Biomass Gasification in an Air-Blown Down-Draft Gasifier: Determination of Tar Compounds from Producer Gas

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The existence of tar compounds in producer gas is one of the major problems found in biomass gasification; these compounds need to be removed before the producer gas can be used. In order to predict the need for producer gas cleaning for catalytic conversion into traffic fuels and chemicals, the gas has to be accurately characterised and defined. In this study, tar compounds from producer gas of two small-scale downdraft gasifiers were collected, identified, and quantified. Based on the results, there were several tar compounds present in the gas flow. Toluene and naphthalene were the most abundant compounds, totalling more than 70% of the total volume of tars while tar concentration levels were in the range of 200 to 400 mg/Nm^3. These concentrations were found to be consistent with values presented for similar-type gasifiers using wood chips.

Keywords: Gasification; Tar; Analysis; Sampling; Down-draft gasifier; Producer gas

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INTRODUCTION

Biomass-based alternatives for energy production are being intensively researched and developed to replace the use of fossil fuels. Biomass is regarded as a renewable material for the production of energy (heat and power), but also as a significant resource for traffic fuels and chemicals produced by catalytic conversion.

Biomass gasification, which can be defined as the thermal treatment of biomass under a restricted supply of oxygen, is one possibility for the conversion of biomass into a useful platform, producer gas, and further to convert purified gas into fuels and chemicals. Synthesis gas is made from producer gas obtained *via* gasification by cleaning the gas to purification levels necessary for each specific application. The resulting producer gas contains CO, H_2, CO_2, and N_2 as its main compounds, in addition to contaminants or impurities such as organic compounds, halides, sulfuric compounds, and alkali metals (Knoef 2005).

Tars are one group of organic compounds present in the producer gas *via* biomass gasification (especially lignocellulosics such as wood chips and pellets). During the gasification process, tar compounds are formed by thermal degradation and conversions of the main components of wood, *i.e.* cellulose, hemicellulose, and lignin. The chemical composition and concentration of tar compounds is dependent on several factors such as the structure of the gasifier, gasification conditions (temperature, feed rate *etc.*), and biomass quality (Knoef 2005; Monteiro *et al.* 2007; Milne and Evans 1998). Tars are defined as organic compounds, mostly aromatic, having a molecular weight higher than that of benzene (Monteiro *et al.* 2007; Milne and Evans 1998). They can be classified according to their chemical composition into five different groups as presented in Table 1. During the gasification processes tar compounds undergo maturation as described in Table 2.

Table 1. Classification of Tars (Knoef 2005; Monteiro *et al.* 2007; Milne and Evans 1998)

Tar class	**Classification**	**Tar compounds**
Class 1	GC undetectable	Very heavy, 7 and higher ring compounds
Class 2	Heterocyclic aromatics	Cyclic hydrocarbons with heteroatoms, highly water soluble, *e.g*. phenol, cresol, and pyridine
Class 3	Light aromatics	Compounds that usually do not cause problems as a result of condensation or water solubility, *e.g*. toluene, styrene, and xylene
Class 4	Light polyaromatics	2 and 3 ring compounds that condense at intermediate temperatures at relatively high concentrations, *e.g.* naphthalene, phenanthrene, and anthracene
Class 5	Heavy polyaromatics	4-6 ring compounds that condensate at high temperature and low concentrations, *e.g*. fluoranthrene, pyrene, chrysene, perylene, and benzoperylene

Most of the gasification processes are unique because of the biomass and gasification conditions used. Therefore tar compounds must be identified and quantified for each type of gasifier individually. A more detailed study on the formation of tars has been presented by Milne and Evans (1998).

