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Tar Content and Composition in Producer Gas of Fluidized Bed Gasification of Wood—Influence of Temperature and Pressure

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In thermochemical biomass conversion processes, especially gasification, the tar content, and composition is a major subject. Because of the various processes examined at VUT, this work picks up the opportunity to compare the different tar amounts and its composition at different temperatures and process parameters. Gasification of biomass was carried out at the 100-kW steam-blown dual fluidized bed gasifier pilot plant III (800–870°C) and the 70-kW air-blown pressurized research unit (800–900°C; 1–5 bar) at VUT. Olivine is a catalyst for tar conversion; hence it was used as bed material in steam gasification and also in pressurized air gasification. For better understanding of tar formation during thermochemical conversion of biomass, the tar content and composition in the producer gas were analyzed with a gas chromatograph coupled with a mass spectrometer.

Basic differences between the two thermochemical conversion processes occurred especially at higher temperatures or higher pressures. The tar composition was shifted to higher molecular tars such as polyaromatic hydrocarbons. Decreasing tar amounts were found at higher temperatures or higher pressures. Therefore, in future, an optimization of gasification processes should be easier to accomplish, which means lower tar content in the producer gas, which results in a better utilization of the biomass. © 2009 American Institute of Chemical Engineers Environ Prog, 28: 372–379, 2009

Keywords: gasification, biomass, GCMS tar composition

INTRODUCTION

The global warming, the increasing CO_2 emissions, the combustion of and dependency on fossil fuels, as well as the high-energy price, have resulted in an increasing demand in renewable energy sources. Biomass, as a renewable energy source, has the potential to contribute to the future energy mix in many countries. At present, renewable energy share in the worlds' total primary consumption is about 11%; it is estimated that renewable energy share will increase to 13% by 2015 [1].

Tar occurs during the gasification process based on a series of complex thermochemical reactions. The reaction conditions are the main influence on tar formation. Tar can consist of over 100 different substances. These substances can polymerize and condense in heat exchangers or on particle filters as well as in pipes, which can lead to blockage and choking. A better understanding of tar formation during thermochemical conversion of biomass is the best way to solve these problems. This work shows the behavior of tar component concentrations at different temperatures and pressures.

At VUT, various gasification processes are investigated, and, therefore, a large data pool is available for comparison. Gasification processes were carried out at a 100-kW dual fluidized bed gasifier (DFB)

Table 1. DFB reactor parameters.

	Gasification zone	Combustion zone
Height (m)	2	5
Diameter (m)	0.31	0.15
Fuel feed	Biomass 20 kg/h dry fuel	Light fuel oil 2 kg/h
Air flow		55 SCM
Steam flow	21 SCM	
Temperatures	700° C . . . 870° C	800°C . . . 950°C
Bed material	Olivine	
Pressure	Atmospheric	

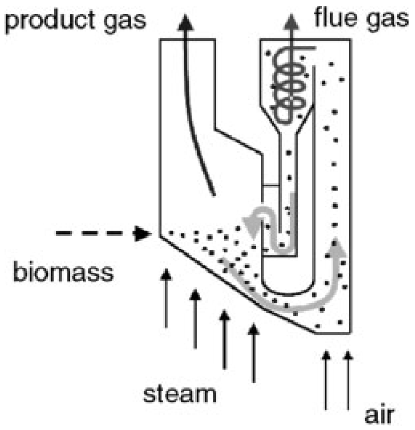

Figure 1. Scheme of DFB gasifier [3].

pilot plant and at a 70-kW pressurized research unit (PRU). In both gasifiers, olivine was used as bed material, because it is known for a catalytically activity for tar conversion [2]. The applied fuels in this study were soft wood pellets and wood chips.

EXPERIMENTAL

Dual Fluidized Bed Steam Gasification

The 100-kW DFB at VUT belongs to the group of circulating fluidized bed reactors. The basic idea of this reactor type is the separation of a steam fluidized gasification zone and an air-fluidized combustion zone. Bed material is continuously circulating between these two zones to provide the heat for gasification. Biomass is fed directly into the gasification zone (bubbling fluidized bed). To supply enough heat in the test facility, besides the gasification char, oil is also burned in the combustion zone (fast fluidized bed). Gas flows out of the gasification zone and combustion zone are measured separately; gas components beside tar are measured with a Rosemount NGA 2000, which is mainly based on infrared absorption. In Table 1, the parameters of the DFB reactor are displayed.

