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Assessment of pollution levels resulting from biomass gasification

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ABSTRACT

In biomass gasification process the producer gas generated can be cleaned by water scrubbing. Some of the organic compounds generated are entrained together with other flue gas dust particles in to the cooling stream. The treatment/disposal of this waste stream remains a challenge because some of the compounds are toxic to humans and the environment. The objective of this study was to assess pollution levels resulting from organic constituents of flue gas filtration in a downdraft gasifier. The study involved assessment of the concentration of polycyclic aromatic hydrocarbons (PAHs) in the liquid effluence. The impacts on human health and environment are also discussed and recommendations on measures to minimize the pollution levels are provided. A downdraft gasifier fed with maize cobs was used and condensates were collected by cooling of producer gas. Samples were preserved in a cooler at about 2 °C for 24 h before analysis using a capillary gas chromatographer connected to a mass spectrometer (GC–MS). The results were that concentrations of: naphthalene was 204.3 mg/m^3, benzene 17.92 mg/m^3, toluene 182.94 mg/m^3, ethylbenzene 202.43 mg/m^3, 1,2-dimethyl benzene 359.28 mg/m^3 and 1,3+1,4-dimethyl benzene 1016.18 mg/m^3. It was observed that the concentrations of naphthalene and xylene were considerably higher than the recommended permissible exposure limits (PELs) on both human health and the environment. On the other hand, the concentrations of benzene, toluene, and ethylbenzene were below the PEL. Generally this study indicated that the liquid effluent meets regulatory standards, but it would be interesting to carryout tests with different biomass fuel types which this study recommends.

Introduction

Biomass gasification is a thermo-chemical conversion process that converts biomass and other solid fuels into gases [1]. According to Larsen et al. [2], the produced gas mainly consists of: 18–20% hydrogen, 18–20% carbon monoxide, 2–3% methane, 8–10% carbon dioxide, 46–56% nitrogen, and traces of other hydrocarbons. Some residue of char is obtained and a host of hydrocarbon compounds called tars are also formed in the process along with water. In practice, gasification can convert 60–90% of the energy stored in the biomass into the gas generated depending on the type of gasifier and the operating condition used [3].

In Uganda, most of the gasification work is being carried out in research institutions and a few prototypes have been developed and tested. These include installations at Makerere University and Kyambogo University, Kampala; King's College Budo, Wakiso; and Nyabyeya Forestry College, Masindi [4]. Other gasifier installations are being commercially operated for power generation and thermal applications like at Muzizi Tea Factory in Kibaale and Ankole Tea Estate in Bushenyi. Recently, a private entity, Center for Renewable Energy and Energy Conservation (CREEC) acquired three 10 kW gek gasifiers under the Millennium Science Initiative (MSI)-Rural Electrification project implemented by the center in collaboration with Makerere University and Pamoja Energy Ltd. Two of these gasifiers have been installed in off grid areas of Gulu and Mityana in the villages of Opit and Ssekanyonyi, respectively to ease processing of agricultural produce from the local farmers.

As biomass gasification gains popularity as a renewable energy technology, it is necessary to ensure that health, safety and environmental issues do not become hurdles to its acceptance in the market. However, today the large scale introduction is hampered by health, safety and environmental issues, among others, which present considerable challenges in the deployment of this technology [5]. In the filtration of producer gas from biomass gasification using water scrubbing it is cooled thereby increasing its energy density for use in gas engines [6]. For instance, a gas temperature reduction of 10% can increase the maximum output of the engine by about 2% [7]. However, the cooling process enhances the condensation of water vapor and some hydrocarbons from the gas causes contamination of the filtering stream [8]. The hydrocarbons, particularly the PAHs from the

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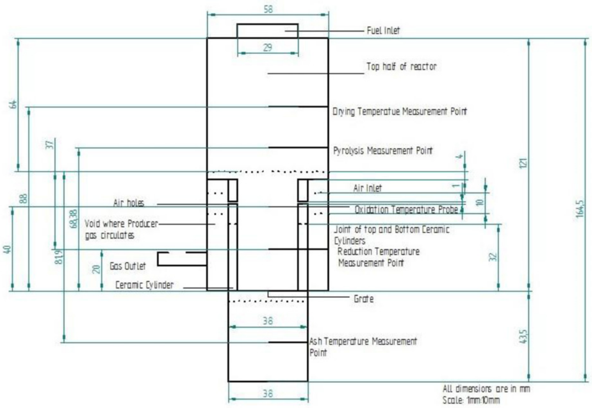

Fig. 1. Sectional view of a downdraft fixed bed gasifier at Makerere University [12].

