

Tar Content and Composition in Producer Gas of Fluidized Bed Gasification and Low Temperature Pyrolysis of Straw and Wood – Influence of Temperature

I. Aigner, U. Wolfesberger, H.Hofbauer*

*Vienna University of Technology (VUT), Institute of Chemical Engineering
Getreidemarkt 9/166, A-1060 Vienna, Austria*

ABSTRACT

The global warming, the increasing CO₂ emission, 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 various ways.

In thermo-chemical biomass conversion processes, especially gasification and pyrolysis, the tar content and its composition is a major subject. Due to the various processes examined at VUT, this work picks up the opportunity to compare the different tar amounts and compositions at different temperatures and process parameters. The tar content and composition in the producer gas of steam gasification of straw and wood as well as the tar yields of low temperature pyrolysis of straw are displayed in the following work.

Gasification experiments were carried out in a 100 kW dual fluidized bed steam gasifier at a temperature range of 700° C to 870° C. Pyrolysis experiments were conducted in a rotary kiln reactor at temperatures between 600° C and 630° C.

For better understanding of tar formation during thermo-chemical conversion of biomass the tar content and composition in the producer gas was analyzed with a gas chromatograph coupled with a mass spectrometer.

Main observation was that at higher temperatures the tar composition is shifted to higher molecular tars as poly aromatic hydrocarbons (PAH). Key tar components at lower temperatures (pyrolysis) are phenols. These results give the opportunity to analyse tar formation in different thermo-chemical conversion steps, therefore, for the future a better understanding of tar formation in large scale facility's should be gained. This means lower tar content in the producer gas for gasification processes and an achievement of required pyrolysis oil yields for pyrolysis. This should lead to higher process efficiencies, in both biomass conversion processes.

Keywords: Pyrolysis, Straw, Biomass, GCMS Tar, Gasification

1. INTRODUCTION

Worlds energy demand, as well as CO₂ emission are increasing rapidly. For the future a reduction of greenhouse gas emissions is a major goal of many countries. Processes like biomass gasification and pyrolysis uses a renewable energy carrier. At present renewable energy share in the worlds total primary consumption is about 11 %, it is expected that the renewable energy share will increase to 13 % by 2015[1]. To optimize both processes research has to be done in many fields. This work should be one step to clarify the difficult subject of tar formation during these processes. Over many years results of different conversion processes have been collected at the VUT and can be displayed in this work now.

The knowledge of tar formation is essential for process stability, as tar condenses and polymerizes in pipes and filters and therefore leads to blockage. In gasification tar reduction is the major goal and in pyrolysis normally maximum pyrolysis oil yields are desired. Tar formation is based on a series of complex thermo chemical reactions. The reaction conditions have a strong influence on tar formation. Tar can consist of over 100 different substances. This work shows the influence of different temperatures on tar component concentrations.

For the steam gasification wood pellets and wood/straw pellets mixtures were used as fuel and olivine as bed material, which is known for its catalytically activity [2]. In the pyrolysis process indoor stored straw was used as fuel.

2. EXPERIMENTAL

2.1. Dual Fluidized Bed Steam Gasification

The 100 kW dual fluidized bed gasifier (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 char in the bed material also oil is added and burned in the combustion zone (fast fluidized bed). Gas flows into the gasification zone and into the combustion zone are measured separately. The main 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.

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

Table 1 DFB reactor parameters

	Gasification zone	Combustion zone
Height [m]	2	5
Diameter [m]	0,31	0,15
Fuel feed	Biomass	Light fuel oil (Auxiliary fuel)
Air flow	20 kg/h dry fuel	2 kg/h
Steam flow	21 SCM	55 SCM
Temperatures	700° C...870° C	800° C...950° C
Bed material	Olivine	
Pressure	Atmospheric	

