

Characterization and Cleanup of Wastewater from Pressurized Entrained Flow Biomass Gasification

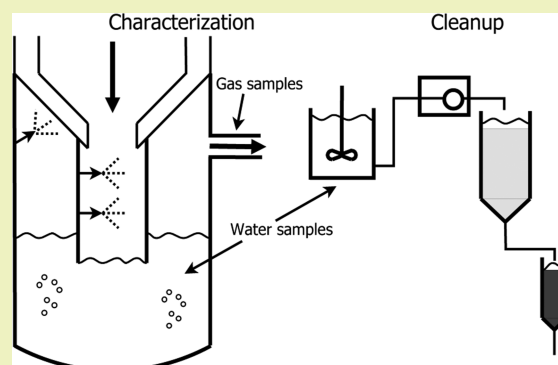
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S Supporting Information

ABSTRACT: Wastewater produced during pressurized entrained flow biomass gasification (PEBG) was characterized and cleaned in order to raise the technology readiness level of the PEBG concept. Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) and thermogravimetric analysis (TGA) were used to study material found in the water. The material was removed using filtration and the concentration of dissolved organic carbon (DOC), polyaromatic hydrocarbons (PAHs) and metals in filtered water was studied using standardized methods. Water was sampled during operation at three oxygen equivalence ratios (λ) and the results were compared to concentrations of gaseous hydrocarbons in the syngas. As λ increased, the amount of soot in the wastewater and the amount of soot precursors in the syngas was reduced. As a result the concentration of particles in the water was reduced and their composition shifted toward a higher percentage of inorganics (ash). PAH concentration trends in the water and in the syngas correlated and dissolved organic material in the water was reduced with increased λ . A particle removal efficiency of 98–99% was achieved using sedimentation and filtration while the DOC was reduced from $\approx 2.5 \text{ mg L}^{-1}$ to below detection limit using granular activated carbon (GAC).

KEYWORDS: Biofuel, Particles, Soot formation, Soot precursors, Sand filtration, GAC contactor



INTRODUCTION

Increased use of energy from renewable sources, according to Directive 2009/28/EC of the European parliament and the council of the European Union, is an important part in promoting the security of energy supply, technological development and innovation.¹ It is further stated by the Directive that it is appropriate to establish mandatory national targets consistent with a 10% share of energy from renewable sources in transport. The European Commission's strategy on clean and efficient vehicles² includes the notion that the internal combustion engine is likely to remain dominant in road vehicles in the short- and medium-term perspective. Internal combustion engine vehicles using liquid biofuels are therefore part of the European Commission's action plan for green vehicles together with electric and hydrogen fuel cell vehicles, which represent the long-term perspective. This action plan will guide policy on clean and efficient vehicles in the European Union.³

The pressurized oxygen-blown entrained flow gasification concept is a thermochemical process that has been used since the 1950s for the production of liquid fossil fuel from coal.⁴ It involves the production of a syngas that is converted to a liquid in downstream catalytic processes. In 2011, a pilot-scale gasifier (maximum 1 MW_{th} fuel capacity, 10 bar(a) pressure) was commissioned to demonstrate the concept for large-scale production of liquid biofuel from solid biomass. This

pressurized entrained flow biomass gasifier (PEBG) consisted of a lock hopper system used for introduction of fuel and O_2 into a ceramic-lined reactor with a conical-shaped outlet and a bubbling water-sprayed quench. Initial work showed that a high quality syngas could be produced from wood powder,⁵ and later work investigated gaseous trace compounds⁶ and submicron particles⁷ in detail. Alternative fuels such as torrefied wood,⁸ biorefinery lignin residue,⁹ and pyrolysis oil¹⁰ were also studied.

However, the bubbling water-sprayed quench has not been investigated in detail. For liquid biofuel production using metal-based catalysts, syngas upgrading will be needed downstream of the reactor to remove acid gases and also trace compounds that can cause fouling and poison catalyst surfaces.¹¹ As the bubbling quench functions as a syngas cleaning step, it needs to be investigated to enable a complete understanding of the PEBG process. In a full-scale operation, the wastewater produced in the bubbling quench will be recirculated. It will need to be cleaned before recirculation because contaminants such as hydrocarbons and particles would otherwise accumulate in the system causing fouling and plugging of spray nozzles. There are several treatment options for water cleanup such as

Received: May 12, 2014

Revised: June 16, 2014

Published: June 17, 2014

coagulation/flocculation,¹² filtration,¹³ and flotation.¹⁴ Wastewater produced during cleaning of raw syngas produced by gasification of coal has previously been treated using flocculation and flotation.^{15–17} A nonpolar flocculation agent with a high affinity for organic material has been added during mixing. This has been followed by phase separation and finally a removal of the nonpolar phase from the water.

