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Research article

The impact of dry torrefaction on the fast pyrolysis behavior of ash wood and commercial Dutch mixed wood in a pyroprobe

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ABSTRACT

In this study torrefied feedstocks, consisting of mixed wood and wood residues torrefied at 300 °C and ash wood torrefied at 250 and 265 °C, were pyrolyzed in a pyroprobe at five pyrolysis temperatures (600–1000 °C) and a fast heating rate (600 °C·s^{-1}) to investigate the effect of torrefaction on the formation of volatiles and their evolution in a 100 kW circulating fluidized bed gasifier. Results showed that torrefaction converted mostly the hemicellulose content of feedstocks. Furthermore, torrefaction resulted in decreasing the bio-oil and gas yields, increasing the char and phenol yields and not affecting the polyaromatic hydrocarbons yield. Phenol and naphthalene showed the largest yield at 600–700 °C and 800–1000 °C, respectively. At such high temperatures, the rest polyaromatic hydrocarbons showed yields similar to phenol's. At 900 °C torrefaction affected mainly the phenolic species, with 4-propyl-phenol being the dominant species of its group for mixed wood and wood residues feedstock. In the gasifier, H_2 and CO_2 yields increased, CH_4 yield remained constant, and CO yield depended on tar conversion and oxidation and steam reactions. The phenol and naphthalene yields further decreased and increased, respectively, whereas, polyaromatic hydrocarbons did not change in the gasifier.

1. Introduction

Biomass conversion to electricity and biofuels has become attractive due to its potential carbon neutrality and its benefits regarding the global warming impact. However, there are aspects of biomass that inhibit its use in different applications, such as its heterogeneous nature (even for the same species), its high moisture content that results in low energy density. Therefore, pretreatment technologies were developed to address such issues. Among the various biomass kinds, wood has gained attention as it is considered second generation biomass and it has a low ash content.

Torrefaction is a promising pretreatment technology which converts biomass to a more coal-alike fuel. It is a mild thermochemical process occurring between 200 and 300 °C in an inert atmosphere. During torrefaction biomass devolatilizes partially, becomes more brittle, hydrophobic, less prone to microbial and fungal degradation and increases its energy density [1]. Torrefied biomass is a potential coal-replacement fuel for boilers with a much lower carbon footprint considering its life cycle [2]. In addition, torrefaction has shown to lower the oxygen content of the biomass and to increase the aromatic fraction of the condensable species during fast pyrolysis for bio-oil production [3,4].

Hemicellulose, cellulose and lignin are the main biocomponents of biomass. These chemical components decompose at different temperature ranges. Hemicellulose is the least thermally stable component due to its amorphous nature, cellulose thermal behavior is due to its relatively strong intramolecular bonds and lignin is a complex, highly branched and heavily crosslinked polymer and therefore it is more thermally stable than the other two components. Hemicellulose decomposes in the temperature range of 200 to 315 °C and its typical products are acetic acid, acetone, furfural, CO, CO_2 and CH_4 [5]. Hemicellulose decomposition is mainly responsible for the release of CO_2. This is mainly due to its higher carboxyl content in comparison to cellulose and lignin which are mainly responsible for CO and H_2 – CH_4 production, respectively [3]. Cellulose decomposition starts approximately at 230 °C and ends at 400 °C and it produces mainly

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levoglucosan which at temperatures exceeding 500 °C vaporizes to contribute almost exclusively to the gas and liquid yields [4]. At lower temperatures active cellulose is generated with a comparatively low degree of polymerization [6]. Due to the action of radicals and increasing temperature, active cellulose undergoes further degradation to generate tar, char and light gases [7–9]. During torrefaction the active cellulose undergoes crosslinking. Severe carbon–carbon crosslinking of cellulose hinders the production of volatiles and results in increasing char production [5]. Thermal degradation of lignin starts at approximately 200 °C, but the main part of its conversion typically occurs at higher temperature, between 400 and 750 °C [10]. Lignin decomposition leads to mainly char and, secondarily, volatiles [11]. At temperatures higher than 500 °C the aromatic rings of lignin rearrange and condense releasing H_2. CO is produced both at higher and lower temperatures from ether groups. CH_4 is mainly produced from a weakly bonded methoxy group, at somewhat lower temperatures [12].

Several researchers [3,13–18] performed fast pyrolysis using a pyroprobe and focussed their studies on the effect of torrefaction of wood, agricultural residues or fractionated bio-polymers on bio-oil components production. These researchers compared torrefied and untreated biomass, but only Neupane et al. [13] and Yang et al. [20] used feedstocks with different degrees of torrefaction. On the other hand, there are researchers [21,22] who focused on investigating high temperature fast pyrolysis, but used a fixed bed reactor, a design that is similar to the pyroprobe's design (see Table 1).