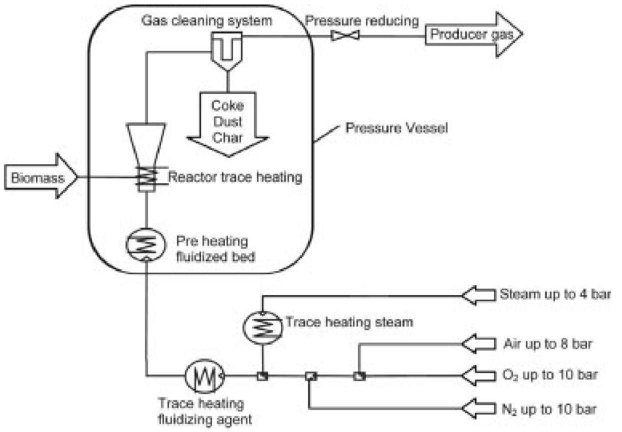

Figure 2. Simplified scheme of PRU gasifier [6].

Table 2. PRU reactor parameters [6].

	Gasifier
Height (m)	0.35
Diameter (m)	0.08
Fuel feed	Wood pellets 4 . . . 6 kg/h dry fuel
Air flow	7.2 SCM
Temperatures	700°C . . . 870°C
Bed material	Olivine
Pressure	1 bar . . . 10 bar
Temperature	750°C . . . 900°C

In Figure 1, the main principle of the DFB gasifier is shown; more technical details are found in Refs. [4, 5]. A demonstration plant (8 MWth) based on the same technology also exists in Austria, Güssing [3].

Pressurized Air Gasification

The PRU realized at the Vienna University of Technology (VUT) is able to operate at temperatures up to 950°C and pressures up to 10 bars, with a thermal fuel power of up to 70 kW at full load. The gasification supported by additional tracing takes place in a bubbling fluidized bed of a defined fluidization quality at temperatures between 750 and 950°C. All hot plant components are situated in a pressure vessel with a volume of 3.5 m^3. The producer gas is measured with the same measurement device as mentioned in Dual Fluidized Bed Steam Gasification section.

Figure 2 shows a simplified flow sheet of the PRU reactor. Detailed information on the PRU can be found in Refs. [6, 7].

Tar Definition and Nature

Hydrocarbon-containing mixtures, which can form liquid or highly viscose to solid deposits by cooling of the gaseous phase down to ambient temperature, are generally called tars. Besides carbon (C) and hydrogen (H), other organic linked elements of the used biomass like oxygen (O), nitrogen (N), or sulfur

Figure 3. Transition of tars dependent on temperature [9].

Table 3. Classification of tar based on molecular weight [12].

Tar class	Class name	Property	Representative compounds
1	GC-undetectable	Very heavy tars, cannot be detected by GC	—
2	Heterocyclic aromatics	Tars containing hetero atoms, highly water soluble compounds	Pyridine; phenol; cresols; quinoline; isoquinoline; dibenzophenol
3	Light aromatic (one ring)	Usually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility	Toluene; ethylbenzene; xylenes; styrene
4	Light PAH compounds (two to three rings)	Two and three rings compounds; condense at low temperature even at very low concentration	Indene; naphthalene; methylnaphthalene; biphenyl; acenaphthalene; fluorene; phenanthrene; anthracene
5	Heavy PAH compounds (four to seven rings)	Larger then three rings; these components condense at high-temperature at low concentration	Fluoranthene; pyrene; chrysene; perylene; coronene

(S) are also found in tar. Tars are generally assumed to be largely aromatic [8].

For the tar classification, various ways are accessible; for instance, the division in primary, secondary, and tertiary tar is shown in the work of various researchers [9–11].

So-called primary tar emerges from the pyrolysis process. The three main components of wood cellulose, hemicellulose, and lignin can be identified as source for the primary tar. Cellulose and hemicellulose, which contain a lot of oxygen, form mainly oxygen rich primary tar products like alcohols, ketons, aldehydes, or carbon acids. On the contrary, bi- and trifunctional monoaromatics mostly substituted phenols occur from lignin. Verifiable substances are, for example, phenol, dimethylphenol, and cresol. The formation temperature for those primary tars.

