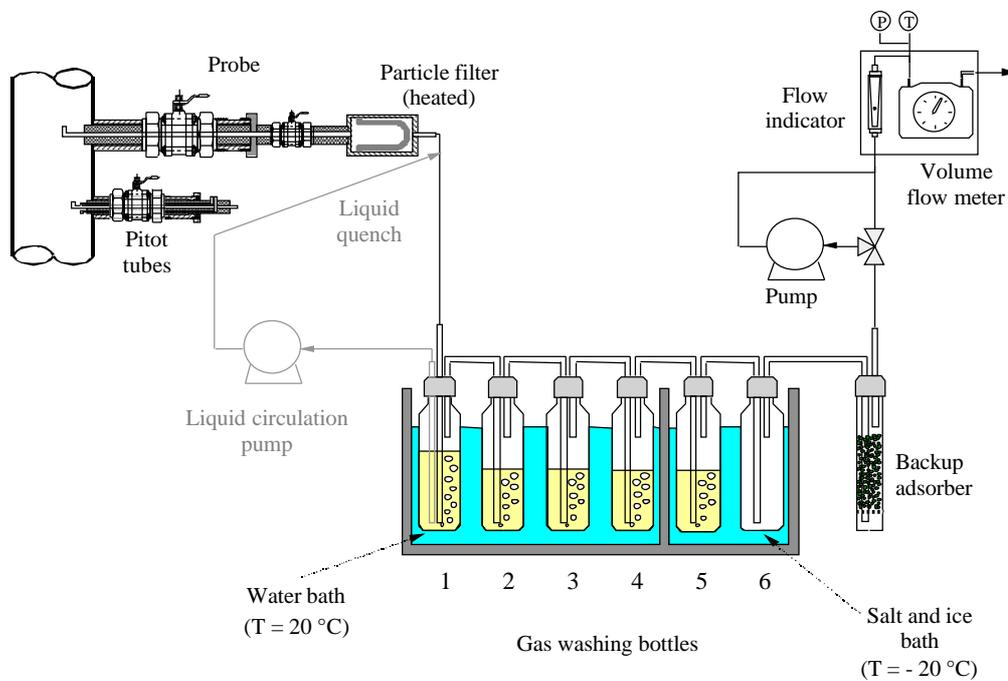
Figure 4.2   *The Guideline sampling set-up*

Atmospheric and isokinetic sampling train for tar and particles with removable probe and pitot tubes for flow measurement. The liquid quench is optional.
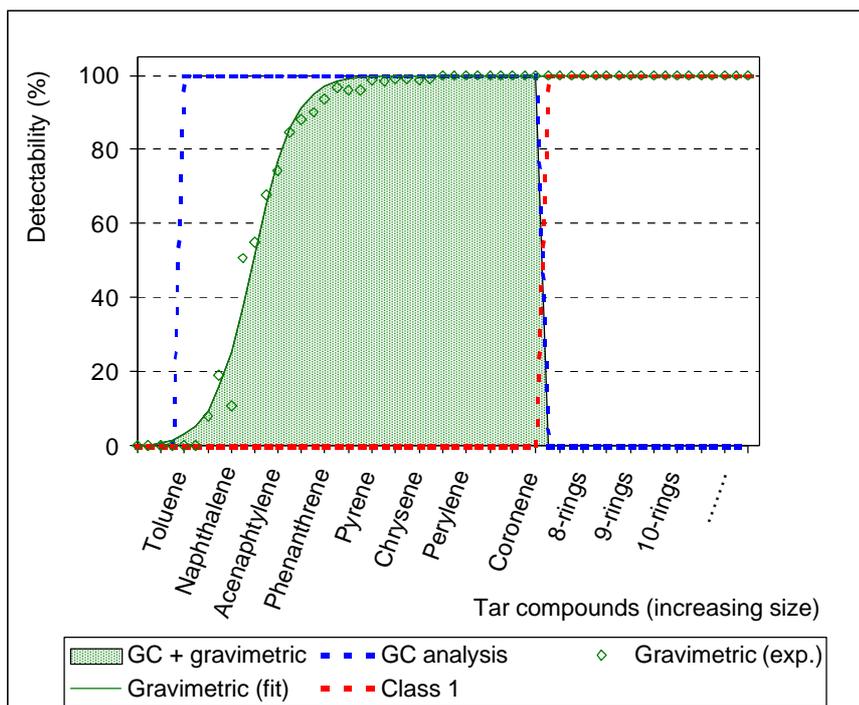

Figure 4.3   *Range of tar compounds covered by the applied tar analysis methods.*

4.4 Presentation of the results

4.4.1 Tar classification

As explained in Chapter 1, a basic notion was that the impact of tar formation on the performance of downstream processes mostly is not related to the lump-sum tar content (expressed, e.g., in g/m_n^3 "tar"), but that problems are merely caused by specific tar fractions or tar compounds. Therefore, much emphasis has been given to the determination of the tar *composition* by measuring individual tar compounds. However, it is also indicated in Chapter 1, that a concise presentation of experimental results and obtaining mechanistic insight would highly benefit from a grouping or classification of these tar compounds. Based on the behaviour of the tar compounds in downstream processes, the classification system presented in Table 1.1 was derived. For each class, Table 4.2 presents the tar compounds considered and the sampling method applied.

Table 4.2   *Example of tar compounds in each tar class in the classification system and applied sampling methods.*

	Name	Sampling method	Tar compounds
Class 1	GC-undetectable	Guideline	Determined by subtracting the GC- detectable tar fraction from the total gravimetric tar concentration.
Class 2	heterocyclic aromatics	Guideline SPA	pyridine, phenol, cresol, quinoline
Class 3	aromatics (1 ring)	Guideline SPA	xylene, styrene, toluene
Class 4	light PAH compounds (2-3 ring)	Guideline SPA	naphtalene, methyl-naphtalene, biphenyl, ethenylnaphtalene, acenaphtylene, acenaphtene, fluorene, phenanthrene, anthracene
Class 5	heavy PAH compounds (4-7 ring)	Guideline SPA	fluoranthene, pyrene, benzo-anthracene, chrysene, benzo-fluoranthene, benzo-pyrene, perylene, indeno-pyrene, dibenzo-anthracene, benzo-perylene

4.4.2 Tar dewpoint

An important thermodynamic property for condensation is the tar dewpoint. The tar dewpoint is the temperature at which the real total partial pressure of tar equals the saturation pressure of tar. ECN developed a dewpoint model for the calculation of tar dewpoints from a given tar composition [26]. The model includes vapour/liquid equilibrium data for the tar compounds in the product gas from a downdraft or fluidised-bed gasifier. The calculation is based on ideal gas behaviour. Raoult's law is applied for the calculation of a mixture of hydrocarbons, using the vapour pressure data of individual compounds. The tar dewpoint is calculated from the tar composition measured with the SPA or Guideline method, i.e.. tars with a molecular size between toluene and coronene. Heavier tars are not considered, but they may be expected to have a relatively high dewpoint at low concentration. Therefore, generally, the calculated tar dewpoint should be considered as an underestimate, the actual dewpoint probably being (somewhat) higher.

In Figure 4.4, the dewpoint for the tar classes 2-5 is given at several concentrations. Even at a low class 5 tar concentration of circa 0.1 mg/m_n^3, the corresponding dewpoint (120°C) exceeds the dewpoint valid for high concentrations of class 2, 3, and class 4 tars (e.g. 1000 mg/m_n^3) at atmospheric pressure. The class 3 tar compounds do not condense at concentrations as high as 10,000 mg/m_n^3.
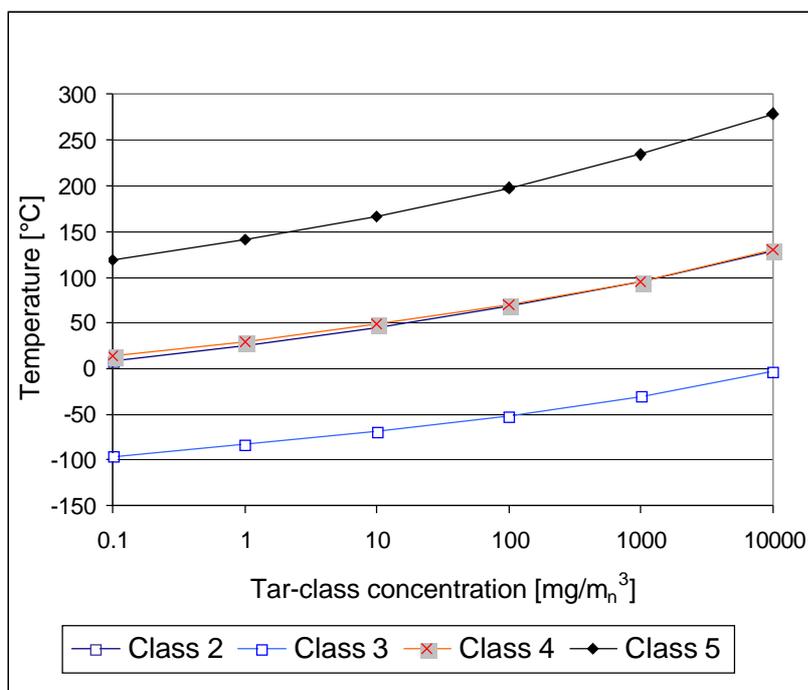
Figure 4.4   *Tar dewpoint at atmospheric pressure vs. tar concentration for different tar classes.*

As an example, Figure 4.5 gives the tar dewpoint calculated from a real tar composition, measured with the SPA method in the product gas from the BFB gasifier WOB at ECN. The tar dewpoint decreases from ca 190°C to 150°C when tars with more than 4 aromatic rings are removed from the tar mixture, which corresponds with the removal of 2 wt% of the total tar amount. Further removal of tars with four aromatic rings lead to a dewpoint of 100°C. At this point 93 wt% of the total amount of tar is still left. From the tar mass fraction curve and the dewpoint curve in Figure 4.5, it can be concluded that the dewpoint is dominated by the molecular size and not by the tar concentration.
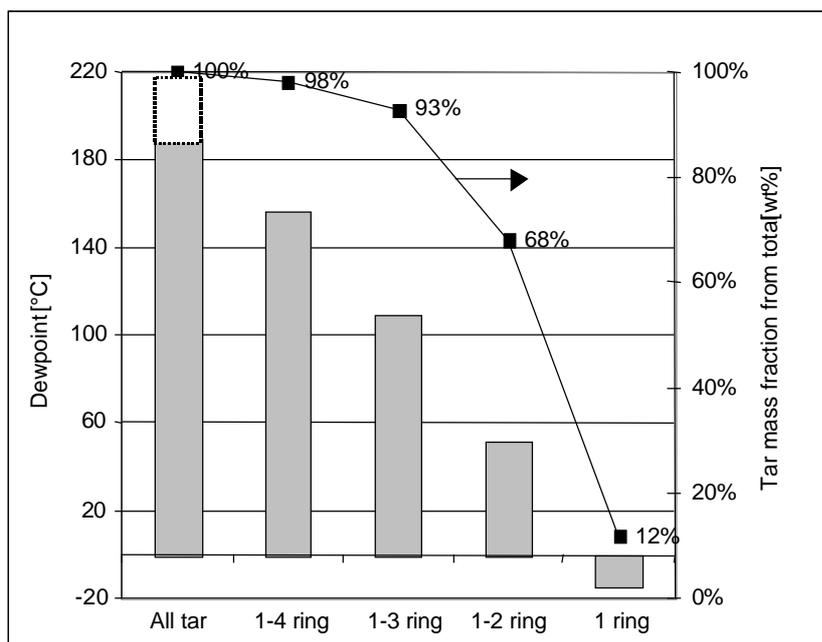
Figure 4.5   *Tar dewpoint for a real tar composition as measured with the SPA method in the BFB gasifier WOB.*

5. RESULTS AND DISCUSSION

In this chapter, the results of the systematic variation of individual fuel properties and gasifier operating conditions are presented and discussed.

5.1 Biomass ash content / char addition

The ash content in biomass is strongly dependent on the type of biomass. Untreated (woody) biomass has normally an ash content of 1-3 wt% and grasses of approx. 7 wt%. The ash content of manure, like chicken or pig manure, is with 30 wt% relatively high. The ash contains several components that may exhibit catalytic activity for tar reduction, and thus can influence the tar composition at the outlet of the gasifier.

In a first simple approach to simulate differences in biomass ash content, experiments have been conducted with different mixtures of biomass and high-ash char. The char was obtained from the secondary cyclone of the 100 kg/h CFB gasifier BIVKIN at ECN during the gasification of Labee demolition wood pellets (ID-code 1448 in the ECN biomass database Phyllis, www.phyllis.nl). The ash content of the char was approx. 40 wt%. In order to change the ash to biomass ratio, the char was fed from a separate bunker and mixed up with the biomass in the feeding screw. Tars were sampled using the SPA method. The specific experimental conditions are given in Table 5.1, and the experimental results in Table 5.2 and Figures 5.1 and 5.2.