Table 2. Formation and Maturation of Tar-compounds at Different Gasification Temperatures (Milne and Evans 1998)

Mixed oxygenates	→	Phenolic esters	→	Alkyl phenolics	→	Heterocyclic esters	→	PAH	→	Larger PAH
400 °C		500 °C		600 °C		700 °C		800 °C		900 °C

The maximum allowable level of tar in synthesis gas depends on the final use of the gas. Milne and Evans have reported limit levels for some applications for various devices: for example, tar concentrations less than 500 mg/Nm^3, 50 mg/Nm^3, and 5 mg/Nm^3 are recommended for compressors, internal combustion systems, and direct-fired industrial gas turbines, respectively. For catalytic methanol synthesis, the content of tar is required to be below 0.1 mg/Nm^3 (Milne and Evans 1998).

The presence of tars in the producer gas and later in the purified synthesis gas is harmful. Tar compounds can affect the gasification equipment and gas purification and catalytic conversion units in a number of ways. Heavier tars are known to polymerise at elevated temperatures in the reactors, causing the clogging of tubing (Knoef 2005; Monteiro *et al.* 2007; Milne and Evans 1998), the main culprits being heavy polyaromatic compounds. These tar compounds form condensates at rather high temperatures even at low concentrations. Moreover, tar can affect the catalyst used by lowering the catalytic activity or completely blocking the catalyst by the formation of carbon-containing substances at the surface of the catalyst. These mechanisms of catalyst deactivation are mostly irreversible. (Shen and Yoshikawa 2013; Ruiz *et al.* 2013)

Most of the catalysts used in the catalytic conversion of synthesis gas are sensitive to contamination by impurities present in the gas. In order to eliminate this problem, gas quality must be characterised, and based on these results, proper cleaning steps necessary for each individual gasifier must be developed. Identification of the components present in the gas and the determination of tar concentrations are most essential for further use of the gas (Monteiro *et al.* 2007; Milne and Evans 1998; Shen and Yoshikawa 2013).

A number of methods are available for the determination of tar compounds. Most of these include absorption of the tars into liquid or a solid phase followed by chemical analysis, chromatographic (gas or liquid chromatography) and gravimetric methods (heavier tars), and to some extent spectrometric methods have also been applied (Brage *et al.* 1997). A validation and optimisation of tar sampling and analysis methods have been performed and published as the Tar Protocol (Good *et al.* 2005).

Many publications describing the mechanism of tar formation and determination of tars in gasification processes have been published. Most of these studies are, however, performed on large-scale gasifiers based on the fluidized-bed type (size 10 to 300 MW). On the other hand, when it comes to small scale, fixed-bed gasifiers (50 to 200 kW), there is little data available on the various tar levels present in the producer gas. Downdraft gasifiers have, in some studies, been reported to produce much lower amounts of tars, 200 to 400 mg/m^3 (Xu *et al.* 2010; Gautam *et al.* 2011), compared to fluidized-bed and updraft gasifiers (Warnecke 2000). For fluidized bed gasifiers, tar levels ranging from 1 to 65 g/m^3 have been reported (Göransson *et al.* 2011).

In this study, two small-scale (150 kWh), wood-fired and air-blown downdraft gasifiers operating at rather high gasification temperatures (1050 to 1200 ºC) were studied in order to obtain more information on the composition of tar and concentrations of individual components present in the producer gas from this type of gasifier. Another aim of this study was to get preliminary information of the cleaning steps needed to purify the producer gas prior to the catalytic production of fuels by the Fischer-Tropsch synthesis method. Tar samples were collected; then the components were separated, identified, and quantified.

EXPERIMENTAL

Gasifiers and Experimental Set-up

Gas sampling was performed in duplicate from two different down-draft gasifiers of the same construction, operating at rather high gasification temperatures of 1050 to 1250 °C. These gasifiers are denoted as gasifier A and B. The producer gas from gasifier A was cleaned by passing the gas through the bed of wood chips and the samples were taken after the cleaning unit. In gasifier B, the gas was cleaned by passing it through a water scrubber while gas samples were taken from the raw gas and after the cleaning unit. A schematic diagram of the gasifiers is presented in Fig. 1. For gasifier A, the samples were only taken from sampling-port 2, whereas for gasifier B, samples were taken from sampling-ports 1 and 2.