Ojha and Vinu [14] pyrolyzed cellulose at 500 °C in a pyroprobe and reported mainly yields of aldehydes/ketones, furans and anhydrosugars. Srinivasan et al. [15] pyrolyzed, at 600 °C, cellulose and torrefied cellulose (at 225 °C for 30 min) in a pyroprobe. They reported no significant mass loss during the torrefaction process, rather than an effect of the process on the structure of the cellulose. They commented that torrefaction modified cellulose structure by altering the C–O–C and glycosidic bonds and reported no phenol yield in both feedstocks pyrolysis tests, and an aromatics yield only during the pyrolysis test of the torrefied cellulose. Wu et al. [18] pyrolyzed three mixtures (two personally prepared mixtures and one natural mixture) of cellulose and hemicellulose at 500–700 °C in a pyroprobe to investigate possible interactions between the polymers. They concluded that for all mixtures, the main condensable products were anhydrosugars, mainly levoglucosan, and acetone and the only quantified non-condensable gas was CO_2. The latter was quantified in larger yields in the mixture with the largest content of hemicellulose. Neupane et al. [13] performed fast pyrolysis of pine wood at 550 °C. They reported an increase in phenol and a minor increase in aromatic hydrocarbons (HC), such as benzene, naphthalene, anthracene, phenanthrene and fluorene, with increasing torrefaction level (225, 250 and 275 °C and 15, 30 and 45 mins). In an earlier study of the same authors [3], they reported a much larger increase of some aromatic HC (such as benzene, toluene, xylenes, indene and styrene) and no influence on the phenolic and naphthalene species upon torrefaction during fast pyrolysis at 650 °C of untreated and torrefied pine wood. Thangalazhy-Gopakumar et al. [17] performed fast pyrolysis of pine wood; they concluded that the bio-oil yield showed a maximum at 550 °C with levoglucosan and other anhydrous sugars being the major compounds. They also reported increasing phenols and toluene yields with increasing temperature, from 550 to 750 °C. Yang et al. [20] reported mainly oxygenated polar species from fast pyrolysis at 500–700 °C of untreated and torrefied switchgrass in a pyroprobe. Torrefaction promoted the production of the anhydrous sugars and, to a slight extent, the phenols, but apart from toluene the authors did not report other aromatics.

Mazlan et al. [21] investigated the effect of fast pyrolysis temperature, from 450 to 650 °C, on two types of untreated hardwood residues in a fixed bed drop-type pyrolyzer under a fast heating rate. They concluded that both feedstocks produced the same maximum amount of bio-oil but at slightly different temperature. When bio-oil yield decreased, non-condensable gases yield increased due to the secondary reactions. The main analyzed constituents of the bio-oil were acetic acid, tetrahydrofuran, and benzene. Zhou et al. [22] performed fast pyrolysis of lignin at 500–900 °C in a fixed bed reactor using a rapid heating rate. They reported that lignin pyrolysis results mainly in solid residue (char), except at 900 °C, where the gas yield exceeds the solid residue yield. The main heavy organic species analyzed were naphthalene and acenaphthylene, especially at 900 °C their yields increased significantly. Previous researchers investigated the effect of torrefaction of wood on fast pyrolysis and focused on selecting these process conditions that would optimize bio-oil production. Furthermore, authors put emphasis on bio-oil constituents, such as anhydrosugars, furans, etc. Therefore, literature is scarce concerning investigating on fast pyrolysis as the first chemical step at high temperature thermochemical reactors. Louwes et al. [23] investigated on fast pyrolysis of one of the two woody feedstocks used in our study, but these authors focused on bio-oil properties and supply chain analysis while using an entrained down-flow reactor.

The aim of this study is to characterize the effect of wood torrefaction on the formation of volatiles during fast pyrolysis, as the latter is the first chemical conversion step of thermochemical-converting technologies. In addition, to our knowledge this is the first time when a commercially available, severely torrefied fuel is characterized, and various non-condensable gases and PAH species are quantified under fast pyrolysis conditions. Furthermore, the pyrolysis volatiles were selected in order to be relevant to gasification's volatiles generated by mixed reactions. Therefore, the results of this study are compared with published results of O_2-steam blown circulating fluidized bed (CFB) gasification using exactly the same feedstocks [24,25] in order to show

Table 1
Literature review of similar pyroprobe research. Only the major identified compounds are reported.