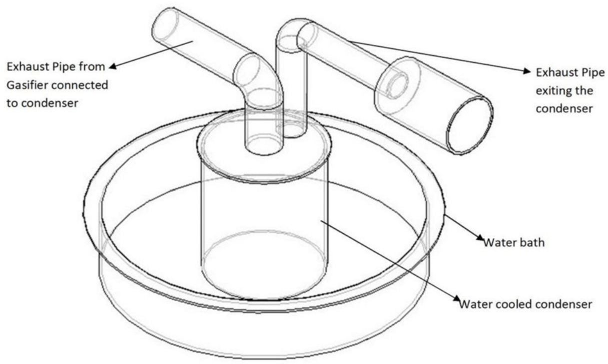

Fig. 2. Water cooled condenser connected to the exhaust pipe.

stream, are carcinogenic and highly toxic that can lead to risks of water pollution, adverse health and environmental effects [9].

The objective of this research was to assess the pollution levels resulting from biomass gasification producer gas filtration effluence. This involved determination of concentration of selected PAHs in the effluence and the comparison with known PEL, the impact on human health and the environment, and proposition measures aimed at minimizing pollution levels resulting from biomass gasification. The study was conducted on a downdraft gasifier test rig at Makerere University using maize cobs as fuel. The downdraft gasifier was chosen because it is suitable for gas engine applications due to the low tar levels it generates compared to the others [6] and is the gasifier type commonly used in small scale applications. The hydrocarbons measured were limited to mono aromatic hydrocarbons and light PAHs that are detectable by gas chromatography [10,11].

Experimentation

Description of gasifier setup and operation

The gasifier system comprised of a reactor, fuel feeding system, air blower connected to a three phase motor, ash collecting system, a gas sampling unit and a condenser coupled to the exhaust pipe. Fig. 1 shows a sectional view of the downdraft fixed bed gasifier that was used to perform the experiments.

The gasifier was first cleaned of tars from previous experiments that had accumulated in it. Charcoal amounting to an average weight of 7 kg was fed into the gasifier to provide a char bed during gasifier start-up. Maize cobs ranging between 9 and 12 kg was then weighed and fed into the reactor. The K-type thermocouples were installed in the pyrolysis zone and gas exit after the cyclone to indicate the temperature variation within the reactor during the gasification process. Temperatures were recorded at 10 min interval using a data acquisition system (87,623 SRP-6-1.5M data logger).

The producer gas generated during gasification of the maize cobs was tested by flaring. The gas samples were then collected for analysis from the gas sampling unit which was turned on once a flare was obtained and ran for more than an hour. In addition, the producer gas was cooled and condensate collected in a condenser that was fabricated and coupled to the exhaust pipe as shown in Fig. 2.

The collected condensate was immediately transferred from the condenser to graduated 250 ml water sampling bottles made of opaque glass to avoid photochemical reactions in water samples. The condensate samples were preserved in a cooler at about 2 °C to minimize the volatilization of the organic compounds with low boiling points and bacterial degradation of the organic compounds. The producer gas exiting the exhaust was flared to avoid emissions into the atmosphere. The operation of the gasifier was stopped once there was a progressive decline in the recommended gasification temperatures of 800–1000 °C [13].

Measurements and analyses

Selected physical and chemical properties of biomass that influence the gasification process were determined. The physical properties included bulk density and particle size. The bulk density was determined according to ASTM E873 while the particle size was determined using a digital vernier caliper. On the other hand, the chemical properties of the biomass were determined by conducting both the proximate and ultimate analyses. The ASTM standard E872 method was used to determine volatile matter. The ash content was determined following the Laboratory analytical procedure (LAP) for determination of ash in biomass developed by the National Renewable Energy Laboratory (NREL/TP-510-42622) [14]. On the other hand the fixed carbon was obtained by difference. The ultimate analysis was conducted to determine the elemental composition (i.e. carbon (C), hydrogen (H) and nitrogen (N)) of maize cobs using ASTM D3178-79 standard. The percentage composition of oxygen was then obtained by difference. The moisture content was determined separately using the oven dry method according to CENT/TS 14774-3 [15].

Producer gas samples were collected using gas sampling bags (Tedlar® bags) with a maximum capacity of 5 l. The samples were then immediately carried to the laboratory for analysis using a gas chromatographer (Shimadzu GC-3BT). Other parameters that were determined included: fuel flow rate, specific load of the reactor, and rate of gas production. See Belonio [16] for details of the procedures.

All chemicals and reagents for analysis were of analytical grade and of highest purity (i.e. >99.999% pure). The use of high purity reagents and solvents helped to minimize interference problems. A PAH reference standard mixture containing the target light PAHs (i.e. naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene) was used in the study. The mixture contained two isotopically labeled PAHs namely, acenaphthalene-d_{10} and phenanthrene-d_{10} as internal standards. For benzene, toluene, ethylbenzene and xylene (BTEX) analysis in the condensate, fluorobenzene (4000 mg/l in methanol) was used as an internal standard while BTEX-gas chromatography standard solution was used as a reference standard mixture. The apparatus used in sample preparation included: measuring cylinders, pipettes, vials, centrifugal tubes, mechanical shaker, centrifuge machine, analytical balance, Agilent GC–MS (6890) in electron ionization mode with split-less injector and capillary column of dimension 30 m × 250 μm × 0.25 μm. Measuring cylinders, vials, pipettes and centrifugal tubes used were cleaned with hexane and dried in an oven at 105 °C. This was done to avoid method interferences due to contaminants in solvents, reagents, glassware, and other sample processing hardware.

