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Research paper

# The effect of torrefaction on the process performance of oxygen-steam blown CFB gasification of hardwood and softwood

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## ARTICLE INFO

## ABSTRACT

Torrefaction is a promising biomass upgrading method, offering advantages in logistics and handling. Gasification is an attractive thermochemical conversion technology due to its flexibility in the product gas end-use. The aim of this paper is to investigate the impact of torrefaction on the gasification performance of a softwood (spruce) and a hardwood (ash). Spruce and ash were torrefied at 260 and 280 °C, and at 250 and 265 °C, respectively, and pelletized. All feedstocks were gasified at 850 °C and atmospheric pressure under oxygen-steam circulating fluidized bed gasification conditions, with magnesite as bed material and with an equivalence ratio (ER) of 0.3 and a steam-to-biomass mass ratio (SBR) of 1.0. Only the torrefied feedstocks were gasified varying ER and SBR values. The results show that torrefaction affected the gasification performance of both feedstocks leading to decreasing the cold gas and carbon conversion efficiencies. For spruce, torrefaction did not affect the permanent gas composition but led to a decrease of the total tar content for both spruce 260 and spruce 280. For ash, torrefaction resulted in decreasing the $CH_4$ volume fraction, and increasing the $H_2$ volume fraction and the total tar content for both torrefaction temperatures. Varying the ER and SBR affected only the Class 3 tars of ash 250. Conclusively, torrefaction of spruce and ash did not offer substantial benefits on the gasification performance under the investigated conditions. It is suggested that research of torrefied wood gasification includes feedstock's chemical analysis and characterization of products obtained under fast devolatilization conditions.

## 1. Introduction

Biomass is envisaged to make a major contribution to the future energy supply. However, untreated biomass is not ideally suited for energy conversion applications. This is due to its generally high moisture mass fraction, which corresponds to a low energy content. Moreover, its main biochemical and mineral compositions vary based on the type of biomass, time and location of cultivation. This makes the conversion of biomass complicated and logistics more expensive. Therefore, efforts are being made to develop upgrading processes which convert biomass into a fuel with superior properties in terms of logistics and end-use. Among biomass kinds, wood is considered an attractive option due to the composition of the contained ash and the fact that it can be the raw material for second generation biofuel production. Wood may be classified in two types, softwood and hardwood; hardwood contains more hemicellulose (the xylan group) and less lignin and cellulose [1], and the hardwood's lignin is considered more unstable to thermal treatment due to the higher mass fraction of syringylpropane units [1,2]. Torrefaction is a thermochemical process, carried out at a relatively low temperature, typically in the range of 230–300 °C, in an oxygen-deficient atmosphere. At this temperature range hemicellulose is expected to be the most converted polymer, followed by

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cellulose and lignin. Hemicellulose starts degrading between 200 and 380 C, with xylan being the most thermally unstable containing monomer at the low temperature side, followed by glucomannan [3]. Thermal degradation of lignin starts approximately at 200 °C but occurs generally at higher temperatures, between 400 and 750 °C [4], and thermal devolatilization of cellulose starts approximately at 230 and finishes at 400 °C [5]. As a result, the extent of the effect of torrefaction on the chemical composition depends on the temperature, the residence time at this temperature and the type of wood. In addition, torrefaction in combination with a densification step is a promising technology for upgrading the biomass into a high quality solid energy carrier. During this process, biomass becomes more coal alike; it has a higher energy density, lower O/C and H/C molar ratios, and it becomes more hydrophobic, more resistant against biological degradation and more brittle. Therefore, torrefaction pretreatment leads to benefits in transportation, handling and storage. Studies have shown that torrefied biomass is a promising feedstock for (entrained flow) gasification and co-firing in coal-fired power plants from an efficiency and environmental point of view, e.g. no additional equipment is needed for grinding and torrefaction offers environmental benefits in terms of climate change impact from a life cycle perspective [6—9].

Different types of gasification reactors exist, such as fixed bed, entrained flow, plasma and fluidized bed. Circulating fluidized bed (CFB) gasification is attractive because the feedstock size is not as critical, as in fixed bed and entrained flow gasification, and scaling up is relatively straightforward [10]. Roracher et al. [11] described that large scale coal and biomass CFB gasification plants exist with capacities up to 100 MW$_{th}$ output, where the product gas is fired in lime kilns, dedicated boilers for power generation or combined heat and power generation. In terms of operational parameters, experimental studies on CFB gasification of wood [12—15] have shown that an increase in the bed temperature leads to an increase in the H$_2$ volume fraction and H$_2$/CO ratio, and a decrease in the tar content of the product gas. In addition, the introduction of oxygen and steam [14,15] appears to improve product gas quality with respect to increasing the H$_2$ volume fraction and decreasing the tar content. Oxygen offers the heat for endothermic processes due to oxidation reactions and steam influences the product gas quality through chemical reactions, such as the water gas shift (WGS), char gasification and steam reforming. The typical range of the equivalence ratio (ER) in gasification is between 0.2 and 0.4; lower values result in low carbon conversion efficiency (CCE), whereas, higher values result in combusting the product gas, thus decreasing its calorific value due to the combustion of H$_2$, CH$_4$ and CO species. Generally, a higher ER results in lowering the total tar content of the

product gas and cold gas efficiency (CGE), and increasing the CCE [16]. In addition, typical steam to biomass mass ratios (SBR) range between 0.5 and 1.5 and increasing the SBR value results in higher H$_2$ and CO$_2$ volume fractions and in lower total tar content in the product gas [10]. Finally, various bed materials can be applied and magnesite has shown benefits, compared to quartz sand, in terms of reducing the tar content [17].

So far, only a limited number of studies [15,18—20] have focused on the effect of torrefaction on the permanent gas composition and tar content in the product gas during wood gasification; an overview is presented in Table 1. In addition, all these studies were restricted to bubbling fluidized bed gasification and the feedstocks used were torrefied on small scale by the researchers, except for the study by Kulkarni et al. [18]. These researchers acquired their feedstock from an American company, i.e. New Biomass Energy, LLC. In general, these authors concluded that torrefaction did not result in improving the gasification performance. Even though, the permanent gas composition remained unaffected and the total tar content decreased, the carbon CCE and CGE decreased as well. Berrueco et al. [15] performed lab-scale O$_2$-steam gasification of Norwegian spruce and forest residues at 850 °C. They presented that increasing the torrefaction temperature from 225 to 275 °C led to an increase in the H$_2$ volume fraction by approximately 1.5 wt%, and a decrease in the total tar content (up to 66 and 85 wt% for spruce and forest residues, respectively). Moreover, these authors presented that an increasing torrefaction temperature led to an increase in char and gas yields, a reduction in the CCE and the CGE did not show a clear trend. Sweeney [20] performed steam gasification at 788 °C, and, although the torrefaction conditions were not mentioned, he reported the same effects of increasing torrefaction degree as Berrueco et al. [15] concerning the product gas constituents' composition and CCE. On the other hand, he reported a decrease in CGE upon torrefaction. Kulkarni et al. [18] performed air-blown gasification of pine wood at 935 °C. These authors also do not mention the torrefaction conditions. They reported that torrefaction led to a decrease in the CGE and no significant changes in product gas constituents' compositions. Woytiuk et al. [19] performed steam-air gasification at 900 °C of willow and torrefied willow at four different torrefaction temperatures. These authors limited their permanent gas results to H$_2$ and CO volume fractions only and concluded that increasing the torrefaction temperature increased the H$_2$ volume fraction and decreased the total tar content up to 47% but only when the torrefaction temperature reached and exceeded 260 °C. Woytiuk et al. did not explain the reasons for this behavior but willow is a hardwood, which as mentioned contains more hemicellulose and more reactive lignin at low temperature. So this result can be attributed to the cellulose not reacting at