Table 5.1   *Impact of ash content: experimental conditions.*

		1	2	3	4
Biomass feedstock		willow	willow	willow	willow
Moisture content	wt%	9.7	9.7	9.7	9.7
Char/biomass ratio	wt%	0	3	5	17
ER	-	0.24	0.23	0.23	0.20
Bed temperature	°C	831	832	829	827
Freeboard temperature	°C	805	806	807	808
Sample period		10:00-10:30	11:46-11:45	13:08-14:37	14:55-15:39

Table 5.2   *Impact of ash content: experimental results.*

Ash/biomass ratio	wt%	Above fluidised bed (Gas residence time = 1.3 s)				After cyclone (Gas residence time = 4 s)			
		0	3	5	17	0	3	5	17
Product gas flow rate (wet)	m_n^3/h	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
CO	vol.%	ND	17.5	18.4	20.2	17.3	17.3	18.1	19.0
H_2	vol.%	ND	6.8	8.5	10.4	7.0	7.0	8.0	10.9
CO_2	vol.%	ND	15.2	14.9	14.7	15.8	15.5	14.9	14.9
CH_4	vol.%	ND	4.6	4.7	4.9	4.9	4.7	4.7	4.8
C_2H_4	vol.%	ND	1.7	1.7	1.8	1.8	1.8	1.9	1.7
H_2O (calc.)	vol.%	ND	14	13	11	15	16	14	0.2
N_2	vol.%	ND	53	50	46	52	52	49	48
C_6H_6	mg/m_n^3	ND	12703	12292	12179	16947	??	17977	16335
Tar dewpoint	°C	ND	176	174	171	199	198	198	192
SPA total	mg/m_n^3	ND	20352	19840	20116	19296	19337	19985	18673
Unknown	mg/m_n^3	ND	4724	4572	4584	2710	2789	2714	2427
Class 1	mg/m_n^3	ND	ND	ND	ND	ND	ND	ND	ND
Class 2	mg/m_n^3	ND	2283	2121	2218	953	792	814	802
Class 3	mg/m_n^3	ND	8505	8407	8616	8745	8637	9492	9103
Class 4	mg/m_n^3	ND	4537	4465	4438	6008	6319	6191	5723
Class 5	mg/m_n^3	ND	304	275	260	881	800	774	618

ND = Not determined. Concentrations (except for H_2O) are given on dry basis. The tar data represent averages of two or three measurements.
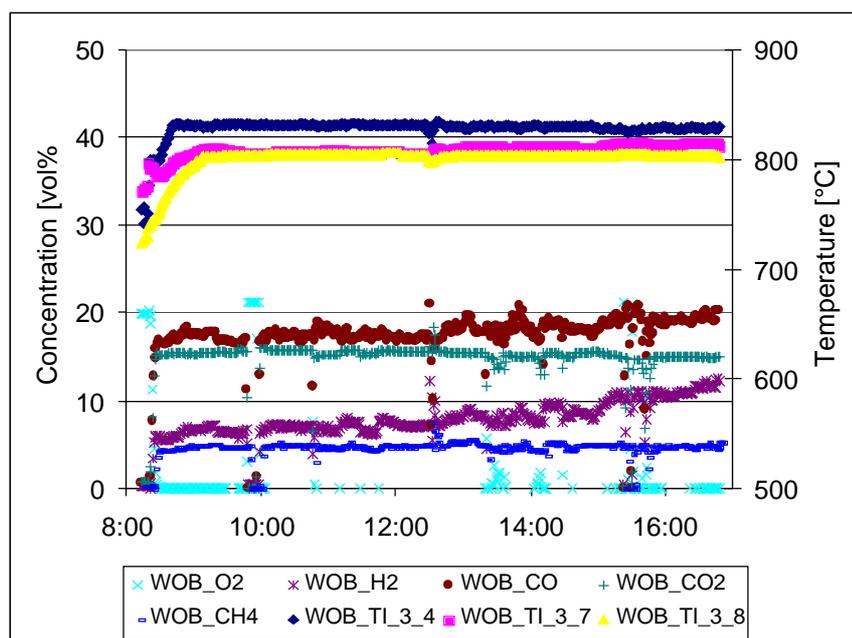
Figure 5.1   *Impact of ash content: gas composition and gasifier operating temperatures.*

WOB TI_3_4 = bed temperature; WOB_TI_3_7 = freeboard temperature bottom; WOB_TI_3_8 = freeboard temperature top.
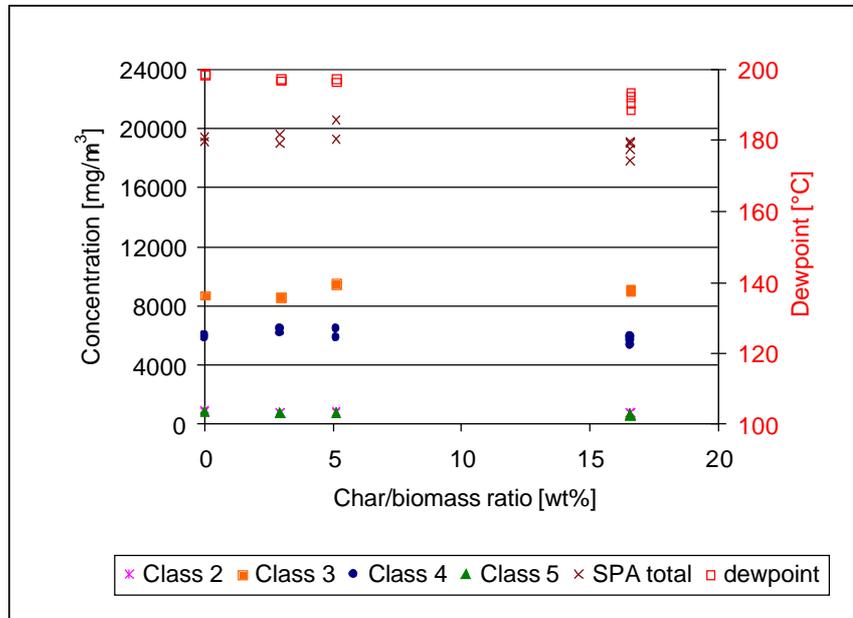
Figure 5.2   *Impact of ash content: tar composition and dewpoint after the cyclone.*

It appears from Table 5.2 and Figure 5.2, that the total tar concentration after the cyclone is hardly influenced when additional char is fed to the gasifier up to a char to biomass ratio of 17 wt%. Also the general tar composition remains the same. The tar dewpoint slightly decreases with the addition of char to the gasifier due to a minor decrease in the class 5 tar concentration. On the other hand, the impact of the gas residence time in the freeboard appears to be significant. Although the total tar concentration remains nearly the same, the tar composition changes considerably. The class 2 tars are for more than 50 % converted. The class 4 and class 5 tars are produced in the freeboard leading to an increase in tar dewpoint. The influence of the gas residence time will be discussed further in Section 5.4.

In literature, high tar conversion rates are reported with char at a temperature of 800-900°C. Most experiments were performed in dense beds of char and at a gas residence time of a few seconds. Despite the high conversion rates obtained by other authors, only minor tar decomposition was obtained in the fluidised-bed experiments. Apparently, the char hold-up in the gasifier or the char activity was too low to obtain substantial tar conversion.

5.2   Biomass moisture content

The moisture content of the biomass can vary significantly and is dependent on the pre-treatment of the biomass. The moisture content of fresh biomass from the forest is relatively high with a typical value of 55 wt%. When a trunk is stored in the forest, the moisture content can decrease to approx. 25 wt%. Additional drying of (chipped) biomass in a biomass dryer can lower the moisture content further. In this section, the influence of the biomass moisture content on tar formation is discussed. To simulate different moisture contents, dry biomass has been mixed off-line with water to obtain a biomass moisture content of 10-45 wt%. The extra heat necessary in the gasifier to evaporate the moisture was supplied by the trace heating of the gasifier. This made it possible to perform the experiments with different biomass moisture contents at a constant gasification temperature and a constant equivalence ratio. The tar composition was determined using the SPA method. The specific experimental conditions are given in Table 5.3, and the experimental results in Table 5.4 and Figures 5.3 and 5.4.

Table 5.3   *Impact of biomass moisture content: experimental conditions.*

		1	2	3
Biomass feedstock		willow	willow	willow
Moisture content	wt%	9.7	26.4	43.2
ER	-	0.24	0.26	0.25
Bed temperature	°C	808	826	810
Freeboard temperature	°C	806	807	804
Sample period		11:40-12:38	10:19-11:02	14:15-15:27

Table 5.4   *Impact of biomass moisture content: experimental results.*

		Above fluidised bed (Gas residence time approx. 1.3 s)			After cyclone (Gas residence time approx. 4 s)		
Moisture content	wt%	9.7	26.4	43.2	9.7	26.4	43.2
Product gas flow rate (wet)	m_n^3/h	1.9	1.7	1.4	1.9	1.7	1.6
CO	vol.%	18.7	17.5	13.6	18.2	16.2	10.4
H_2	vol.%	8.4	7.6	10.3	8.9	9.3	14.9
CO_2	vol.%	14.9	14.6	16.9	15.5	15.7	20.7
CH_4	vol.%	5.2	4.8	4.4	5.3	4.8	4.6
C_2H_4	vol.%	1.9	1.9	1.7	2.1	1.9	1.6
H_2O (calc.)	vol.%	14	24	33	14	23	31
N_2	vol.%	47	49	48	45	47	46
C_6H_6	mg/m_n^3	10927	10497	9561	15284	15177	12894
Tar dewpoint	°C	161	173	166	185	185	176
SPA total	mg/m_n^3	14264	15124	9222	14176	11400	8485
Unknown	mg/m_n^3	2297	2734	846	1090	758	360
Class 1	mg/m_n^3	ND	ND	ND	ND	ND	ND
Class 2	mg/m_n^3	1522	2131	1035	593	490	187
Class 3	mg/m_n^3	6609	5913	4641	6186	5234	4017
Class 4	mg/m_n^3	3636	4070	2514	5721	4383	3581
Class 5	mg/m_n^3	199	277	186	586	535	340

ND = Not determined. Concentrations (except for H_2O) are given on dry basis. The tar data represent averages of two or three measurements.
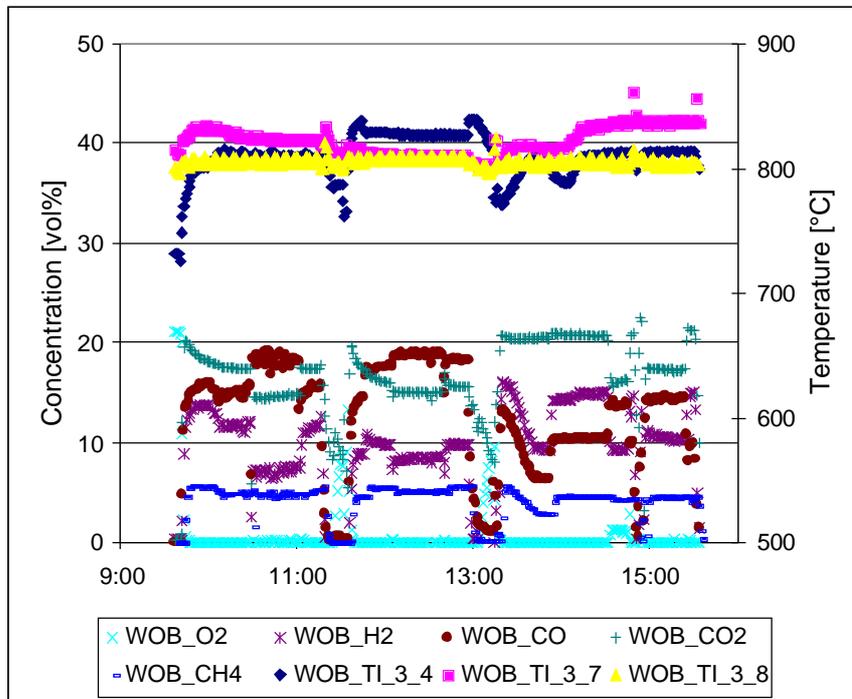
Figure 5.3   *Impact of biomass moisture content: gas composition and gasifier operating temperatures.*

*WOB TI_3_4 = bed temperature; WOB_TI_3_7 = freeboard temperature bottom; WOB_TI_3_8 = freeboard temperature top.*
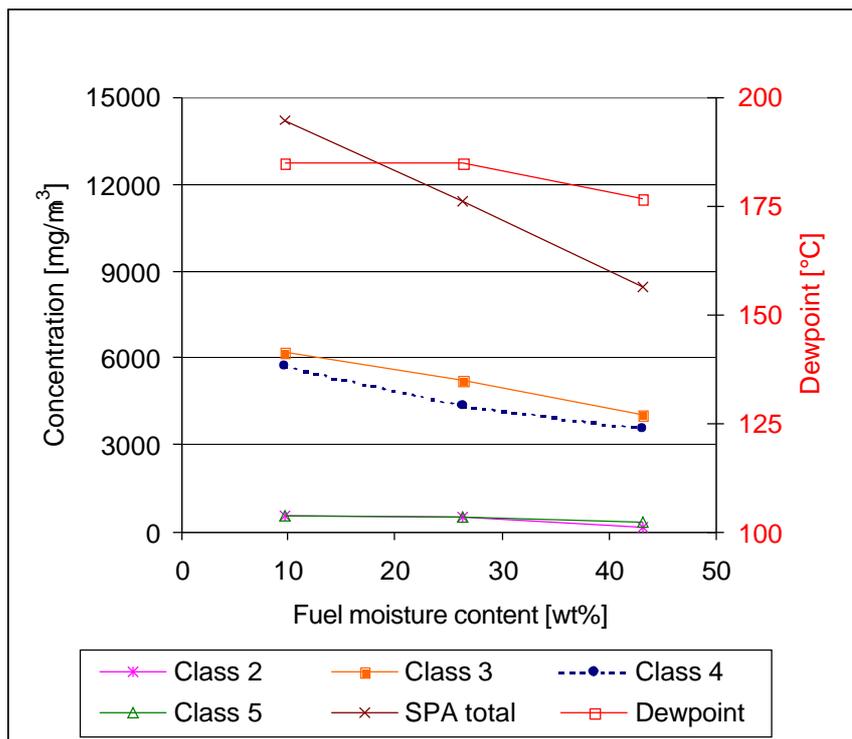

Figure 5.4   *Impact of biomass moisture content: tar composition and dewpoint after the cyclone.*

Significant variations in product gas composition can be observed from Figure 5.3 and Table 5.4. The H_2O, CO_2, and H_2 concentration increases and the CO concentration decreases with increasing moisture content (and increasing gas residence time). This is likely to be the result of the water gas shift reaction in which H_2 and CO_2 is produced by the conversion of CO with H_2O.