In this work, wastewater collected during PEBG operation at three temperatures were characterized with regard to concentration and composition of both particles and dissolved material. A cleanup method designed to remove the particles and dissolved material was tested at the bench scale. A comparison with concentrations of gaseous hydrocarbons in the syngas downstream of the bubbling quench was also carried out.

EXPERIMENTAL SECTION

PEBG Gasifier. The PEBG gasifier has been described in detail previously.⁵ In short, the PEBG gasifier consisted of a lock hopper system used for introduction of fuel and O₂ into a ceramic-lined reactor with a conical-shaped outlet and a bubbling water-sprayed quench (Figure 1). The reactor had an inner diameter of 0.52 m and a

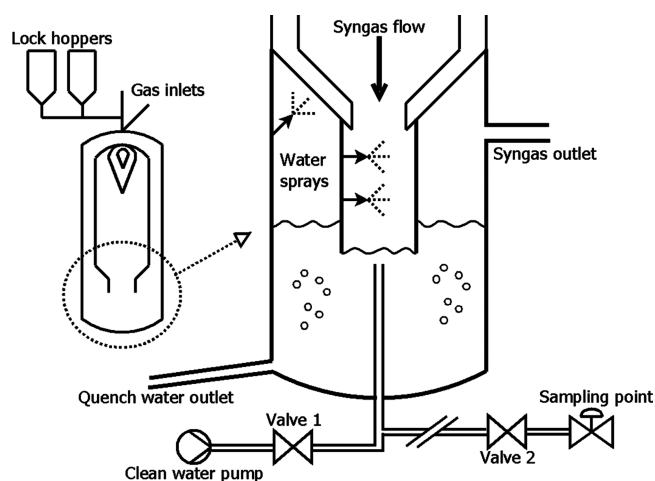


Figure 1. Simplified schematic of the PEBG system (left) and detailed schematic of the water sampling system (right).

vertical reactor wall length of 1.67 m. The quench tank had an inner diameter of 0.88 m, and the water level was kept at a height of ≈ 0.7 m during operation. Hence, the amount of wastewater inside the quench was kept at ≈ 400 kg. Downstream of the bubbling quench, the syngas flow was directed through a syngas outlet with a gas analysis sampling point to a flare, while quench water was directed through a sedimentation tank to an outlet. Note that the gas investigated here is a raw syngas that would need further upgrading prior to conversion to liquid fuel. However, the term “syngas” is used throughout this work for brevity and consistency.

Sampling. The water sampling system comprised a vertical tube (ID 36 mm, length 760 mm) with its end below the water level in the bubbling quench, two horizontal tubes (ID 17 mm), a pump, two interlocking valves (1 and 2), and a needle valve used as a sampling point (Figure 1). During gasification operation, valve 1 was opened, while valve 2 was closed to maintain a flow of clean water (2 L min^{-1}) upward through the vertical tube to prevent quench water from entering the water sampling system during operation. During sampling, valve 2 and the needle valve were opened, while valve 1 was closed to allow a flow of quench water to the sampling point. The flow through the needle valve was monitored via visual inspection to ensure that all clean water had been flushed from the sampling system. The flow was then maintained for 1 min before a 1 L clear glass bottle,

1 L green glass bottle, and two 25 L plastic containers were filled to the top with raw water and sealed. The clear glass bottle was immediately placed in a refrigerator kept at $5 \text{ }^\circ\text{C}$ and awaited analysis as described below. The water in the 1 L green glass bottle was immediately filtered through a quantitative filter with pore sizes of $1\text{--}2 \mu\text{m}$ (00H grade, Munktel, Sweden) and stored in a refrigerator kept at $5 \text{ }^\circ\text{C}$ prior to quantification of polyaromatic hydrocarbons (PAHs). The 25 L plastic containers were stored in a pilot hall at $\approx 15 \text{ }^\circ\text{C}$ and awaited water treatment experiments. Organic material can attach to the walls of plastic containers. Therefore, glass bottles were used during sampling of water that were to be used for characterization to avoid losses of both particles and dissolved organic material. However, given that 50 L of water was needed for water treatment, it was impractical to use glass containers during sampling of water used for water treatment.

Gas samples were collected from the syngas outlet (Figure 1) at a gas analysis sampling point using 10 dm^3 foil gas sampling bags as described in detail previously.⁹ The gas samples were analyzed using a CP-3800 gas chromatograph (Varian, Inc.) with a flame ionization detector (FID) for quantification of CH₄, C₂H₂ + C₂H₄, C₂H₆, and C₆H₆. Note that C₂H₂ and C₂H₄ did not separate on the column used.