**Table 1**
Overview of bubbling fluidized bed gasification studies with torrefied wood.

| Reference | Power level (W) | Gasification agent | Temperature (°C) | Biomass | Particle size[b] (µm) | Torrefaction temperature (°C) | Bed material |
|---|---|---|---|---|---|---|---|
| [18] | 20,000 | Air | 790, 935, 1000 | Untreated pine | 850 | — | Sand |
| | | | | Torrefied pine | 850 | n.d. | |
| [15] | 2,000[a] | Oxygen, steam | 900 | Untreated spruce | 6000 | — | Silica sand |
| | | | | Torrefied spruce | 6000 | 225, 275 | |
| | | | | Untreated wood residues | 6000 | — | |
| | | | | Torrefied wood residues | 6000 | 225, 275 | |
| [20] | 200,000 | Steam | 780 | Untreated pine | 950 | — | Sand |
| | | | | Torrefied pine (brown) | 950 | n.d. | |
| | | | | Untreated pine (dark) | 950 | n.d. | |
| [19] | 30,000[a] | Air, steam | 900 | Untreated willow | n.d. | — | Silica sand |
| | | | | Torrefied willow | n.d. | 240, 260, 270, 280 | |

[a] Capacity was not mentioned, therefore it is calculated based on used feeding rate.
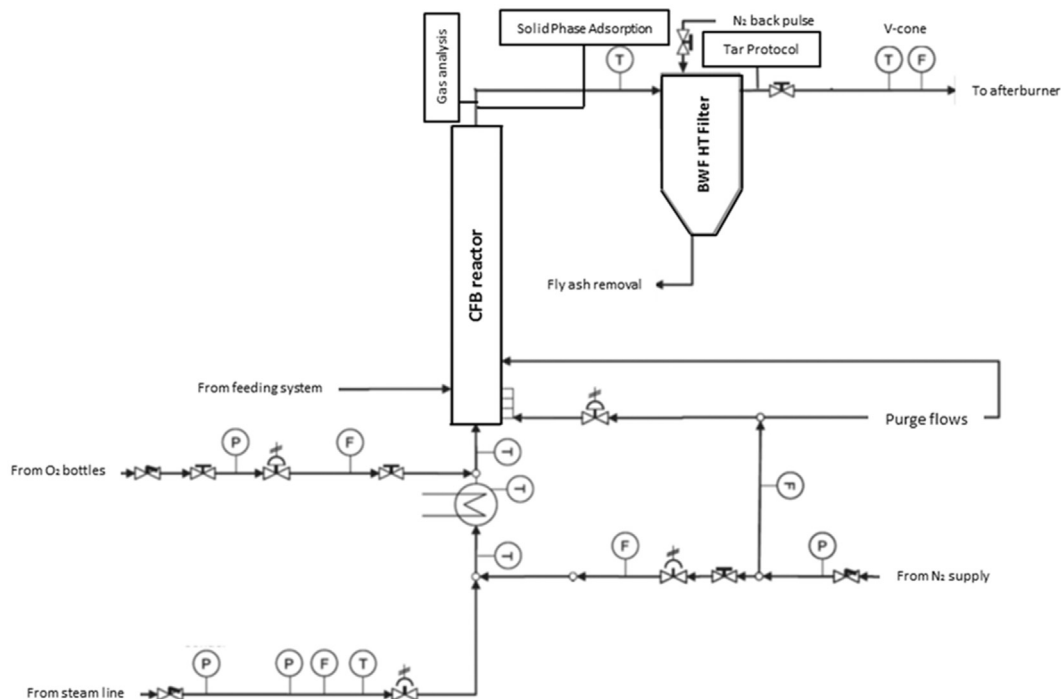[b] The particle size concerns the biomass.

**Fig. 1.** TU Delft CFB gasifier experimental test rig.

low torrefaction temperature, thus increasing its content in the torrefied willow while maintain unstable sugar groups.

As pointed out above, there has been only limited, and in several



**Fig. 2.** CFB gasifier with the eight thermocouples ($T_1$-$T_8$) and eight differential pressure meters (symbols 1–10, excluding symbol 7). $P_R$ corresponds to a single absolute manometer and $T_{in}$ to a thermocouple to measure the inlet temperature of the fluidization medium [14].

aspects contradictory, research on fluidized bed gasification of torrefied biomass. Furthermore, so far no research has been carried out regarding the impact of torrefaction on oxygen-steam blown CFB gasification, presenting in detail the permanent gas composition of torrefied hardwood gasification or reporting a wide range of tar species formed. Therefore, the aim of this study is to investigate the impact of torrefaction on the permanent gas composition, tar composition, CCE and CGE during atmospheric oxygen-steam CFB gasification of hardwood and softwood. Since torrefaction shows advantages in logistics, can its combination with gasification performed under typical operating conditions in industrial relevant application applications lead to even larger benefits?

## 2. Materials and methods

### 2.1. Experimental test rig geometry and functionality

The experimental test rig at TU Delft consisted of a 100 kW$_{th}$ CFB gasifier followed by a candle filter unit, and equipped with a gas supply system, a solids supply system and analytical equipment. A schematic of the experimental rig is presented in Fig. 1.

The riser had a length of approximately 5.5 m and an inner diameter of 83 mm. The downcomer had an inner diameter of 54 mm. The cyclone had an inner diameter of 102 mm and a total height (excluding the flanges) of 630 mm. The reactor was made of stainless-steel AISI310, DIN 1.4845 for the parts exposed to high temperature and in contact with the reactants and the products. The other parts were made of stainless-steel AISI316, DIN 1.4404 [17]. The reactor temperature was controlled via monitoring eight K-type thermocouples. Seven of them were located in the riser, whereas one was located in the downcomer. Eight differential pressure meters were installed to measure the pressure drop along the installation and to check the circulation of the solids. A schematic of the reactor is presented in Fig. 2.