In the product gas after the cyclone, the total tar concentration decreases from 14 to 8 g/m_n^3 when the fuel moisture content increases from 10 to 45 wt%. Also the individual tar classes decrease in concentration with increasing moisture content. Although the class 2 tar concentration decreases, complete elimination of class 2 tars was not obtained at the given gasification temperature of 800-825°C. The formation of heavy class 5 tar is suppressed and the tar dewpoint slightly drops when the fuel moisture content exceeds 30 wt%. Over the freeboard, the class 5 tar concentration increases leading to an increasing tar dewpoint.

Fuel with high moisture content needs extra energy for the evaporation of water and heating of the water vapour. In a large-scale gasifier, the extra heat can/will be generated by increasing the ER in the gasifier. This will lead to even lower tar concentrations. However, this may result also in a decrease in cold gas efficiency, and a drop in energy efficiency. Also the gas volume flow will increase due to both the increasing fuel moisture content and the increasing ER. This results in an increase in the size of unit operations downstream the gasifier. For many applications, the loss in energy efficiency and the increasing size of unit operations will probably outweigh the advantage of lower class 2 and class 5 tar concentrations. However, this might not be the case for indirect biomass co-combustion.

5.3 Biomass lignocellulose composition

De-polymerisation of the three lignocellulose components of biomass is an important reaction step in the conversion of biomass. Since the monomer structures of lignin and cellulose or hemicellulose differ significantly, the final tar composition is expected to depend on the lignocellulose composition of the biomass.

To investigate the influence of the lignocellulose composition, beech, willow and cellulose were used as feedstock for the gasifier. Fuel specifications are given in Section 4.1. The gasifier was operated at a temperature of 800°C and 900°C. After the cyclone, the tar composition was measured according to the SPA method. The specific experimental conditions are given in Table 5.5 and the experimental results in Table 5.6.

Table 5.5   *Impact of lignocellulose composition: experimental conditions.*

		1		2	3	4	5	6
Biomass feedstock		beech	beech	beech	willow	willow	cellulose	cellulose
Lignin content	wt.%	24	24	24	18	18	0	0
Moisture content	wt.%	10.2	10.2	10.2	9.7	9.7	0	0
ER	-	0.25	0.26	0.25	0.24	0.27	0.32	0.32
Bed temperature	°C	806	830	902	801	898	827	900
Freeboard temperature	°C	776	800	873	776	875	796	863

Table 5.6   *Impact of lignocellulose composition: experimental results.*

		Beech 24 wt% lignin			Willow 18 wt% lignin		Cellulose 0 wt% lignin	
		806°C ER=0.25	830°C[*1] ER=0.26	902°C ER=0.25	801°C[*1] ER=0.24	898°C ER=0.27	827°C ER=0.32	900°C ER=0.32
CO	vol.%	16.7	16.8	16.8	16.3	16.0	15.4	15.3
H_2	vol.%	8.5	8.4	11.2	8.0	11.4	8.9	11.7
CH_4	vol.%	5.0	5.0	4.6	4.8	4.1	3.9	3,7
CO_2	vol.%	15.7	15.6	15.4	16.3	15.8	15.7	15.7
N_2	vol.%	51[*2]	52[*2]	49[*2]	53.7	52.8	52.0	49.9
H_2O (calculated)	vol%	15.6	15.5	12.9	16.2	11.7	10.8	8.8
Tar dewpoint	°C	178	179	198	172	203	168	180
SPA total tar	g/m_n^3	10.0	7.6	8.1	10.2	9.6	3.2	2.7
Unknown		1702	963	671	1941	1134	465	257
Class 1	mg/m_n^3	ND	ND	ND	ND	ND	ND	ND
Class 2	mg/m_n^3	1089	471	27	1511	41	125	10
Phenol	mg/m_n^3	1015	425	12	1245	2	112	10
Class 3 (excl. toluene)	mg/m_n^3	1359	756	336	2369	562	430	145
Class 4	mg/m_n^3	5495	5024	6310	3967	6231	2011	1991
Class 5	mg/m_n^3	311	352	762	409	1070	213	333

ND = Not determined. Gas samples were taken after the cyclone. Concentrations (except for H_2O) are given on dry basis.
*1: carbon mass balance is for 92-93 % complete instead of 97-99 %.
*2: estimated concentration based on mass balance.

The composition of the permanent gases is comparable for the three fuels, except for the water concentration. For cellulose, the low water concentration is a result of the low moisture content of the feedstock. The total tar concentration for beech and willow is substantially higher (2-4 times) than for cellulose. The tar composition, however, seems to be comparable and only dependent on the gasification temperature. Despite the factor two or three difference in tar concentration, the tar dewpoint is only slightly lower for cellulose than for willow or beech.

The ER in the cellulose experiments is relatively high in comparison with the beech and willow experiments. For an appropriate evaluation and interpretation of the tar results, the influence of the ER on the total tar concentration should be explained first.

Kinosha et al. [27] and Narvaez et al. [11] both investigated the influence of the ER on the total tar concentration in a fluidised-bed gasifier. According to Kinosha et al., the tar concentration decreases with 30 % when the ER increases from 0.22 to 0.32 at a bed temperature of 700°C. An increasing availability of oxygen, which reacts with volatiles in the oxidation zone (Figure 2.1) zone, is mentioned as the main reason for a decreasing tar concentration. Narvaez et al. reported a decrease in tar concentration of approximately a factor 2, when the ER increases from 0.25 to 0.32 at a bed temperature of 800°C.

Based on these literature data, the high ER of 0.32 in the cellulose experiments cannot completely explain the difference in tar concentration between the cellulose, and willow or beech experiments. Based on the results obtained by Narvaez et al. and Kinosha et al. a factor 1.5 or 2 lower tar concentration would be expected due to the difference in ER. The factor 3 difference in tar concentration is therefore probably not only determined by the difference in ER.

For the class 2 concentration, a difference would be expected based on the thermal conversion characteristics of the lignocellulose components. When lignin and cellulose, present in willow and beech, degrade by structural de-polymerisation, than the primary tars will have a molecular structure with similar functional groups as the monomer (as has been shown by Milne and

Evans). The molecular structure of a lignin monomer contains a hydroxide, alkyl and sometimes a methoxy group attached to a phenyl group. This molecular structure is a logical precursor for phenol. The monomer of cellulose is glucose and does not contain a phenyl group. The primary tars from cellulose and hemicellulose are furfural derivates and anhydrosugars like levoglucosan. The furfural and anhydrosugars decompose at a temperature of 800°C and form compounds that hardly contain oxygen resulting in a low class 2 tar concentration. Therefore, the difference in monomer structure between cellulose and lignin largely contributes to the explanation for the difference in class 2 concentration between willow or beech and cellulose. At 900°C, the decomposition rate of phenol (see Figure 3.2) is fast, which explains the low concentration of phenol at 900°C in all cases.

Also differences in class 4 and 5 tar concentration between willow or beech and cellulose might be attributed to differences in lignocellulose composition of the feedstock. The class 4 and 5 tars are mostly PAH compounds. The molecular structure of lignin in beech or willow contains an aromatic functional group. Therefore, products from the thermal conversion of the lignin are logical precursors for the formation of these PAH compounds. On the other hand, cellulose does not contain these aromatic functional groups. However, it has been proven by several authors that PAH compounds may be formed from cellulose through other mechanisms, viz. via intermediates such as reduced sugars (e.g., levoglucosan [28]), unsaturated hydrocarbons [19], and furfural derivates together with acetaldehyde [29]). Nevertheless, the production of class 4 and 5 tars via these formation reactions is less pronounced.

The alkyl substituted, class 3 tar concentration is for willow and beech a factor 3 higher than for cellulose. Since these tar compounds are only slightly contributing to the tar problems of wastewater production and do not cause problems of fouling, an extensive literature survey for the formation of alkyl substituted compounds has not been made. The alkyl-substituted compounds may directly be formed from primary or secondary tars but might also be formed by the attachment of alkyl groups to benzene. At a temperature of 900°C, the alkyl-substituted tars are thermally unstable and decompose, which explains the low class 3 tar concentration at 900°C.

Generally, the heavy PAH compounds in the product gas determine the dewpoint. Although the concentrations of the class 4 and 5 tars are a factor three lower for cellulose, the dewpoint is only 10-20°C lower. That means that fouling due to tar condensation will happen at similar process conditions. However, due to the lower tar concentrations, the amount of condensed tar species will be substantially lower for the cellulose case.

5.4 Gasifier operating conditions (temperature and gas residence time)

Both the temperature as well as the gas residence time in a gasifier strongly influences the tar composition and concentration in the product gas. The tar composition is a result of multiple consecutive reactions. Each reaction has a certain reaction time for completion. The gas residence time determines how many, and to what extent, consecutive reactions can take place at a certain temperature. In this section, tar formation in relation to the gasification temperature and gas residence time is evaluated.

5.4.1 Gas residence time

To determine the relation between tar formation and gas residence time, gas sampling has been performed at different heights in the freeboard of the gasifier. By this sampling at different freeboard heights (as well as sampling after the cyclone), the gas residence time could be varied between 1.2 and 5.4 s. Experiments were done in two days. The specific experimental conditions are given in Table 5.7, and experimental results are presented in Table 5.8 and Figures 5.5 and 5.6.

Table 5.7 *Impact of gas residence time: experimental conditions.*

Gas residence time	s	1.2	2.0	3.7	4.1	4.9	5.4
Biomass feedstock		willow	willow	willow	willow	willow	willow
Moisture content	wt%	9.7	9.7	9.7	9.7	9.7	9.7
ER	-	0.22	0.22	0.22	0.22	0.23	0.23
Bed temperature	°C	827	828	828	828	828	828
Freeboard temperature	°C	808	812	810	809	805	805
Sample day		9 April	9 April	9 April	9 April	6 April	6 April
Sample period		11:00-11:50	15:55-16:15	13:30-14:09	10:20 and 15:40	11:36-12:33	11:15 and 13:30

Table 5.8 *Impact of gas residence time: experimental results.*

Gas residence time	s	1.2	2.0	3.7	4.1	4.9	5.4
CO	vol.%	19.2	19.5	18.9	18.9	18.1	18.1
H_2	vol.%	8.2	8.8	9.1	9.0	7.3	7.8
CO_2	vol.%	14.7	14.5	14.8	15.0	14.6	15.4
CH_4	vol.%	4.9	5.1	5.2	5.3	4.8	4.8
C_2H_4	vol.%	1.9	1.9	2.0	2.0	1.9	1.9
H_2O (calc.)	vol.%	14	13	14	13	13	13
N_2	vol.%	49	49	49	49	51	51
C_6H_6	mg/m_n^3	13754	15049	17317	18619	16829	18719
Tar dewpoint	°C	177	187	195	198	193	198
SPA total	mg/m_n^3	22629	20691	20854	18623	17524	17845
Unknown	mg/m_n^3	4970	4073	3329	2292	2296	1920
Class 1	mg/m_n^3	ND	ND	ND	ND	ND	ND
Class 2	mg/m_n^3	2589	1687	1026	865	872	739
Class 3	mg/m_n^3	9842	9137	9092	8646	7813	8198
Class 4	mg/m_n^3	4926	5344	6710	6018	5882	6120
Class 5	mg/m_n^3	303	449	697	803	661	869

ND = Not determined. Concentrations (except for H_2O) are given on dry basis.
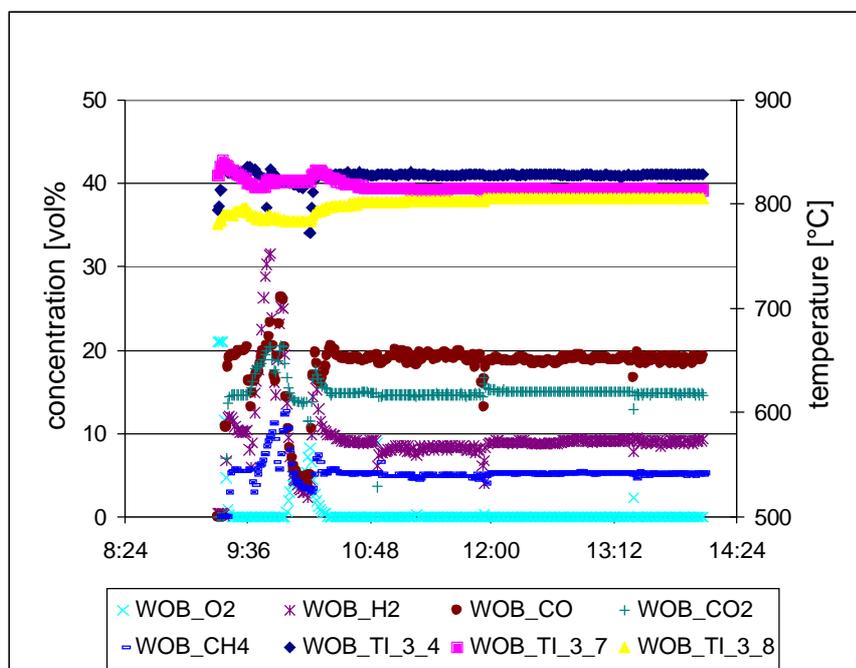
Figure 5.5   *Impact of gas residence time: gas composition and gasifier operating temperatures on April 9th.*