Preparation of standard solutions for PAH determination

Five standard solutions each containing the target compounds were prepared by diluting to 1.0, 0.75, 0.50, 0.25 and 0.1 ppm of 10 ppm of each PAH standard mixture with 20 ml of hexane. A pipette was used to measure the respective volumes calculated according to Eq. (1):

$$C_1V_1 = C_2V_2 \tag{1}$$

where C = concentration (ppm) and V = volume (ml).

To all of the solutions 0.5 µg each of the internal standards was added. The solutions were transferred into capped and sealed vials ready for analysis. The standard solutions obtained were used for creating calibration curves for evaluation of method linearity and spiking the samples for quantitative determination of the PAHs.

Calibrations

Calibration curves were obtained using a series of varying concentrations (i.e. 1.0, 0.75. 0.50, 0.25, and 0.1 ppm) of a standard mixture containing each of the targeted aromatic hydrocarbon. The several dilutions of PAH and BTEX-GC standard mixtures made were analyzed to determine the limit of detection (LOD), limit of quantitation (LOQ), relative standard deviation (RSD) and coefficient of correlation (r). The LOD and LOQ were determined from the plot of response factor versus concentration. The LOD was determined using Eq. (2) while the limit of quantitation was determined using Eq. (3) [17].

$$\mathrm{LOD} = \frac{3.3 \times \mathrm{SD}}{\mathrm{Slope}} \tag{2}$$

$$\mathrm{LOQ} = \frac{10 \times \mathrm{SD}}{\mathrm{Slope}} \tag{3}$$

where SD is the standard deviation of the response.

PAH extraction by shaking

In a 50 ml glass vial, 20 ml of sample was measured using measuring cylinders and mixed with 10 g of anhydrous sodium sulphate. The purpose of the anhydrous sodium sulphate was to remove any water that would otherwise mix with the solvent prior to injection of the prepared sample in to the GC. 20 ml of the organic solvent (i.e. hexane) and 100 µl of the internal standards were added to the mixture and the solutions mixed by mechanical shaking at 200 rpm for 20 min at room temperature. The two phases formed were separated by centrifugation at 1500 rpm for a period of 30 min. The extracted samples were purified by passing them through a silica gel column prepared by loading 10 g of activated silica gel onto a chromatographic column. The organic phase was then transferred into 20 ml glass test tube after which a 2 µl aliquot of the final solution of each test sample was then injected in the GC–MS for analysis.

Recovery studies

Prior to extraction, two surrogate standards were added to the sample to monitor the recovery of the different target compounds. The surrogate standards used included: acenaphthene d_{10}, and phenanthrene-d_{10} for PAH analysis. These were used to monitor method performance and the samples were subjected to the same extraction procedures as described above. The surrogate percent recovery was calculated using Eq. (4).

$$\%\text{surrogate recovery} = \frac{Q_d}{Q_a} \times 100 \tag{4}$$

where Q_d is the quantity determined by analysis and Q_a is the quantity added.

GC–MS conditions

The GC–MS was used to detect and quantify the target aromatic hydrocarbons in the condensate. Helium (>99.999% pure) was used as the carrier gas and the column head pressure was maintained at 25.83 kPa to give an approximate flow rate of 1 ml/min with an injection port configured in the split-less mode with all injection volumes at 2 µl. The injection port and detector temperatures were maintained at 250 °C and 300 °C, respectively. The initial column oven temperature was held at 50 °C for 0.4 min and was programmed to 195 °C at a 25 °C/min rate for 1.5 min, then 8 °C/min to 265 °C for 0 min and finally to 315 °C at 20 °C/min rate where it was held for 1.25 min. The overall GC programmed time was 20.2 min. The mass spectrometer was used in electron ionization mode by electron impact (70 eV).

Table 1
Properties of maize cobs.

	Measured value
Physical properties	
Bulk density (kg/m^3)	358.99 ± 40.42
Particle size (mm)	91.20 ± 18.05
Proximate analysis (wt.%)	
Ash	3.39 ± 0.51
Volatile matter	77.85 ± 0.62
Fixed carbon	18.81 ± 0.80
Ultimate analysis (wt.%)	
Carbon	46.57 ± 0.20
Hydrogen	6.41 ± 0.33
Nitrogen	0.96 ± 0.26
Oxygen (by difference)	46.06 ± 0.11
Moisture content	13.55 ± 0.99

Identification and quantitation of the hydrocarbons

Identification of the targeted compounds was based on the retention time and mass spectra match against the calibration standards. The integrated programs of the GC–MS were used to quantify the concentration of the individual target compound. Overall quantification was based on the following targeted ions (m/z): naphthalene, 128; acenaphthylene, 152; acenaphthene, 154; fluorene, 166; phenanthrene, 178; anthracene, 178. The limit of detection for each target aromatic hydrocarbon was established from calibration.