Samples were collected during three campaigns carried out using biomass particles with a mass mean particle size (d_{50}) of approximately $130 \mu\text{m}$, at a pressure of 7 bar(a), with a fuel load of 80 kg h^{-1} (equal to $420 \text{ kW}_{\text{th}}$) at oxygen equivalence ratios (λ) of 0.35, 0.425, and 0.50. λ is defined here as the ratio of supplied O₂ to the stoichiometric amount of O₂ needed for complete combustion. Further details of the water sampling are given in the Supporting Information.

Characterization. Filtration was carried out on the water sampled in the clear 1 L glass bottles using quantitative filters with pore sizes of $1\text{--}2 \mu\text{m}$ (00H grade, Munktel, Sweden). Particle concentration was determined by weighing filter papers and filtered water according to a regime described in the Supporting Information.

Morphology and elemental composition of particulate matter were investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) using a XHR-SEM (Magellan 400, FEI Company, The Netherlands) equipped with a X-Max 80 mm² SDD X-ray detector (Oxford Instruments, England). Pieces of filter paper containing particles were loaded onto sample holders for analysis. When necessary, samples were sputter-coated with tungsten using a BAL-TEC MED 020 vacuum coating system to reduce interference from charging. EDS analysis was carried out at 10 kV and 0.2 nA.

Thermogravimetric analysis (TGA) was used to investigate inorganic (ash) content through mass loss during heating in air using a Netzsch STA 409 Thermogravimetric analyzer. Particles were placed in an Al₂O₃ crucible and heated to $225 \text{ }^\circ\text{C}$ at $7.5 \text{ }^\circ\text{C min}^{-1}$ and then to $550 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$ and kept at $550 \text{ }^\circ\text{C}$ for 1 h. This temperature program was in accordance with Swedish standard SS 1871771 (SMS reg. 120.9171) for determination of inorganic (ash) content of material formed during gasification. A blank run (without particles) was carried out so that corrections for buoyancy effects could be made.

Filtered water from the 1 L clear glass bottle was used for analysis of dissolved organic carbon (DOC) and of refractory metals (Al, Si, Ca, and Fe) by an accredited laboratory (ALS Scandinavia AB, Sweden). DOC is defined by European standard EN 1484 as “the sum of organically bound carbon present in water originating from compounds which will pass a membrane filter of pore size of $0.45 \mu\text{m}$ ”. DOC was analyzed using IR detection according to a method based on CSN EN 1484 and SCN EN 13370. Note that this analysis does not give information on the nature of the organic substance. Refractory metal concentration was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) according to a modified version of U.S. EPA method 200.7. pH was determined using a T50 titrator equipped with a DG 113-SC pH probe and a compact stirrer (Mettler Toledo, Switzerland).

Water from the 1 L green glass bottle was used for quantification of the 16 PAHs included in U.S. EPA method 8270 by an accredited laboratory (ALS Scandinavia AB, Sweden) using a method based on CSN EN ISO 6848 and U.S. EPA 8270.

Water Treatment. Water treatment was carried out at the bench scale on wastewater sampled in the 25 L plastic containers using sedimentation followed by sand filtration for removal of particles and a granular activated carbon (GAC) contactor for removal of dissolved organic material (Figure 2). The 25 L plastic container was vigorously

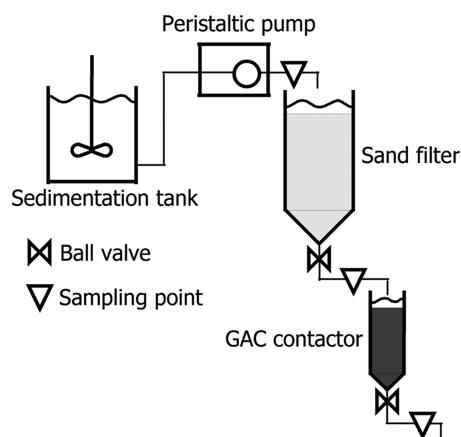


Figure 2. Schematic of the bench-scale water treatment setup.

shaken in order to resuspend particles that had settled during storage. Treatment was then carried out as a batch process using 9 L of sampled wastewater.

Sedimentation was carried out in a 10 L plastic sedimentation tank in three steps: (i) mixing with a flocculation agent, (ii) flocculation, and (iii) settling. For full-scale operation of this water treatment setup, light hydrocarbons such as pentane, toluene, or naphtha would likely be used as flocculants.^{15,16} For this work, a high purity toluene product (Merck, Germany) with well-known physical and chemical properties was used to enable a detailed investigation of the interaction between particles and flocculant.