WOB TI_3_4 =bed temperature; WOB_TI_3_7 = freeboard temperature bottom; WOB_TI_3_8 = freeboard temperature top.
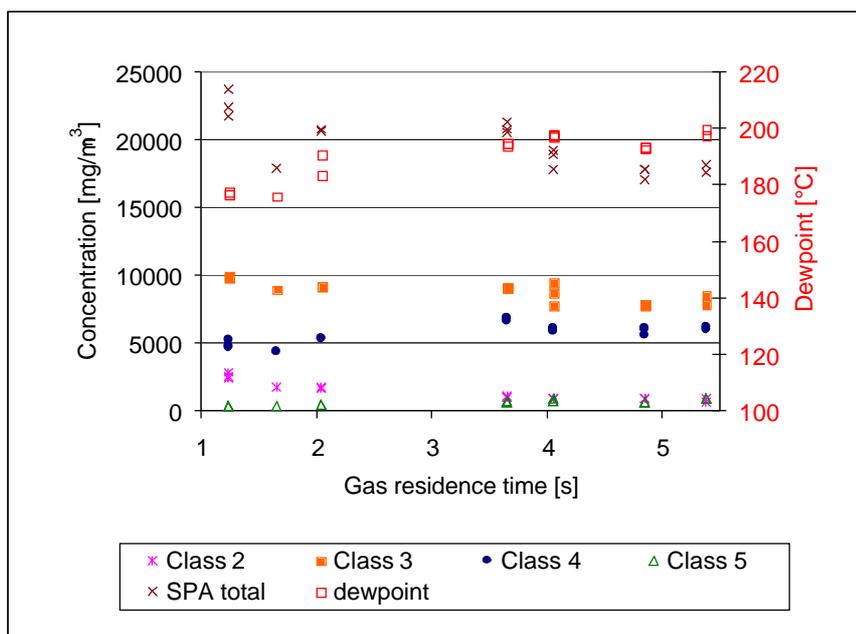
Figure 5.6   *Impact of gas residence time: tar concentration and dewpoint.*

It appears that the gas residence time has a significant impact and that this impact is in general agreement with the trends derived from literature and described in Chapter 3. Due to combination of several gas phase reactions, like water gas shift (WGS), reforming, polymerisation and cracking reactions, the total tar concentration in the product gas decreases with increasing gas residence time. With respect to the individual tar classes, the class 4 and

heavy class 5 tar concentration increase, while the class 2 and 3 tar concentrations decrease with increasing gas residence time. The tar dewpoint increases with increasing gas residence time, which is due mainly to the increase in class 5 tar concentration. However, the tar dewpoint seems to level off at a residence time longer than 3 s.

5.4.2 Gasification temperature

To determine the influence of the gasification temperature on tar formation, the gasification temperature has been increased from 750°C to 900°C with steps of 50°C. The equivalence ratio, ER, was kept constant. Tar measurements were performed after the cyclone according to the SPA method. The specific experimental conditions are given in Table 5.9, and the experimental results in Table 5.10 and Figures 5.7 and 5.8.

Table 5.9   *Impact of gasification temperature: experimental conditions.*

		1	2	3	4	5
Biomass feedstock		willow	willow	willow	willow	willow
Moisture content	wt%	7.8	7.8	7.8	7.8	7.8
ER	-	0.26	0.26	0.25	0.25	0.25
Bed temperature	°C	732	758	801	853	899
Freeboard temperature	°C	686	728	776	823	878
Sample period		8:19-9:06	9:31-10:07	10:31-11:09	11:32-12:13	12:36-13:11

Table 5.10   *Impact of gasification temperature: experimental results.*

Bed temperature	°C	732	758	801	853	899
CO	vol.%	15.5	16.4	18.7	17.5	19.0
H_2	vol.%	5.4	7.2	9.2	7.4	10.7
CO_2	vol.%	16.3	16.4	15.6	15.3	15.0
CH_4	vol.%	4.1	4.8	5.4	4.9	5.2
C_2H_4	vol.%	1.4	1.6	2.0	2.0	1.8
H_2O (calc.)	vol.%	13	13	11	12	10
N_2	vol.%	58	58	55	53	50
C_6H_6	mg/m_n^3	5884	8072	11746	14322	19005
Tar dewpoint	°C	145	139	172	190	203
SPA total	mg/m_n^3	16977	18303	18325	16041	13456
Unknown	mg/m_n^3	3749	2380	1801	1369	1004
Class 1	mg/m_n^3	ND	ND	ND	ND	ND
Class 2	mg/m_n^3	3476	3403	1651	436	157
Class 3	mg/m_n^3	7923	9871	10497	8539	5018
Class 4	mg/m_n^3	1739	2522	3967	4906	5842
Class 5	mg/m_n^3	89	127	409	791	1434

ND = Not determined. Gas samples were taken after the cyclone. Concentrations (except for H_2O) are given on dry basis. The tar data represent averages of two or three measurements.
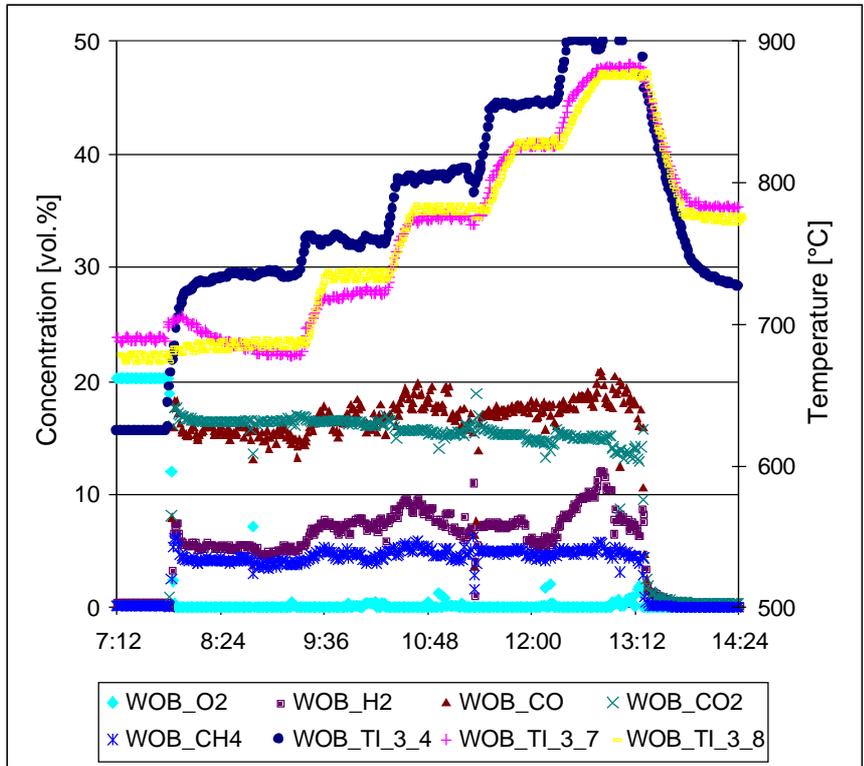
Figure 5.7 *Impact of gasification temperature: gas composition and gasifier operating temperatures.*

WOB TI_3_4 = bed temperature; WOB_TI_3_7 = freeboard temperature bottom; WOB_TI_3_8 = freeboard temperature top.
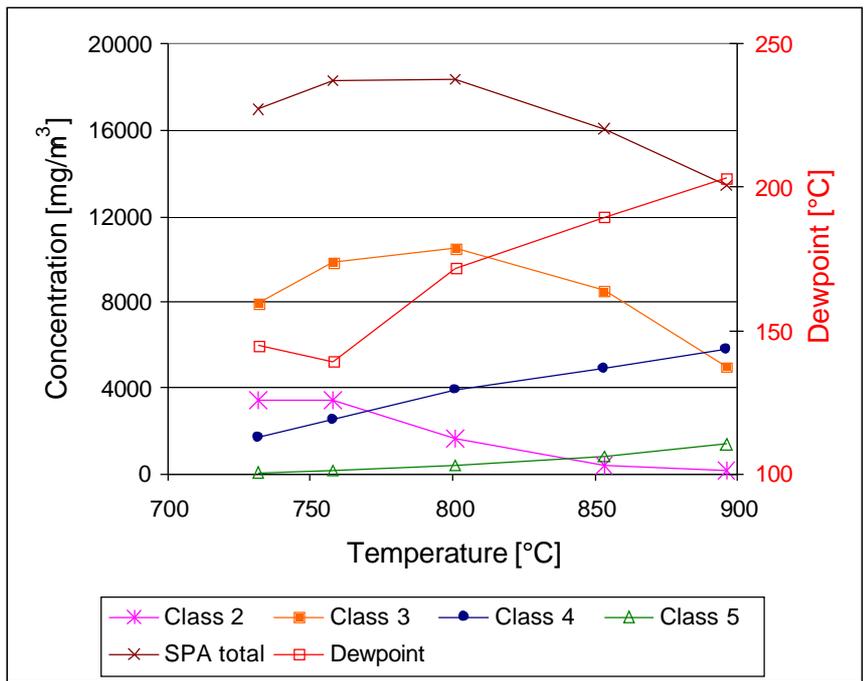

Figure 5.8 *Impact of gasification temperature: tar concentration and dewpoint.*

The gasification temperature appears to have a large impact, in particular on the tar composition. The class 2 tars are almost decomposed at a gasification temperature of 850°C. On the other hand, the class 4 and heavy class 5 tar concentration continuously increases with increasing temperature, leading to a continuous increase in tar dewpoint from 145°C at 730°C to 203°C at 900°C. The class 3 (light) tar compounds go through a maximum at 780-800°C, just as the total tar concentration.

The mechanisms for the formation of heavy, class 5 tars are not fully understood. Two opposite mechanisms can determine the production of heavy tars with increasing temperature. On the one hand, class 5 tar compounds might be produced from the decomposition (cracking) of heavy/large class 1 tar compounds. On the other hand, the class 5 tars can be a product from lighter (class 2, 3 and 4) tar compounds, due to PAH growth reactions. Both mechanisms will increase the class 5 tar concentration with increasing temperature. Since heavy, class 5 tar compounds dominate the tar dewpoint, which means that even at low concentrations these compounds start to condense at relatively high temperature, it is important to aim at a better understanding of the mechanisms of class 5 tar formation.

The concentration and composition of class 1 tar has not been considered thus far. However, the GC-undetectable class 1 tar may contain very heavy tar compounds (larger than coronene) with a high dewpoint. In that case, not to include these compounds in the dewpoint calculation leads to an underestimation of the tar dewpoint. Therefore, it was decided to repeat the gasification temperature variation experiments, now paying specific attention to the formation and fate of class 1 tars. To this purpose, tar measurement was conducted with the "advanced" Guideline method, meaning that the gravimetric tar fraction was redissolved and analysed for class 2-5 tars to obtain the "true" class 1 tar fraction. In addition, some attempts were made to obtain a qualitative impression of the composition of the class 1 tar fraction by using HPLC analysis.

Furthermore, it was decided to conduct the experiments in a more realistic manner by simultaneously changing the gasification temperature and the equivalence ratio (ER) in agreement with full-scale gasifier operating practice.

5.4.3 Gasification temperature with variation in ER

On industrial scale, the gasification temperature is determined by the equivalence ratio (ER) in the gasifier. The air inlet temperature, heat losses in the gasifier, the carbon conversion and the biomass moisture content determine the ER - temperature relation for a gasifier. On laboratory scale, the high heat losses would result in an unrealistic high ER. To compensate for the heat losses, lab-scale gasifiers are electrically heated with trace heating, which allows decoupling of ER and gasification temperature.

In order to obtain results that are more representative for gasifiers at commercial scale, the ER - temperature relation for a 50 MW_{th} atmospheric, air-blown fluidised-bed gasifier, operated on woody biomass, has been determined and was used for the experiments. This means that the airflow was increased according to this relation when the gasification temperature was increased. The following assumptions were made for the calculation of the ER - temperature relation:
- Commercial scale: 50 MW_{th}
- Carbon conversion = 93 %
- Air pre-heating = 100°C
- Heat loss = 2.7 % (LHV basis)
- Biomass moisture content = 9.5 wt%
- Gas composition calculated with an in-house, semi-empirical gasification model.

The ER - temperature relation is given in Table 5.11.

Table 5.11 *ER - temperature relation for a 50 MW$_{th}$ atmospheric, air-blown fluidised-bed biomass gasifier.*

Test	Gasification temperature	ER
1	750°C	0.22
2	800°C	0.24
3	850°C	0.25
4	900°C	0.27
5	950°C	0.28

During the fluidised-bed gasification experiments, gas analysis and sampling were performed just above the sand bed and after the cyclone. The tar dewpoint was calculated from the GC-detectable tar fraction and, therefore, may be an underestimate of the actual tar dewpoint. The specific experimental conditions are given in Table 5.12, and the experimental results in Table 5.13 and Figures 5.9 and 5.10.