Reference	Feedstock	Temperature (°C)	Heating rate ($°C·s^{-1}$)	Holding time (s)	Non-condensable gases	Oxygenated hydrocarbons	Non-oxygenated hydrocarbons
[14]	Cellulose	500	20,000	50	CO_2	Acetaldehyde, 5-hydroxymethylfurfural	–
[15]	Torrefied and untreated cellulose	600	n.d.	n.d.	–	Levoglucosan	Aromatics[a]
[18]	Cellulose-hemicellulose mix	500–700	20,000	15	CO_2	Levoglucosan, acetone	–
[17]	Pine wood	450–750	100	30	–	Guaiacols, phenols	Toluene
[13]	Torrefied and untreated pine wood	550	2000	90	–	Phenols, guaiacols	Naphthalene, anthracene, phenanthrene and fluorene
[3]	Torrefied and untreated pine wood	650	2000	n.d.	–	Phenols, guaiacols	Naphthalene
[20]	Torrefied and untreated Kanlow switchgrass	500–700	1000	n.d.	–	Benzofuran, phenols	Toluene, benzene

[a] No species are reported, however they concern non-oxygenated hydrocarbons with one or two rings structure.

the evolution of non-condensable gas species and selected organic species, such as phenol and PAH, in the gasifier. The results presented in this paper will provide information regarding the mentioned organic species and gas evolution under relevant conditions for thermochemical processes.

2. Experimental section

2.1. Feedstock

Five wood samples were tested, torrefied mixed wood, torrefied ash wood and their parent materials. Torrefied Torrcoal pellets (coded as BT: "Black Torrcoal" feedstock) consist of mixed wood and wood residues and it is a solid biofuel already available on the Dutch market. The fuel was acquired from Torr®Coal International B.V., where it was torrefied in an indirectly heated rotary drum reactor at approximately 300 °C for < 10 min. Torrefied ash wood pellets, of the species *Fraxinus excelsior*, were acquired from Van den Broek B.V. (The Netherlands) and torrefied by the Energy research Centre of the Netherlands (ECN) at a 50 kg·h^{-1} directly heated moving bed pilot plant at two temperatures, 250 °C (coded as ash 250) and 265 (coded as ash 265) °C for 30 min. Both parent materials, i.e. untreated ash pellets and untreated Torrcoal pellets (coded as WT: "White Torrcoal" feedstock), were received from the same sources as the torrefied feedstocks. All feedstocks were ground and manually sieved into a size < 70 μm.

2.2. TGA

The proximate analysis was performed via thermogravimetric analysis and is presented in Table 2 [24,25]. For this purpose a TA Instruments SDT Q600 thermogravimetric analyzer (TGA) was used and a heating rate of 20 °C·min^{-1} in a N_2 atmosphere was applied. Details regarding the TGA instrument have been described in [26]. The samples were placed in alumina cups in the apparatus in amounts varying between 3 and 15 mg and the purge flow rate was 100 ml·min^{-1}. Experimental runs were performed in a nitrogen atmosphere. The TGA runs started with a temperature equilibration at 30 °C, after which a drying step followed (heating up to 120 °C at 20 °C·min^{-1} with a holding time at 120 °C of 30 min). The next step was the devolatilization, with the selected heating rate of 20 °C·min^{-1}, up to 900 °C. The holding time at 900 °C was again 30 min. In addition, the torrefaction degree was calculated based on the anhydrous weight loss divided by the initial volatile mass fraction on a dry basis and is presented in Table 2.

$$\text{Torrefaction degree} = (m_{\text{final}} - m_{\text{initial}})_{\text{dry}}/\text{volatile matter}_{\text{initial,dry}}$$

The increase of the moisture content upon torrefaction of ash wood is attributed to the water addition to facilitate pelleting. Based on the proximate analysis of BT and ash 265, the fixed carbon and volatile contents are similar despite the difference in wood origin and the torrefaction temperature. Lastly, the elemental analysis of the feedstocks can be found in [24,25].

Table 2
Proximate analysis, bio-chemical analysis and torrefaction degree of used feedstocks.

	Untreated ash	Ash 250	Ash 265	WT	BT
Moisture[a]	4.6	5.7	5.8	5.9	4.1
Volatile matter[b]	79.2	72.4	68.6	76.8	66.2
Fixed carbon[b]	20.2	27.0	30.5	21.8	32.2
Ash content[b]	0.5	0.5	1.0	1.4	1.6
Hemicellulose[b]	36.0	16.3	11.3	25.4	10.0
Cellulose[b]	33.2	34.9	34.3	41.1	35.1
Lignin[b]	30.8	48.8	54.4	33.5	54.9
Torrefaction degree (%)	–	8.6	13.4	–	13.8

[a] On as received basis.
[b] On dry basis.