Because of increasing temperature and presence of an oxidant (oxygen, air, or steam), a part of the cellulose-contributed primary tars react to small gaseous molecules. The residual primary tar forms secondary tar, which are composed of alkylated mono- and diaromatics including heteroaromatics like pyridine, furan, dioxin, and thiophene. The most common reaction for transformation of primary tar into secondary tar is the elimination of small gaseous molecules. Such processes are dehydration, decarboxylation, and decarbonylation.

Over 800°C tertiary tar can be found. Tertiary tars are also called recombination or high-temperature tars. Typical tertiary tars are benzene, naphthalene, phenanthrene, pyrene, and benzopyrene (polynuclear aromatic hydrocarbons; PAH). Tertiary tar structures cannot be found in natural biomass, which was used in the experiments. They can emerge from small molecules fragments as allyl-, aryl-, and alkyl radicals, which result from homolytic cleavage of the secondary tar.

Tertiary tar can also be formed at lower temperatures and a possible mechanism is the 2 + 4 cycloaddition according to Diels–Alder, which forms additional cyclohexene rings followed by an aromatization due to dehydrogenation respectively dehydration.

Figure 3 shows the transition of tars as a function of process temperature as discussed in Ref. [9].

Another approach for classification of tars is based on molecular weight of the compounds [12] (Table 3).

Because all classifications interleave at the boundaries, there is not one true definition, but rather all classifications are an attempt for better understanding of the tar nature.

Measuring Techniques

The analysis, calculation, and sampling for GCMS tar follows the method described in Ref. [13], which is used as guideline at the VUT.

The method has been adopted for the possibilities and needs based on [14]. The applied method is used to measure the dust, entrained char, and tar content in a gas stream together with the water content. The principal fundamentals are the impinger method. For tar measurement, a gas stream is isokinetically taken for a certain period of time. Before every sampling,

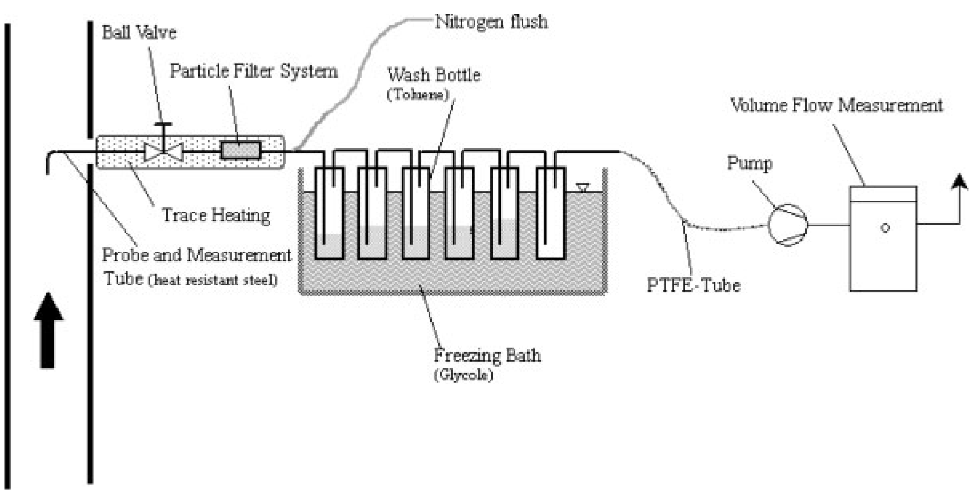

Figure 4. Tar sampling scheme [4].

Table 4. Measured GCMS components combined in substance groups [15].

Substance groups	Component
Phenols	Phenol; 2-methylphenol; 4-methylphenol; 2,6-dimethylphenol; 2,5-dimethylphenol; 2,4-dimethylphenol; 3,5-dimethylphenol; 2,3-dimethylphenol; 3,4-dimethylphenol; 2-methoxy-4-methylphenol; catechol
Furans	Benzofuran; 2-methylbenzofuran; dibenzofuran
Aromatic compounds	Phenylacetylene; styrene; mesitylene; indene
Aromatic nitrogen compounds	Isoquinoline; indole; carbazole; quinoline
Naphthalenes	Naphthalene; 2-methylnaphtalene; 1-methylnaphtalene
Polyaromatic hydrocarbons (PAH) (without naphthalenes)	Biphenyl; acenaphtylene; acenaphtene; fluorene; anthracene; phenanthrene; 4.5-methylphenanthrene; 9-methylanthracene; fluoranthene; pyrene; benzo[a]anthracene; chrysene; benzo[b]flouranthene; benzo[k]flouranthene; benzo[a]pyrene; benzo[g,h,i]perylene; indeno[1,2,3-cd]pyrene
Guaiacols	guaiacol; eugenol; isoeugenol