Table 5.12 *Impact of gasification temperature at varying ER: experimental conditions.*

		1	2	3	4	5
Biomass feedstock		willow	willow	willow	willow	willow
Moisture content	wt%	7.8	7.8	7.8	7.8	7.8
ER	-	0.23	0.24	0.26	0.27	0.29
Bed temperature	°C	759	807	854	906	955
Freeboard temperature	°C	721	770	823	874	924
Sample period		13 May 8:51-11:12	13 May 13:20-15:02	14 May 9:30-11:08	15 May 9:42-11:14	16 May 8:25-9:33

Table 5.13 *Impact of gasification temperature at varying ER: experimental results.*

Bed temperature	°C	759	807	854	906	955
CO	vol.%	16.5	16.3	15.2	16.0	17.0
H_2	vol.%	6.9	8.0	10.4	11.4	12.3
CO_2	vol.%	16.2	16.3	16.6	15.8	14.8
CH_4	vol.%	4.9	4.8	4.5	4.1	3.8
C_2H_4	vol.%	1.7	1.9	1.7	1.3	0.7
N_2	vol.%	55	54	53	53	53
C_6H_6	mg/m$_n^3$	6890	8979	10897	12338	12276
Tar dewpoint	°C	194	188	195	207	220
Guideline total	mg/m$_n^3$	54058	26205	19613	14398	11843
Unknown	mg/m$_n^3$	14527	6951	5063	3177	2452
Class 1	mg/m$_n^3$	17504	6367	4173	2152	1865
Class 2	mg/m$_n^3$	7301	1579	186	41	17
Class 3	mg/m$_n^3$	7015	4967	3314	1596	541
Class 4	mg/m$_n^3$	6900	5413	5912	6231	5401
Class 5	mg/m$_n^3$	466	492	753	1070	1522

Gas samples were taken after the cyclone. Concentrations are given on dry basis. The tar data correspond to a single measurement.
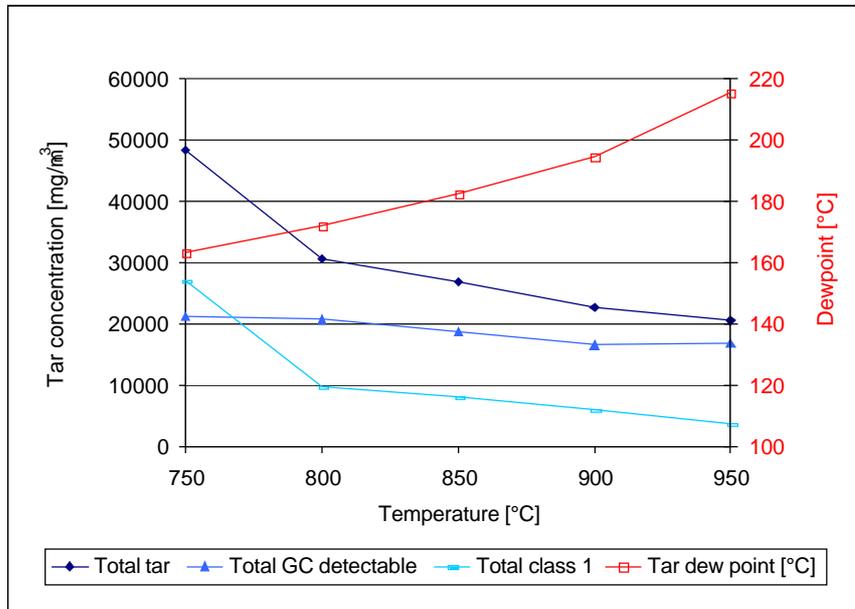
Figure 5.9   *Impact of gasification temperature at varying ER: tar concentration and dewpoint just above the sand bed.*
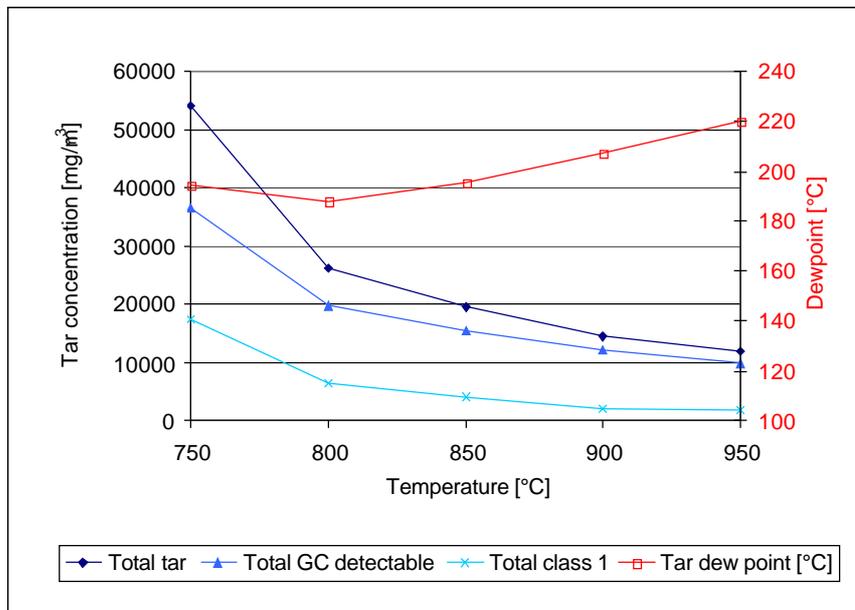

Figure 5.10 *Impact of gasification temperature at varying ER: tar concentration and dewpoint after the cyclone.*

Figure 5.10 reveals a decrease in total tar concentration in the product gas after the cyclone by a factor of five, when the gasification temperature is increased from 750 to 950°C. Both the class 1 tar concentration as well as the GC-detectable tar concentration (tar with a molecular mass between toluene and coronene) decreases in concentration with increasing gasification temperature. However, despite the factor five decrease in total tar concentration, the tar dewpoint increases.

Detailed tar composition

In order to better understand the mechanisms of tar formation and decomposition inside the gasifier, the tar compounds have been have been regrouped in the following 3 groups: alkyl-substituted tar compounds, heterocyclic tar compounds and PAH compounds without substituted groups. This grouping corresponds to the division made by Milne and Evans: primary tars, secondary tars, tertiary tars.

The results for the alkyl-substituted tar compounds are given in Figures 5.11 and 5.12 for samples obtained just above the sand bed and after the cyclone respectively. At low temperature (750-800°C), the alkyl-substituted tars are produced in the freeboard of the gasifier. At high temperature (850°C-950°C), the alkyl-substituted tar compounds are decomposed. At 950°C, this decomposition is almost complete.

From Figure 3.2 it appears that the thermal decomposition of indene starts at a temperature of 750°C, and at 850°C, 50 % conversion is reached after 2 s gas residence time. In the gasification experiments, however, indene is still present at a temperature of 950°C and a residence time of approx. 4 s (see Figure 5.12). Comparing these results leads to the conclusion that, probably, indene (or more in general, alkyl-substituted tar) is produced in the freeboard of the gasifier.
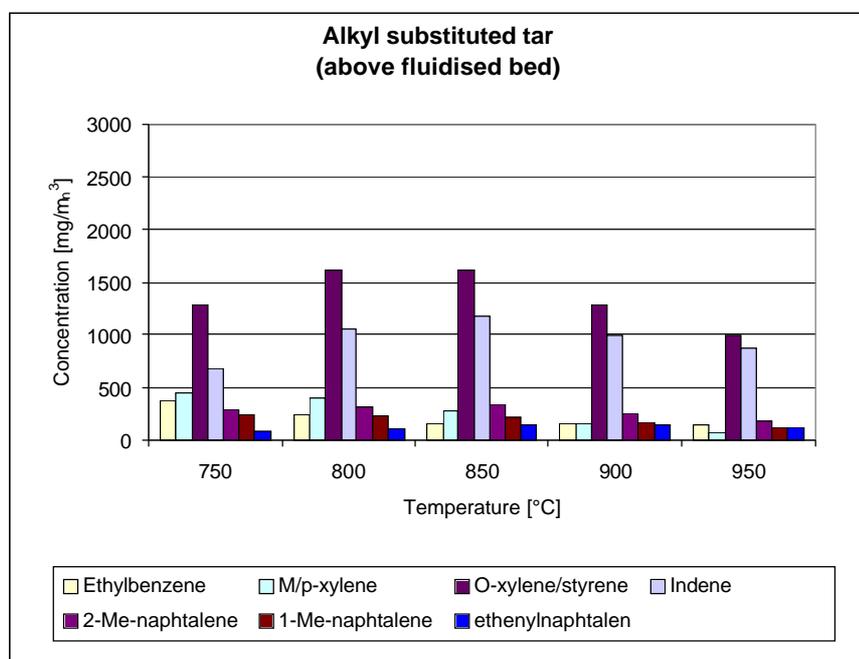

Figure 5.11 *Tar compounds with an alkyl-substituted group sampled just above the sand bed at different gasification temperatures.*

Alkyl substituted tar
(after cyclone)
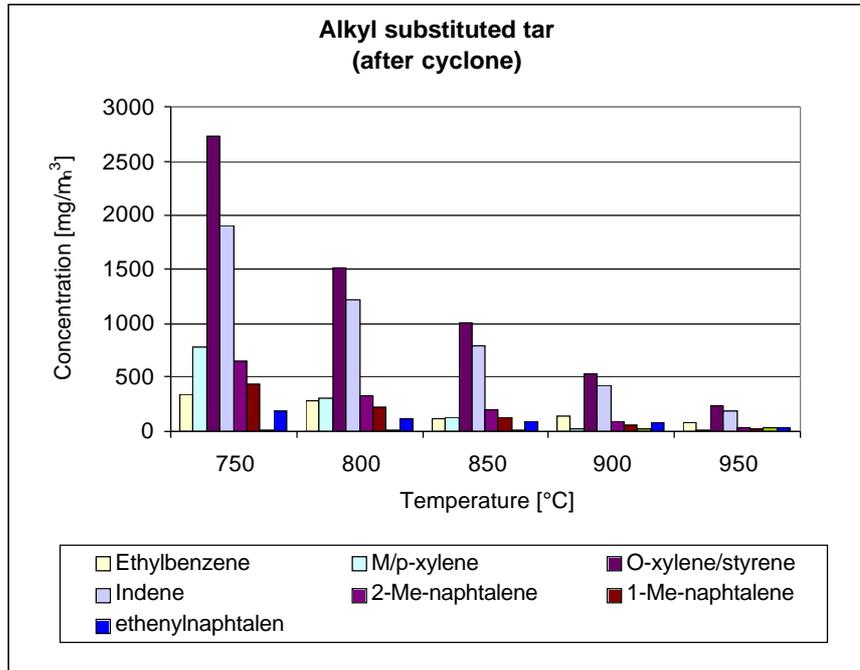
Figure 5.12 *Tar compounds with an alkyl-substituted group sampled after the cyclone at different gasification temperatures.*

Heterocyclic tar compounds, sampled just above the sand bed and after the cyclone at different gasification temperatures with varying ER, are presented in Figures 5.13 and 5.14 respectively.

**Heterocyclic tar**
(above fluidised bed)
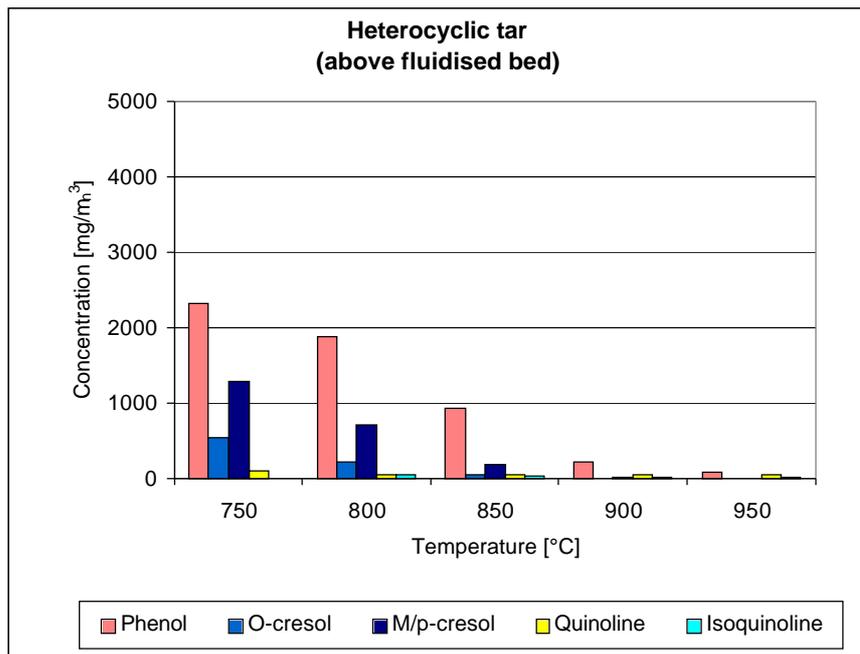
Figure 5.13 *Heterocyclic tar compounds sampled just above the sand bed at different gasification temperatures.*
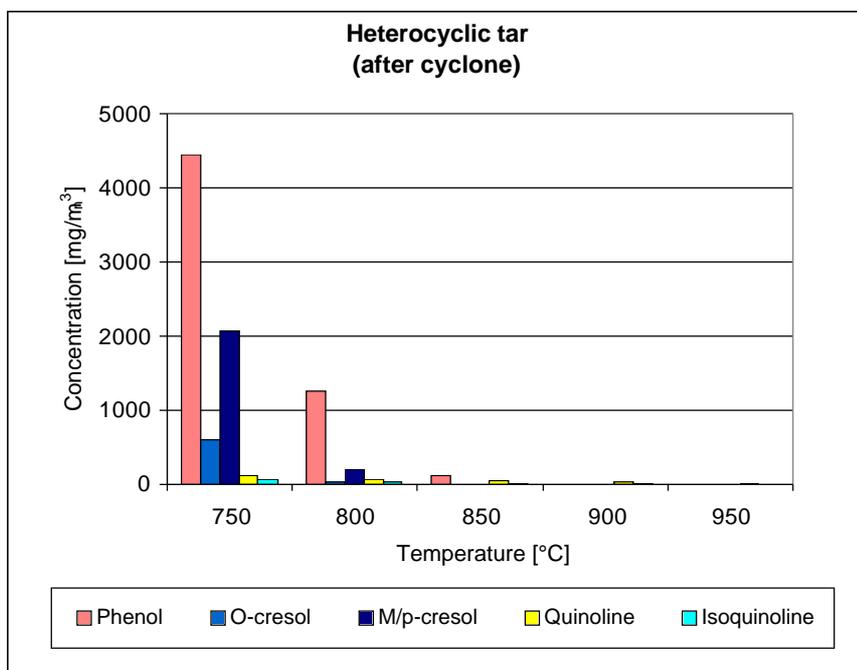
Figure 5.14 *Heterocyclic tar compounds sampled after the cyclone at different gasification temperatures.*

At a temperature of 750°C, heterocyclic tars are produced in the freeboard of the gasifier. At 800°C, the conversion rate becomes appreciable, resulting in a decrease in heterocyclic tar concentrations in the freeboard. Already at a temperature of 850°C and a gas residence time of approx. 4 s (sampling after the cyclone), the heterocyclic tars are completely decomposed. At a residence time of approx. 1.3 s (sampling just above the bed), the temperature should be increased to 950°C to obtain the same effect.