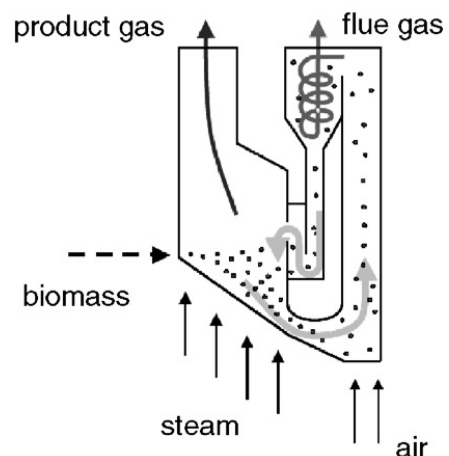


Fig. 1 Scheme of DFB gasifier [5]

2.2. Low Temperature Pyrolysis Biomass Pilot Plant

The pyrolysis tests were conducted in an indirect heated rotary kiln reactor at the low temperature pyrolysis biomass pilot plant Dürnröhr (EVN). The heat needed in the rotary kiln reactor is supplied indirectly over the reactor wall. The pyrolysis gas temperature at the outlet of the rotary kiln is between 450° C and 650° C. The reactor is a cylindrical vessel, inclined slightly to the horizontal, which rotates slowly around its axis. As the reactor rotates, material gradually moves down towards the lower end, and may undergo a certain amount of stirring and mixing. This reactor is typical used for low temperature pyrolysis because of the longer residence times and an unproblematic continuous feeding and discharge of the solid components. The applied fuel was indoor stored wheat straw. Further technical information is found in [6].

2.3. Tar Definition and Nature

Generally, tars are hydrocarbon containing mixtures, which can form liquid or highly viscous to solid deposits by cooling of the gaseous phase down to ambient temperature. Besides the main

elements carbon (C) and hydrogen (H) other elements like oxygen (O), nitrogen (N) or sulfur (S) are found in tar. Tars are generally assumed to be largely aromatic [7].

For the tar classification various ways are accessible, for instance the division in primary, secondary and tertiary tar shown in the work of various researchers [8 - 10].

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 e.g. phenol, dimethylphenol and cresol. The formation temperature for those primary tars lies between 200° - 500° C.

Due to 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 tars form secondary tar, which are composed of alkylated mono- and diaromatics including heteroaromatics like pyridine, furan, dioxin and thiophene.

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 be also 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 2 shows the transition of tars as a function of process temperature as discussed in [8].



Fig. 2 Transition of tars dependent on temperature [8]

Another approach for classification of tars is based on molecular weight of the compounds [11] summarized in table 2.

Table 2 Classification of tars based on molecular weight [11]

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 (1 ring)	Usually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility	Toluene; ethylbenzene; xylenes; styrene
4	Light PAH compounds (2-3 rings)	2 and 3 rings compounds; condense at low temperature even at very low concentration	Indene; naphthalene; methylnaphthalene; biphenyl; acenaphthalene; fluorene; phenanthrene; anthracene
5	Heavy PAH	Larger then 3 rings; these	Fluoranthene; pyrene;

compounds (4-7 rings)	components condense at high-temperature at low concentration	chrysene; perylene; coronene
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Since 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.

2.4. Measuring Techniques

The analysis, calculation, and sampling for GCMS tar follows the method described in [12], which is used as guideline at the VUT. In Figure 3 the main principle of the tar sampling is shown, detailed information can be found in [13].