The gas cleaning unit consisted of a high-temperature filter unit containing four woven ceramic candles (BWF, Germany) operating
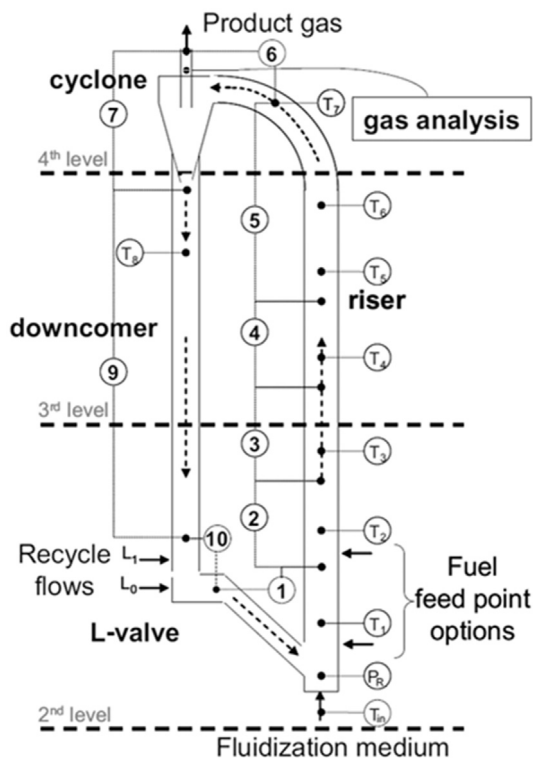
at 450 °C. The product gas was finally flared downstream this unit.

The capacity of the solids feeding system was approximately 100 kW fuel thermal input. This corresponded to approximately 20 kg.h$^{-1}$ of biomass. Furthermore, two other kinds of solids could be fed simultaneously, e.g. bed material. Details about the supply systems of solids and gases can be found elsewhere [14,17].

For the data acquisition, an in-house implemented Supervision, Control, And Data Acquisition (SCADA) package was combined with a Programmable Logic Controller (PLC, make ABB, type SattCon200) for test rig control. The test rig was operated with three PCs in the control room. The process data were logged with a frequency of 0.1 Hz [14,17].

## 2.2. Analytical techniques

In the current experiments, sampling of the gas, tar and solids was carried out downstream the gasifier. Solid residue samples were retrieved from the downcomer after each successful experiment, when the gasifier was cooled down and inertized. The product gas was sampled in the Gas Analysis position, just downstream the riser. The sampled product gas passed through a heated (at 300 °C) particle filter (glass wool) and via two water- and ice-cooled condensers to achieve moisture removal. The final traces of moisture were removed using calcium oxide in the tests 2 and 3, and sicapent was used in the others. The product gas was analyzed on-line using a Varian μ-GC CP-4900 equipped with two column modules, that measured continuously the volumetric concentration of the CO, H$_2$, CH$_4$, CO$_2$ and N$_2$ (1 m COX column) and that of benzene, toluene and xylenes (BTX) (4 m CP-Sil5 CB column). The gas composition data from the μ-GC were obtained with intervals of 3 min. In addition, an NDIR analyzer (Hartmann & Braun Uras 10P) monitored the CO$_2$ and the CO and a paramagnetic analyzer measured the oxygen concentration (Hartmann & Braun Magnos 6G) with a time interval of 2 s. The water volume fraction of the product gas was determined gravimetrically via sampling a measured flowrate of the product gas for a determined timeframe. The sampled gas was cooled down in a condenser immersed in a mixture of salt, ice and water. The weight of the condenser was determined before and after this sampling. Tar was sampled in the Tar Protocol position downstream the BWF filter (Fig. 1). The tar samples were collected according to the tar standard method [21] and were analyzed using an HPLC equipped with a UV and fluorescence analyzer (Knauer), and a reverse phase column (Kromasil Eternity C18 5 μm 150 × 4.6 mm). 20 μL of filtered sample was injected in the column and a gradient elution with methanol – water was performed for 50 min. The UV detector was set at 254 nm. The quantification was performed by external calibration using triplicate data point and standard tar compounds in appropriate concentration range. All coefficients of determination (R$^2$) exceeded 0.990. Only in one test (#8), solid phase adsorption (SPA) samples were analyzed (in the same HPLC) and used, even though the trapping efficiency of the SPA method for BTX species is considered lower than the tar standard [22]. This was decided due to the fact that the tar standard resulted in unrealistically low tar values for that test; the tar standard results of the test 8 can be found in the supplementary information. It must be noted that the SPA sample was acquired just downstream the riser, as in the Gas Analysis position. For that test, only the phenol value from the tar standard measurement was used, while the data for the rest of the tar species were obtained by SPA sampling.

## 2.3. Biomass feedstock, bed material and gasification char

### 2.3.1. Biomass feedstock characterization

Six samples of biomass feedstock were tested; two of them

consisted of untreated pure wood and the rest were their torrefied products. Softwood (spruce, of the species *Picea abies*) and hardwood (ash, of the species *Salix viminalis*) were tested. Debarked and chipped ash and spruce wood were obtained from Van den Broek B.V. (The Netherlands) and short rotation coppice willow of the Salix family obtained from SGB (UK). Torrefaction and subsequent pelleting were conducted by the Energy research Centre of the Netherlands (ECN) [23]. ECN torrefied the untreated wood feedstocks at its pilot plant, in a directly heated moving bed, with a 50 kg.h$^{-1}$ capacity. The final torrefaction temperature and the residence time at the torrefaction temperature, along with the calculated torrefaction degree are presented in Table 2. The untreated wood samples were pelletized at a Dutch company, Comgoed Biomassa. All the feedstocks had an outer diameter of 6 mm and length of approximately 2 cm, to facilitate feeding in the gasifier. The elemental composition of the feedstocks was analyzed at the University of L'Aquila, Italy, with a PerkinElmer Series 2 CHNS/O 2400 analyzer. The proximate analysis was performed via thermogravimetric analysis at Technical University of Delft. For this purpose a Thermal Advantage SDT Q600 thermogravimetric analyzer (TGA), was used; details regarding the TGA instrument and the procedure have been described elsewhere [24], and the feedstocks were ground and sieved manually ≤75 μm particle size to ensure homogeneity. The feedstocks elemental analysis average results, proximate analysis average results, with standard deviation in parenthesis, and lower heating values (LHV) are presented in Table 3. In addition, the torrefaction degree was calculated, i.e. the anhydrous weight loss or the reduction of the volatile mass fraction upon torrefaction divided by the initial volatile mass fraction on an a dry basis (see Table 2). Based on the elemental analysis data of the feedstock samples and data for various fuels obtained from the Phyllis2 online database [25], a Van Krevelen diagram (Fig. 3) has been drawn to show the changes in the feedstock due to torrefaction. It is confirmed that torrefaction decreased the O/C and H/C ratios for both wood types.

### 2.3.2. Bed material

Calcined magnesite was used as the bed material. It is a mineral consisting mainly of MgO and smaller fractions of CaO, Fe$_2$O$_3$ and silica. Magnesite was considered a favorable bed material due to its low silica mass fraction, acceptable price (same order of magnitude as sand), and previous experimental results. The use of magnesite showed a remarkable increase in the H$_2$ volume fraction, a doubled H$_2$:CO ratio and a decrease in the total tar content, with respect to the use of silica sand [17]. More information regarding the magnesite can be found in a previous research paper from our group [14,17].