In practice, sedimentation was carried out by adding wastewater to the 10 L plastic sedimentation tank. Toluene was added, and the wastewater was mixed for 30 s at 800 rpm using a CAT R50 stirrer. Flocculation was carried out by stirring at 30 rpm for 15 min followed by settling for an additional 15 min. For full-scale operation, the material removed from the water can then be used as fuel for a gas generator.¹⁷ The toluene dose was adjusted according to the particle concentration so that 1 g of toluene was added for each gram of particles. In other words, the weight ratio of the quantity of toluene and particles was 1:1. Both the dosing and mixing used in step (i) was based on the work by Mondria and Logman,¹⁶ while the flocculation regime was based on bench-scale work by Jarvis et al.¹⁸ Settling time was based both on the work by Jarvis et al.¹⁸ and on the recommendations of Potter and Richter.¹⁵

After the sedimentation step, water was pumped to a sand filter at a flow rate of 0.1 L min⁻¹ using a peristaltic pump (model 520S, Watson Marlow, United Kingdom). The sand filter was constructed from a 1 L separation funnel (inner diameter 80 mm) filled with a 40 mm high layer of gravel with a particle size of 8–16 mm at the bottom. Above the gravel was a bed of sand 200 mm in height (used as filtration media) with a particle size of 0.5–1.0 mm. The gravel and sand were separated by a sheet of filter fabric. This is a common sand filter design used in full-scale applications.¹⁹ The surface overflow rate was 19.9 mm min⁻¹, which resulted in a contact time of 10 min. Sand filters used previously for pilot-scale work have been larger (300 mm inner diameter, 1 m bed height) and used higher surface overflow rates (133–150 mm min⁻¹) resulting in contact times of 6–7.5 min.^{18,20} Note that the flow rate used here was dictated by the dimensions of the downstream GAC contactor where it was essential that a given contact time was achieved (see below). Between water treatment runs, the sand filter was backwashed with tap water to remove particles filtered from the wastewater during the previous run.

After the sand filter, water was allowed to flow directly through a GAC contactor. To prepare the GAC contactor, activated carbon pellets were crushed and sieved through a 500 μm and 250 μm mesh to prepare GAC particles with particle sizes of 250–500 μm . The crushed particles were rinsed with tap water to remove fines and dried at room temperature in a fume cupboard. The GAC particles were then poured into a chromatographic column (inner diameter 40 mm) with a glass frit at the bottom (type P2 with a pore size of 40–100 μm). The particle bed height was 280 mm. Given the water flow rate of 0.1 L min⁻¹, the surface overflow rate was 80 mm min⁻¹ and the contact time was 3.5 min. The aim was to simulate a full-scale GAC contactor, and they use GAC particles with a diameter of ≈ 1 mm and a contact time of 10–15 min.^{21–23} To calculate the corresponding contact time for a large-scale treatment plant, it was assumed that intraparticle diffusivity increases linearly with a reduction in GAC particle size. Consequently, a smaller particle size can compensate for a shorter contact time (eq 1). This is referred to as the constant diffusivity approach to compare bench-scale and full-scale GAC contactor tests and has been reviewed in detail by Nowack et al.²¹ The approach has been shown to enable bench-scale tests to simulate full-scale operation²⁴ and has been used previously to study water treatment.^{21,23} Equation 1 shows the assumed relationship between contact time and GAC particle size.²¹ According to eq 1, the contact time in the bench-scale setup described here using 250–500 μm particles correspond to a contact time of 7–14 min in a full-scale plant using 1 mm particles. Fresh GAC particles were added prior to each treatment.

$$\frac{\text{Particle size}_{\text{Full scale}}}{\text{Particle size}_{\text{Bench scale}}} = \frac{\text{Contact time}_{\text{Full scale}}}{\text{Contact time}_{\text{Bench scale}}} \quad (1)$$

Water samples were collected in 1 L green glass bottles during water treatment after each treatment step. The sedimentation step was carried out before any sampling was carried out. Water was then pumped through the sand filter and the GAC contactor for 10 min before the water flow from the sedimentation tank was directed to a glass bottle for 10 min (hence, filling it with 1 L of water). During sampling, the flow through the sand filter and GAC contactor was stopped using ball valves (Figure 2). After sampling, the water was directed through the sand filter and GAC contactor again. Water was then sampled after the sand filter and GAC contactor in the same manner (i.e., filling another sample bottle for 10 min while stopping the flow downstream of the sampling point). The sampling regime allowed for 3 bed volumes of water to pass through the sand filter and GAC contactor prior to sampling after them. This ensured that the sample was representative of wastewater having been subjected to water treatment.