2.3. Pyroprobe

Pyrolysis experiments were performed in a commercial pyrolyzer, i.e. pyroprobe, model 5150, CDS Analytical Inc. The probe had a computer-controlled heating element, which surrounded the sample contained in a quartz tube (approximately 25 mm long and 1.9 mm inner diameter). A second heated zone with a longer packed tube (114 mm long and 1.9 mm inner diameter) at 50 °C was positioned downstream to the valve oven, which was approximately at 325 °C, and acted as the first trapping zone for the heavy condensable species (hereafter referred to as 'trap'). At the end of this quartz tube, an impinger bottle filled with 2 ml of isopropanol (IPA) was connected, acting as the final condenser for lighter aromatics. Pyrolysis experiments were performed at five temperatures (600, 700, 800, 900 and 1000 °C) at a constant heating rate of 600 °C·s^{-1} and holding time of 10 s. The pyroprobe run started with packing 30 ± 1 mg of feedstock sample in the quartz tube which was at room temperature, and the nitrogen flow was fixed at approximately 18 ml·min^{-1}. The set points (heating rate, final temperature and holding time) of the test were imposed using a device-control software. To begin, the temperature of the accessory was increased to 300 °C at a heating rate of 100 °C·min^{-1} and an de-gassed syringe was connected to the exhaust line of the gases to collect the produced gases just before the pyrolysis process started. The next step was the initiation of the pyrolysis process with the selected set points; heating rate, holding time (at final temperature) and the final temperature, between 600 and 1000 °C. Only two experiments with BT feedstock were performed with an extended holding time to investigate the remaining unreacted volatile mass fraction in the solid residue. When the run had finished the gas-filled syringe was connected to the micro-GC and the gases were injected for analysis, and the condenser was removed and weighed. The trap was rinsed with 3 ml of IPA in a test tube and the resulting solution was mixed with the contents of the impinger bottle. The dissolved species were then filtered via a paper filter in order to remove any particles, and the 5 ml solution was collected in a vial for analysis. After the accessory was cooled down to, at least, 50 °C the sample holder was removed and weighed. All pyroprobe runs were duplicated at least once and the average values and standard deviations are calculated. Table 3 shows the experimental matrix of pyroprobe experiments. Lastly, researchers have reported that at such high temperatures (T > 550 °C) a heating lag occurs [27]. However, the quantification of species such as phenols and PAH, and their behavior show that this effect is minimized in the pyroprobe.

2.4. Circulating fluidized bed gasification

The experimental test rig at TU Delft consisted of a 100 kWth steam-oxygen blown CFB gasifier followed by a candle filter unit, and it was equipped with a gas supply system, a solids supply system and analytical equipment. The candle filter unit consisted of a high-

Table 3
Fast pyrolysis experimental matrix.

Parameters		Untreated ash	Ash 250	Ash 265	WT	BT
Final temperature (°C)	600	X	X	X	X	X
	700	X	X	X	X	X
	800	X	X	X	X	X
	900	X	X	X	X	X
	1000	X	X	X	X	X
Holding time at final temperature (s)	10	X	X	X	X	X
	30					X
	60					X
Heating rate (°C·s^{-1})	600	X	X	X	X	X

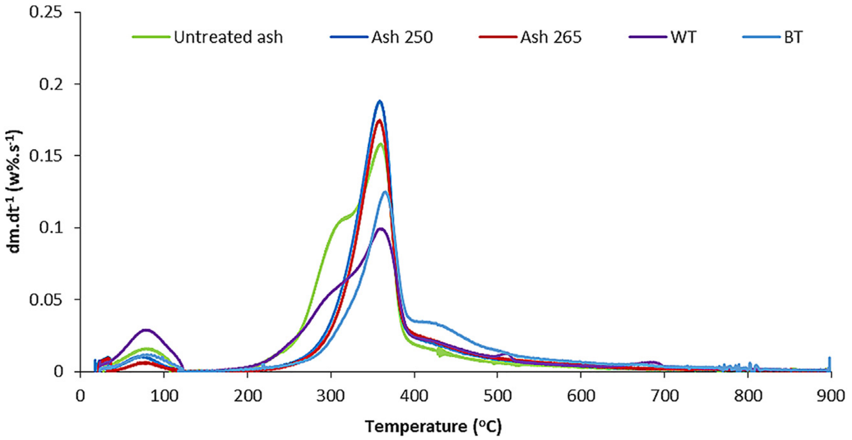

Fig. 1. dTG of ash wood and Torrcoal wood samples (heating rate = 20 °C·min^{-1}, N_2 = 100 ml·min^{-1}).

temperature filter unit containing four woven ceramic candles (BWF, Germany) operating at 450 °C and 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. In addition, two other kinds of solids could be fed simultaneously, e.g. the magnesite as bed material; magnesite is a mineral consisting mainly of MgO. Details about the gasification rig can be found elsewhere [24,25].