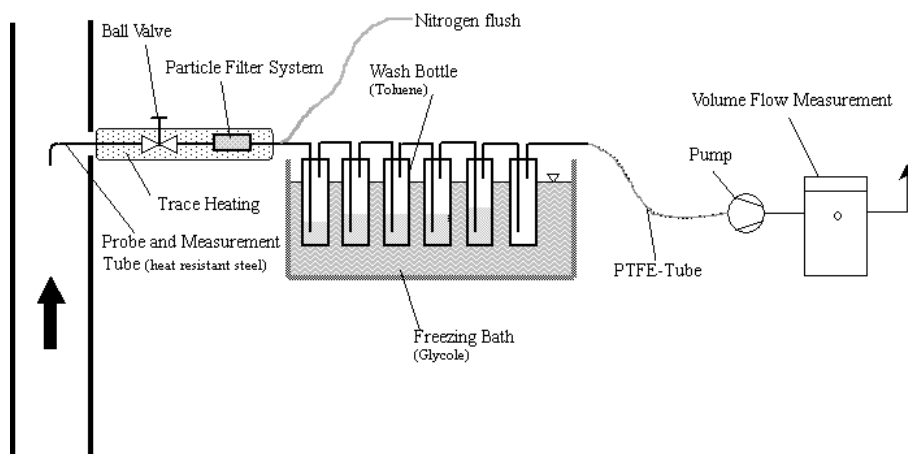


Fig. 3 Tar sampling scheme [4]

2.4.1. 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 (manufacturer: 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 (SIR) is used as scanning mode.

2.4.2. GCMS Tar Evaluation

For a better and easier interpretation of the results the measured components were combined to substance groups [6] shown in table 3. The substance groups were chosen due to the related chemical structure and properties as well as formation groups.

Table 3 Measured GCMS components combined in substance groups [6]

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-Methylnaphthalene; 1-Methylnaphthalene

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

3. RESULTS AND DISCUSSION

3.1. Tar Content and Composition in Producer Gas of DFB Steam Gasification

The steam gasification experiments were carried out with different fuels. Because of the low ash melting point of straw, only straw/wood mixtures could be gasified at temperatures above 700°C. Two different kinds of mixtures were used. On the one hand wood pellets and straw pellets were fed separately in the gasifier (mixture ratio 13% straw/87% wood Fig. 4, experiment numbers 1 – 3, Fig. 7). On the other hand pellets containing straw and wood were used (mixture ratio 20% straw/80% wood and 40% straw/40% wood Fig. 4, experiment numbers 4 – 11, Fig. 7). Figure 4 displays the average tar content in steam gasification producer gas and the corresponding gasification temperature. Lower tar contents are recognized for mixtures with straw and wood. It can be seen also that the kind of mixture (direct or mixed pellets) is an insignificant influence compared to the temperature.

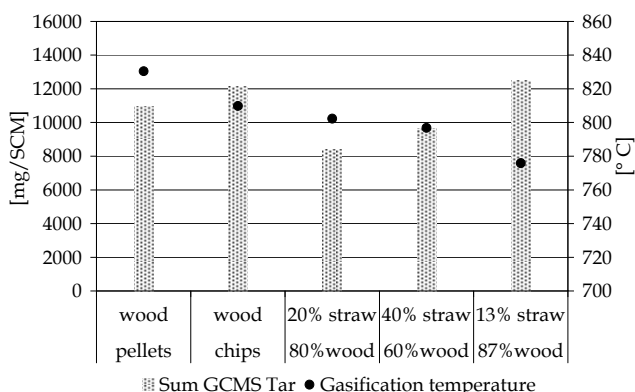


Fig. 4 Average sum of GCMS tar content for wood and different straw wood mixtures during gasification

Wood Chips – Tar Composition

Wood chips in the size of 11 – 20 mm were gasified at different temperatures. The resultant change of the relative tar content is seen in Figure 5 and Figure 6 [14]. The relative contents of naphthalenes and PAHs are significantly increasing and the relative contents of aromatic compounds and phenols are decreasing. Due to tar formation theories (Fig. 2) this trend was expected.

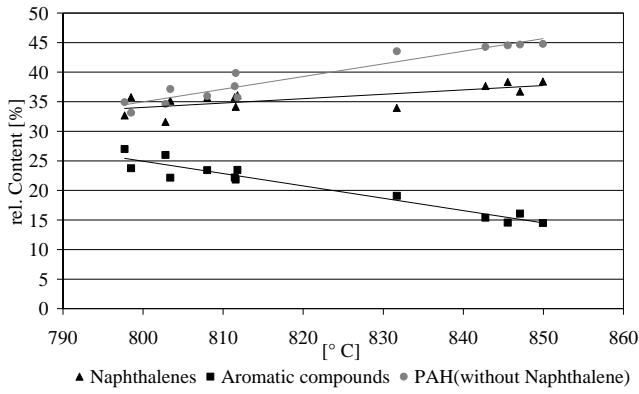


Fig. 5 Relative content of naphthalenes, aromatic compounds and PAH for wood chips [14]