Results and data analysis

Selected properties of biomass

The physical and chemical properties of the maize cobs that were used as samples in this study are shown in Table 1.

From the results obtained as highlighted in Table 1, the fuel mean bulk density was 358.99 kg/m^3. The high variability of bulk densities may be attributed to variation in grain quality. The bulk density of the maize cobs was high compared to that reported by Lubwama [12] and Brunner et al. [18] and therefore advantageous because it represents a high energy content for a biomass fuel. The mean particle size of 91.20 mm was suitable for the downdraft gasifier according to a size range of 10–300 mm in a study by Ming [19]. The mean ash content of the six test samples was 3.39%. This suggests that the maize cobs may exhibit some slagging tendencies if the gasification temperature is not kept to below 1000 °C [18]. According to FAO [7], slagging can lead to excessive tar formation and/or complete blocking of the reactor thus affecting smooth operation of the gasifier, but generally no slagging is observed with fuels having ash contents below 5–6% when low temperatures are involved. The average value of volatile matter recorded was 77.85%. This is close to the volatile matter of 78.7% reported by Chang et al. [20] and Tsai et al. [21]. Turare [22] also reports that the volatile matter content of crop residues lies between 63 and 80% which conforms to the results of the authors. The high value of the volatile matter content presents a risk of more tar production which causes problems to internal combustion engine [22]. However, the increase in volatile matter also improves biomass

Table 2
Gasification parameters.

Particular	Value
Fuel flow rate (kg/h)	11.40 ± 0.93
Specific load of reactor (kg/m^2 h)	185.14 ± 15.14
Condensate collected ($\times 10^{-6}$ m^3/kg fuel h)	8.5 ± 1.8
Specific gas production rate (N m^3/h m^2)	8907.6 ± 3024.1

reactivity and results in higher conversion efficiency [23]. The fixed carbon of the maize cobs was found to be 18.81%. This is close to the fixed carbon of 16.1% reported by Chang et al. [20] and Tsai et al. [21]. Demirbas [24] reported that biomass has low fixed carbon content (15–25 wt.%) which conforms to the values obtained by the authors. Higher values of fixed carbon are preferred for a gasifier to operate better since the fixed carbon produces char which is utilized to thermally crack the tar during the gasification process [25]. In addition, biomass with high content of fixed carbon has a higher energy density resulting in a high energy throughput of the gasifier [26].

The carbon and hydrogen content in the biomass was 46.57% and 6.41% respectively. These are close to the carbon and hydrogen content of 46.8% and 6% respectively reported by Chang et al. [20] and Tsai et al. [21]. Demirbas [24] also asserts that carbon content of biomass is about 45% which is close to the value obtained by the authors. On the other hand, Jenkins [27] reported that the hydrogen content of biomass is about 6% which conforms to the results obtained by the authors. Biomass with high carbon and hydrogen are desirable for energy applications because most of the biomass energy is derived from the chemical bonds of C and H [26]. The nitrogen and oxygen content was found to be 0.96% and 46.06% respectively. The nitrogen content recorded was slightly higher than that reported by Chang et al. [20] and Tsai et al. [21]. The high nitrogen content implies a danger of fuel NO_x formation during thermochemical conversion. The high nitrogen content in the biomass also leads to dilution of syngas due to evolution of nitrogen gas in the producer gas. Jenkins [27] reported that the nitrogen content of biomass varies from 0.2% to more than 1%. The slight variations from the composition of biomass reported in literature may be as a result of differences in geographical location, variety, climate conditions and harvest methods [28]. On the other hand, the moisture content of 13.55% db for maize cobs favored downdraft gasification. According to FAO [7], downdraft gasifiers need reasonably dry fuels (less than 25% moisture dry basis) to reduce on the tar entrainment problem.

Gasification parameters

The mean fuel flow rate, specific load of the reactor, specific gas production rate and amount of condensate collected per kg fuel per hour are given in Table 2.

The mean fuel flow rate of the gasifier was 11.4 kg/h. The specific load of reactor was 185.14 kg/ (m^2 h). According to Goorts [8], the characteristic value of specific loads of the reactor falls between 500–2000 kg/(m^2 h). The low value of the specific load may be explained by the high heat loss in the reactor resulting in lower overall thermal efficiency of the gasifier. The heat energy that can be used in the quick volatilization process and in the degradation of the char is lost; the fuel has a longer residence time resulting into low specific load. The mean amount of condensate collected was 8.5 $\times 10^{-6}$ m^3/(kg fuel h) while the mean specific gas production rate was 8907.6 N m^3/(h m^2). Hariie [29] suggests an optimum value of specific gas production rate of 9000 N m^3/(h m^2) and going by that, the experimental value of specific gas production rate was close to the optimum value implying that the gasifier was operating at nearly optimum conditions.