2.5. Analytical equipment

The gas analysis was performed using a Varian μ-GC CP4900 equipped with a column module which separates the gas species N_2, H_2, CO, CO_2 and CH_4 (1 m CP-COX column), which are then detected via a TCD detector and quantified. In addition, the (trapped) condensable species were analyzed using a KNAUER HPLC and the trapped condensable species of only two experiments were analyzed using a GCxGC-FID analysis setup available at the University of Groningen [28]. The HPLC was equipped with a UV and fluorescence detector (Knauer), and two reverse phase columns, one for phenol (Kromasil Eternity C18 5 μm 150 × 4.6 mm) and the other for PAHs (i.e. from naphthalene to indeno(1,2,3-cd)pyrene) (UltraSep ES PAH QC, 60 × 2.0 mm). For the hemicellulose, cellulose and lignin compositions, the two-step hydrolysis based on the (modified) NREL method [29] was followed and the hydrolysed samples were analyzed in a KNAUER HPLC. The latter was equipped with a Refractive Index (RI) detector and a Phenomenex Rezex RPM-Monosaccharide Pb^{2+} column for glucan, xylan, galactan, arabinan and mannan quantification. The modification of the National Renewable Energy Laboratory (NREL) method concerned the use of barium hydroxide octahydrate ($Ba(OH)_2{\cdot}8H_2O$) instead of the recommended calcium carbonate ($CaCO_3$) base for the neutralization step. This modification was necessary due to the apparent interference of the sulfate anion with measurement of the peak, as explained by [30]. The chemical composition results are presented in Table 2. Yu et al. [31] have shown that phenol is mainly derived from lignin and it was observed that no PAH are formed below 800 °C. Therefore, phenol is quantified for the whole temperature range and the PAH for temperatures between 800 and 1000 °C. In addition, it was decided to analyze these organic compounds as phenol is mainly derived from lignin, which is expected to increase in mass fraction upon torrefaction, phenol is converted to PAH at elevated temperature and phenol and PAH are species formed during CFB gasification. For the analysis of the phenol from fast pyrolysis, 20 μL of filtered sample were injected in the column and a gradient elution with methanol and water was performed for 5 min and the UV detector was set at 254 nm. For the analysis of the PAH from fast pyrolysis, 20 μL of filtered sample were injected in the column and a gradient elution with acetonitrile and water was performed for 17 min. The quantification was performed by external calibration using standard tar compounds and the quantitative analysis was obtained on the basis of the external calibration. The calibration was performed using triplicate data points. All coefficients of determination (R^2) exceeded 0.990. The external calibrations were prepared for aromatic hydrocarbons, such as phenols and from naphthalene to indeno(1,2,3-cd)pyrene. In addition, for compounds analyzed during CFB gasification, the samples were collected with the tar standard method [32] 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). A detailed description of the equipment used along with the followed procedure can be found elsewhere [24,25]. Lastly, bio-oil samples of WT and BT experiments at 900 °C were sent to the University of Groningen for bio-oil analysis, monomers and oligomers detection, such as alkyl-phenolics, aromatics and aliphatic HC. The detailed GCxGC-FID description along with the followed procedure can be found elsewhere [28].

3. Results and discussion

3.1. Biomass characterization

Fig. 1 shows the differential thermogravimetric data of untreated ash, torrefied ash woods, WT and BT. Torrefaction resulted in a minimal effect regarding the peak mass loss value of the feedstocks, in increasing the fixed carbon and the ash contents at the highest torrefaction temperatures (Table 2) and the decomposition of the torrefied feedstocks started at a higher temperature. In addition, torrefaction resulted in increasing the lignin content and the ratios of cellulose to hemicellulose and lignin to hemicellulose, this was confirmed by the hydrolysis results (Table 2) and as part of the hemicellulose was converted, the "shoulder" on the left side of Fig. 1 has disappeared. It has been reported before that the conversion of hemicellulose up to 275 °C is attributed to the fragmentation of monosaccharide units, the cleavage of glycosidic bonds and the decomposition of the side chains [9]. It should be stressed that even though ash 265 and BT result in practically the same torrefaction degree, the effect of torrefaction on the cellulose content is different. For ash 265, torrefaction resulted in increasing the cellulose content, whereas for BT the cellulose content decreased upon torrefaction. This behavior is a combination of the torrefaction temperature, the torrefaction residence time, and the type of wood. Torrcoal company uses a mixture of hardwood, softwood and wood residues and operates at high torrefaction temperature which results in larger cellulose conversion. On the other hand, ECN torrefied hardwood at lower temperature than Torrcoal but using a much longer torrefaction residence time. The latter resulted in larger hemicellulose conversion upon torrefaction. However, in both cases the total sum of