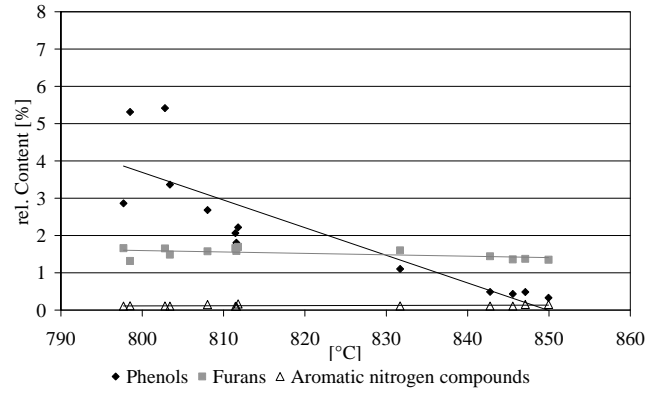


Fig. 6 Relative content of phenols, furans and aromatic nitrogen compounds for wood chips [14]

Straw / Wood Pellets Mixtures – Tar Composition

Different straw mixtures were gasified at temperatures between 755° C and 803° C. Figure 7 shows no significant change in the relative tar content. The main influence is the temperature, which is shown in experiments 1 to 3 (Fig. 7).

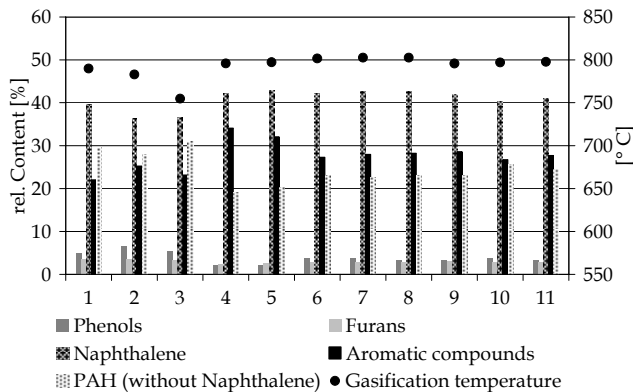


Fig. 7 Relative content of GCMS substance groups for mixtures of straw and wood

Table 4 displays the main experimental parameters which are the type of fuel and temperature for the experiments shown in Figure 7.

Table 4: Experimental parameters for Figure 7; * Percent of nominal power

Experiment number	1	2	3	4	5	6	7	8	9	10	11
Fuel	87 %* Wood pellets 13 %* Straw pellets	Mix pellets	Mix pellets	80 %* Wood 20 %* Straw	Mix pellets	Mix pellets	80 %* Wood 20 %* Straw	Mix pellets	Mix pellets	60 %* Wood 40 %* Straw	Mix pellets
Gasification temperature	789	783	755	796	797	802	803	803	796	797	798

More information about the producer gas composition for smaller molecules like CO, CO₂, H₂, CH₄, and higher gaseous hydrocarbons can be found in [14 - 16].

3.2. Tar Content and Composition of Low Temperature Pyrolysis

In Figure 8 the temperature dependency of the sum of GCMS tars is displayed. During pyrolysis operation the sum of the GCMS tars ranges between 27-42 g/SCM.