Sampled water was filtered using filter papers that had been handled as the filter papers used for characterization (Supporting Information). Particles were quantified as described above and filtered water was analyzed for DOC.

RESULTS AND DISCUSSION

Characterization. The particle concentration in the raw wastewater decreased as λ (and thus also the temperature) increased (Table 1). For example, the particle concentration was ≈ 5 times higher at $\lambda = 0.35$ (1260 °C) compared to $\lambda = 0.50$ (1460 °C). The gaseous hydrocarbon concentrations in the syngas also decreased as λ was increased (Table 1). For example, $\text{C}_2\text{H}_2 + \text{C}_2\text{H}_4$ was reduced from 200 to 6 ppm, while C_6H_6 was reduced from 31 to essentially 0 ppm. Note that C_2H_2 and C_2H_4 did not separate on the GC column used here. C_2H_2 and C_6H_6 concentrations of 3200 to 500 and 1100 to 100 ppm, respectively, were observed during previous PEBG campaigns carried out at 2 bar(a) and 0.20 MW_{th} with λ between 0.35 and 0.50 (1130 to 1340 °C).⁶ Material from the wastewater collected during those campaigns was found to consist mainly of soot. C_2H_2 and C_6H_6 are known soot

Table 1. Wastewater and Syngas Characteristics at Different Gasifier Conditions

| gasifier conditions | | | |
|---|--------|-------|------|
| oxygen equivalence ratio (λ) | 0.35 | 0.425 | 0.50 |
| temperature ($^{\circ}\text{C}$) | 1260 | 1360 | 1460 |
| wastewater characteristics | | | |
| pH | 7.3 | 7.2 | 7.6 |
| particle concentration (mg L^{-1}) | 82.1 | 25.7 | 15.9 |
| DOC (mg L^{-1}) | 2.6 | 2.4 | 2.2 |
| PAH sum 16 ^a ($\mu\text{g L}^{-1}$) | 510 | 6 | 27 |
| refractory metals ^b (mg L^{-1}) | 41.9 | 38.8 | 35.5 |
| gaseous hydrocarbons | | | |
| CH_4 (ppm) | 13,300 | 3,095 | 52 |
| $\text{C}_2\text{H}_2 + \text{C}_2\text{H}_4$ (ppm) | 200 | 25 | 6 |
| C_2H_6 (ppm) | 7 | 1 | 2 |
| C_6H_6 (ppm) | 31 | 3 | 0 |

^aSum of the 16 PAHs quantified with the U.S. EPA 8270 method. ^bAl, Si, Ca, and Fe.

precursors.²⁵ If the particles collected here also consisted mainly of soot, then the decrease in concentrations of both wastewater particles and gaseous soot precursors with increased λ could be attributed to a reduction in soot formation in the PEBG.

SEM imaging of the material filtered from the wastewaters sampled in the clear 1 L glass bottles showed that the particles had similar morphologies and sizes at all λ s investigated here. Material formed at $\lambda = 0.35$ was deemed representative of material found in all three waters and consisted of agglomerated spherical particles with diameters of ≈ 50 – 100 nm (Figure 3).

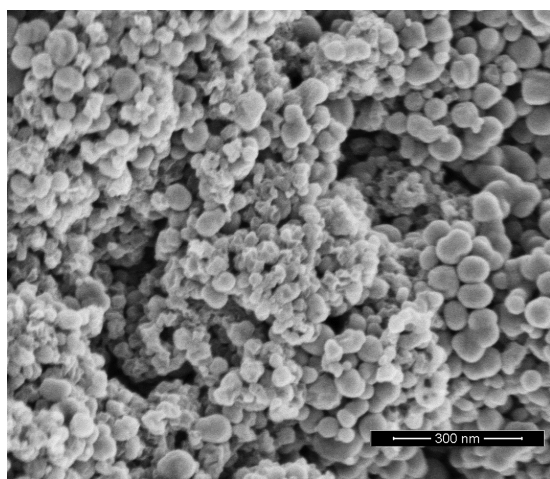


Figure 3. SEM image (100,000 \times magnification) of material filtered from the water sampled during PEBG operation at $\lambda = 0.35$.