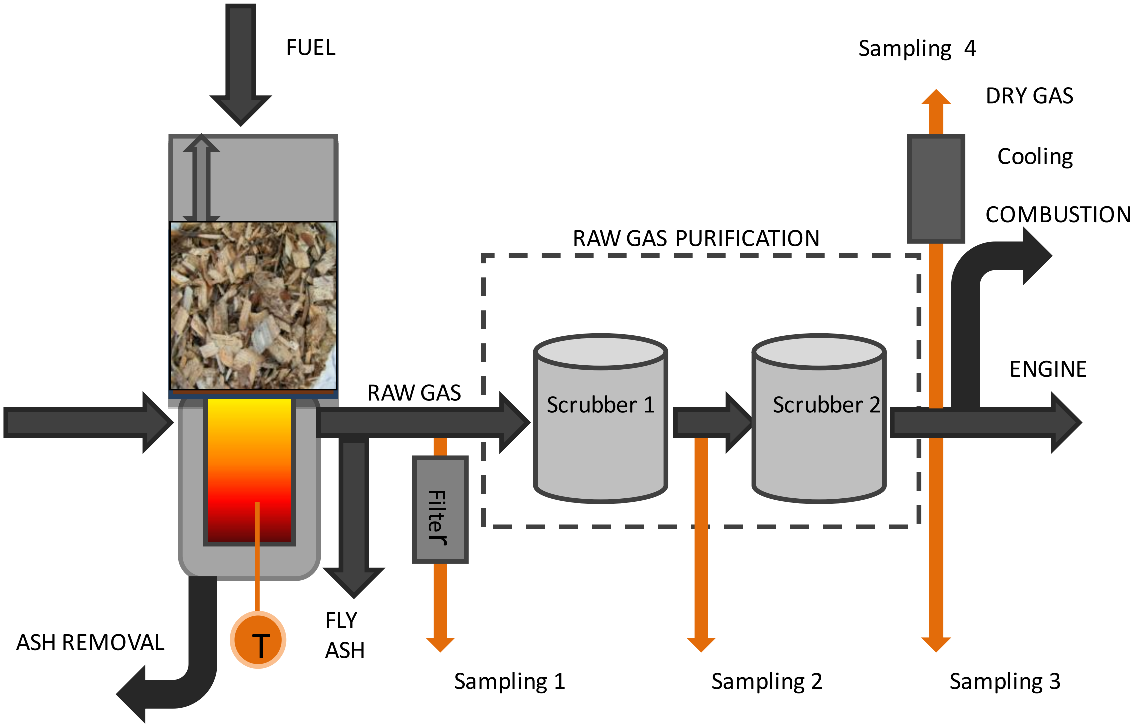

Fig. 1. A schematic diagram of the gasifiers and gas-cleaning systems studied. For gasifier A, samples were taken from sampling-port 2, whereas for gasifier B, samples were taken from sampling-ports 1 and 2.

Samples were also taken from the wood-chips used for gasification and analysed at the Finnish Forest Research Institute **(**Metla) for heat values and elemental analysis of H, C, N, and metals. H, C, and N were analysed using specific elementary analysers, while metals in the samples were analysed by ICP-MS after microwave assisted digestion in nitric acid-hydrogen peroxide. Results from these analyses are presented in Table 3. H, C, and N were measured using standard, validated procedures. Gasification conditions were also recorded and presented in Table 4.

Tar Sampling

All sampling procedures for tar compounds were performed when the gasifiers were operated in steady-state conditions. A sampling unit was constructed according to the Tar Protocol (Good *et al.* 2005), as illustrated in Fig. 2.