Figures 5.15 and 5.16 show the formation of PAH compounds without substituted groups as a function of gasification temperature. It appears that most PAH compounds are formed in the freeboard at a temperature of 750-900°C. Above a temperature of 900°C, the concentration of large PAH compounds (pyrene-coronene) further increases, but the concentration of small PAH compounds like biphenyl and phenanthrene levels off or starts to decrease. Similar effects can be observed with increasing residence time. The naphthalene concentration (not shown because of its high values) continuously increases from 0.5 to 3.5 g/m_n^3 with increasing temperature at a residence time of 1.3 s. At a residence time of 4 s, the naphthalene concentration increases from 2 g/m_n^3 at 750°C to 3.5 g/m_n^3 at 900°C, and levels of to 3 g/m_n^3 at 950°C.
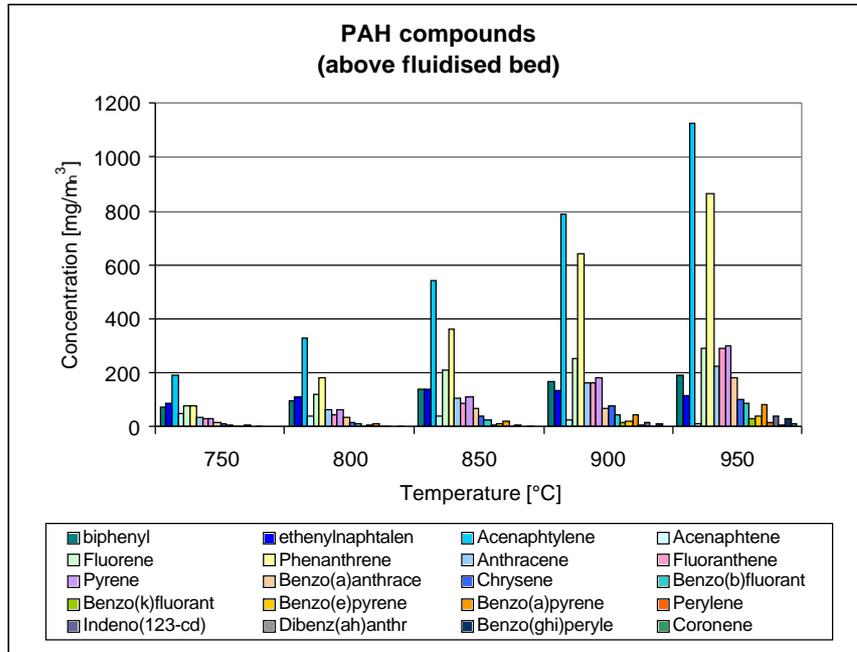
Figure 5.15 *PAH tar compounds without substituted groups sampled just above the sand bed at different gasification temperatures.*
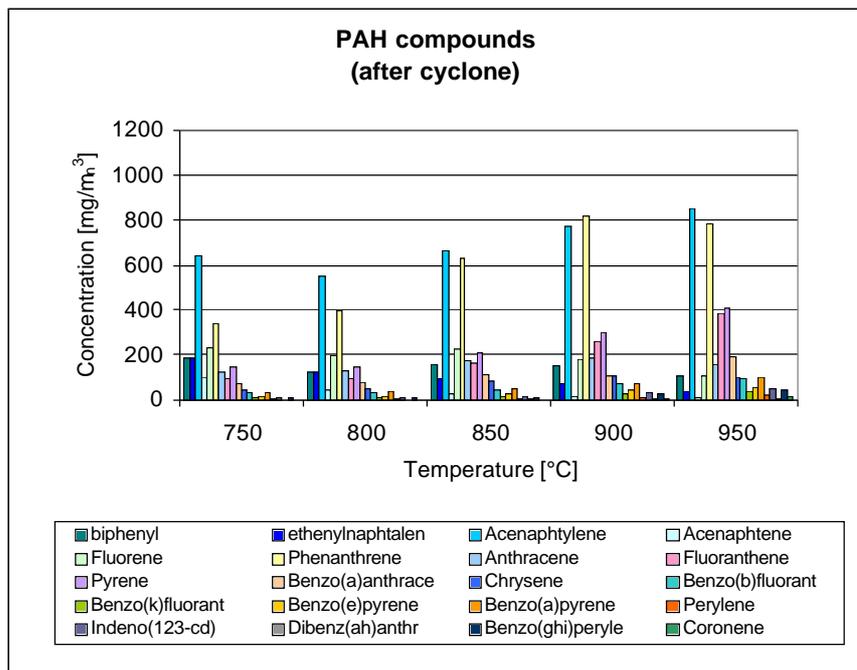
Figure 5.16 *PAH tar compounds without substituted groups sampled after the cyclone at different gasification temperatures.*

Mechanisms of heavy tar formation

As mentioned in the previous section, two mechanisms may be responsible for the observed production of class 5 tar compounds. On the one hand, the class 5 tars could be the products from the cracking of even heavier tar compounds that form part of the GC-undetectable class 1 tars. This seems not to be contradicted by the experimental results, as it appears that the increase in class 5 tars is accompanied by a decrease in class 1 tars. On the other hand, the class 5 tars could also be the products of PAH growth reactions involving small PAH compounds or unsaturated hydrocarbons.

The PAH growth reactions have been studied extensively with respect to soot formation in flames. Light (class 4) PAH compounds can recombine to produce one larger PAH compound. Biphenyl is a clear example of this growth mechanism, being the result of the recombination of two phenyl (benzene) radicals. Unsaturated C2-C4 hydrocarbons can also form PAH compounds in isomerisation reactions. Isomerisation reactions yield PAH compounds without single C-C-bonds between the phenyl groups. Pyrene, benzoghi)perylene and coronene are examples of isomerisation products. Ethylene and acetylene are examples of unsaturated hydrocarbons, which are present at low concentration in fluidised-bed gasifier product gas.

In order to verify the occurrence and importance of class 5 tar formation through the decomposition of class 1 tars, a HPLC analysis of the gravimetric tar fraction has been performed. This HPLC analysis allowed a qualitative analysis of PAH compounds with a molecular mass larger than coronene (i.e., tars heavier than class 5 tars). Figures 5.17 and 5.18 give the response of the UV detector of the HPLC analyser as function of the retention time, starting after the elution of coronene at a retention time of 10 minutes.

The retention time of a certain tar compound in the HPLC diagram is dependent on its polarity. A compound with high polarity, like phenol, will have a short retention time, while a compounds with a low polarity, like coronene, will have a long retention time. The polarity of aromatic compounds decreases with increasing number of aromatic rings. The response signal of the detector is linear dependent on the concentration of the compound in the gravimetric tar sample, according to the law of Lambert Beer. When the concentration of the compound increases the peak area will also increase, generally resulting in higher peaks. The response is also dependent on the molecular structure of a compound. The response factor as well as the retention time for each compound must be determined by calibration. In this limited, first effort, this calibration has not been performed yet. However, the HPLC analysis results can still be used to obtain qualitative results.
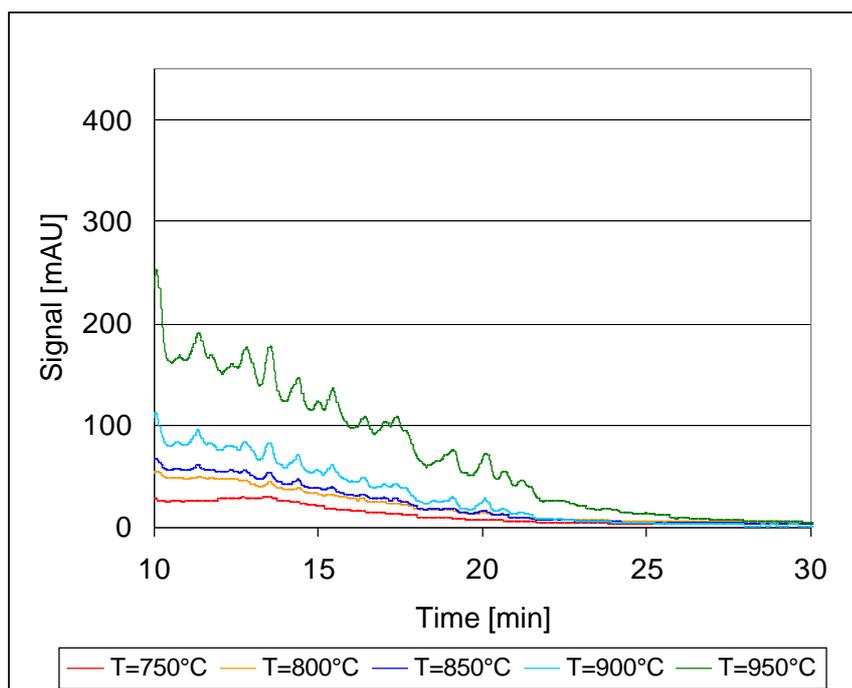
Figure 5.17 *HPLC analysis of gravimetric tar sampled just above the sand bed at different gasification temperatures.*
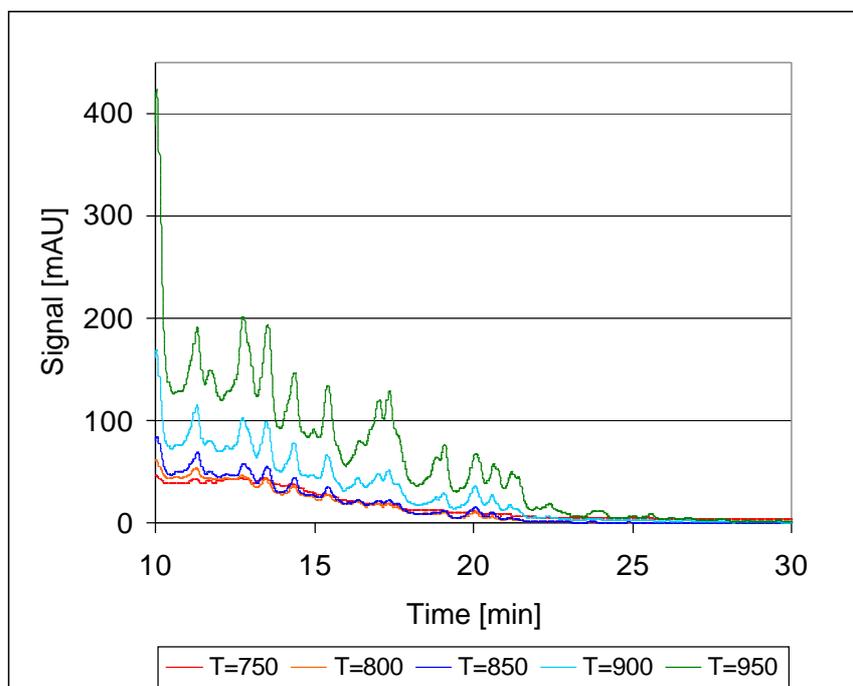
Figure 5.18 *HPLC analysis of gravimetric tar sampled after the cyclone at different gasification temperatures.*

The 'hill' in the HPLC diagrams of Figures 5.17 and 5.18 is due to the presence of a fairly high concentration of light hydrocarbons in the gravimetric tar sample. Generally, these hydrocarbons have a lower retention time than coronene. Due to the high concentration, however, the hydrocarbons elute also at higher retention time, disturbing the diagram. The peaks on the 'hills' are of most interest, since they indicate the presence of hydrocarbons with a lower polarity than coronene.

The absence of these peaks in the HPLC diagrams for the gravimetric tar samples taken at 750-800°C is an indication that at low temperature, large PAH compounds are hardly present in the tar sample. Above 850°C, the peaks increase considerably in height with increasing gasifier temperature as well as gas residence time. Apparently, above 850°C large PAH compounds (larger than coronene) are produced by the PAH growth reaction mechanism.