The particle morphology was similar to that of soot particles found in wastewater during previous PEBG campaigns using the same fuel as here⁶ and of particles from a bench-scale entrained flow gasifier using wood as fuel.²⁶

The elemental composition of the particles produced during the $\lambda = 0.35$ campaign was dominated by C (96 wt %), and it was concluded that they consisted almost entirely of soot. This was expected as previous work have shown that during gasification²⁷ and pyrolysis,²⁸ at temperatures between 1000 and 1400 $^{\circ}\text{C}$, the particles that form consist of soot. Soot particles collected from the syngas, after the bubbling quench,

during previous PEBG campaigns were similar in composition to the particles produced during the $\lambda = 0.35$ campaign.⁷ They were also similar with regards to size and morphology. Investigations using transmission electron microscopy (TEM) showed that the soot particles consisted of inner cores surrounded by outer shells.⁷ This was explained by recirculation of the particles in the gasifier flame where an outer shell is added with each recirculation. If so, the particles passed the bubbling quench unaltered. In other words, their composition, size, and morphology were the same inside and after the quench.

With increasing λ , the composition of the particles changed toward a reduced amount of C and an increased amount of O and refractory metals (Figure 4). This was in agreement with

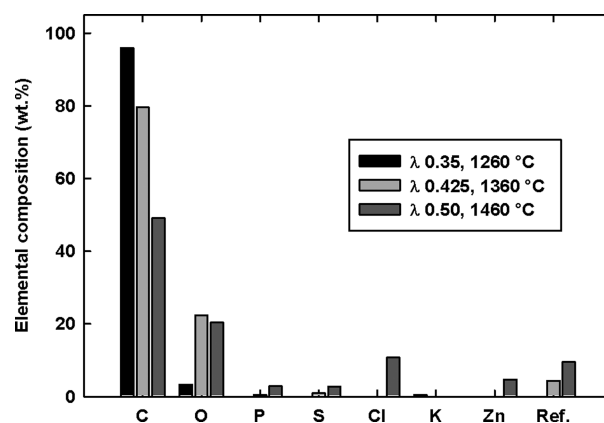


Figure 4. Elemental bulk composition from SEM-EDS analysis of particles filtered from the water sampled during PEBG operations at $\lambda = 0.35$, $\lambda = 0.425$, and $\lambda = 0.50$. Ref. = refractory metals (Al, Si, Ca, and Fe).

the observation that charging was higher when the material collected at higher λ was investigated because charging is induced by refractory metals. Coating was needed to successfully carry out EDS analysis of material collected at $\lambda = 0.5$ without significant interference from charging. A dramatic reduction in C content was observed from $\approx 96\%$ at $\lambda = 0.35$ to $\approx 80\%$ at $\lambda = 0.425$ and further to $\approx 50\%$ at $\lambda = 0.50$. This was in agreement with the TGA data as the particles formed at $\lambda = 0.35$ displayed a mass loss of 90.7%, while the particles formed at $\lambda = 0.425$ displayed a mass loss of 86.2%. TGA was not carried out for particles formed at $\lambda = 0.50$ because a representative sample could not be produced. The fraction of soot (and thus C) in the particles was therefore lower at higher λ , whereas the refractory metal fraction of the particles was increased. However, the refractory metal concentration in the filtered water was fairly constant across all λ s (Table 1). It is therefore likely that the composition of the particles changed because the amount of soot was reduced, while the amount of refractory metals remained constant.

Out of the refractory metals in particles formed at $\lambda = 0.425$ and 0.50, the contributions from Fe and Al were 66.7–67.3 and 12.6–17.3 wt %, respectively, while the contributions from Fe and Al to the refractory metals in the water were 0.01–0.08 and 0.01–0.04 wt %, respectively. The over representation of Fe and Al in the particles was attributed to the flocculating effect of Fe and Al on organic compounds in water. The pH of the wastewaters was between 7.3 and 7.6 and in this pH range Fe and Al form hydroxides when they are in a water solution.²⁹

These hydroxides are known to form agglomerates with organic material through a mechanism referred to as sweep flocculation.^{30,31} It is possible that through this mechanism, Fe and Al were removed from the water column and became enmeshed in the particles. Fe and Al salts are commonly used in water treatment to remove dissolved organic material²⁹ and could replace the GAC contactor used here. However, this would require additional tanks for mixing, flocculation, and sludge removal.