Producer gas analysis

Three gas samples were analyzed using the micro-GC to determine the percentage composition of the gas. These were normalized and the results are shown in Table 3.

The percentage composition of noncombustible nitrogen (i.e. 62.91%) in the producer gas was higher than the composition (i.e. 50–54%), reported by FAO [7] for typical downdraft gasifier. This in effect reduced the heating value of the producer gas. The relatively high content of N_2 may be attributed to the high content of the fuel bound nitrogen which was found to be 0.96% of the dry fuel. According to Zhou et al. [30], the content of fuel nitrogen in biomass feedstock significantly affects the formation and evolution of nitrogen species during biomass gasification. On the other hand, the percentage composition of CO and H_2 were lower than those reported by FAO [7]. According to FAO [7], gas composition of a typical downdraft gasifier include: CO (17–22%) and H_2 (12–20%). CO_2 was within the range reported by FAO [7] (i.e. CO_2 (9–15%)).

Reactor temperature

The temperatures were measured in selected zones of the reactor which included: the drying zone, pyrolysis zone, oxidation zone, reduction zone and the gas exit after the cyclone. The average temperatures recorded in the zones of the reactor are shown in Table 4.

From Table 4, the average temperature in the drying zone was 101.19 °C, pyrolysis zone 389.03 °C, oxidation zone 882.14 °C, reduction zone 769.12 °C and gas exit after the cyclone 171.30 °C. The pyrolysis temperature of 389.03 °C was suitable for formation of primary tars. However, as the producer gas passed through the oxidation and reduction zones, the primary tars were thermally cracked to secondary and tertiary tars. According to Morf et al. [31], primary tars are formed at temperatures between 200 and 500 °C, secondary tars at temperatures between 500 and 800 °C while tertiary tars at temperatures greater than 800 °C. Ledesma et al. [32] however, reports that very small amounts of tertiary compounds can also be formed in the range of temperatures used in pyrolysis reactors (350–600 °C). The constituents in the tertiary tars are polycyclic aromatic hydrocarbons [33]. On the other hand, the constituents in the secondary tar and tertiary tar include the monoaromatic hydrocarbons [31].

Analysis of selected aromatic hydrocarbons in the condensate

Selected PAH analysis

Fig. 3 shows a typical chromatogram obtained from GC–MS analysis of sampled condensate for selected PAH. The peaks corresponding to the target PAH compounds include: naphthalene with retention time of 5.608 min, acenaphthylene 7.287 min, acenaphthalene 7.527 min, fluorene 8.297 min, anthracene 10.248 min, phenanthrene 10.249 min, fluoranthene 13.142 min, pyrene 13.720 min, benz(a) anthracene 17.350 and benzo(a) pyerene 19.546 min.

Out of the calibrated light polycyclic-aromatic components, naphthalene was the only detected light polycyclic aromatic hydrocarbons by the GC–MS with an average concentration of 204.25 mg/m^3. This may be attributed to the less reactivity of naphthalene than the other light polycyclic hydrocarbons [34]. Naphthalene is a stable aromatic compound that can survive at temperatures higher than 1000 °C [34]. The other light polycyclic aromatic hydrocarbons (i.e. acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene) are easily broken down to heavy polycyclic aromatic hydrocarbons at temperatures higher than 1000 °C hence their very low concentrations which could not be detected by the GC–MS. The results are in conformity with findings from previous researchers; Romar et al. [35] reported naphthalene as one of the most abundant tar components that were identified during biomass gasification in an air-blown

Table 3
Normalized percentage composition of producer gas from maize cobs.

	% H_2	% N_2	% CO	% CH_4	% CO_2	%Total
Normalized component	8.79	62.91	13.65	2.04	12.61	100.00
SD	0.02	0.36	0.52	0.17	0.56	

Table 4
Average temperature in the selected zones of the reactor.

	Drying zone	Pyrolysis zone	Oxidation zone	Reduction zone	Gas exit after the cyclone
Mean temp. (°C)	101.19	389.03	882.14	769.12	171.30
SD (°C)	39.45	205.44	116.32	160.08	52.24

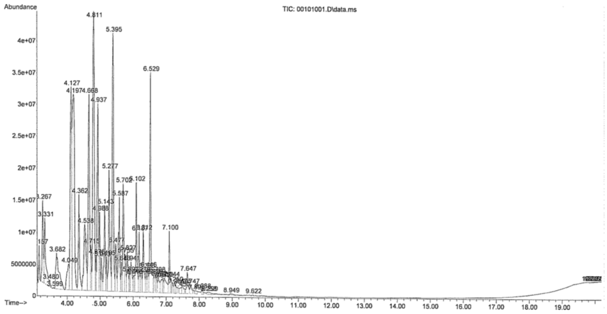

Fig. 3. A typical chromatogram obtained from GC–MS analysis of sampled condensate for selected PAH.

