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Article in *Fuel* · October 2016

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Characterisation of the producer gas from an open top gasifier: Assessment of different tar analysis approaches



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HIGHLIGHTS

- Comprehensive screening of the tar in the raw producer gas of an open top gasifier.
- Total tar is mainly composed of light aromatic compounds (benzene and toluene).
- Similar gravimetric tar content operating the gasifier with Casuarina woodchip and coconut shell.
- Gravimetric tar in the raw gas of the investigated open top gasifier is 50–80 mg N m⁻³.

ARTICLE INFO

Article history:

Received 14 April 2015

Received in revised form 20 April 2016

Accepted 21 April 2016

Keywords:

Tar analysis

Open top gasifier

GC–MS

Gravimetric approach

Gasification

ABSTRACT

The paper addresses a comprehensive screening procedure of the tar present in the raw producer gas generated by an open top downdraft gasifier developed at the Indian Institute of Science (IISc), Bangalore. The main objectives of this research are the comparison of different approaches for the sampling and analysis of tar (i.e. GC–MS and gravimetric methods), and the assessment of the capability of this gasifier to produce low-tar producer gas.

The results of the GC–MS analysis of the collected samples showed that tar is mainly composed of light aromatic compounds, where benzene and toluene account for about 70% of the total detected tar. Contrastingly, the gravimetric tar is roughly one order of magnitude lower than the total tar that was determined by GC–MS analysis on the collected samples. The light and heavy polycyclic aromatic hydrocarbons (PAH) compounds that have a molecular weight higher than 150 g mol⁻¹ account for the gravimetric tars, but the main fraction is GC-undetectable. The two approaches for the analysis of tar have different capabilities and the choice of either the approaches would strongly depend on the selected gasification technology. The detailed experimental analysis evidenced that the IISc open-top reactor design results in a low tar content in the producer gas. The gravimetric tar in the raw gas were measured at 50–80 mg N m⁻³, with minimum dependence on the choice of the feedstock used (i.e. Casuarina wood chip or coconut shell).

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1. Introduction

Biomass is a renewable source of energy that can be converted into heat, liquid or gaseous fuel forms using thermo-chemical processes such as combustion, pyrolysis and gasification. In particular, gasification is considered as an interesting and an efficient process to expand the utilisation of biomass. Air/steam blown biomass gasification enables the conversion of the solid fuel into a combustible gas commonly known as producer gas. The composition

of the producer gas mainly depends on the feedstock characteristics and also on the conditions of the gasification process (i.e. temperature, gasifying agent, pressure, etc.). The chemical and physical characteristics of the feedstock play a vital role in the overall thermochemical process. The sub-process, pyrolysis, greatly depends on both fuel properties as well as process conditions, which influences the overall gasification conditions. As an example, the composition and the heating value of the producer gas, depending on the different oxidants, are reported in Table 1 [1,2]. Producer gas can be used in various prime movers (internal combustion engine and gas turbine) for the combined production of heat and power applications. The producer gas has a high potential to replace fossil

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Table 1
Producer gas composition with different oxidants [1,2].

Oxidant	Composition (vol.%)					LHV (MJ/N m ³)
	H ₂	CO	CO ₂	CH ₄	N ₂	
Air	9–10	12–15	14–17	2–4	56–59	3–6
Oxygen	30–34	30–37	25–29	4–6	–	10–15
Steam/CO ₂	24–50	30–45	10–19	5–12	–	12–20
Oxy-steam	45–51	13–25	15–20	1–4	–	7–10

fuel for decentralised energy generation, but it contains some undesired compounds (e.g., tar, particulate, fly ash, etc.) that need to be reduced to guarantee an acceptable operation of the prime mover.

The presence of tar in the producer gas is one of the key technology barriers for the use of the gasification systems for engine applications [3,4]. Tar is a bituminous oil present in the producer gas in vapour phase that is difficult to remove with a simple condensation or cleaning since it may cause the clogging of filter and valves and also the corrosion of the metallic components [5]. For this reason, several methods for the reduction of tar have been tested as a part of gasification system. These methods included the gasification technology itself, the gasifier design, appropriate operating conditions and the use of bed additives or catalysts [6–8]. Tar-free producer gas, downstream of the gasifier, can be obtained by the use of tar-cracker reactors and mechanical gas filtration setups [9,10]. The desirable concentrations of tar depend on the intended use of producer gas in downstream prime movers for CHP applications. The internal combustion engine is considered to be more tolerant to tar than the gas turbine. The tar limit is around 100 mg N m⁻³ for internal combustion engines operating in the naturally aspirated mode, while it is 5 mg N m⁻³ for turbocharged engines and gas turbines [11–13]. The solid oxide fuel cells are not particularly sensitive to tar content in the producer gas [14] but it is still desirable to have low tar levels and the effect of the fuel gas impurities on fuel cells is not well documented in scientific literature.