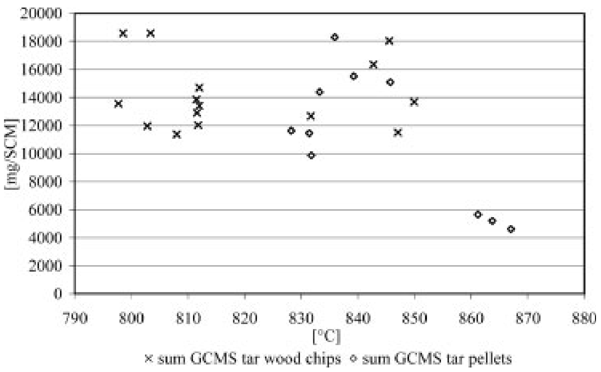

Figure 5. Temperature dependency of sum GCMS tars of wood chips and pellets.

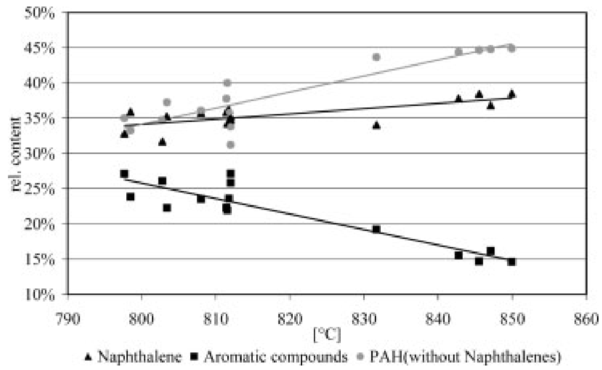

Figure 6. Wood chips: relative content of naphthalenes, aromatic compounds, and PAH*.

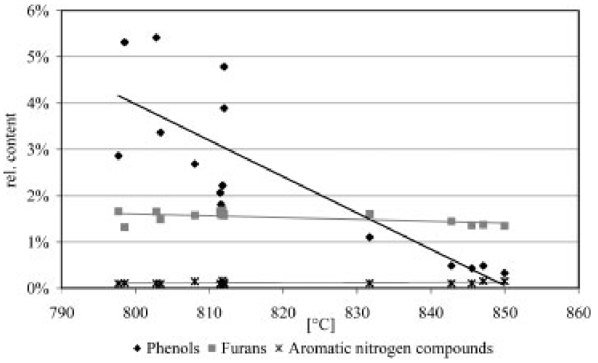

Figure 7. Wood chips: relative content of phenols, furans, and aromatic nitrogen compounds*.

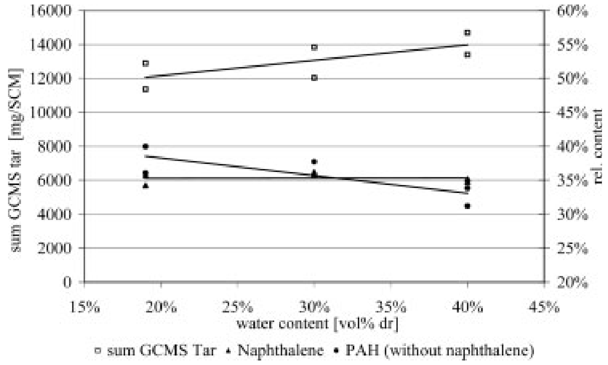

Figure 8. Dependency of water content and sum GCMS tars as well as relative content of naphthalenes and PAH [16]*.

the probe is flushed with nitrogen for cleaning purposes.