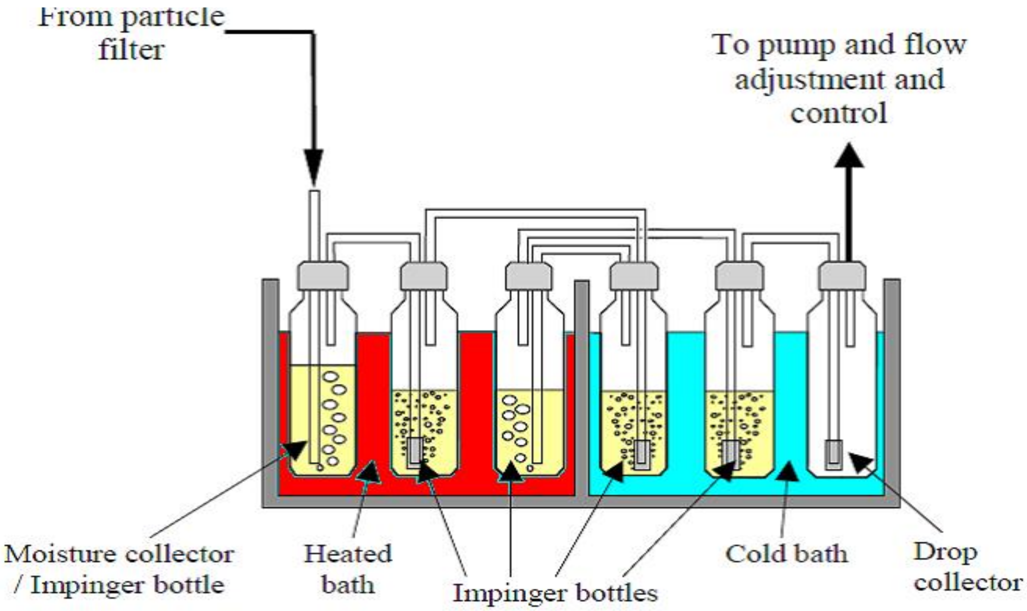

Fig. 2. Set-up of the sampling unit used for the collection of tar-samples according to the Tar Protocol. Adapted from (Good *et al.* 2005)

The sampling unit consisted of six impinger bottles, five (numbers 1 to 5) of which were filled with propan-2-ol while the sixth bottle (number 6) was left empty. Bottles 1, 2, and 4 were kept at a temperature of +35 °C while bottles 3, 5, and 6 were kept at -20 °C. In addition, bottles 2, 3, 5, and 6 were equipped with glass-frits (G3) in order to increase the dispersion of gases in the trapping solutions. Bottle 1 was connected to the sampling port of the gasifiers by a heated Teflon-tubing while gas was pumped through the bottles at a known velocity with the aid of a pump connected to bottle 6. In the normal tar collection, 120 dm^3 of gas was pumped from the sampling port of the gasifiers for a period of 30 min with a flow rate of 4 dm^3/min for quantitation. After sampling the contents, all bottles were combined into a volumetric flask. The lines and flasks then were washed with pure propan-2-ol and made up to obtain the final volume. In the case of quantitation of tars, a small volume of internal standard, o-terphenyl, 50 µg/µL, was added according to the Tar Protocol before making up the correct volume.

Chromatographic Analysis and Quantification

Before chemical analysis, the samples were protected from light and stored at +5 °C. Aliquots of the combined solution were transferred to auto-sampler bottles and analysed with gas chromatography-mass spectrometry (GC-MS, Agilent 7980, Agilent 5975C) in a HP-5MS column (60 m x 250 µm x 0.25 µm) using gas flow and temperature settings as published in the tar-sampling protocol (Good *et al.* 2005). The oven program was as follows: 3 min at 40 °C followed by a temperature ramp of 5 °C/min to 300 °C, a 10 min hold at 300 °C, and a total analysis time of 48 min. The injector was kept at 300 °C, and the injected sample volume was 1 µL, with a split ratio of 1:50. Individual compounds were compared to and identified from a (National Institute of Standards and Technology) NIST library according to their fragmentation patterns in the MS detector. Compounds identified but having a low identification probability are marked as "unknown", and are included in the total tar concentration. Usually the concentrations of the individual unknown compounds are < 0.5 mass-% of the total tar mass.