Besides the determination of the tar concentrations, it is essential to identify the compounds that are critical for the operation of the system. As an example, the internal combustion engine is particularly sensitive to the heavy tar, which is usually deposited in the engine manifold and on the cylinder wall. The polycyclic aromatic hydrocarbon (PAH) compounds do not cause deposition problems but could affect the pollutant emissions of the engine exhausts and also the wastewater from the gas conditioning units [15]. Milne et al. [11] established a thumb rule for the formation of tar depending on the gasifier design; updraft gasifiers at 100 g N m⁻³, fluidised bed gasifiers at 10 g N m⁻³ and downdraft gasifiers with less than 1 g N m⁻³. Furthermore, they suggested a classification of tar into four product classes: primary products that are characterised by cellulose, hemicellulose and lignin-derived methoxyphenols; secondary products that are characterised by phenolics and olefins; alkyl tertiary products that are mainly methyl derivatives of aromatic compounds; and the condensed tertiary products which are PAH series without substituents. These four categories of tar correspond to different maturation temperatures; primary products are cracked before the tertiary products appear. The updraft gasifiers produce mainly primary tar with some degree of secondary tar. The fluidised bed gasifiers produce secondary and tertiary tar and the downdraft gasifiers produce mainly tertiary tar [11]. Overall, the tar concentration depends on several parameters such as temperature, pressure, moisture/size/ash content of the feedstock, gasifying medium, catalyst and additives, equivalence ratio (ER) and residence time.

Temperature is considered as a fundamental parameter for the formation and maturation of tar. Higher operating temperatures reduce the overall tar production; however, it causes a progressive aromatisation of the evolved compounds [16–18]. A well-known scheme developed by Elliott [19] summarises the maturation of tar with the temperature, which indicates the formation of mixed oxygenates at 400 °C, phenolic ethers at 500 °C, alkyl phenolics at 600 °C, heterocyclic ethers at 700 °C, PAH at 800 °C and larger PAH at 900 °C.

Besides the classification scheme proposed by Milne et al. [11], another classification of tar into five classes is based on the solubility and condensability of different tar compounds [20]. An increase in temperature promotes the decomposition of class 1 (GC-undetectable) and class 2 (heterocyclic aromatics) tar while it fosters class 3 (light aromatic) and class 5 (heavy PAH compounds) tar [20,21]. According to Bergman et al. [22], the tar dew-point is a key parameter to assess the condensation issues and it depends on the tar concentration. Bergman et al. [22] defined the correlation for each tar class and highlighted that the class 5 compounds dominate the dew-point of tar, since at low concentrations (<1 mg m⁻³) a dew-point below 100 °C can be obtained [17]. Based on its concentration in the producer gas, class 2 (heterocyclic aromatics) and class 4 (light PAH compounds) tar should be partially removed to avoid condensation that can foul engines and turbines [5].

A high operating temperature decreases the tar content but can also lead to lower gas heating value and lower char conversion due to a higher risk of sintering [23]. Moreover, increasing the ER leads to lower tar production due to a higher amount of oxygen for the oxidation of the volatile matter; nevertheless, the remaining tar undergoes a progressive aromatisation. The optimal ER values are a trade-off between gas quality, process efficiency and tar production [16].

A study carried out by Yu et al. [24] showed the tar formation for major biomass components (i.e. cellulose, hemicellulose and lignin). PAHs represented the largest component of gasification tar. The relative fractions of PAHs for cellulose, lignin and hemicellulose increased with temperature from approximately 65–70% at 800 °C to approximately 90–95% at 1000 °C. Lignin, due to its molecular structure, has a higher tar yield and produces more stable components (PAHs derived primarily from phenols and its derivatives). For cellulose and hemicellulose, PAHs are derived primarily from benzene, toluene, ethylbenzene and xylene isomers (BTEX) and miscellaneous hydrocarbons.