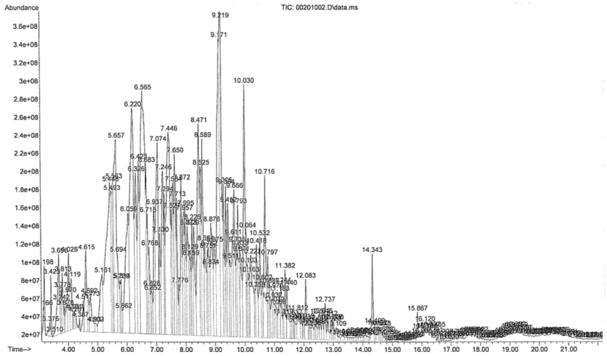

Fig. 4. A typical chromatogram obtained from GC–MS analysis of sampled condensate for BTEX.

downdraft gasifier using woodchips as biomass fuel. Milne and Evans [36] also reported that at a temperature of 900 °C, naphthalene is the major component in tars.

Comparing the concentration total weighted average (TWA) of 52.35 mg/m^3 and short term exposure limit (STEL) of 78.53 mg/m^3 for naphthalene [37], the range observed in these tests of between 176.01 and 220.30 mg/m^3 was considerably high. This indicates that the condensate generated from producer gas cooling presents a high risk to cause both health and environmental effects. According to NIOSH [38] the following are the probable health effects due to naphthalene exposure:

- When naphthalene vapors are inhaled for example when producer gas escapes to the environment through producer gas leakages, it can cause headache, weakness, nausea, vomiting, sweating, confusion, jaundice and dark urine.
- In contact with the skin, naphthalene may be absorbed into the skin which results into a yellowish skin.
- Naphthalene also has effects on the eyes which results into the development of cataract and yellowish eyes (jaundice).
- If ingested, naphthalene may cause abdominal pain, diarrhea, convulsions, unconsciousness and may result in death if ingested in high concentrations.
- Short term exposure to naphthalene may cause lesions of blood cells (hemolysis) while long term exposure may cause chronic hemolytic anemia.

Other effects include kidney and liver damage which may occur from either breathing or eating naphthalene. However, the levels of naphthalene at which each of the above mentioned effects can occur are not known. On the other hand, the probable environmental effects due to naphthalene exposure include: high toxicity to aquatic organisms and may cause long-term effects in the aquatic environment [39].

BTEX analysis

The light aromatic hydrocarbons analyzed in the condensate included: benzene, toluene, ethylbenzene, 1,2-dimethylbenzene and 1,3 + 1,4-dimethylbenzene. These are also commonly referred to as BTEX. Fig. 4 shows a typical chromatogram obtained from GC–MS analysis of sampled condensate for BTEX. The peaks corresponding to the target BTEX compounds include: benzene with retention time of 9.603 min, toluene 6.052 min, ethylbenzene 8.783 min, 1,2-dimethylbenzene 9.046 min and 1,3 + 1,4-dimethylbenzene with retention time of 9.604 min.

Table 5 shows the average concentration of the targeted light aromatic hydrocarbons.

Xylene is one of the monoaromatic hydrocarbon constituents formed as a result of thermal cracking of primary tars to secondary tars during pyrolysis [31]. The presence of xylene in the condensate may be as a result of low temperatures in some zones of the reactor that could not allow sufficient thermal cracking of the secondary tar to tertiary tars. The low temperature might have been caused by the heat losses experienced in some sections of the reactor. Gauma et al. [40] reports that majority of tar compounds observed in downdraft gasifiers are tertiary condensed tars due to thermal cracking inside the gasifier. On the other hand, the presence of monoaromatic hydrocarbons including benzene, toluene and ethylbenzene is characteristic of downdraft gasifiers. These belong to secondary/tertiary compounds category [31].

The high variability in the concentrations of the respective light aromatic hydrocarbons may be attributed to the volatile nature of the compounds. The average concentration of benzene in the condensate (i.e. 17.92 mg/m^3) was below the permissible exposure limit of 30 mg/m^3 reported by ACGIH [41] this would suggest that no adverse health and environmental effects would result from exposure due to benzene. The average concentration of toulene of 182.94 mg/m^3 (or 0.182 mg/l), was well below the permissible exposure range of 10 and 90 mg/l reported by Environment Canada [42]. Generally, toxic effects

Table 5
Concentration of targeted light aromatic hydrocarbons.