### 2.4. Gasification conditions

The gasification experiments were performed, at approximately 850 °C and atmospheric pressure. The experiments were carried out varying ER and the SBR as presented in Table 4. It must be noted that the results of two additional tests are presented in the supplementary material to explain the reasons for using the SPA

**Table 2**
Torrefaction parameter specifications.

| Biomass code | Temperature (°C) | Residence time (min) | Torrefaction degree (d.b. wt%) |
|---|---|---|---|
| Ash 250 | 250 | 30 | 8.6 |
| Ash 265 | 265 | 30 | 13.4 |
| Spruce 260 | 260 | 30 | 9.3 |
| Spruce 280 | 280 | 30 | 10.5 |

**Table 3**
Wood and torrefied wood proximate and ultimate analyses with standard deviation values.

| Biomass | Ultimate analysis, wt% | | | | | Proximate analysis, wt% | | | | LHV[c,d] (MJ.kg$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | C[a] | H[a] | N[a] | S[a] | O[a,b] | Moisture[a] | Volatile matter[d] | Fixed carbon[d] | Ash[d] | |
| Untreated ash | 46.6 ± 3.43 | 5.9 ± 0.32 | 0.1 ± 0.06 | 0.8 ± 0.18 | 41.5 ± 3.86 | 4.6 ± 0.02 | 79.2 ± 0.31 | 20.2 ± 0.30 | 0.5 ± 0.19 | 16.4 |
| Ash 250 | 50.6 ± 0.28 | 5.5 ± 0.02 | 0.1 ± 0.10 | 0.8 ± 0.05 | 36.8 ± 0.41 | 5.7 ± 0.08 | 72.4 ± 0.68 | 27.0 ± 0.30 | 0.5 ± 0.04 | 16.7 |
| Ash 265 | 51.8 ± 0.74 | 5.3 ± 0.13 | 0.1 ± 0.06 | 0.7 ± 0.05 | 35.3 ± 0.62 | 5.8 ± 0.02 | 68.6 ± 0.57 | 30.5 ± 0.47 | 1.0 ± 0.00 | 17.2 |
| Untreated spruce | 47.1 ± 0.42 | 5.7 ± 0.16 | 0.1 ± 0.01 | 0.8 ± 0.02 | 40.3 ± 0.25 | 5.9 ± 0.06 | 82.1 ± 0.01 | 17.5 ± 0.01 | 0.3 ± 0.03 | 16.2 |
| Spruce 260 | 51.4 ± 1.48 | 5.6 ± 0.16 | 0.1 ± 0.01 | 0.8 ± 0.01 | 37.0 ± 1.49 | 5.4 ± 0.16 | 74.5 ± 1.76 | 25.2 ± 1.34 | 0.3 ± 0.01 | 17.5 |
| Spruce 280 | 52.0 ± 1.00 | 5.5 ± 0.06 | 0.1 ± 0.07 | 0.7 ± 0.06 | 36.0 ± 1.07 | 4.8 ± 0.11 | 73.5 ± 0.02 | 26.1 ± 0.02 | 0.4 ± 0.04 | 17.6 |

[a] On an a.r. basis.
[b] O mass fraction is calculated by difference.
[c] Calculated based on [26].
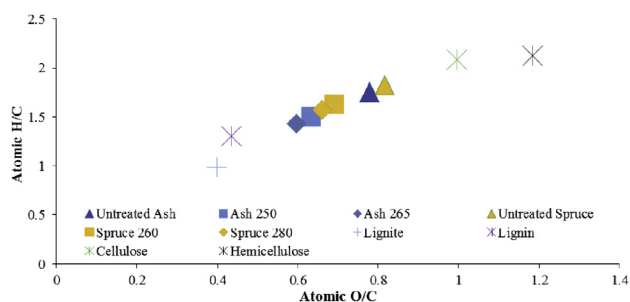[d] On a dry basis.



**Fig. 3.** Van Krevelen diagram; tested biomass feedstocks compared with lignite and bio-polymers (source for untested samples is Phyllis2 database [25]).

All gas volumes concentrations and tar species content reported in this work concern the steady state operation and are on a dry, nitrogen-free (dnf) basis. The $CO_2$, $H_2$, CO, $CH_4$, and BTX volume fractions presented are the average values during the steady state operation. Moreover, the standard deviations of these gas species are presented. For water, no standard deviation value is presented due to the nature of the measurement method used. As described above, during the steady state only one measurement for the water quantification was performed. The tar yield (wt%) concerns the steady state operation as well and it is presented on a dry ash-free (daf) basis of supplied feedstock. Finally, process key parameters, such as CCE, CGE, etc. and mass balance calculations are presented in Table 5. The latter was based on the inflow measurements ($O_2$,

**Table 4**
Experimental matrix.

| Test | Biomass | Fuel flow rate (kg.h$^{-1}$) | ER (-) | SBR (-) | Temperature (ºC) | Pressure (kPa) | Steady state (min) |
|---|---|---|---|---|---|---|---|
| 1 | Untreated ash | 12.0 | 0.31 | 1.00 | 841 | 108 | 133 |
| 2 | Ash 250 | 12.0 | 0.30 | 1.00 | 849 | 125 | 202 |
| 3 | Ash 250 | 12.0 | 0.36 | 0.85 | 849 | 136 | 116 |
| 4 | Ash 265 | 12.0 | 0.36 | 0.88 | 854 | 131 | 61 |
| 5 | Ash 265 | 13.0 | 0.31 | 1.00 | 848 | 109 | 187 |
| 6 | Ash 265 | 13.0 | 0.35 | 0.85 | 846 | 110 | 190 |
| 7 | Untreated spruce | 12.0 | 0.30 | 1.00 | 839 | 109 | 140 |
| 8 | Spruce 260 | 12.4 | 0.31 | 1.00 | 848 | 110 | 183 |
| 9 | Spruce 260 | 12.9 | 0.36 | 0.85 | 842 | 108 | 180 |
| 10 | Spruce 280 | 12.6 | 0.36 | 0.85 | 845 | 108 | 180 |
| 11 | Spruce 280 | 12.6 | 0.31 | 1.00 | 843 | 1.08 | 181 |

results instead of tar standard results for one gasification experiment (test 8). The selection of conditions was based on typical operating conditions in relevant industrial applications. Torrefied material needed higher ER that untreated biomass due to its lower $O_2$ and higher fixed carbon mass fractions. In Table 4, the temperature concerned the average temperature in the reactor measured from the eight thermocouples (see Fig. 2). Similarly, the pressure was monitored by an absolute pressure sensor installed in the bottom part of the riser. Lastly, the two dimensionless ratios have been determined, the ER was determined based on equation (1), ER was controlled via gas mass-flow control and maintain a constant feedstock flow rate. The SBR was determined based on equation (2).

$$ER = \frac{external\ O_2\ fed/fuel\ fed\ (daf)}{stoichiometric\ O_2\ requirement/unit\ of\ fuel\ input\ (daf)}$$

(1)

$$SBR = steam\ mass\ flow/fuel\ feed\ flow$$ (2)

steam and feedstock) and streams (permanent gases, tars and solid residue) that exit the reactor, thus, a mass balance error is calculated and presented in Table 5. The equations for determination of the CGE and CCE can be found in the supplementary material.