Few studies on the tar analysis of a gasifier operated with coconut shell are present in scientific literature. Sheeba et al. [25] tested coir pith in a circulating fluidised bed gasifier at varying temperatures (650–1020 °C) and ER (0.18–0.31) and estimated a tar content of in the range of 7–11 g m⁻³. Senapati and Behera [26] tested coconut coir in a prototype of entrained flow gasifier at different temperature (976–1100 °C) and ER (0.21–0.30) and estimated the tar content to be in the range of 4.8–26.3 g m⁻³. However, the literature lacks a detailed analysis of tar compounds in the producer gas when the gasifier is operated with coconut shell.

In the present work, a comprehensive screening of the tar present in the raw producer gas were carried out for a small open top gasifier (~1 kg h⁻¹ biomass input) operated with Casuarina wood chip and coconut shell as fuels. The tar analyses were further addressed with two different approaches available in the scientific literature which include gas chromatography–mass spectrometry (GC–MS) analysis and the gravimetric approach. Additionally, the tar collection using two different solvents, isopropyl alcohol (IPA) and hexane were addressed to compare their capability to dissolve tar compounds, which impacts their estimation. The study focuses comparing some of the methods used for characterising tar and

also compares the performance of the solvents used for the collection of tar.

2. Experimental setup

2.1. Open top gasifier

The gasifier considered here is a 1 kg/h biomass gasification which is a scaled down design of the open top twin fire gasifier developed at the Indian Institute of Science, Bangalore [27]. This downdraft gasifier comprises of a 0.8 m long and 0.103 m internal diameter cylindrical reactor with an open top and air nozzles in the oxidation zone. The residual char and ash are periodically removed using a bottom screw-type char extraction unit. This design is particularly suitable for generating low-tar producer gas. The dual air entry (through the top and the nozzles) enables the upward movement of the flame front leading to the establishment of a larger heating zone, greatly improving the gas residence time. The elongated residence time of the gas in the high temperature environment, along with the hot reactive char, ensures better cracking of higher molecular weight (MW) compounds. Furthermore, the tar cracking improves the overall gasification efficiency [28–30]. The gas cleaning and cooling unit, which comprises of a cyclone separator, water scrubber, water chiller and a fabric filter, is a synchronised and customised accessory along with the gasification unit. Fig. 1 shows the typical layout of an open top downdraft gasifier used in the current study. The biomass gasifier configuration is identical to the setup used by Dasappa et al. [31]. The producer gas was drawn for sampling before the gas conditioning section at the reactor outlet, and the tar collection procedure is described in Section 2.2. The gasifier was operated with two different feedstocks, casuarina wood chips and coconut shells. Both the materials were oven dried with the moisture content around 5 wt.%, calculated on a wet basis. During the tar sampling, both the temperature of the oxidation zone and the composition of the producer gas were continuously monitored and recorded.

2.2. Tar sampling system

The tar sampling methodology has adapted features from UNI EN 15439–2008 and the test set up has been evaluated earlier using methoxy benzene as the solvent [32]. The apparatus used for the collection of tar consists of one empty bottle (moisture trap) and four bottles filled with a solvent (impinger bottles); all placed in

an ice water bath. As depicted in Fig. 2, the setup is equipped with a flow metre to measure the volumetric flow rate, a vacuum pump to draw the producer gas, and a burner to flare the producer gas. Furthermore, a cotton and calcium chloride filter for filtering and desiccation purposes is added after the impinger bottles when analysing the producer gas composition using a micro GC. The tar sampling was carried out using two different solvents; IPA (polar solvent) and hexane (non-polar solvent). Hexane has a lower boiling point, compared to IPA and hence a larger evaporation of the solvent is expected. Nevertheless, hexane is a non-polar solvent and could differently impinge on tar capture. All the bottles were kept in an ice bath at 0 °C and atmospheric pressure (~89.5 kPa). The volumetric flow rate, bubbling through the impinger bottles, was set at 0.36 m³ h⁻¹ with a sampling time of 1.5 h and 4 h for hexane and IPA, respectively. A lower sampling time was used with hexane, which has a lower boiling point, to avoid an excessive evaporation of the solvent. The raw gas at the sampling point had a temperature of around 330 °C.

For each test, the content of the impinger bottles and the rinsate from both connection tubes and impinger bottles were mixed. Finally, the sample was filtered using a paper filter and stored in an air tight bottle at a temperature of 5 °C. A sub-sample (10 ml) of each filtered solution was stored for the determination of the individual tar compounds using GC–MS analysis. The remaining part was used for the determination of the gravimetric tar using solvent evaporation at ambient temperature (~30 °C) and ambient pressure (~89.5 kPa). The residues, after the gravimetric procedure, were re-dissolved in 10 ml of IPA and analysed utilising GC–MS analysis. The experiments were repeated three times for each feedstock (i.e. Casuarina wood chip and coconut shell) and each solvent (i.e. IPA and hexane). The results of the experiments are reported in the following sections labelled by their corresponding trial numbers (i.e. 1, 2 and 3) and the indication of the solvent used (i.e. “ipa” for IPA and “hex” for hexane).