Concentration (mg/m^3)					
Run	Benzene	Toluene	Ethylbenzene	1,2-Dimethylbenzene	1,3 + 1,4-Dimethylbenzene
1	12.89	190.54	228.42	401.01	1002.42
2	20.92	188.98	165.57	311.99	956.47
3	18.64	179.82	203.25	367.87	1192.63
4	19.23	172.43	212.46	356.23	873.21
Mean	17.92	182.94	202.43	359.28	1016.18
SD	3.02	7.32	23.11	31.86	117.18

of toluene on aquatic organisms are observed with concentrations ranging between 10 and 90 mg/l. It may therefore be concluded that toulene pollution levels resulting from the condensate could not cause significant toxicity in aquatic life [42]. The concentration of ethylbenzene (i.e. 46.63 ppm or 202.43 mg/m^3) in the condensate was well below the permissible exposure limit of 100 ppm (435 mg/m^3) as a total weighted average (TWA) for up to a 10-h workday and 125 ppm (545 mg/m^3) as a short-term exposure limit reported by NIOSH [43]. It may also therefore be concluded that ethylbenzene pollution levels resulting from the condensate could not cause significant health effects on humans. On the other hand, the total concentration of xylene (i.e. 1,2-dimethylbenzene and 1,3 + 1,4-dimethylbenzene) in the condensate (i.e. 318.30 ppm or 1356.46 mg/m^3) was considerably higher than the permissible exposure limit of 100 ppm (or 435 mg/m^3) and 150 ppm (or 655 mg/m^3) as a total weighted average and short term exposure limit respectively reported by ACGIH [44] thus presenting a potential to cause both health and environmental effects. According to United States Public Health Service [45], the probable health effects due to xylene exposure include: irritation of the skin, eyes, nose, and throat, difficulty in breathing, impaired function of the lungs, delayed response to a visual stimulus, impaired memory, stomach discomfort and possible changes in the liver and kidneys. Both short- and long-term exposure to high concentrations of xylene can also cause effects on the nervous system such as headache, lack of muscle coordination, dizziness and confusion. According to Environment Australia [46], the probable environmental effects due to xylene exposure include; high acute toxicity to aquatic life and can cause injury to various agricultural and ornamental crops. It also has high chronic (long-term) toxicity to aquatic life. However, there are no sufficient data to predict the acute or chronic toxicity of xylene to birds or land animals [47].

Results of calibration

For both the selected light polycyclic aromatic hydrocarbons and the light aromatic hydrocarbons, a linear relationship was obtained with correlation coefficients from the linear regression of 0.991 and above. The correlation coefficient (r) is evaluated as a measure of acceptability for which a value of 1.00 represents a perfect correlation although in practice, a value of r greater than 0.990 is considered satisfactory [48]. Other analytical parameters for the chromatographic method such as percent relative standard deviations (% RSD), limits of detection (LOD), limits of quantitation (LOQ) are provided in Table 6. The LOD and LOQ were determined from Eqs. (2) and (3), respectively.

The LOD for the targeted hydrocarbons ranged between 0.05 and 0.11 μg/ml, with naphthalene, acenaphthylene and toluene having the highest while benzene and xylene having the lowest. This signifies that any of the targeted hydrocarbons that fell below the respective LOD values in the course of analysis could not be detected by the MSD and would therefore fall below the non-detectable limit. The LOQ, ranged between 0.16 and 0.33 μg/ml with naphthalene and acenaphthylene having the highest while benzene and xylene had the lowest. The percent relative standard deviation (% RSD) ranged between 2.88 and 6.35% with acenaphthylene having the highest while 1,3 + 1,4-dimethylbenzene had the lowest. According to Driscoll et al. [49], precision is acceptable if percent relative standard deviation (% RSD) is less than 20%.

Matrix spike for the aromatic hydrocarbons

The performance of the GC–MS was determined by assessment of the surrogate standard compound recoveries. The samples were spiked with a known concentration of a surrogate standard of 1 ppm of each target compound and the spike was injected into the GC–MS for analysis. The GC–MS was run in selective ion mode (SIM) mode. The concentrations of the target compounds after analysis and the corresponding percentage recoveries are shown in Table 7. The percentage recoveries were determined using Eq. (4).

From Table 7, the percentage recoveries ranged between 70% and 103%. For surrogate percent recovery to be acceptable it must fall between 60 and 120% [50].

Measures to minimize pollution levels resulting from biomass gasification

The measures to minimize pollution levels resulting from biomass gasification that are responsible for causing a high risk to both health and environment have been classified under primary measures and secondary measures. The primary measures aim at reducing tar production within the gasifier which results into a less contaminated waste water thus reduced disposal and treatment costs. On the other hand, the secondary measures aim at cleaning the producer gas downstream of the gasification reactor.