To estimate the total detectable tar content of the sample (quantification), peak areas were grouped, and concentrations were calculated as naphthalene equivalent according to the sum of the peak areas compared to the peak area of the internal standard. The concentrations were finally calculated as a total mass of tars (naphthalene equivalents) per volume of gas. Quantitation of individual tar components and total tar content in the gas was performed on the samples collected from gasifier B. Samples from gasifier A were only used for separations, identification, and calculation of the distribution of the individual tar components.

RESULTS AND DISCUSSION

Tars from two different down-draft gasifiers were collected and analysed. A typical chromatogram of the tar compounds from gasifier A and B are presented in Figs. 3A and 3B, respectively. Corresponding percentage appearance of tar compounds are presented in Table 6.

Table 3. Analysis Results of the Chips Used for Gasification and the Ash Produced during the Gasification Process

Parameter	Unit	Value, wood chips	Value, ash
Moisture	%	21.0	7.5
Organic content	%	98.1	84.8
Ash	%	1.9	15.2
Higher heating value (HHV(dry))	MJ/kg	19.9	-
Lower heating value (LHV(dry))	MJ/kg	18.5	-
Lower heating value as received (LHV)	MJ/kg	14.1	-
H	% of d.s.	6.0	1.0
C	% of d.s.	50.5	85.0
N	% of d.s.	2.3	1.6
Al	mg/kg	222	1520
B	mg/kg	2.8	68.6
Ca	mg/kg	1580	36700
Cd	mg/kg	0.083	1.1
Cr	mg/kg	2.3	120
Cu	mg/kg	2.1	53.7
Fe	mg/kg	387	3240
K	mg/kg	830	7720
Mg	mg/kg	351	5610
Mn	mg/kg	101	2320
Na	mg/kg	35.3	354
Ni	mg/kg	0.70	104
P	mg/kg	149	4040
Pb	mg/kg	<1.05	10.2
S	mg/kg	128	2240
Zn	mg/kg	26.6	540

d.s. = Dry substance

Table 4. Process Conditions during the Steady-state Operation of the Gasifier (Muilu and Pieniniemi 2011)

Property	**Value**
Feedstock mass flow, kg/h	45
Air flow, Nm^3/h	52
Air temperature, °C	16
Reactor temperature, °C	1050-1200

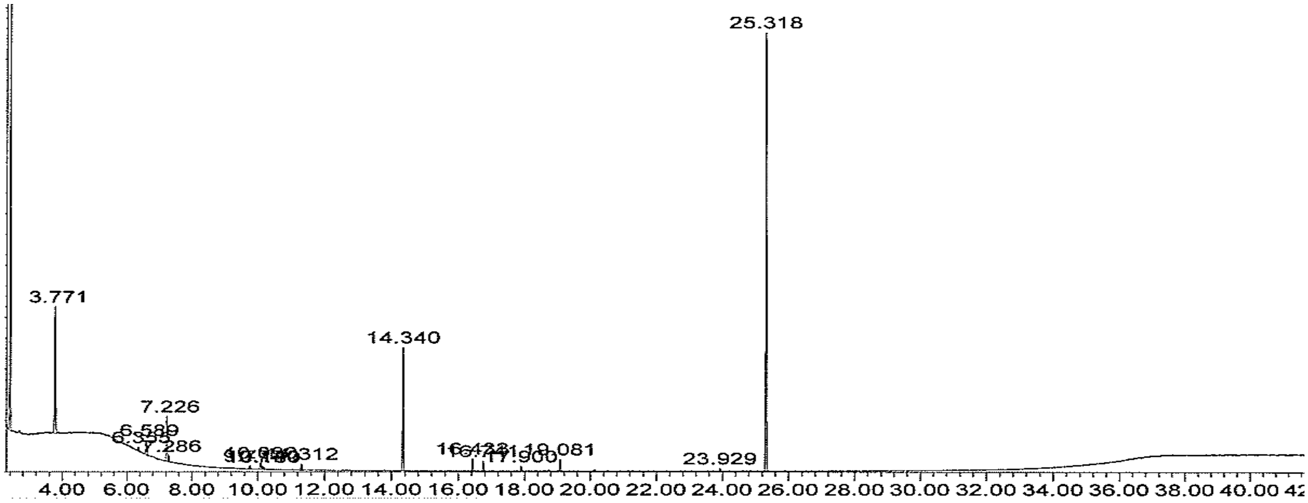

Fig. 3A. A typical chromatogram obtained from GC-MS analysis of sampled tars (from gasifier B). The main peaks are found at retention times 2.38 min, benzene, 3.77 min toluene, 14.34 min naphthalene, and 25.31 min internal standard (o-terphenyl)