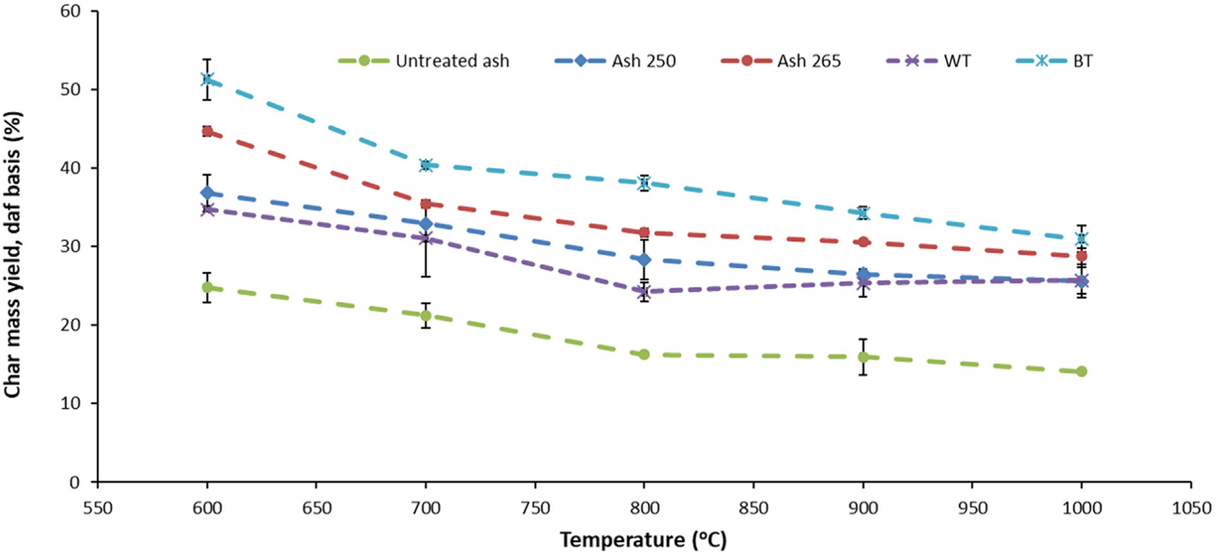

Fig. 2. Mass yield of char versus temperature during fast pyrolysis.

hemicellulose and cellulose contents decreased upon torrefaction.

3.2. *Pyroprobe results*

3.2.1. *Char*

Torrefaction resulted in increasing the char mass yield, as presented in Fig. 2. Ash 265 and BT resulted in the largest char mass yield for the entire temperature range due to their increased lignin content [22], and ash 250 resulted in a slightly lower mass yield than ash 265 for the entire temperature range. In addition, increasing the devolatilization temperature leads to decreasing the char mass yield. The char mass yields of the torrefied ash wood species did not result in a large difference, except at the lowest temperature of 600 °C where the difference is approximately 10%. At 1000 °C the char mass yield of the ash 250 and ash 265 matches their fixed carbon contents. However, for untreated ash, the char yield at 1000 °C was lower than its fixed carbon content. The latter may be attributed to secondary reactions.

Regarding the Torrcoal feedstocks, the WT char mass yield reaches a plateau at 800 °C, whereas, BT char mass yield tends towards a plateau at 1000 °C. The latter was confirmed with two additional tests performed with a higher holding time (see Table 3) and resulted in minor changes in the char mass yield values. The final char yield of BT matches its fixed carbon content; however for WT the char mass yield is larger than its fixed carbon content. The latter is due to part of volatiles condensed at such high temperature, as a WT char yield plateau is observed at 800 °C and not at the highest pyrolysis temperature. This difference in the final char yields in relation to the fixed carbon contents for both TW and untreated ash wood may be attributed to the different hemicellulose and cellulose contents that both feedstock exhibit. A higher hemicellulose content (e.g. untreated ash) results in a higher CO_2 yield [18]. On the other hand, a higher cellulose content (e.g. TW) results in a larger levoglucosan yield that would result in more secondary char formation (see Fig. 2). Another reason for this difference can be the secondary decomposition of char for the formation of non – condensable gases [12].