The gas enters the heated-sampling line, which consists of a cyclone and a glass wool filled filter cartridge, where dust is separated. Afterward, the gas is led through six impinger bottles. The impinger bottles are filled in total with 500 mL of toluene (50 mL, 100 mL, 100 mL, 100 mL, 150 mL, and 0 mL). For better condensation and absorption, the impinger bottles are situated in a cooling pond, which is cooled down to −10°C by a cryostat (ethylene–glycol). Generally, in the first impinger bottle, the aqueous phase condenses. A scheme of the tar-sampling system is shown in Figure 4.

The liquid phases in the impinger bottles are unified, and the aqueous phase is separated from the toluene phase. The amount of toluene is determined, and a 10-mL sample is taken for GCMS analysis.

Additionally, the dust has to be extracted to gain a total amount of the GCMS tar. For this purpose, a soxhlet extraction with isopropanol (IPA) is carried out. A 10-mL GCMS sample of the IPA phase is taken.

GCMS Equipment

The GCMS consists of an Autosystem XL GC (manufacturer: Perkin Elmer) and a TurboMass MS (manufacturer: Perkin Elmer) with positive electron impact ionization. The oven temperature program starts at an initial temperature of 60°C and ends at 290°C with various temperature ramps in between. The GC column is a DB-17MS MS-capable capillary column (Agilent). The capillary column has a length of 30 m, an inner diameter of 250 μm, and a film thickness of 5 μm. To quantify the different substances, selected ion recording is used as scanning mode.

GCMS Tar Analysis

All samples were diluted, this means that to 500 μL of the sample 480-μL solvent and 20-μL internal standard (1,2,3,4-tetrahydronaphthalene) were added.

For a better and easier interpretation of the results, the measured components were combined to substance groups [15] shown in Table 4. The substance groups were chosen due to the related chemical structure and properties as well as formation groups.

RESULTS AND DISCUSSION

Tar Content and Composition in Producer Gas of DFB Steam Gasification

All results presented in chapter 3 are referred to dry producer gas. The fuels wood chips and wood pellets show similar total tar contents at the same temperature. At temperatures from 798 to 867°C, the sum of GCMS tars ranges between 4500 and 18,500 mg/SCM. A slightly decrease of tar concentration can be recognized at temperatures up to 850°C, higher temperatures cause a more significant decrease (see Figure 5).

Wood Chips

As shown in Figure 6, the main components at gasification of wood chips are the tertiary tars naphthalenes and PAH as described in Tar Definition and Nature section. Because of the tar formation process, at higher temperatures, the relative content of those two substance groups increases. On the opposite, the relative content of the groups aromatic compounds (see Figure 6), phenols, and furans (see Figure 7) decrease at the displayed temperature range (798–850°C). The relative low content of aromatic nitrogen compounds (see Figure 7) shows no significant temperature dependency at the investigated temperatures.

The fuel water content has an effect on the tar composition and content (see Figure 8) but compared to the temperature dependency the influence is insignificant.

Wood Pellets

The relative content of naphthalenes increases with increasing temperature (828–867°C), while the aromatic compounds slightly decrease. The PAHs (without naphthalenes) show an unexpected behavior, because their relative concentration is decreasing at higher temperatures (above 860°C; Figure 9). To clarify these results, further investigations are neces-

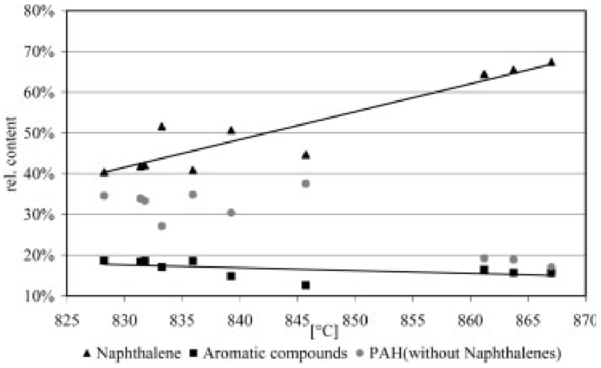

Figure 9. Wood pellets: relative content of naphthalenes, aromatic compounds, and PAH [17]*.