2.3. GC–MS analysis

The samples collected by means of the tar sampling equipment were analysed by a gas chromatograph *Clarus 680* – *Perkin Elmer* coupled with a mass spectrometer (*Clarus SQ8T* – *Perkin Elmer*). The GC *Clarus 680* was equipped with a 30 m length and 0.25 mm internal diameter capillary column (*Elite-5 MS*; phase reference – 5% diphenyl and 95% dimethyl polysiloxane, low bleed column). The GC oven temperature was programmed as follows: hold at 30 °C for 5 min, a ramp of 10 °C min⁻¹ up to 150 °C,

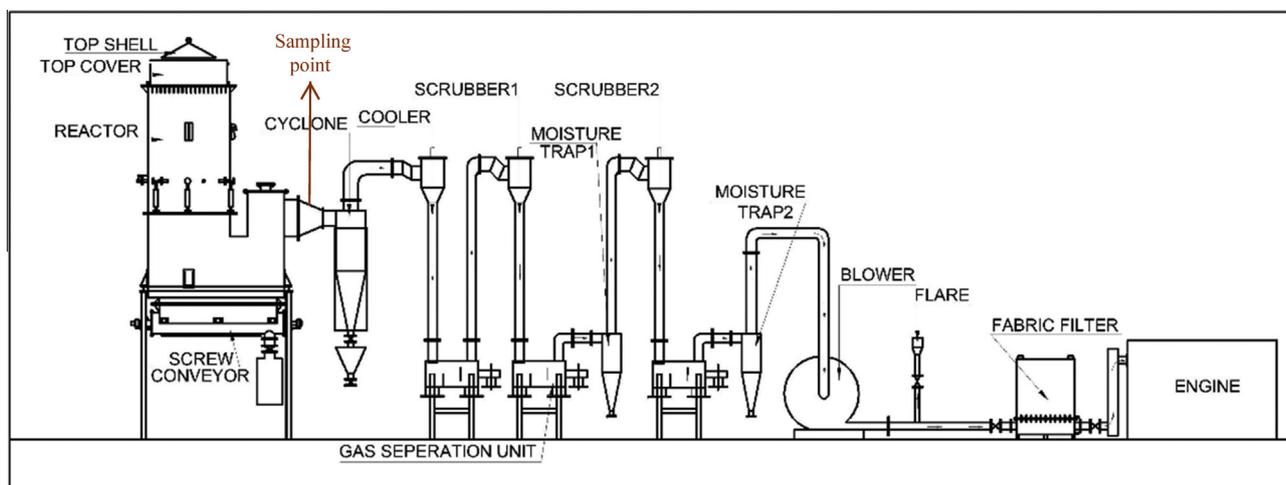


Fig. 1. Typical layout of an open top downdraft gasifier.

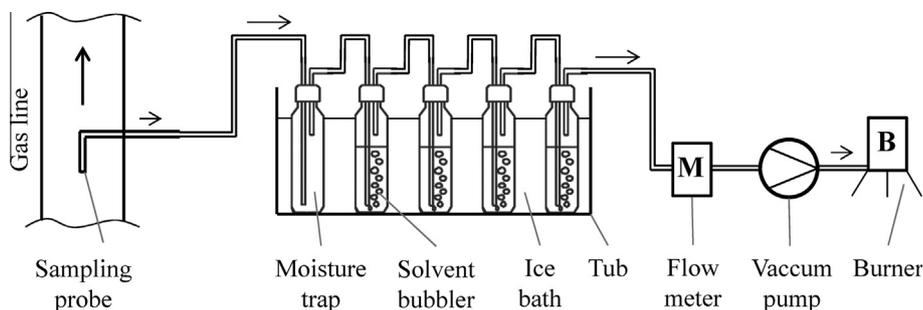


Fig. 2. Scheme of the tar sampling system.

followed by another ramp of 25 °C min^{-1} up to 320 °C . The carrier gas was high purity helium (99.999 vol.%) with a flow rate of 1.0 ml min^{-1} . The injector temperature was set at 300 °C and the injection volume at $0.5\text{ }\mu\text{l}$ with a split ratio of 30:1. The transfer line and the ion source temperature were set at 200 °C and 180 °C , respectively. The MS was operated in electron ionisation mode (70 eV), full scan mode (range: $30\text{--}300\text{ Da}$) and with a solvent delay of 2.7 min . The detected peaks were identified by means of NIST spectral library 2.0 g (2011). Furthermore, the quantification of the main compounds (i.e. benzene, toluene, styrene, phenol and naphthalene) was carried out through MS detector in SIR (single ion recording) mode and by means of external standards.