3.2.2. *Trapped bio-oil*

The untreated feedstocks resulted in a higher trapped bio-oil mass yield for the entire temperature range [4] (see Fig. 3) due to the torrefaction reducing the volatile content of the biomass. The amount of volatiles released during torrefaction occurs due to hemicellulose and to a lesser content cellulose decomposition which are the main sources of

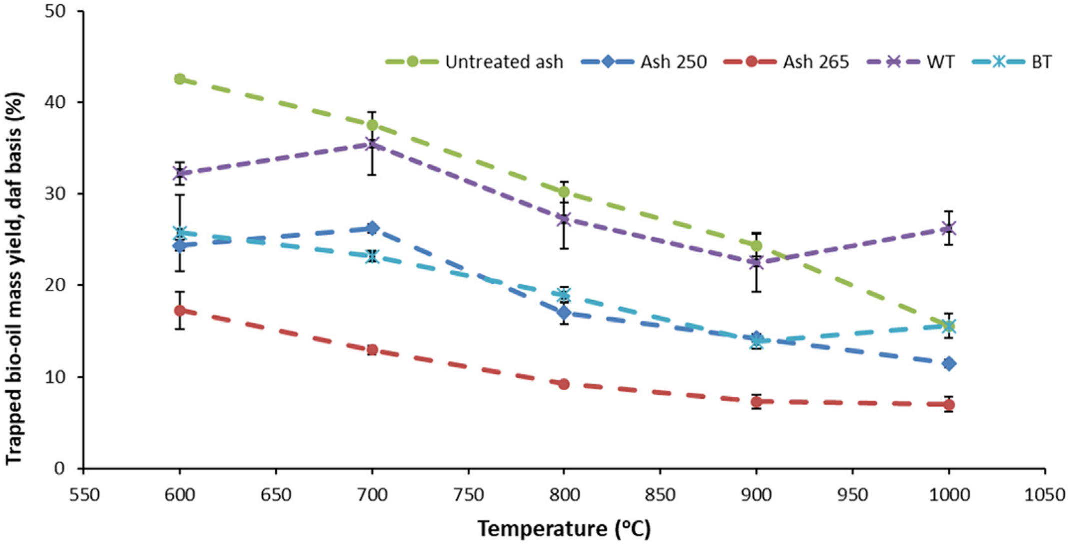

Fig. 3. Mass yield of total trapped bio-oil versus temperature during fast pyrolysis.

liquid products. Furthermore, the severe carbon–carbon crosslinking of the biomass carbohydrates prevents the production of both liquid and gaseous products and favours char production. For ash wood samples, the bio-oil yield decreases with increasing pyrolysis temperature, consistent with reported results [17]. Untreated ash and ash 250 bio-oil yields decrease during the entire temperature range. Ash 265 resulted in the lowest bio-oil yield during the entire temperature range and its bio-oil yield reaches a plateau at 900 °C. For Torrcoal wood samples, increasing the devolatilization temperature resulted in decreasing the bio-oil yield at higher temperature than 700 °C and up to 900 °C, then it stabilized. The reduction of the bio-oil mass yield occurs with a simultaneous increase of the gas yield (see Fig. 4), showing that part of the bio-oil produced is converted to non-condensable gases [21].

3.2.3. Non-condensable gas

As torrefaction reduces the volatile content of the feedstocks, the torrefied samples resulted in a lower non-condensable gas mass yield than the untreated samples, see Fig. 4. The gas mass yield for all feedstocks increases with increasing pyrolysis temperature. For ash wood samples, the gas yield is approximately the same until 700 °C; from 700 to 1000 °C untreated ash results in higher gas yield than ash 250 and 265. This shows that secondary reactions, such as reforming reactions, that occur between 700 and 1000 °C and produce gases, mostly CO based on the analyzed gases, are more common in untreated ash wood tests [33]. For Torrcoal feedstocks, WT results in a higher gas yield, except at 1000 °C when BT matches the gas yield of WT.