## 3. Results and discussion

### 3.1. Feedstock characterization

The feedstocks were characterized for their slow devolatilization behavior in a $N_2$-atmosphere. The changes in the mass loss rate versus temperature curves, as presented in Figs. 4 and 5, are generally a result of the changes in the chemical composition upon torrefaction. Torrefaction resulted in converting part of the hemicellulose for both untreated woods, as the "shoulder" part of the mass loss rate peak graph disappeared. It has been reported before that the mass loss of hemicellulose up to 250 °C and 275 °C is attributed to the cleavage of glycosidic bonds and the decomposition of side chains, and the fragmentation of monosaccharide units,

respectively [27]. As a consequence, both feedstocks are expected to contain higher lignin and cellulose mass fractions than their parent materials. The 20 and 15 °C increase in torrefaction temperature resulted in minimal changes in the mass loss rate peak of spruce and ash.

### 3.2. Permanent gas species and BTX composition

The internal reactor pressure and the differential pressures for the tests 2–4 resulted in sub-optimal char circulation conditions due to the excessive presence of carbonaceous solids in the entire downcomer which prevented proper circulation. Therefore, it is expected that less char was recirculating in the gasifier, which resulted in affecting the gas-solid reactions. The permanent gas, the total tar yield and process key parameters are, therefore, expected to be affected. The data of internal reactor pressure and differential pressure can be found in the supplementary material.

Torrefaction has a small impact on the permanent gas composition during gasification as presented in Figs. 6 and 7. It resulted in only a marginal increase of the $CO_2$ volume fraction of spruce 280, decreasing the $CH_4$ volume fraction of ash 265 and increasing the $H_2$ volume fraction of ash 250 and 265. The other gases remained unaffected. The $H_2/CO$ ratio varied between 2.0 and 2.8, but in most experiments is approximately 2.4. This increase in the $H_2$ volume fraction, the decrease in $CH_4$ volume fraction and the slight increase in the $CO_2$ volume fraction has been reported before [15,18,19]. These changes are attributed to the changes in the chemical composition upon torrefaction in combination with chemical reactions taking place in the gasifier simultaneously. As torrefaction results in decreasing the contribution of devolatilization on the formation of the product gas, gasification reactions become more relevant, especially char gasification reactions as the fixed carbon mass fraction increases upon torrefaction [28] and steam is employed in our rig. For torrefied spruce feedstocks, the effect of torrefaction on the permanent gases is in agreement with previous gasification studies with softwood [15,18]. As hemicellulose (mainly) and to a certain extent cellulose are expected to decrease due to the torrefaction conditions [3,5], a larger volume fraction of CO is expected as it is a common main product of lignin and cellulose devolatilization. In addition, more CO is expected to be produced as a product of to the tar reduction reactions (see Fig. 12). However, due to the fed $O_2$, CO is converted to $CO_2$. In addition, our hardwood results are in agreement with [19], $H_2$ is the only affected gas species and increases upon torrefaction. The reason why torrefaction affected only the $H_2$ is not clear. However, it must be noted that as ash wood contains mainly xylan which is significantly unstable at low temperature [3] and lignin that is more reactive at low temperature [23], thus this volatile part of ash wood was converted, resulting in unaffected cellulose due to the torrefaction temperature [15,18]. In fact the cellulose mass fraction either remained the same or increased slightly. Based on this hypothesis, the tar content is expected to increase and, as the remaining lignin is reactive at higher temperature, the $H_2$ volume fraction is expected to increase as well [29].

Given the small changes in the permanent gas composition between test 4 and 6, both with ash 265, one can conclude from Fig. 8 that the impact of the poor circulation on the permanent gas composition was small. In addition, torrefaction influenced the water volume fraction of the product gas (see Table 5). Experiments with spruce 280 and ash 265 resulted in a higher water volume fraction than spruce 260 and ash 250, respectively, showing that the product gas contained water that was either formed during the $H_2$ oxidation or steam that did not react with other species.

Increasing the ER and decreasing the SBR results in decreasing the $H_2$ volume fraction and increasing the $CO_2$ volume fraction (see Fig. 6). This effect, of increasing ER, is known and has been confirmed before in different gasifiers. However, CO and $CH_4$ do not show this trend. The unchanged CO volume fraction is possibly due to the contribution of the Boudouard reaction due to the increased fixed carbon content of the torrefied woods. Whereas, regarding the $CH_4$, Petersen and Werther [30] have reported that the $O_2$ reacts faster with other species, such as $H_2$, CO and char rather than oxidizing the $CH_4$. The same effect is also observed with steam, which reforms other hydrocarbons, rather than $CH_4$.

Based on the μ-GC analysis of the product gas, torrefaction resulted in reducing the benzene and toluene volume fractions of ash 265, spruce 260 and 280, in line with what has been reported in literature [18], but torrefaction did not affect the BTX volume fractions of ash 250 (Figs. 8 and 9). Due to the reduction of the volatile content in the torrefied woods, a decrease in BTX was expected as it was presented in our other study with commercial torrefied wood as feedstock [31]. Only the gasification of ash 250 did not result in a lower BTX volume fraction. This is attributed to (already mentioned) effect of torrefaction on the chemical composition of ash woods. Given the small changes in the permanent BTX composition between tests 4 and 6, with ash 265, one can conclude from Fig. 10 that the impact of the poor circulation on the BTX composition was small. Simultaneously increasing the ER and decreasing the SBR did not affect the BTX volume fraction significantly for both feedstocks.

### 3.3. Tar species content, yield and classes

Torrefaction resulted in decreasing the total tar content of both torrefied spruce woods, and marginally increasing the total tar content of both torrefied ash woods, as shown in Figs. 11 and 12. Untreated and torrefied ash resulted in lower total tar contents than untreated and torrefied spruce. This is attributed to the higher cellulose and lignin mass fraction that softwoods contain [1,32]. In addition, for each tar compound, gasification of untreated ash results in lower contents than untreated spruce (Fig. 11). For phenol, this was expected due to the typically higher lignin mass fraction of softwoods with respect to hardwoods [1] and due to the fact that phenol is considered to be formed mainly from lignin [32,33].

Upon torrefaction of the spruce, the total tar content reduction was 30% and 13% for spruce 260 and spruce 280, respectively (see Fig. 10). Such a reduction upon torrefaction has also been observed for softwood in other gasification studies [15,18] and for hardwood, when torrefied at 260 °C or higher temperatures [19]. Based on the gasification studies that have reported the chemical composition, it can be said that in both studies [18,19] the tar content decreases due to the significant decrease of the holocellulose content, so our result is attributed to that effect of torrefaction. Increasing the torrefaction temperature, from 260 to 280 °C, resulted in a further decrease for almost all tars species, but phenols and toluene. This is explained by the fact that the SPA sampling was performed for the spruce 260 experiment and it is reported that the SPA sampling shows a lower trapping efficiency for the BTX species [22]. Therefore, increasing the torrefaction temperature is expected to decrease all tar species.