3. Results and discussion

3.1. Process characterisation

The temperature in the oxidation zone and composition of the raw gas were monitored and no substantial differences in the temperature and gas composition were observed while operating the gasifier with casuarina and coconut shell. The temperature in the oxidation zone was $900 \pm 50\text{ °C}$ with both the feedstock and the composition of the producer gas was: $13.2 \pm 0.8\%$ CO, $13.0 \pm 2.1\%$ H₂, $1.8 \pm 0.2\%$ CH₄, $14.2 \pm 1.9\%$ CO₂ and $57.8 \pm 1.7\%$ N₂. The lower heating values (LHV) of the producer gas were $3.12 \pm 0.22\text{ MJ kg}^{-1}$ and $3.03 \pm 0.11\text{ MJ kg}^{-1}$ for Casuarina wood chip and coconut shell, respectively. These values are in accordance with the nominal ones, using Casuarina as the biomass feed and the gasifier itself operated at standard design conditions (89.5 kPa ambient pressure, and 25 °C ambient temperature, biomass composition of CH_{1.4}O_{0.6} with a moisture content of 5 wt.%, 0.34 wt.% ash content and air to fuel ratio = 1.5–1.8 [31]).

3.2. Calibration curves

The quantification of the main compounds was carried out by means of external standards, which were used to create the calibration curves. Each calibration curve represents a linear regression calculated for three points at different concentrations and therefore corresponds to different area of the chromatogram peak. The area was elaborated on the basis of the signal recorded by the MS detector operating in SIR mode. The chromatogram starts at 2.7 min because of the solvent delay (time required by the solvent to leave the column). The analysis was repeated three times for each point and the average value is reported in Fig. 3.

The compounds that have not been calibrated with the external standards were quantified by means of estimated calibration curves that were determined on the basis of the correlation between the calibration curves (reported in Fig. 3), and the molecular weight of the compounds. Each compound has its own correlation between area and concentration as shown in Fig. 3, which

highlights the correlation between calibration curves and the molecular weight. For a predetermined concentration, a higher molecular weight correlates to an enhanced signal from MS detector and therefore results in a higher area of the chromatogram peak. The MW for the calibrated compounds is reported within parentheses: benzene (78.11 g mol^{-1}), toluene (92.14 g mol^{-1}), phenol (94.11 g mol^{-1}), styrene (104.15 g mol^{-1}), naphthalene (128.17 g mol^{-1}). In the graphs, benzene and naphthalene are displayed in the opposite extremes of the curves stack since they are considerably different in terms of MW. For each un-calibrated compound, an estimated calibration curve was elaborated on the basis of the calibration curves displayed in Fig. 3 and the corresponding MW. Therefore, for each un-calibrated compound, it is possible to estimate its concentration in the sample by means of the estimated calibration curve.

3.3. GC–MS analysis and gravimetric tar

The quantification of the tar compounds in the raw gas was performed with the GC–MS analysis of the collected samples. The concentration of each compound was calculated by means of the detected area and the calibration curve. The area was elaborated on the basis of the signal recorded by the MS detector operating in full scan mode. All the analyses were repeated twice and the average values are reported in Tables 2 and 3.

Tables 2 and 3 refer to the producer gas from casuarina wood chip and coconut shell, respectively. The results are reported using both IPA and hexane as the solvent. No considerable differences are observed using IPA or hexane. Nevertheless, IPA is easier to handle since its boiling point is higher compared to the one of hexane. Tables 2 and 3 report the average values calculated, considering the samples from specific feedstock and solvent (i.e. IPA or hexane). Only gravimetric tar is calculated for the sample “1_hex”, for both Casuarina wood chip and coconut shell. This is due to the fact that the samples were extensively used towards establishing the results from the GC–MS analysis. Furthermore, the total amount of tar (measured and estimated) and the percentage of estimated tar on the total one are reported in Tables 2 and 3. The order of magnitude of the total tar content is in accordance with the scientific literature that reports a value of about 1 g N m^{-3} for a downdraft gasifier [11]. The detected compounds are mainly class 3 tar (i.e. light aromatics). Benzene and toluene account for an average share of 70% of the total detected tar for both the feedstocks. Gravimetric tar is considerably lower (almost one order of magnitude) than the total tar detected in the collected samples. This is due to the evaporation of the lighter compounds (e.g., benzene, toluene, etc.) during the gravimetric procedure. Only heavy hydrocarbons are expected to be present in the gravimetric tar residues (this is further discussed in Section 3.4). The determination of tar content has to be restricted to include just the harmful compounds, according to the downstream application. As an