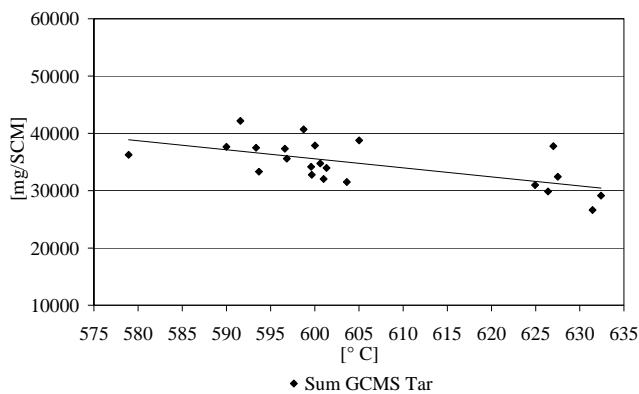


Fig. 8 Temperature dependency of sum GCMS tars for straw during pyrolysis [6]

Due to the lower temperature and the lack of a gasification agent the tar contents obtained in pyrolysis are extremely higher than in gasification producer gas. As observed for gasification also a decrease in the tar content with increasing temperatures is noted (Figure 8).

Figure 9 and 10 show the relative tar composition of pyrolysis producer gas at a temperature range from 578° C to 632° C.

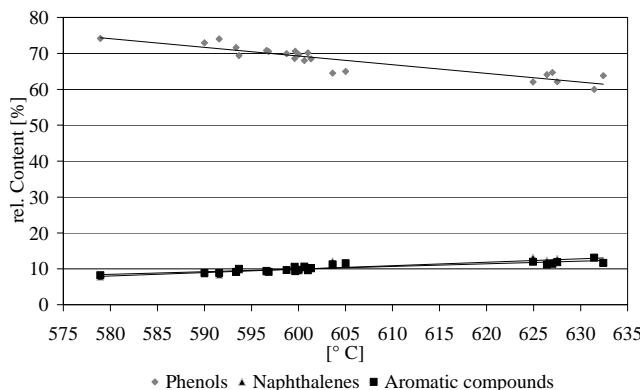


Fig. 9 Temperature dependency of relative tar content of phenols, naphthalenes and aromatic compounds for pyrolysis of straw [6]

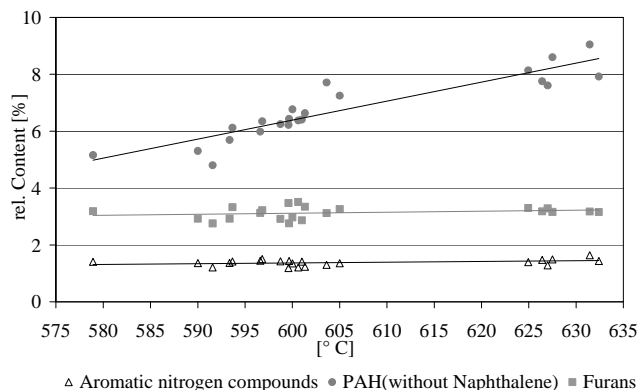


Fig. 10 Temperature dependency of relative tar content of aromatic nitrogen compounds, PAH and furans for pyrolysis of straw [6]

The decrease of the phenols (Figure 9) with increasing temperature can be explained by the primary tar transition to secondary tar, thus a reduction of the phenols. In Figure 10 a slight decrease of higher pyrolysis gas temperature of the furans and aromatic compounds with nitrogen can be observed. The explanation for this decrease is similar to the phenols reduction.

On the contrary, an increase in the amount of aromatic compounds, naphthalenes (Figure 9) and PAHs can be observed (Figure 10). This increase occurs at higher temperatures because secondary tars (aromatic compounds) as well as tertiary tars (naphthalenes and PAHs) are formed at these temperatures.

3.3 Comparison of Tar from Gasification with Tar from Pyrolysis

As expected the tar composition in pyrolysis producer gas is different from the tar composition in steam gasification. The main pyrolysis producer gas component, phenols, is only a by-product at gasification. The reason is – as mentioned before – that phenols are a primary tar component, which is reformed to smaller (gaseous) or larger components at higher temperatures.

At pyrolysis temperatures from 600° C to 630° C a slight increase of aromatic compounds is noted, whereas at gasification temperatures from 800° C to 850° C the relative content of aromatic compounds is decreasing again. Aromatic compounds are mainly secondary tars which begin to

form during pyrolysis. If a reaction partner is available and the temperature is increasing to higher temperatures (800° C – 850° C), mainly tertiary tars, as naphthalenes and PAH, are formed. Therefore, the higher concentration of naphthalenes in gasification producer gas, as well as their increase with rising gasification temperatures, is a logical consequence.