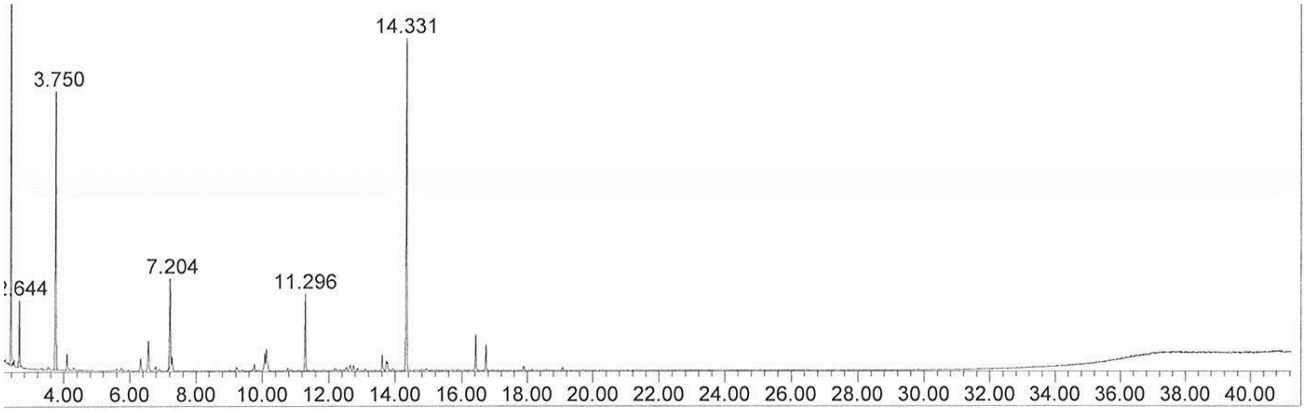

Fig. 3B. A typical chromatogram obtained from GC-MS analysis of sampled tars (from gasifier A). The main peaks are found at retention times 2.38 min, benzene, RT 2.64 min, unknown; 3.75 min toluene, 7.20 min styrene, 11.29 min indene, and 14.33 min naphthalene

Based on the results presented in Fig. 3A and 3B and in Table 5, there were only a few major tar compounds present in the producer gas after the gas cleaning units of the gasifiers. Even though benzene is not regarded as a tar compound, the concentration of benzene is included in Table 5, while the concentrations of real tar compounds are given in line 2 of Table 5 (benzene excluded from calculations). Toluene and naphthalene are the most abundant tar compounds identified, representing more than 70% of the total GC-detectable amount of tars in the samples. This is consistent with the results presented by Gautam *et al.* (2011) who concluded that toluene (28%) and naphthalene (18%) were the main components from a down-draft gasifier. Surprisingly, in this study no phenolic tar compounds could be detected. This finding is inconsistent with the study of Gautam *et al.* (2011), where phenolic compounds were reported at levels ranging between 7 and 70 mg/Nm^3.

In Table 6 the concentrations of total tar before and after the gas cleaner calculated as naphthalene equivalents are presented. The concentrations of some major tar compounds in the gas before and after the gas-cleaner of gasifier B are presented in Fig. 4. Surprisingly, the tar-levels were the same or in some cases even higher after the cleaner (water) compared to the levels obtained from the raw gas. These results indicate a very low capacity of the cleaner to separate tar-components; the results might even indicate a faulty or overloaded cleaner. The results obtained in this study concerning tar-levels in raw and cleaned gas are consistent with previous as yet unpublished results.