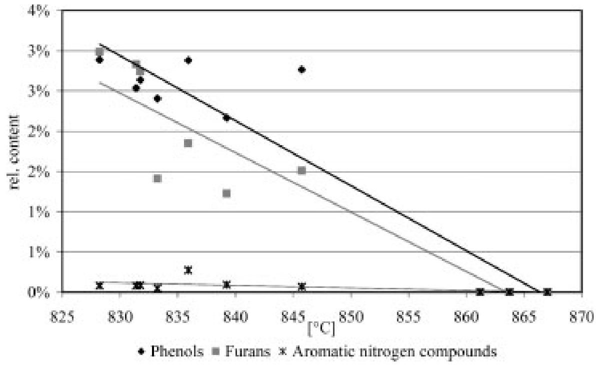

Figure 10. Wood pellets: relative content of phenols, furans, and aromatic nitrogen compounds [17]*.

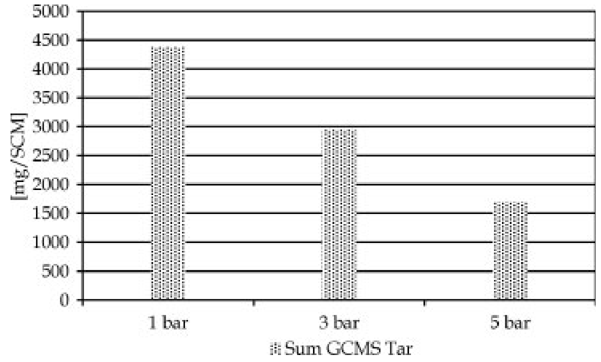

Figure 11. Sum GCMS tars at 1, 3, and 5 bar at 825°C.

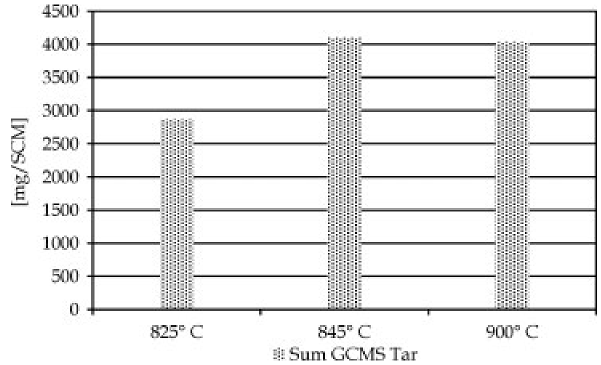

Figure 12. Sum of GCMS tars at 825°, 845°, and 900°C at 5 bar.

sary. In Figure 10, the temperature behavior of phenols, furans, and aromatic nitrogen compounds is shown. The relative content approaches nearly 0% at temperatures above 860°C.

Tar Content and Composition of PRU Air Gasification

Figure 11 displays tar concentrations and its interdependency of pressure. The tar content declines from 4500 to 1700 mg/SCM with increasing pressures of 1–5 bar at 825°C. On the other side, Figure 12 shows the tar content behavior at increasing temperatures and same pressure (5 bar). The graph points out an increase of the tar content at ascending temperatures. This can be partly explained by different fluidization parameters as it was not possible to vary only the temperature and to keep all other parameters constant. Especially, the residence time is one of these parameters, which cannot be controlled absolutely. With increasing pressure, the gas speed is decreasing due to density influence of pressure on the gaseous phase. Therefore, the residence time is increasing, and the connected tar content is decreasing (see Figure 11). If the temperature is increasing at same pressure, the gas speed is increasing, and therefore the residence time is decreasing by what the tar content is increasing (see Figure 12). This incident is a good example for the difference between scientific experience with thermodynamics and the complex impact that construction of plants gives on different reactions.

The tar composition at 5 bar is displayed in Figure 13 and at 3 bar in Figure 14. At 5 bar (see Figure 13), a decrease of the relative content of phenols (6%–1%), furans (4%–2%), and aromatic compounds (19%–14%) with rising temperatures is recognizable as well as an increase of PAHs (20–26%). Naphthalenes show no relevant influence of the temperature at 5 bar. With increasing temperatures at 3 bar (see Figure 14), the relative naphthalenes content rise from 46 to 75% and the PAH concentration slightly declines from 20% to 18%. The other substance groups as phenols (3%–1%), furans (5%–1%), and aromatic compounds (24% to 5%) show the same interdependency as at 5 bar.

Producer Gas Composition

The producer gas composition for wood chips and pellets of steam gasification as well as pressurized air gasification of wood pellets is displayed in Table 5.