The HPLC analysis results provide evidence that the PAH growth mechanism mainly determines the production of class 5 tars. This mechanism is consistent with the mentioned PAH growth mechanism published by Bruinsma and Moulijn [19]. The class 4 tars are intermediate compounds in this mechanism. That means that large compounds, which exhibit a high dewpoint at relatively low concentration, will be produced to a larger extent with increasing temperature.

Class 1 tar composition
The increasing production of heavy PAH compounds with increasing temperature seems in conflict with the decreasing class 1 tar concentration. The class 1 tars were defined as tars that cannot be detected with a GC. Heavy non-polar PAH compounds stick on the non-polar GC column and are not eluted which makes the measurement of these compounds with the current GC method not possible. It was expected that these non-polar heavy PAH compounds would dominate the class 1 tar composition. However, the high concentration of class 1 tars at low gasification temperatures seems not in agreement with the low concentration of heavy PAH compounds at these temperatures. It appears that the class 1 tar comprises a second group of tar compounds.

It is postulated that this second group consists of primary and secondary tars according to the classification of Evans and Milne (see Chapter 2). The composition of primary tars is close to the composition of the biomass itself, and is determined by the monomer structures of the lignocellulose components in the biomass. Secondary tars are decomposition products of primary tars. Due to the high oxygen (and nitrogen) content of woody biomass, the primary and secondary tars will both have a relatively high oxygen (and nitrogen) content as well.

Furthermore, the primary and secondary tars, containing hetero-elements, generally have a high polarity, which makes them difficult to analyse with both GC-FID equipped with a non-polar column and with the applied HPLC method.

To verify this hypothesis, the gravimetric tars have been subjected to an ultimate analysis. The results are presented in Tables 5.14 and 5.15 for tar samples taken just above the sand bed and after the cyclone respectively. The element composition of the class 1 tar fraction has been obtained by subtracting the element composition of the GC-detectable tar fraction in the gravimetric tars from the element composition of the gravimetric tars.

Table 5.14   *Ultimate analysis of gravimetric tars and the GC-undetectable fraction (class 1 tar), sampled just above the sand bed.*

Bed temperature (°C)	O grav.	O class 1	C grav.	C class 1	H grav.	H class 1	N grav.	N class 1
759	15	24	56	62	5	6	4	4
807	12	21	70	58	6	7	6	7
854	11	22	70	54	7	9	5	7
906	8	22	68	59	5	6	4	7
955	4	13	73	74	5	6	2	3

Element concentrations in wt%.

Table 5.15   *Ultimate analysis of gravimetric tars and the GC-undetectable fraction (class 1 tar), sampled after the cyclone.*

Bed temperature (°C)	O grav.	O class 1	C grav.	C class 1	H grav.	H class 1	N grav.	N class 1
759	12	21	68	59	6	7	5	13
807	11	27	68	50	6	7	4	16
854	8	28	71	51	6	8	4	13
906	6	35	75	45	5	6	2	14
955	4	29	78	38	5	8	3	25

Element concentrations in wt%.

The results should be interpreted with precautions, because the element weight fractions total between 80 and 95 wt%. In order to find the missing 5-20 wt%, the ash concentration in the gravimetric tar sample was determined from the 759°C gravimetric tar sample. However, the ash content appeared to be very low (0.25 wt%) and cannot explain the missing 5-20 wt%.

Nevertheless, the tables show that the oxygen content of the gravimetric tars decreases with increasing temperature and with increasing gas residence time. At a gasifier bed temperature of 955°C the oxygen content has almost disappeared. The decrease in oxygen content for the GC-detectable tars is even more pronounced, as can be seen from Figures 5.13 and 5.14. After the cyclone, the class 2 tars have disappeared almost completely at a temperature of 850°C.

The oxygen content in the class 1 tars is higher than in the gravimetric tars in all cases, and remains constant or even increases with increasing bed temperature. Apparently, the oxygen

content in the GC-detectable tar fraction of the gravimetric tars is considerably lower than in the class 1 tars. The increase in oxygen content in the freeboard is not well understood.

In conclusion, class 1 tar indeed appears to contain a substantial fraction of hetero-elements containing compounds, which are likely to be primary or secondary tars. This also implies that the water solubility of tars may be underestimated considerably when the evaluation is based on the class 2 tar content only.

5.5   Tar production in BFB vs. CFB gasifiers

In this section, the influence of the fluidisation regime on the tar composition will be evaluated. The experiments in the previous sections were all conducted in a bubbling-fluidised-bed gasifier. For the gasification of biomass on commercial scale, both bubbling-fluidised-bed (BFB) and circulating-fluidised-bed (CFB) gasifiers can be selected. Knowledge about the influence of the type of fluidised-bed gasifier on the tar composition is essential for the translation of the experimental results presented in this report to commercial-scale installations.

The difference between a BFB and CFB gasifier lies mainly in the gas velocity and the resulting axial solids distribution. The BFB gasifier is characterised by a dense bed with an "empty" freeboard. A CFB gasifier is characterised by a dense and a lean bed, and does not have a distinct solids separation between the freeboard and the bed. The solids promote a uniform axial temperature distribution. With the absence of solids in the freeboard of the BFB gasifier, the temperature in the freeboard can drop due to endothermic reactions.

The tar composition in the product gas strongly depends on the axial temperature profile, but may also depend on the hydrodynamics in the gasifier in a different way. In a CFB gasifier, biomass particles can be carried over the top. This can result in pyrolysis products at the exit of the gasifier, which experienced a shorter residence time than would be expected based on the average gas residence time in the gasifier. In a BFB gasifier, biomass particles cannot reach the exit of the gasifier due to the presence of a freeboard. Although the biomass particles are mixed up in the bed, the long residence time in the freeboard equilibrates the differences in residence time of the pyrolysis gas in the fluidised bed itself.

To get an impression of the relation between tar production in BFB and CFB gasifiers, the experimental data obtained from the 1 kg/h BFB gasifier WOB have been compared to data obtained from the 100 kg/h CFB gasifier BIVKIN at ECN. Details of this gasifier can be found elsewhere [30]. In the CFB gasifier, Labee demolition wood pellets (ID-code 1448 in the ECN biomass database Phyllis, www.phyllis.nl) were used as feedstock. In Figure 5.19, tar class concentrations in both gasifiers are presented as fractions of the total tar concentration.

The data from both gasifiers show a similar temperature dependency. The class 4 and class 5 fractions increase, and the class 2 tar fraction decreases with increasing temperature. The contribution of the remaining tars (class 3 and unknowns, not shown) decreases from approx. 50 wt% to 20 wt%, when the gasification temperature increases from 750°C to 950°C. When the BFB (WOB) data are analysed in more detail, than three different curves can actually be distinguished for the class 4 fraction. The large closed triangles belong to samples taken just above the bed with willow as feedstock. The upper small closed triangles belong to samples taken after the cyclone with beech as feedstock. The small closed triangles in between belong to samples taken after the cyclone with willow as feedstock. For the class 2 and 5 tars the subdivision can only be made for samples taken above the bed and after the cyclone.

It appears that the tar composition of samples taken at the outlet of the CFB gasifier is more comparable to samples taken after the cyclone of the BFB gasifier than to samples taken just above the sand bed. The gas residence time, on the other hand, is in the CFB gasifier with approximately 1 s comparable to the gas residence time just above the bed of the BFB gasifier.

From this, it would be expected that the composition at the outlet of the CFB-gasifier would match with the composition just above the sand bed in the BFB-gasifier.
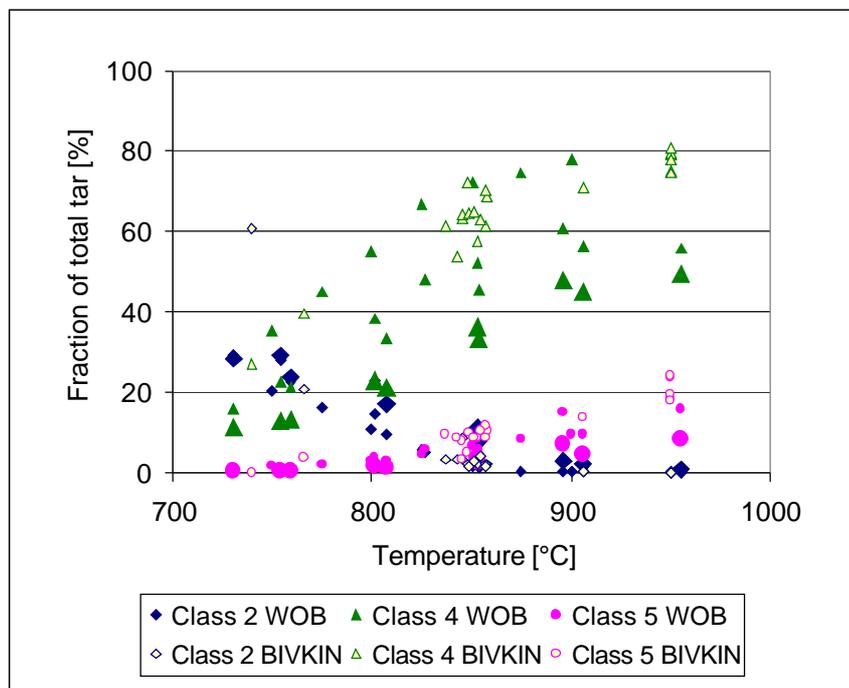

Figure 5.19 *Tar composition vs. gasification temperature for the BFB (WOB) and CFB (BIVKIN) gasifiers at ECN.*

The gasifiers were operated on woody biomass. WOB data were obtained just above the sand bed (large closed symbols) and after the cyclone (small closed symbols).

This apparent contradiction may be due to a temperature drop in the freeboard of the BFB gasifier and/or differences in feedstock. The temperature drop in the freeboard can be as high as 30°C. Such a temperature drop can significantly influence the tar composition, as has been discussed extensively in the previous Section. The impact of the temperature drop on the tar composition is similar to the impact of a longer gas residence time.

Evidence of a larger (pyrolysis) gas residence time distribution in the CFB gasifier cannot be found in Figure 5.19. A larger residence time distribution would result in a larger class 2 contribution and a smaller class 4 and 5 contribution, but the opposite has been observed. However, this was probably also not to be expected for the rather large Labee fuel pellets. It is most likely that they stay in the bottom section of the CFB-gasifier during the main part of the pyrolysis phase.

In conclusion, it appears that the tar data obtained in the lab-scale BFB-gasifier are quite representative for a CFB-gasifier, provided that differences in gasification temperature and gas residence time are taken into account, and provided that the CFB-gasifier is operated on relatively large/heavy fuel particles. The previous sections in this report provide data to account for the differences in gasification temperature and gas residence time. Furthermore, it is indicated qualitatively how the tar composition in the product gas of a CFB-gasifier may change, when smaller, lighter fuel particles are fed that do not stay in the bottom section during the pyrolysis phase.

6. CONCLUSIONS

The overall objective of the project has been to assist designers and operators of fluidised-bed biomass gasification based systems by providing detailed data concerning the impact of fuel properties and gasifier operating conditions on the resulting tar content and composition, and concerning the underlying mechanisms. The tar content and composition have been interpreted in terms of their impact on the performance of downstream equipment using a dedicated tar classification system. In this respect, water solubility and condensation behaviour, expressed in terms of the tar dewpoint, were identified as the most important tar properties. Attention has been paid mostly to atmospheric-pressure, air-blown bubbling-fluidised-bed (BFB) gasification of woody biomass, but circulating-fluidised-bed (CFB) gasification was addressed as well.

In the experimental programme, the impact of three fuel properties (ash content, moisture content and lignocellulose composition) and two operating conditions (gasification temperature and gas residence time) has been determined. In general, these parameters were varied independently, i.e. while keeping the others constant. Also the equivalence ratio ER was mostly kept constant, which was made possible by the trace heating on the wall of the lab-scale gasifier.

Variation of the **ash content** in the bed, simulated by co-feeding high-ash char (approx. 40 wt% ash), had a negligible impact up to the maximum tested char/biomass ratio of 17 wt%.

An increase in **moisture content** from 10 to 45 wt%, simulated by mixing dry biomass off-line with water, led to a total tar concentration decreases from 14 to 8 g/m_n^3. Also all the individual tar classes showed a clear decrease. However, the highly water-soluble heterocyclic compounds (class 2 tars) could not be eliminated completely at the given gasification temperature of 800-825°C and approx. 4 s gas residence time, and the tar dewpoint only showed a slight decrease. Fuel with high moisture content needs extra energy for the evaporation of water and heating of the water vapour. In a large-scale gasifier, the extra heat can/will be generated by increasing the ER in the gasifier. This will lead to even lower tar concentrations (due to both a dilution effect and an increased oxygen availability). However, this may result also in a decrease in cold gas efficiency, and a drop in energy efficiency. Also the gas volume flow will increase due to both the increasing fuel moisture content and the increasing ER. This results in an increase in the size of unit operations downstream the gasifier. For many applications, the loss in energy efficiency and the increasing size of unit operations will probably outweigh the advantage of lower class 2 and class 5 tar concentrations. However, this might not be the case for indirect biomass co-combustion (see below).

The **lignocellulose composition** seems to have some effect on the total tar concentration, while having no significant effect on the tar composition. Experiments with a fuel prepared from pure cellulose gave lower tar concentrations than experiments with willow and beech. Despite the lower tar concentrations, the tar dewpoint remained nearly the same. This means that fouling due to tar condensation will happen at similar process conditions. However, due to the lower tar concentrations, the amount of condensed tar species will be substantially lower for the cellulose case.