DOC was slightly reduced as λ was increased (Table 1). PAH concentration was reduced by 95% as λ was increased from 0.35 to 0.50, but there was no trend across all three waters (Table 1). Note that it is the sum of the concentrations of the 16 PAHs quantified with the U.S. EPA 8270 method that is given in Table 1. The concentrations of the individual PAHs are given in the Supporting Information. The PAHs that were quantified in the wastewater were not quantified in the syngas, which means that a direct comparison between PAH content in wastewater and syngas was not possible. However, C_6H_6 was quantified in the syngas and is used here as a marker for PAHs because it is a precursor to the higher MW PAHs quantified in the wastewater.³² The C_6H_6 concentration in the syngas was reduced from 31 to essentially 0 ppm as λ was increased from 0.35 to 0.50 (Table 1). Consequently, there was a similarity in PAH concentration trends in both wastewater and syngas. The increase in λ resulted in a rise in temperature from 1260 to 1460 °C, and investigations using drop tube furnaces have shown that PAH yield in the gas phase is reduced with increased temperature.^{27,28} High temperatures promote the formation of OH radicals, which in turn promote PAH oxidation with subsequent formation of lower MW PAHs, which are more readily combusted.²⁵ It is reasonable to assume that the PAHs formed upstream of the bubbling quench and that a given portion of them were retained in the bubbling quench while the rest remained in the syngas. The reduction in DOC was also attributed to higher combustion with subsequent conversion of organic material to gaseous compounds, which readily passed through the bubbling quench.

Water Treatment. Samples taken after the sedimentation tank and after the sand filter showed significant reduction in particle concentrations compared to raw wastewater. The DOC was partly reduced during sedimentation, but it was unaltered over the sand filter and finally significantly reduced over the GAC contactor (Figure 5). Note that the detection limit of the DOC method was 0.5 mg L⁻¹. Two out of three DOC results after the GAC contactor were below this detection limit but are listed in Figure 3 as 0.5 mg L⁻¹, even though the true DOC could be much lower.

The reduction in particle concentration during sedimentation, consisting of (i) mixing with a flocculation agent, (ii) flocculation, and (iii) settling, is valuable as a reduced particle load onto the sand filter means that it can be backwashed less often. Backwashing was only carried out here between runs as the amount of particles introduced to the sand filter was not enough to saturate it. Sedimentation reduced the particle concentration by 88%, 73%, and 29% during treatment of water sampled during PEBG operations at $\lambda = 0.35$, $\lambda = 0.425$, and $\lambda = 0.50$, respectively (Figure 5). Hence, sedimentation was more efficient at removing particles when the particle concentration was high and less efficient when the concentration was low. This was attributed to the fewer number of particle collisions that occurred during the flocculation stage according to Von Smoluchowski's model for orthokinetic flocculation describing

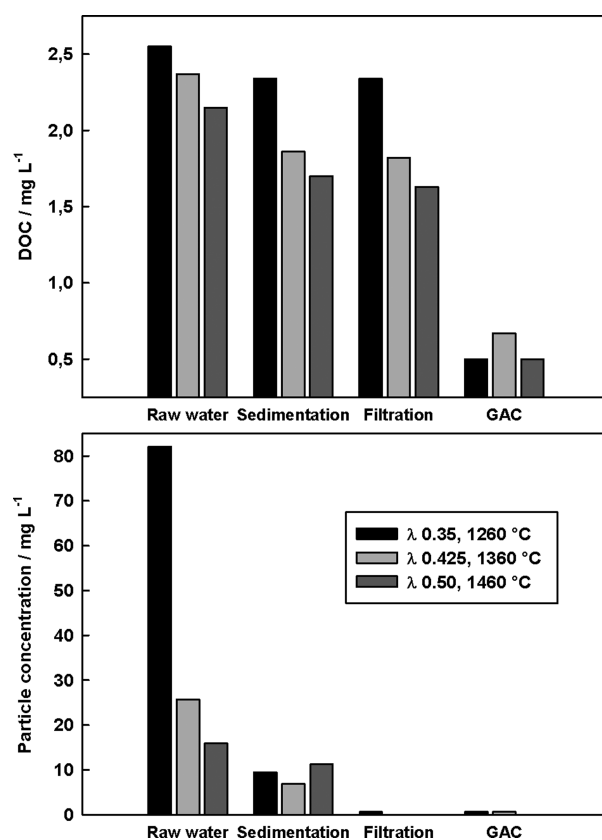


Figure 5. DOC and particle concentrations through the water treatment steps.

the number of collisions between two particles moving in laminar flow (eq 2).³³

$$H_{ij} = \frac{4}{3} n_i n_j R_{ij}^3 \frac{dv}{dz} \quad (2)$$

In this model H_{ij} = the number of contacts between i and j particles per unit time, n_i , n_j = respective number of concentrations of i and j particles, R_{ij} = radius of interaction of the two particles, and dv/dz = velocity gradient in laminar flow.³³

The aim of the flocculation step was to increase particle size. This increased sedimentation and simplified sand filtration as larger particles are deposited faster and are easier to remove using sand filtration than smaller ones. The dominating mechanism was assumed to be bridging or clumping of the particles by toluene, thus forming agglomerates that grow upon particle collision. However, apart from particle collisions, successful flocculation also relies on an affinity for the flocculant to the particles. As revealed by EDS analysis, the particles contained soot (C) and inorganics (Al, Si, Ca, and Fe) in varying compositions depending on the conditions under which they were formed. When added to water, inorganics such as Al, Ca, and Fe form hydrophilic compounds,^{29,34} which have a stronger affinity for water than for toluene. Hence, the affinity for the toluene to particles containing high amounts of inorganics will be lower than to those containing low amounts. Consequently, reduced particle removal efficiency with increased λ could also be attributed to a lower affinity of the flocculant for the particles.