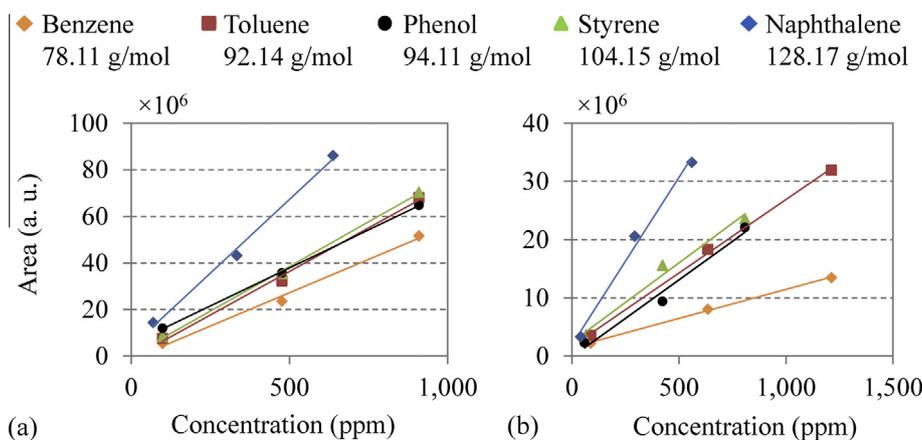


Fig. 3. Calibration curves; IPA as solvent (a), hexane as solvent (b).

Table 2
Quantification of tar compounds (mg N m^{-3}) in the raw gas when the gasifier is operated with Casuarina woodchip.

Sample #	IPA (solvent)				Hexane (solvent)			
	1_ipa	2_ipa	3_ipa	Avg. ipa	1_hex	2_hex	3_hex	Avg. hex
Benzene	160 ± 37	102 ± 18	108 ± 14	123 ± 66	–	93 ± 14	116 ± 21	104 ± 34
Toluene	86 ± 12	68 ± 9	64 ± 5	73 ± 26	–	117 ± 17	98 ± 13	108 ± 30
Styrene	38 ± 2	0	7 ± 1	15 ± 3	–	35 ± 4	22 ± 3	28 ± 7
Phenol	0	25 ± 3	0	8 ± 1	–	10 ± 3	16 ± 4	13 ± 7
Naphthalene	4 ± 2	33 ± 4	0	12 ± 7	–	2 ± 1	1 ± 1	2 ± 3
Furans ^a	0	0	0	0	–	5	4	4
Cycloheptatriene ^a	0	0	0	0	–	2	0	1
Furfurals ^a	0	3	0	1	–	8	4	6
Dimethyl heptene ^a	0	0	0	0	–	0	0	0
Ethylbenzene ^a	7	10	0	6	–	16	10	13
Xylenes ^a	10	13	0	8	–	20	13	16
Anisole ^a	0	4	0	1	–	5	2	4
Benzofurans ^a	12	17	0	9	–	13	7	10
Indenes ^a	8	19	0	9	–	9	6	8
Acetic acid ^a	0	0	19	6	–	0	8	4
Cresols ^a	0	0	0	0	–	1	0	0
Cyclohexane ^a	3	0	5	3	–	0	0	0
Total GC–MS	327	294	201	274	–	337	309	323
Total estimated ^a (%)	12	22	12	15	–	24	18	21
Gravimetric tar	73	41	30	48	72	45	60	59

^a Concentration calculated by means of estimated calibration curves.

example, considering an internal combustion engine, the organic compounds with a boiling point lower than about 100 °C (e.g. benzene and toluene) need not be considered [11].