Increasing the **gasification temperature** from 750 to 900°C at constant ER appeared to have a large impact on tar formation, in particular on the tar composition. The class 2 tars were decomposed almost completely at 850°C and higher. On the other hand, the 2-3 ring PolyAromatic Hydrocarbon (PAH) compounds (class 4) and the 4-7 ring PAH compounds (class 5) concentration continuously increased with increasing temperature, leading to a continuous and substantial increase in tar dewpoint. The class 3 light aromatic compounds went through a maximum at 780-800°C, just as the total tar concentration.

Since it was realised that in an actual, industrial-scale gasifier, there is a coupling between the gasification temperature and the equivalence ration ER, additional experiments were conducted with a simultaneous, coupled variation of the gasification temperature and ER (higher ER to get higher temperature). These experiments gave a strong decrease in total tar over the temperature range of 750-950°C. However, here again the tar dewpoint showed an increase due to an increase in heavy PAH compounds (class 5 tar), despite the diluting effect of a higher ER. A more detailed analysis, focussing on the heavy tar fraction in particular, revealed that the heavy PAH compounds are formed by dimerisation reactions of two PAH compounds or by cyclisation or polymerisation reactions of unsaturated C2-C4 hydrocarbons like acetylene and ethylene. These latter compounds are produced in the decomposition of aromatic as well as linear hydrocarbons.

Finally, increasing the **gas residence time** (in the freeboard of a BFB gasifier) was found to have a similar, but much smaller, effect than increasing the gasification temperature.

The reported results of lab-scale BFB gasification were found to be representative for CFB gasification as well, provided that differences in gasification temperature and gas residence time (distribution) are taken into account. The report contains data to account for these differences.

Primary measures
Based on the findings concerning the impact of fuel properties and gasifier operating conditions on tar content and composition, conclusions may be drawn concerning the possibilities of tar control by primary measures. To this purpose, a distinction should be made between firing the product gas in a coal-fired boiler (indirect co-firing) or in a stand-alone boiler on the one hand, and more advanced applications of the product gas on the other hand.

In indirect co-firing, the product gas is used as a secondary fuel for the main (coal-fired) boiler. Generally, the product gas temperature is kept as high as possible to prevent tar-induced problems. In that case, the gas will not be cooled to temperatures below the water dewpoint. Therefore, tars with a high water solubility (class 2) do not pose a problem. However, the gas cooling will require in most cases a mild control of the heavy PAH content in the product gas. Generally, primary measures in the form of a proper selection of fuel properties and gasifier design and/or operating conditions seem to offer enough possibilities to avoid severe tar-induced fouling problems. The same holds for the case, where the product gas is kept at high temperature and then fired in a stand-alone boiler.

More advanced applications, such as firing the product gas in a gas engine or a gas turbine, or using the product gas for the production of gaseous or liquid fuels, generally require a much cleaner product gas and often require the product gas to be cooled down to (near-)ambient temperature. In these cases, generally, primary measures will not suffice to meet the requirements concerning tar content and composition, and secondary tar removal will be necessary. However, primary measures may be applied then to optimise the tar composition for these secondary removal processes or for gas cooling and cleaning processes in general. For example, if water scrubbing is applied, primary measures may be used to fully decompose the highly water-soluble class 2 tars, leading to a considerable reduction in wastewater treatment cost.

Recommendation
Given the important role of the class 1 tar fraction and its complex composition, it is recommended to put more effort in the determination of the composition of this tar class in future work.

ACKNOWLEDGEMENTS

REFERENCES

[1]   Kiel, J.H.A., *et al.:* "Primary measures to reduce tar formation in fluidised-bed biomass gasifiers - final report SDE-project P1999-012". Report ECN-C--04-014, ECN, Petten, 2004.

[2]   Neeft, J.P.A., and Berends, R.H.: "Inventariserende studie - deel 1: Primaire maatregelen (voorkomen teervorming of in-bed verwijderen) ter verlaging van teerproductie bij wervelbedvergassers". ECN-TNO report, 2001 (in Dutch).

[3]   Evans, R.J., and Milne, T.A.: "Chemistry of tar formation and maturation in the thermochemical conversion of biomass". In: Developments in thermochemical biomass conversion - vol.2, Bridgwater, A.V., and D.G.B.Boocock, D.G.B. (Eds.), Blackie Academic & Professional, London, pp.803-816, 1997.

[4]   Evans, R.J., and Milne, T.A.: "Molecular characterization of the pyrolysis of biomass. 2. Applications". Energy Fuels, vol.1(4), pp.311-319, 1987.

[5]   Milne, T., Abatzoglou, N., and Evans, R.J.: "Biomass gasifier "tars": their nature, formation and conversion". Report NREL/TP-570-25357, NREL, Golden, Colorado, USA, 1998.

[6]   Neeft, J.P.A.: "Tars from thermochemical conversion of biomass and waste. Definitions, formation, properties and sampling and analysis". Report ECN-C--99-102, ECN, Petten, 2000. (in Dutch).

[7]   McGrath, T., Sharma, R., and Hajaligol, M.: "An experimental investigation into the formation of polycyclic-aromatic hydrocarbons (PAH) from pyrolysis of biomass materials". Fuel, vol.80(12), pp.1787-1797, 2001.

[8]   Devi, L., Ptasinski, K.J., and Janssen, F.J.J.G.: "A review of the primary measures for tar elimination in biomass gasification processes". Biomass and Bioenergy, vol.24, pp.125-140, 2003.

[9]   Kurkela, E.: "Formation and removal of biomass-derived contaminants in fluidized-bed gasification processes". VTT Publications 287, VTT, Espoo, Finland, pp.1-47, 1996.

[10]   Gil, J., Corella, J., Aznar, M.P., and Caballero, M.A.: "Biomass gasification in atmospheric and bubbling fluidized bed: effect of the type of gasifying agent on the product distribution". Biomass and Bioenergy, vol.17, pp.389-403, 1999.

[11]   Narváez, I., Orío, A., Corella, J., and Aznar, M.P.: "Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of the produced raw gas". Ind.Eng.Chem.Res., vol.35(7), pp.2110-2120, 1996.

[12]   Cypres, R., and Lejeune, C.: "Craque thermique de m-crésol, du bènzene, du toluène et du phénol entre 650 et 850°C". Ann. Mines Belgique, vol.7-8, pp.1091-1109, 1965.

[13]   Cypres, R., and Bettens, B.: "Mecanismes de fragmentation pyrolytique du phenol et des cresols". Tetrahedon, vol.30, pp.1253-1260, 1974.

[14]   Cypres, R., and Bettens, B.: "Study of the cracking mechanisms of phenanthrene and perhydrophenanthrene labelled in specific positions by ^{14}C and ^{3}H". Fuel, vol.65(4), pp.507-514, 1986.

[15]   Jess, A.: "Mechanisms and kinetics of thermal reactions of aromatic hydrocarbons from pyrolysis of solid fuels". Fuel, vol.75(12), pp.1441-1448, 1996.

[16]   Boroson, M.L., Howard, J.B., Longwell, J.P., and Peters, W.A.: Product yields and kinetics from the vapour phase cracking of wood pyrolysis tars. AIChEJ, vol.35(1), pp.120-128, 1989.

[17] Kaupp, A.: "Gasification of rice hulls - theory and praxis". Vieweg, Braunsweig, Germany, 303 p., 1984.

[18] Bredael, P., Braekman-Danheux, C., and Vinh, T.H.: "Pyrolysis of naphthalenic detivatives 3. Pyrolysis of naphthols, hydronaphthols and perhydronaphthols". Fuel, vol.62(10), pp.1193-1198, 1983.

[19] Bruinsma, O.S.L., and Moulijn, J.A.: "The pyrolytic formation of polycyclic aromatic hydrocarbons from benzene, toluene, ethylbenzene, styrene, phenylacetylene and n-decane in relation to fossil fuels utilisation". Fuel Process. Technol., vol.18(3), pp.213-236, 1988.

[20] Kabe, T., Godo, M., Ishihara, A., Qian, W.H., Otsuki, S., and Mukai, K.: "Estimation of the behaviour of hydrogen in naphthalene in pyrolysis of coal tar using tritium tracer methods". Fuel, vol.77(8), pp.815-820, 1998.

[21] Devi, L., Smits, B.A., Ptasinski, K.J., Janssen, F.J.J.G., Bergman, P.C.A., and Kiel, J.H.A.: "Catalytic decomposition of tars from biomass gasifier". Proc. Int. Nordic Bioenergy Conf. and Exhibition, ISBN 952-5135-26-8, pp.418-420, 2003.

[22] Devi, L., Pol, W.L.C. van, Ptasinski, K.J., and Janssen, F.J.J.G. : "Catalytic decomposition of biomass tars; olivine as a prospective catalyst for biomass gasification processes". Paper presented at the 2003 AIChE annual meeting, San Francisco, USA, 16-21 November 2003.

[23] Devi, L., Ptasinski, K.J., Janssen, F.J.J.G., Paasen, S.V.B. van, Bergman, P.C.A., and Kiel, J.H.A.: "Catalytic decomposition of biomass tars: use of dolomite and untreated olivine". Paper submitted to Renewable Energy, 2003.

[24] Brage, C., Yu, Q., Chen, G., and Sjöström, K.: "Use of amino-phase adsorbent for biomass tar sampling and separation". Fuel, vol.76, pp.137-142, 1997.

[25] Neeft, J.P.A., et al.: "Tar guideline - a standard method for measurement of tars and particles in biomass producer gases". Proc. 12th European Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection, Amsterdam, 17-21 June 2002, published by ETA-Florence and WIP-Munich, pp.469-472, 2002.

[26] Further information on the dewpoint calculation method, developed by ECN, can be obtained from the dedicated web-site www.thersites.nl.

[27] Kinoshita, C.M., Wang, Y., and Zhou, J.: "Tar formation under different biomass gasification conditions". J. Anal. Appl. Pyrolysis, vol.29(2), pp.169-181, 1994.

[28] Shafizadeh, F.: "Thermal Conversion of cellulosic Materials to Fuels and Chemicals". Wood and Agriculture Residues, pp.415-438, 1983.

[29] Pastorova, I., Botto, R.E., Arisz, P.W., and Boon, J.J.: "Cellulose char structure: a combined analytical Py-GC-MS, FTIR and NMR study". Carbohydrate Research, vol.262, pp.27-47, 1994.

[30] Drift, A. van der, Doorn, J. van, and Vermeulen, J.W.: "Ten residual biomass fuels for circulating fluidized-bed gasification". Biomass and Bioenergy, vol.20(1), pp.45-56, 2001.

APPENDIX A   FUEL COMPOSITION

General properties

ECN-Phyllis ID-number	922
Classification	Untreated wood
Subgroups	Willow
Supplier	-
Type	-

		Willow chips
Proximate analysis		
Moisture (ar)	wt%	4.1
Ash (db, 550 °C)	wt%	2.1
Volatile matter (db)	wt%	82.8
Fixed carbon (db, calc.)	wt%	
Ultimate analysis (daf)		
C	wt%	50.5
H	wt%	6.1
O	wt%	39.8
N	wt%	0.89
S	wt%	0.05
Cl	wt%	0.015
F	wt%	< 0.0005
Br	wt%	ND
Calorific value (db)		
HHV	kJ/kg	20833

Elemental analysis (db, mg/kg)

Al	30	Fe	39	Pb	ND
As	1.3	Hg	ND	Sb	ND
B	9.2	K	2400	Se	ND
Ba	ND	Mg	510	Si	88
Ca	6000	Mn	8.5	Sn	ND
Cd	ND	Mo	ND	Sr	ND
Co	0.6	Na	170	Te	ND
Cr	2.9	Ni	10	Ti	1.3
Cu	3.6	P	700	V	0.2
				Zn	100

ar = as received, db = dry basis, daf = dry and ash free basis, ND = not determined
< x.xx = below detection limit

General properties
ECN-Phyllis ID-number   -
Classification   Untreated wood
Subgroups   Beech
Supplier   J. Rettenmaier & Söhne
Type   Chips, Räuchergold HBK 750/2000

		Beech chips Räuchergold HBK 750/2000
Proximate analysis		
Moisture (ar)	wt%	10.2
Ash (db, 550 ºC)	wt%	1.04
Volatile matter (db)	wt%	83.0
Fixed carbon (db, calc.)	wt%	16.0
Ultimate analysis (daf)		
C	wt%	48.8
H	wt%	6.0
O	wt%	44.5
N	wt%	0.14
S	wt%	0.017
Cl	wt%	0.005
F	wt%	< 0.0005
Br	wt%	ND
Calorific value (db)		
HHV	kJ/kg	19071

Elemental analysis (db, mg/kg)

Al	48	Fe	27	Pb	< 5.2		
As	< 0.82	Hg	< 0.013	Sb	< 0.83		
B	3.7	K	1173	Se	1.4		
Ba	11	Mg	365	Si	168		
Ca	2707	Mn	51	Sn	< 0.61		
Cd	< 0.08	Mo	< 0.84	Sr	4.4		
Co	24	Na	13	Te	ND		
Cr	< 0.49	Ni	< 0.90	Ti	1.5		
Cu	1.7	P	88	V	< 0.09		
				Zn	2.8		

ar = as received, db = dry basis, daf = dry and ash free basis, ND = not determined
< x.xx = below detection limit