Figure 11 shows the average tar composition for straw pyrolysis and wood/straw steam gasification. For each process two typical temperatures were chosen.

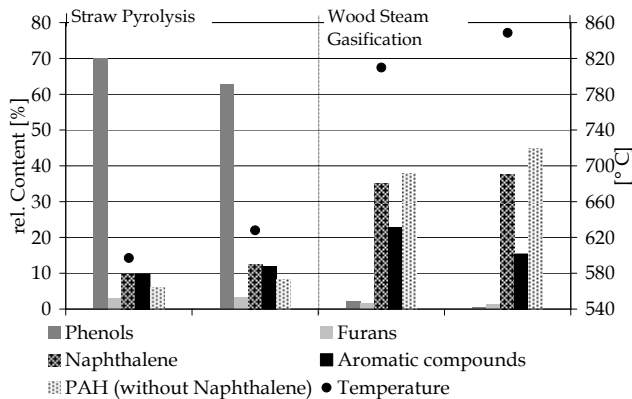


Fig. 11 Comparison of relative tar composition of pyrolysis and steam gasification at different temperatures [6][14]

In average the relative concentration of furans stays the same for gasification and pyrolysis as shown in Figures 12 and 13. The concentration of aromatic nitrogen compounds is relatively low with only one percent in pyrolysis producer gas, and no aromatic nitrogen compounds are found in gasification.

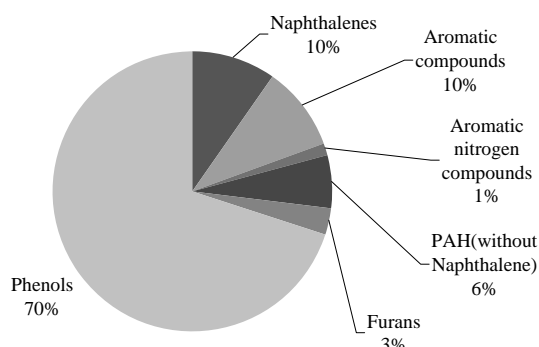


Fig. 12 Average tar composition in pyrolysis producer gas [6]

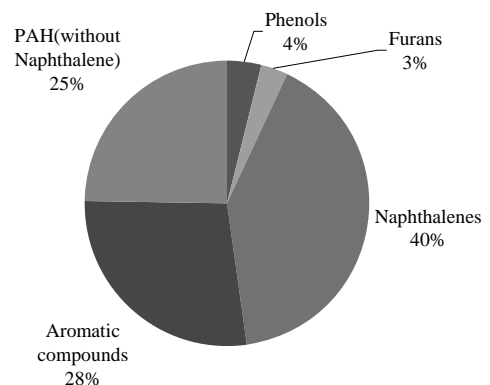


Fig. 13 Average tar composition in steam gasification producer gas [14]

4. CONCLUSION

At Vienna University of Technology (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 from a 100 kW dual fluidized bed (DFB) gasifier and a low temperature pyrolysis biomass pilot plant were chosen.

The tar content in steam gasification producer gas is a major influence factor in producer gas quality. On the other hand the tar yields in pyrolysis vapors are essential for pyrolysis processes. Therefore, the tar formation, tar contents, and tar composition at different process conditions are important features for these processes and thus an important research field.

Main tar components for wood gasification as well as for wood-straw co-gasification are naphthalenes. Their relative content is rising with increasing temperatures.

In pyrolysis phenols are the main components (60 % – 75 %). Phenols as primary tars are known to occur at low temperatures (Fig. 2). With increasing temperatures the phenols are decreasing, and with a reaction partner they are reduced further to less than 5 % relative content at gasification producer gas.

These results give an excellent insight into tar composition and formation. Further 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 [17]. For pyrolysis more studies are carried out currently and new results in this field can be expected within the next years.

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