The results can be compared in terms of tar content depending on the used feedstock. Coconut shell has higher values for most of the compounds. The total amount of tar for coconut shell is 489 mg N m^{-3} (IPA as solvent) and 405 mg N m^{-3} (hexane as solvent) while for Casuarina wood chip it is 274 mg N m^{-3} (IPA as solvent) and 323 mg N m^{-3} (hexane as solvent). Benzene and toluene are the compounds that mainly enhance the difference of the total tar determined by means of GC–MS analysis. The gravimetric tar is similar for both the feedstocks because the lighter compounds (e.g., benzene, toluene, etc.) are evaporated during gravimetric procedure. The evaluated values are 48 mg N m^{-3} (IPA as solvent) and 59 mg N m^{-3} (hexane as solvent) for Casuarina wood chip, and 52 mg N m^{-3} (IPA) and 79 mg N m^{-3} (hexane) for coconut shell.

From the available literature there are several studies about the characterisation of tar. However, the differences in the gasification technology, reaction temperatures and the choice of feedstock make it difficult to compare the results. The results of the present study agree with the generalised tar composition for a downdraft gasifier, concluding that tar is mainly composed of tertiary

aromatics (e.g., benzene, naphthalene, phenanthrene and pyrene) and tertiary alkyl aromatics (e.g., toluene, indene, phenol) [11]. These results are also in accordance with Hernández et al. [16], concluding BTEX to be the main constituents of tar (comprising 60–70 wt.%). Similar results were obtained from the characterisation of tar content in the producer gas generated in a downdraft type fixed bed gasification system using dried sewage sludge as the fuel [33]. However, Jordan and Akay [34] found results significantly deviating from the generalised tar composition outlined by Ref. [11]. They characterised the tar produced by the gasification of cane bagasse in a 50 kW_{el} air-blown downdraft autothermal gasifier, and showed that the main compounds of tar are 4-methylphenol, 1,2-benzediol, styrene, m-xylene and pyrene.

The fluidised bed design, if compared to the downdraft one, generates a producer gas with a higher tar content, mainly due to the lower gasification temperature, while the tar composition depends also on the gas residence time [33,34]. In particular, the class 4 and heavy class 5 tar concentration increase, while the class 2 and 3 tar concentrations decrease, with increasing the gas residence time [34]. According to Nemanova et al. [35], the main tar components of an atmospheric fluidised bed gasifier are naphthalene (58.7%), phenanthrene (6.6%), indene (6.1%). The analysis

Table 3Quantification of tar compounds (mg N m⁻³) in the raw gas when the gasifier is operated with coconut shell.

Sample #	IPA (solvent)				Hexane (solvent)			
	1_ipa	2_ipa	3_ipa	Avg. ipa	1_hex	2_hex	3_hex	Avg. hex
Benzene	292 ± 43	86 ± 9	268 ± 13	215 ± 65	–	141 ± 21	193 ± 29	167 ± 50
Toluene	156 ± 34	55 ± 9	225 ± 15	146 ± 65	–	109 ± 14	87 ± 22	98 ± 37
Styrene	59 ± 10	0	7 ± 2	22 ± 4	–	33 ± 15	26 ± 13	29 ± 29
Phenol	10 ± 3	44 ± 2	16 ± 4	23 ± 13	–	32 ± 16	46 ± 9	39 ± 27
Naphthalene	2 ± 2	32 ± 3	0	11 ± 12	–	1 ± 1	2 ± 2	2 ± 4
Furans ^a	0	0	0	0	–	4	0	2
Cycloheptatriene ^a	0	0	0	0	–	0	0	0
Furfurals ^a	12	9	0	7	–	10	3	7
Dimethyl heptene ^a	0	0	0	0	–	0	0	0
Ethylbenzene ^a	13	4	1	6	–	9	4	7
Xylenes ^a	20	10	0	10	–	16	9	13
Anisole ^a	0	3	0	1	–	2	7	5
Benzofurans ^a	29	20	0	16	–	18	17	18
Indenes ^a	22	21	0	14	–	11	14	12
Acetic acid ^a	16	24	0	13	–	4	8	6
Cresols ^a	0	0	0	0	–	1	0	0
Cyclohexane ^a	5	0	4	3	–	0	0	0
Total GC–MS	637	308	521	489	–	392	418	405
Total estimated ^a (%)	18	30	1	16	–	19	15	17
Gravimetric tar	50	44	63	52	138	54	46	79

^a Concentration calculated by means of estimated calibration curves.

by Michel et al. [36] with a fluidised bed steam gasifier reported the presence of PAHs (naphthalene, anthracene and biphenylene) as the largest tar fractions. In this case, naphthalene was the dominant compound with the concentrations varying from 30% to 70%, depending on the catalyst used. Similar results were described by Koppatz et al. [37] that showed PAHs as the main tar components, where naphthalene concentrations ranged from 30% to 45%, depending on the catalyst used.