Upon torrefaction of the ash wood, the total tar content increased for ash 250 and ash 265 by 34% and 18%, respectively (see Fig. 10). This increase in tar formation and it is partly attributed to less gas-solid reactions, due to the reactor pressure and the sub-optimal recirculation conditions of test 2, and partly to the effect of torrefaction on the chemical composition, since there were no recirculation issues in test 5. The former can be checked with the effect of the circulation conditions on tar classes for tests 4 and 6 (see Fig. 12). Thus, gasification of ash 250 would still result in increased tar content. Whereas, the chemical composition concerns

the formation of primary tars. Since most of the tars derive from the holocellulose mass fraction and the hemicellulose mass fraction does decrease in our torrefaction conditions [3], the volatile content might not have decreased in the torrefied ash feedstocks to an extent that the formation of tar species, which polymerize and convert to heavier species than phenol, is reduced. The same reason can be the source of the deviating result of Woytiuk et al. [19] for their lowest torrefaction temperature as in these researchers' feedstock and our feedstock the cellulose part is not expected to be affected with torrefaction. Regarding the tar compounds for the torrefied ash woods, increasing the torrefaction temperature did not affect any tar compound significantly, but phenol and naphthalene. This change in the phenol content can be explained by the higher $H_2$ volume fraction of the ash 250 product gas which results in enhancing the hydrodeoxygenation of oxygenated tar compounds, i.e. phenol compounds [34]. The latter is among the reasons why the ash 265 resulted in a lower naphthalene content than the ash 250.

The results of classified tar species are presented in Figs. 11 and 12; this classification system is based on the solubility, chemical composition and condensation behavior of various tar compounds [35]. For both wood types, the majority of tars formed during gasification belong in Classes 3 and 4. Tars of these two classes are formed from primary tars due to decomposition of holocellulose and lignin. Increasing the torrefaction temperature resulted in a higher phenol content (Class 2 tars) for both woods, indicating that the lignin mass fraction increased [32]. Regarding spruce, our results show that the torrefaction resulted in lower tar yields than untreated spruce. Class 2 and Class 3 tars strongly decreased for spruce 260, while increasing the torrefaction temperature from 260 to 280 °C led to an increase in tar yield again. However, in the spruce 260 experiment, the SPA sampling was used; therefore if the Class 2 tars and the toluene are not considered, increasing the torrefaction temperature did not really affect all the tar classes, but Class 4 which increased marginally. On the contrary, torrefaction of ash resulted in increasing the tar yield and the Classes 3—5, even if taking into account the sub-optimal recirculation. The effect of sub-optimal recirculation conditions is more relevant for tars than permanent gases and BTX. A comparison between tests 4 and 6 shows that there is a slight increase for Class 2 (phenol) tars and a larger increase for Class 3 tars in the test 5 with the sub-optimal solids circulation. This shows that tars that exists in these two classes did not convert, due to the reduced gas-solid reactions. In addition, an unchanged cellulose mass fraction upon torrefaction may also contribute to that observation.

The simultaneous increase in the ER and decrease in the SBR resulted in no significant impact on the tar compounds for spruce 260 and spruce 280, and in slight impact for ash 250 and ash 265 (see Figs. 13 and 14). This effect was also observed in our previous study with commercial torrefied wood feedstock [31]. The combined increase in the ER and decrease in the SBR resulted in a decrease of the Class 3 tars (due to toluene) and naphthalene for ash 250 and a decrease in the naphthalene for the ash 265. In general, increasing the ER and decreasing the SBR at 850 °C resulted in decreasing Class 2 tars (phenol) and the lighter PAH for ash 265 and ash 250, respectively. In both cases, converted products of such tar compounds formed heavier PAHs, and CO, $CO_2$ (see Fig. 7), and $H_2$ are released.

### 3.4. Process key parameters

Based on mass balance calculations, various process key parameters have been calculated, such as the CCE, CGE and others (Table 5). As expected due to the higher volatile mass fraction, the CCE and CGE values are the highest in the experiments with untreated woods. Furthermore, an increase in the ER showed a increasing effect on the CCE and a decreasing effect on the CGE. Only for ash 250 and spruce 260, increasing the ER did not result in increasing the CCE and decreasing the CGE, respectively. While the former is attributed to the sub-optimal recirculation conditions, the latter is explained with the increase in the gas yield. Lastly, for both feedstocks, torrefaction resulted in a reduction of the gas heating value per biomass input. This reduction is more pronounced for torrefied ash due to the higher fixed carbon mass fraction.

Torrefaction decreased the CCE, CGE for both torrefied spruce woods and decreased the gas yield of spruce 280. Our spruce results regarding the effect of torrefaction on CCE and CGE are in agreement with Sweneey [20]. This researcher reported a decrease in both process parameters when torrefied samples were gasified. On the other hand, Berrueco et al. [15] reported that torrefaction resulted in decreasing the CCE but not a clear trend regarding the CGE was observed with their feedstocks. They reported that regarding torrefied forestry residues increasing the torrefaction temperature resulted in increasing the CGE. However, the volatile matter of their feedstock is not much decreased at 225 °C, rather than at 275 °C. Their increase in the CGE is explained with an increase of the total gas yield (with the most severely torrefied fuel), rather than with the quality of the combustible gas volume fraction.

**Table 5**
Process key parameters.

| | Untreated ash | Ash 250 | Ash 250 | Ash 265 | Ash 265 | Ash 265 | Untreated spruce | Spruce 260 | Spruce 260 | Spruce 280 | Spruce 280 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Test | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| ER | 0.31 | 0.30 | 0.36 | 0.36 | 0.31 | 0.35 | 0.30 | 0.31 | 0.36 | 0.36 | 0.31 |
| SBR | 0.10 | 1.00 | 0.85 | 0.88 | 1.00 | 0.85 | 0.10 | 1.00 | 0.85 | 0.85 | 1.00 |
| CCE | 102.1 | 78.0 | 72.3 | 75.4 | 90.6 | 93.7 | 95.6 | 89.1 | 99.3 | 87.1 | 81.6 |
| CGE | 62.0 | 52.1 | 46.0 | 44.9 | 58.3 | 54.3 | 60.0 | 53.4 | 56.2 | 46.7 | 48.2 |
| $H_2$/CO | 2.4 | 2.8 | 2.2 | 2.2 | 2.5 | 2.1 | 2.4 | 2.3 | 2.0 | 2.2 | 2.4 |
| CO/$CO_2$ | 0.32 | 0.30 | 0.34 | 0.32 | 0.33 | 0.32 | 0.31 | 0.30 | 0.31 | 0.27 | 0.28 |
| Water[a] | 42.8 | 51.9 | 40.2 | 49.0 | 53.0 | 44.1 | 44.4 | 39.7 | 38.2 | 44.0 | 45.6 |
| Gas yield[b] | 1.7 | 1.4 | 1.3 | 1.3 | 1.7 | 1.7 | 1.6 | 1.6 | 1.7 | 1.5 | 1.5 |
| LHV[c] | 7.0 | 6.8 | 7.2 | 6.5 | 6.6 | 6.2 | 6.8 | 6.5 | 6.5 | 6.2 | 6.5 |
| LHV[d] | 11.7 | 9.8 | 9.2 | 8.7 | 11.3 | 10.5 | 11.0 | 10.4 | 11.2 | 9.2 | 9.5 |
| Mass balance error[e] | −2.8 | −6.1 | −22.6 | −14.7 | 8.7 | 1.7 | −1.9 | −10.9 | −3.5 | −2.1 | −5.6 |

[a] Vol% on as received basis.
[b] In $m^3 \cdot kg_{daf}^{-1}$.
[c] In $MJ \cdot m^{-3}$ (STP).
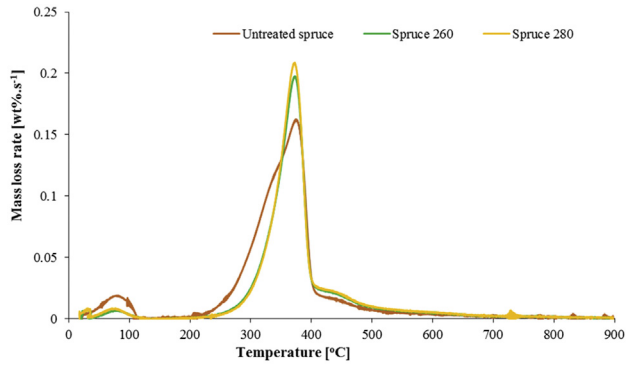[d] In $MJ \cdot kg_{daf}^{-1}$.
[e] In %.