Table 5. Total Concentrations of GC-detectable Tars (mg/Nm^3) from Gasifier B **

	Before cleaner	**After cleaner**
Benzene included in calculations	382	398
Benzene excluded from calculations	143	211
Unknowns*	17	27

* Compounds identified with low probability are referred to as unknowns.
** Benzene is included in the calculations on the first line even if it not is regarded as a tar compound.

Table 6. Distribution of the Main Tar Components in Gasifier A and Gasifier B

Compound	**Gasifier A**	**Gasifier B (before cleaner)**	**Gasifier B (after cleaner)**
Toluene	55 %	43,8 %	32.0 %
Styrene	11 %	11.8 %	12.5 %
Naphthalene	30 %	25.4 %	29.7 %

Under the sampling and chromatographic conditions used in this research according to the Tar Protocol, no or only trace levels of heavier tar compounds could be detected. Because of the nature of tars, especially tars from class 3 and class 4, the authors are aware of the risk that these compounds form condensates in the lines prior to the sampling unit and might not appear in the chromatograms.

Data similar to those from gasifier A are not available for gasifier B. In the case of gasifier B, samples were taken after the cleaner; these samples were only used for chromatographic separation and identification of the tar components.

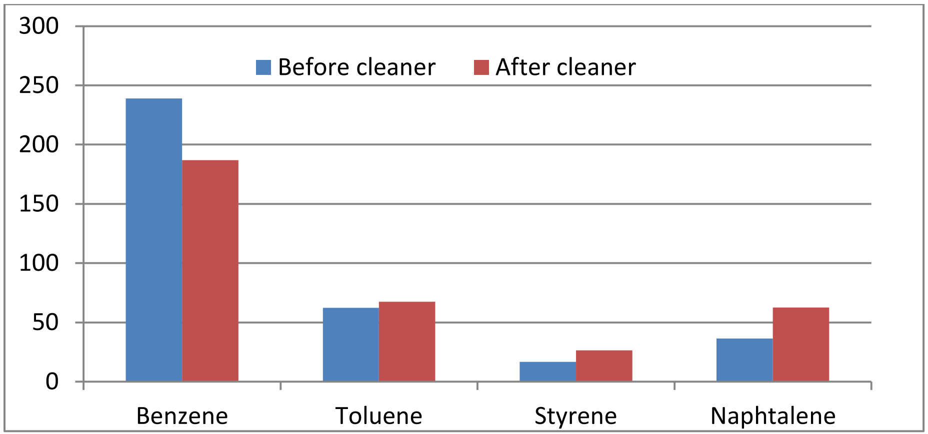

Fig. 4. Concentrations (mg/m^3) of some major tar components before and after the gas-cleaner stage used in gasifier B

CONCLUSIONS

1. Tars are very difficult to sample and analyse, resulting in many research groups developing their own analysis methods, which makes it difficult to compare results. To avoid this discrepancy, we have adopted the Tar Protocol for the sampling and analysis of tars in this study.
2. The tar levels obtained in this study were in line with the results of (Xu *et al.* 2010) (376 mg/Nm^3), whose samples were obtained from a gasifier of about the same size as those used in this study. Normally much higher tar levels have been reported, but in most of these cases larger gasifiers have been used. It is surprising that there is no or little change in the tar levels before and after the water cleaner for gasifier B, indicating a fouled or an overloaded cleaner. As a result of the aromatic nature of tars, water is not regarded as the best solvent for tar-removal.
3. In this study, no phenolic tar compounds were detected. According to the maturations scheme presented in Table 2, phenolic tar compounds are formed in temperatures ranging from 500 to 600 °C. The high gasification temperatures used in this study might be the reason for this observation.
4. The measured tar levels were still much higher than the maximum levels suggested for catalytic purposes. In order to use the gas for catalytic conversion the tar level has to be strongly reduced by either physical removal of the tars or by catalytic cracking of the compounds.
5. Catalytic cracking might be a better option because it will result in an increased level of hydrogen and carbon monoxide in the synthesis gas. This route provides the subject for future investigations.

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