In the present study, the concentration of naphthalene in the producer gas of the open top gasifier is significantly lower. Contrary to benzene, naphthalene is particularly sensitive to the temperature and it undergoes two different reactions; the naphthalene polymerisation leading to soot formation, and the naphthalene cracking leading to lighter species, such as benzene [38,39]. In the open top reactor, the higher residence time (as mentioned in Section 2.1), besides the high temperature of the oxidation section, promotes the naphthalene conversion to benzene. Hence the major compounds that we have recorded are benzene and toluene for both Casuarina wood chip and coconut shell.

Further, as indicated in Tables 2 and 3, the quantification of the tar concentrations using the gravimetric method yielded tar concentrations in the range of 50–80 mg N m⁻³. The magnitude of tar concentrations, as measured in the open top downdraft gasifier used in this study, revealed lower tar concentrations compared to other established gasifiers, such as the air-blown updraft gasifier in Harbøre (80 g N m⁻³) and the steam fluidised-bed gasifier in Güssing (1.5–4.5 g N m⁻³) [40]. Moreover, the tar level is only marginally higher than the one from “Viking” gasifier (15 mg N m⁻³), that has an extremely low tar concentration thanks to the two-stage gasification process [41].

3.4. GC–MS analysis on gravimetric tar residues

The residues, obtained after gravimetric tar, were re-dissolved in 10 ml of IPA and analysed by means of GC–MS. Most of the detected compounds have MW higher than 150 g mol⁻¹ due to the expected evaporation of the lower molecular weight hydrocarbons during the gravimetric sampling procedure. The detected compounds are mainly class 4 (light PAH compounds) and class 5 (heavy PAH compounds) tar. For both Casuarina wood chip and coconut shell the main compounds detected on the gravimetric

tar residues are acenaphthylene, methylparaben, dibenzofuran, fluorene, phenanthrene, anthracene, pyrene, fluorantene and benzo[a,b,c]fluorene. According to several authors [38,42,43], compounds such as fluorantene and pyrene are soot precursors, moreover, class 1 tar (GC-undetectable compounds [20]) are the primary soot components.

The gravimetric procedure preserves only the heavier compounds and the main fraction is GC-undetectable. However, among those detected by the GC–MS analysis, it was not possible to estimate their concentration due to the considerable difference of MW with respect to the standard compounds used to create the calibration curves (as observed in Section 3.2).

Clearly, the gravimetric tar provides useful information when the gasifier is coupled to internal combustion engines or gas turbines since they are particularly sensitive to the heavy tar compounds. Furthermore, the desired end use applications of producer gas, such as fuel cells could exclusively benefit from the detailed GC–MS analysis of lighter tar compounds.

4. Conclusions

The results of tar characterisation are similar if IPA or hexane is used as the solvent. The GC–MS analysis on the collected samples showed that tar is mainly composed of light aromatic compounds, where benzene and toluene account for about 70% of the total detected tar. The amount of gravimetric tars was approximately one order of magnitude lower than the tar amount detected in the collected samples by means of GC–MS analysis. The GC–MS analysis of the gravimetric tar detected compounds with MW greater than 150 g mol⁻¹ (light and heavy PAH compounds), but the principal fractions remained undetectable using the GC–MS method. The two approaches for the determination of tar in the producer gas, GC–MS and gravimetric analysis, have varied capabilities, and the choice of the developed method strongly depends on the gasifier technology used. Higher tar fractions were detected when coconut shell was used in the gasification process and the compounds that particularly formed with enhanced concentrations were benzene and toluene. Besides benzene and toluene concentrations, the gasification of casuarina wood chip as well as coconut shell has similar tar fractions in the producer gas.

Conclusively, the open top downdraft showed satisfactory performance with respect to the reduced generation of tar and clean producer gas owing to the increased residence time in the high temperature zone, compared to the closed top designs. Regardless of the used feedstock (i.e. Casuarina wood chip or coconut shell), the gravimetric tar in the raw producer gas was approximated measured in the range of 50–80 mg N m⁻³.

Acknowledgements

This work were supported by the Autonomous Province of Bolzano and SAHYOG project (www.sahyog-europa-india.eu). The authors gratefully thank “Eco-Research” for the technical support during the analysis of the samples and the National Combustion Center for Research and Development at IISc Bangalore for the GC–MS facility.

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