**Fig. 4.** Rate of mass loss vs temperature (dTG) curves for slow devolatilization of untreated and torrefied spruce feedstocks (heating rate = 20 °C.min$^{-1}$, N$_2$ = 100 mL.min$^{-1}$).



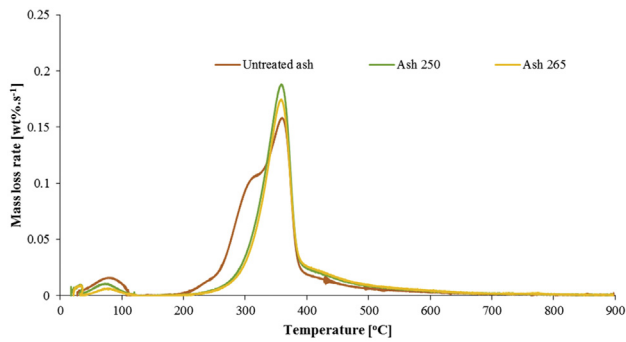**Fig. 5.** Rate of mass loss vs temperature (dTG) curves for slow devolatilization of untreated and torrefied ash feedstocks (heating rate = 20 °C.min$^{-1}$, N$_2$ = 100 mL.min$^{-1}$).
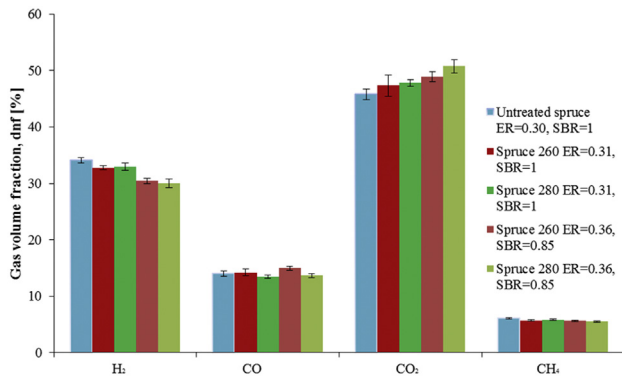


**Fig. 6.** Gas composition measured during spruce feedstocks experiments (at 850 °C).



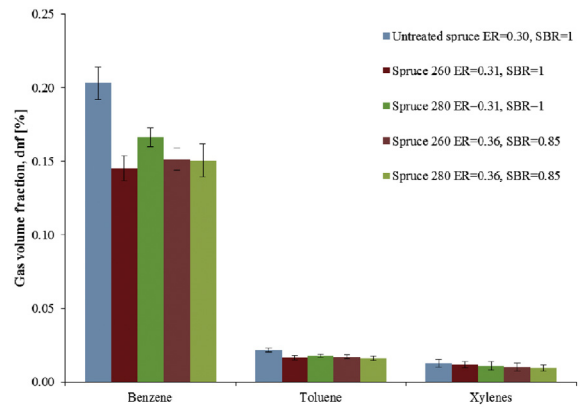**Fig. 7.** Gas composition measured during ash feedstocks experiments (at 850 °C).



**Fig. 8.** BTX composition measured by μGC during spruce feedstocks experiments (at 850 °C).
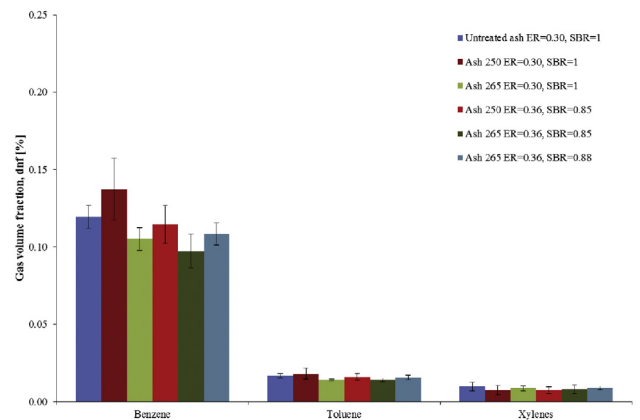


**Fig. 9.** BTX composition measured by μGC during ash feedstocks experiments (at 850 °C).

Torrefaction of ash did not show benefits in increasing the CCE, CGE, gas yield and LHV (MJ.kg$_{daf}^{-1}$) of the product gas. However, when comparing ash 250 and ash 265, these process parameters appear to improve with increasing torrefaction temperature. This was unexpected and not reported before in literature. However, it can be explained if one compares tests 4 and 6, which under the same gasification conditions resulting in large difference in the CCE and CGE. Therefore, both CCE and CGE would be expected to decrease upon torrefaction of ash but not to the extent that we observed. Lastly, the gas yield was mainly also affected due to the elevated pressure and resulted in the significant difference of the CGE between the ash 265 and ash 250.

## 4. Conclusions

Subjecting woody biomass to a combination of torrefaction and subsequent densification offers clear benefits in logistics and handling operations. Therefore, in this study, for the first time oxygen-steam blown circulating fluidized bed gasification experiments have been performed with untreated and torrefied softwood and hardwood to determine additional benefits in this end-use option. The examined operational conditions were relevant to
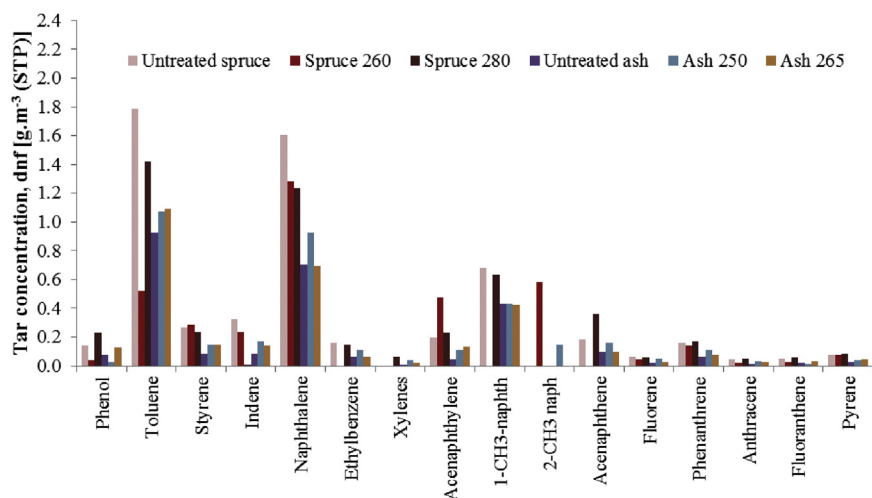
**Fig. 10.** Tar content in the product gas for spruce and ash feedstocks (at 850 °C, ER = 0.30 and SBR = 1) measured with tar standard method.
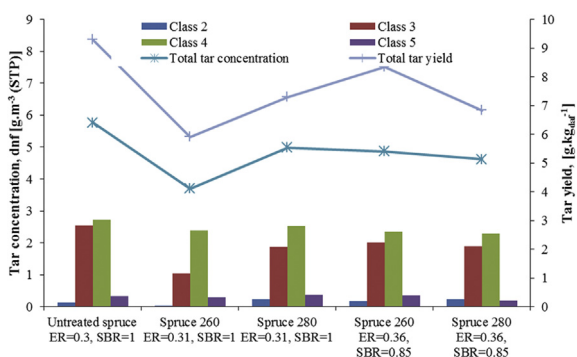