H_2 and CO concentrations rise with increasing temperatures and CO_2 and CH_4 decline at DFB steam

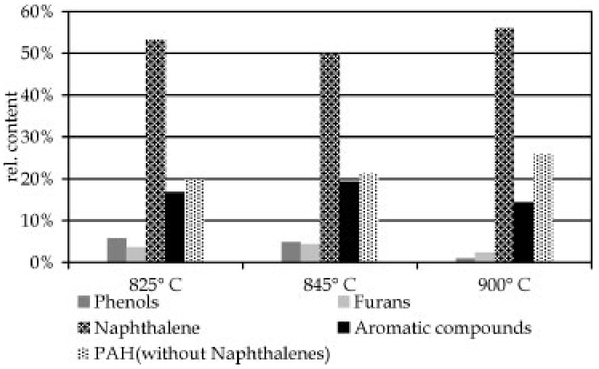

Figure 13. Tar composition at 5 bar and 825°, 845°, and 900°C

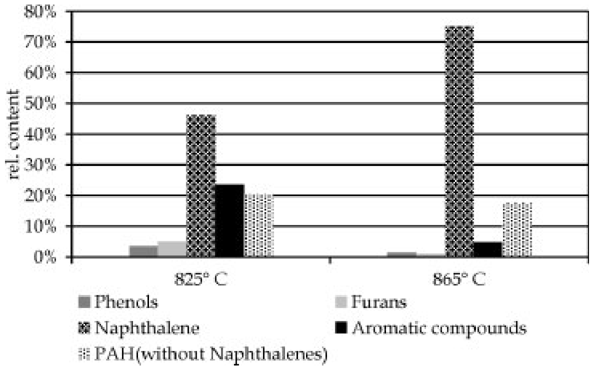

Figure 14. Tar composition at 3 bar and 825° and 865°C.

gasification. Same effects are observable in PRU gasification. With rising pressure, different effects occur, CO_2 is rising and CO decreasing, and the change in CH_4 and H_2 concentration is insignificant at pressures from 1 to 5 bar. More details of the DFB producer gas composition can be found in Ref. [16], and further information of the PRU producer gas composition is mentioned in Ref. [6].

CONCLUSION

At VUT, the tar compositions and concentrations have been observed over a long period of time and for different processes. Hence, the authors have picked up the opportunity to summarize and analyze those results. For this work, results form a 100-kW DFB gasifier and the 70-kW PRU both situated at VUT laboratories were chosen.

The tar content is a major quality characteristic for the use of gasification producer gas. As shown in this work, temperatures and pressures have a significant influence on tar concentration. For example, the tar content of the DFB producer gas declines about 13.7 g/SCM at a temperature range from 798 to 867°C. A rise in pressure (1–5 bar) also leads to a notable decrease of tar concentrations in PRU producer gas from 4.4 to 1.7 g/SCM. In the examined gasification processes, naphthalenes are the main substances, which can be explained due to the tar formation pathways. In this work, it is shown that the relative content of naphthalenes is significantly rising with temperature in steam gasification as well as at pressurized gasification at 3 bar. The main primary tar components (phenols) as well as the main secondary aromatic tars are in most cases declining with rising temperature and/or pressure.

Table 5. Main components of producer gas of DFB and PRU.

Gas components	DFB [vol % dr]	PRU [vol % dr]
N_2	—	38.6−66.3
CO	17.6−25.7	8.8−22.0
CO_2	18.9−28.7	14.6−18.2
CH_4	8.4−11.5	2.9−5.9
H_2	31.8−42.4	5.8−20.4

Also, it is seen that parameters like pressure and temperature have influence on the product gas composition in many ways. If the oxygen to fuel ratio as the fluidization gas flow stay the same, temperature and pressure affect the gas speed and therefore depending on the gasifier construction impact the tar contend in the producer gas.

These results give a further insight into tar composition and formation. Experience at VUT shows that results for plants of this small size are representative also for larger gasification plants of the same type, and, therefore, extremely valuable for up scaling of gasification processes [18].

NOMENCLATURE

SCM	Standard cubic meter; 1013 mbar; 20°C
vol % dr	Volume percent on dry basis
PAH	Polyaromatic hydrocarbons without naphtalenes
GCMS	Gas chromatograph coupled with a mass spectrometer

SYMBOL

*	Lines in the diagrams should only be seen as help for the reader and do not indicate a linear relationship

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