After sedimentation and sand filtration, the particle concentration had been reduced by 99–100%. The particle

concentration after the GAC contactor was comparable but slightly higher than after the sand filter during water treatment of all three waters, resulting in total particle removal of 98–99% for the whole treatment process. This was attributed to the release of GAC fines.

DOC was partly removed during sedimentation, which was attributed to transport of dissolved organic compounds from the water phase to the toluene during the flocculation step. Organic compounds will more readily dissolve in an organic solvent such as toluene than in water. Sedimentation removed 22% and 21% of the DOC during treatment of water sampled during operation at $\lambda = 0.425$ and $\lambda = 0.50$, respectively, but only 8% during treatment of water sampled during operation at $\lambda = 0.35$. In other words, almost 3 times as much DOC was removed from the $\lambda = 0.425$ and $\lambda = 0.50$ waters compared to the $\lambda = 0.35$ water, and this was attributed to the contribution to DOC of residual flocculant (toluene) in the water. All three waters had similar DOC concentrations (2.2–2.6 mg L⁻¹), while the particle concentration of the $\lambda = 0.425$ and $\lambda = 0.50$ waters were much lower than the $\lambda = 0.35$ water (15.9 and 25.7 mg L⁻¹ compared to 82.1 mg L⁻¹) (Table 1, Figure 5). A total of 1 mg of toluene was added for each mg of particles, and as a result, the amount of toluene added to the $\lambda = 0.35$ water was 3 and 5 times higher than to the other waters. Toluene (C₇H₈) contains 91.2 wt % C; hence, 14.5–74.9 mg L⁻¹ of C was added during sedimentation. This means that only a few percent of the added toluene had to remain in the water after sedimentation in order for the DOC to be affected. Metal salt-based coagulants are used for water treatment in the same way as toluene has been used here, and previous work has shown that 3–14% of these coagulants remain after treatment.³⁵

Sand filtration had insignificant effects on the DOC concentration as expected, and after sand filtration, the DOC concentrations were 2.3, 1.8, and 1.6 mg L⁻¹ for the $\lambda = 0.35$, $\lambda = 0.425$, and $\lambda = 0.5$ waters, respectively. After the GAC contactor, the DOC concentrations had been reduced to 0.5, 0.7, and 0.5 mg L⁻¹, respectively, which is equivalent to reductions of 79%, 63%, and 69% across the GAC contactor. Total reduction over the entire treatment process was 80%, 71% and 77%, respectively, which was similar to previously published results.^{21,23} Nowack et al.²¹ and Hooper et al.²³ reported 83% and 87% removal from water with initial total organic carbon (TOC) of 3.0 and 1.5 mg L⁻¹ and pH of 7.3 and 6.4, respectively.

CONCLUSIONS

The particles in the wastewater consisted of soot and refractory metals, and as λ was increased, both of the amounts of soot precursors in the downstream syngas and amount of soot in the wastewater was reduced. As a result of reduced soot formation, the concentration of particles was reduced, and their composition shifted toward a higher percentage of inorganics (ash). Fe and Al hydroxides were taken up from the water by the particles through sweep flocculation. PAH concentration trends in the wastewater and in the downstream syngas correlated and dissolved organic material in the wastewater was reduced with increased λ .

The water treatment successfully removed particles and dissolved organic material from all three investigated wastewaters. For a more comprehensive understanding of the treatment process, the affinity of the flocculant to particles with different composition during sedimentation should be inves-

tigated. Quantification of residual flocculant in the water after sedimentation is also suggested. The next step toward developing a treatment system for wastewater derived from full-scale PEBG is to move from the bench-scale batch process presented here to a continuous pilot-scale process.

ASSOCIATED CONTENT

Supporting Information

Details of the sampling regime, including gasifier operating conditions during sampling, details of the sample filtration process, including sample handling, and concentrations of individual PAHs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Norrbotten Research Council. The PEBG campaigns have been operated with financial support from the Swedish Energy Agency, IVAB, Sveaskog, and Smurfit Kappa Kraftliner. Partial funding also came from Bio4Energy and the Swedish Centre for Biomass Gasification. The authors also thank all ETC personnel involved in the experimental campaigns.

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