**Fig. 11.** Content and yield of total tar and tar classes measured during spruce feedstocks experiments (at 850 °C and 1 bar).

typical operating conditions in industrial relevant applications.

It is concluded that torrefaction affected the product gas composition for both types of wood only to a small extent. For the torrefied spruce woods, torrefaction did not affect the permanent gases and resulted in decreasing the BTX volume fraction and total

tar content for both spruce 260 and 280. A simultaneous increase of the ER and decrease of the SBR did not affect the tar classes. For the torrefied ash woods, torrefaction resulted in increasing only the $H_2$ volume fraction for both ash 250 and 265, and decreasing the $CH_4$ volume fraction for ash 265, affecting the BTX volume fraction for ash 265 and, surprisingly, torrefaction resulted in increasing the total tar content for both ash 250 and 265. The simultaneous increase of the ER and decrease of the SBR resulted in decreasing the Class 3 tars for ash 250 and slightly decreasing the Class 2 tars for ash 265. Lastly, for both wood species the majority of the tars belonged in Classes 3 and 4.

Torrefaction of spruce and ash woods resulted in a limited impact on product gas constituents' composition, but the CCE and the CGE decreased significantly. Therefore, purely from an end-use perspective it is not recommended to replace these untreated spruce and untreated ash woods with these torrefied versions during oxygen-steam blown CFB gasification at 850 °C. Future research of gasification of torrefied wood species should include feedstock chemical analysis and characterization of products obtained under devolatilization conditions. The former will quantify the effect of torrefaction conditions on the hemicellulose, cellulose and lignin, whereas the latter, investigates the formation of primary tars.
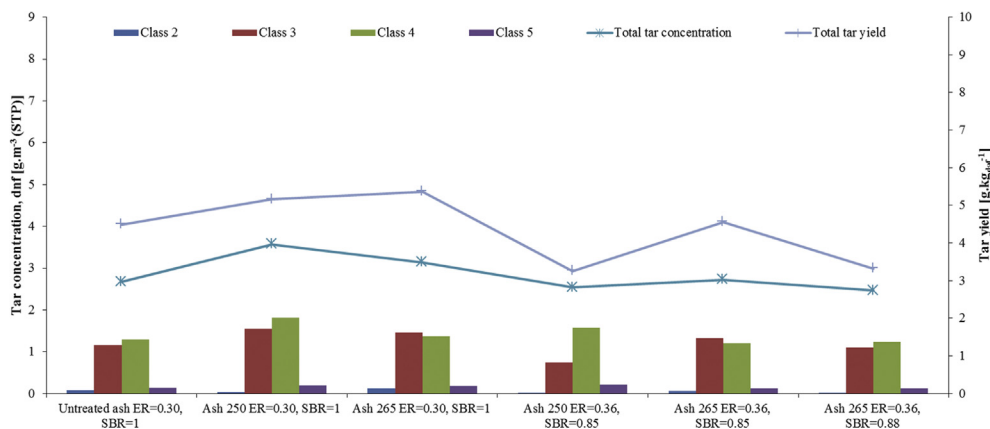


**Fig. 12.** Content and yield of total tar and tar classes measured during ash feedstocks experiments (at 850 °C and 1 bar).
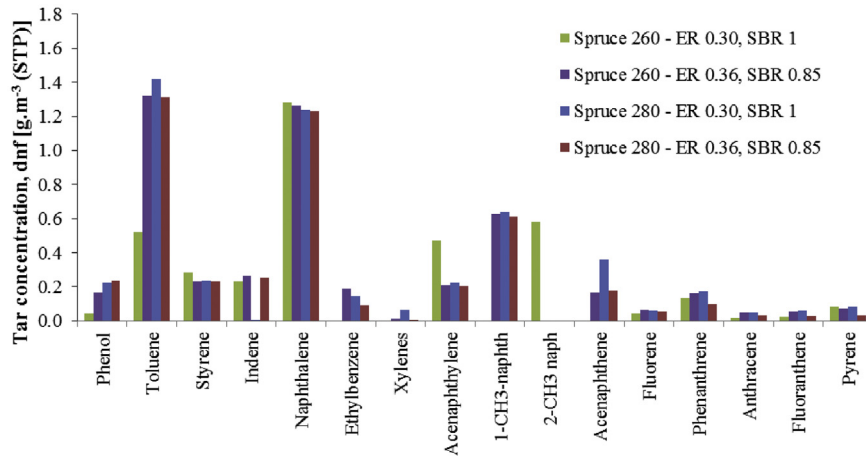
**Fig. 13.** Tar content in the product gas measured during the torrefied spruce experiments (at 850 °C).
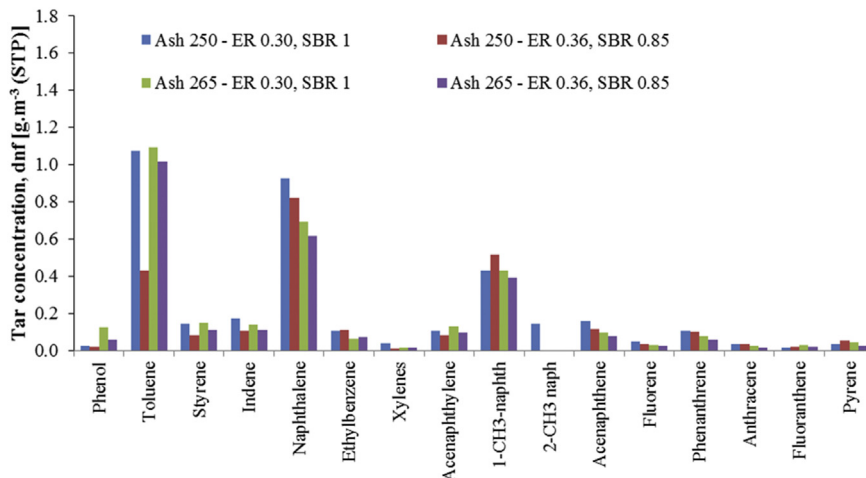


**Fig. 14.** Tar content in the product gas measured during the torrefied ash experiments (at 850 °C).

## Acknowledgments

## Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.biombioe.2017.09.001.

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