Primary measures

The quantity and effluent strength of condensate generated from producer gas cleaning and cooling directly depends on the quantities and characteristics of tar produced respectively. For example, in commercial applications where larger quantities of tar may be produced, intensive producer gas cleaning may be required which results into higher quantities of condensate generated. It is therefore important to seek measures that reduce the tar production during biomass gasification which in the long run minimizes the need for producer gas cleaning, thus less condensate generated. The primary measures are very important especially if the downstream gas utilization process such as in engine applications is bound to be negatively affected by depositions of tar. In such cases, it is possible to generate as little tar as possible. The primary measures may include use of well designed small downdraft gasifiers (30 to a few 100 kW) where an even distribution of air in the oxidizing zone is achieved and thereby successfully converting the tar [51]. However, such a system requires a pilot filter that holds back the remaining tar and requires regular maintenance [51]. Other primary measures include proper selection of gasifier operating conditions such as temperature, equivalence ratio, gasifying medium, use of catalysts, and longer residence time of producer gas in the reactor. Another approach is to apply staged gasification in

Table 6
Correlation coefficient, % RSD, LOD and LOQ for the target compounds.

Compound	Correlation coefficient, r	% RSD	LOD (μg/ml)	LOQ (μg/ml)
Naphthalene	0.991	3.72	0.11	0.33
Acenaphthylene	0.992	5.27	0.11	0.33
Acenaphthene	0.996	2.88	0.07	0.21
Fluorene	0.998	2.96	0.06	0.17
Anthracene	0.993	4.16	0.07	0.29
Phenanthrene	0.995	3.92	0.08	0.24
Benzene	0.998	3.13	0.05	0.16
Toluene	0.992	5.97	0.11	0.32
Ethylbenzene	0.993	5.40	0.10	0.29
1,2-Dimethylbenzene	0.998	3.14	0.05	0.16
1,3 + 1,4-Dimethylbenzene	0.991	6.35	0.05	0.16

Table 7
Matrix spike and percentage recoveries.

Target compounds	Conc. added (mg/m^3)	Conc. after analysis (mg/m^3)	% Recovery
Naphthalene	5.24	4.29	82
Acenaphthylene	6.22	6.40	103
Acenaphthene	6.22	5.78	93
Fluorene	6.79	5.91	87
Phenanthrene	7.28	5.10	70
Anthracene	7.28	5.75	79
Benzene	3.19	2.30	72
Toluene	3.77	3.62	96
Ethylbenzene	4.34	3.73	86
1,2-Dimethyl benzene	4.34	3.26	75
1,3 + 1,4-Dimethyl benzene	4.34	3.17	73

which the primary pyrolysis process and the following oxidation and reduction reaction steps are separated. As a result, very low concentration of condensable hydrocarbons can be achieved. The remaining species are also condensed on separated particles in the subsequent filter systems [51].

Secondary measures

The conventional method of producer gas wet scrubbing is a secondary method for cleaning the producer gas downstream of the gasification reactor. These result into a condensate which may be highly toxic and carcinogenic due to the presence of some polycyclic aromatic hydrocarbons (PAH) and BTEX among others. As a result, the tar–water mixture requires separation and further treatment before disposing it to the environment. The waste water treatment systems may be based on physical, chemical and biological processes as described in details by Lettner et al. [52]. Before choosing the appropriate treatment system, a techno-economic evaluation must be carried out to ascertain the competitiveness of the process [33]. There are a few technologies that have been developed and tested for treatment of the wastewater generated from biomass gasification. Examples include TARWATC technology used for treatment of tar-water mixture in the Danish Haboøre-project [53]. Another waste water treatment technology is the tar cleaning system (OLGA) proposed by the research center of the Netherlands (ECN) and the Dutch company Dahlman [54]. The technology is able to separate both heavy and light tars and keeps them as much as possible away from the also condensing water. In both technologies, the tar liquid is then re-injected into the gasifier for further conversion [55]. In summary a combination of both primary and secondary measures could be employed to reduce the pollution levels that result from biomass gasification.

Conclusion

As biomass gasification gains popularity as a renewable energy technology, it is necessary to ensure that the health, safety and environmental issues do not become a hindrance to its acceptance in the market. This study provides vital information to operators of gasifiers, engineers, policy makers, investors and other stakeholders who are the market actors of the technology about the health, safety and environmental aspects that may arise due to waste water generated during biomass gasification. From the analysis of the waste water, it was found that the concentration of naphthalene was 204.3 mg/m^3, benzene 17.92 mg/m^3, toluene 182.94 mg/m^3, ethylbenzene 202.43 mg/m^3, 1,2-dimethyl benzene 359.28 mg/m^3 and 1,3 + 1,4-dimethyl benzene 1016.18 mg/m^3. It was observed that the concentrations of naphthalene and xylene were considerably higher than the recommended permissible exposure limits (PEL) on both human health and the environment. On the other hand, the concentrations of benzene, toluene and ethylbenzene were below. Generally this study indicated that the liquid effluent meets regulatory standards, but it would be interesting to carryout tests with different biomass fuel types which this study recommends.

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