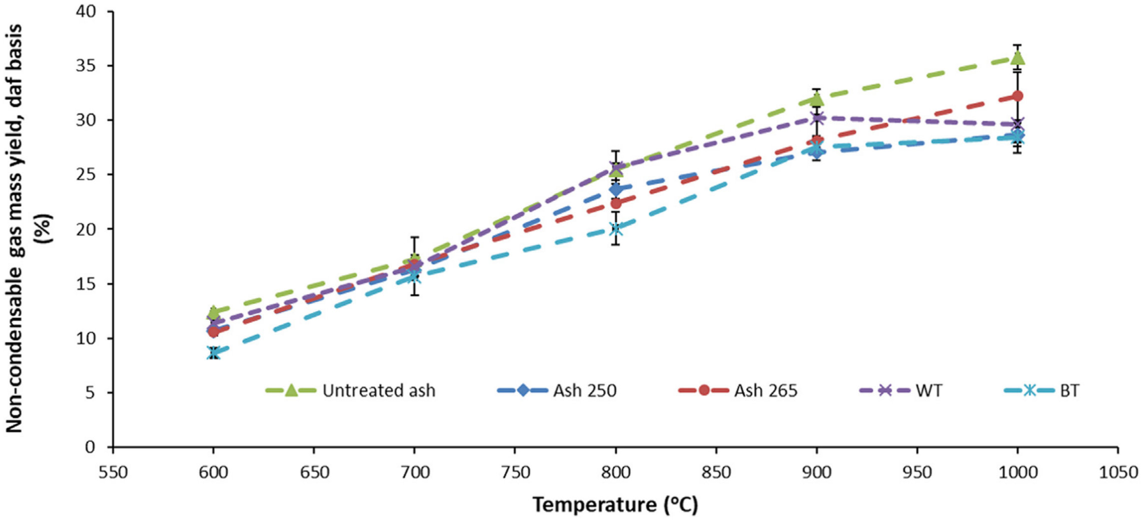

Fig. 4. Mass yield of measured non-condensable gases versus temperature during fast pyrolysis.

Fig. 5 presents the mass yields of measured individual permanent gas species, CO_2, CO, CH_4 and H_2. All feedstocks show a similar behavior, the yield of these gas species increases with devolatilization increasing temperature. At lower temperature CO_2 is the dominant gas; however, at 800 °C and at higher devolatilization temperatures, CO becomes the gas with the largest mass yield, consistent with the reported results [26,34].

Even though the untreated feedstocks are both wood in origin, they show differences in the mass yields of CO and CO_2 in the entire temperature range. Their yields for both gases are approximately the same at 600 °C. WT pyrolysis results in higher CO_2 yield than untreated ash pyrolysis; whereas, untreated ash results in higher CO yield than WT. This difference is attributed to their different chemical compositions, WT has a larger hemicellulose content than untreated ash [18] and secondary reactions of the pyrolysis products. In addition, upon torrefaction both CO and CO_2 mass yields decreased due to the conversion of hemicellulose and the reduction of the volatile content during torrefaction.

CH_4 and H_2 mass yields are much lower than the mass yields of CO and CO_2. Both untreated feedstocks show similar mass yields of CH_4 and H_2 up to 900 °C, but at 1000 °C untreated ash results in higher mass yields. Torrefaction of ash resulted in increasing to a small extent only the mass yields of CH_4 until 800 °C, at higher temperature this change is within the error margin between untreated ash and torrefied ash woods. For Torrcoal samples, torrefaction resulted in no significant changes for both CH_4 and H_2.

3.2.4. Phenol and PAHs

Phenol and PAH yields generally decrease and increase, respectively, with increasing devolatilization temperature. This effect of temperature on the phenol yield is consistent with literature [13,20,35]. Phenol mainly derives from lignin degradation [3,36] and at high temperature (> 850 °C) phenol is converted mainly to non-oxygenated aromatics (naphthalene and benzene) and secondly to non-condensable species (CO and CO_2), instead of char [35,37]. As torrefaction typically results in increasing the lignin content [4], torrefied feedstocks are expected to result in a higher phenol yield. This was observed with all torrefied feedstocks except for WT and BT at 700 °C, given the high standard deviation, they result in approximately the same phenol yields. Regarding the PAH yield, all the analyzed species, but naphthalene, resulted in approximately the same yield as the phenol yield for higher temperature than 800 °C. For all feedstocks, the dominant PAH compound is naphthalene [22].

Fig. 6 shows that torrefaction of WT results in increasing the mass yield of phenol but it does not affect significantly the mass yields of other PAH compounds. Even though torrefaction results in decreasing the volatile content of BT, the increase in the lignin content counters the effect on the PAH yield. Phenol is a PAH precursor and BTEX compounds that are produced in cellulose and hemicellulose pyrolysis are also PAH precursors [13]. Additionally, the small increase of produced H_2 can be an indicator of phenol cracking, but also of H_2 abstraction as part of the HACA sequence [14]. Therefore, it is fair to assume that both mechanisms contribute to PAH formation in the present cases. In addition, increasing the devolatilization temperature results in increasing all the PAH compounds and decreasing the phenol. A plateau for the phenol yield is observed at 800 °C and 900 °C for WT and BT, respectively. However, the phenol reduction is greater than the PAH increase. Based on this result, the PAH are formed only from a part of the converted phenol, the rest of the converted phenol results in non-condensable gases (such as CO) or organic species that are not measured (such as benzene). In addition Fig. 8 shows the relation between

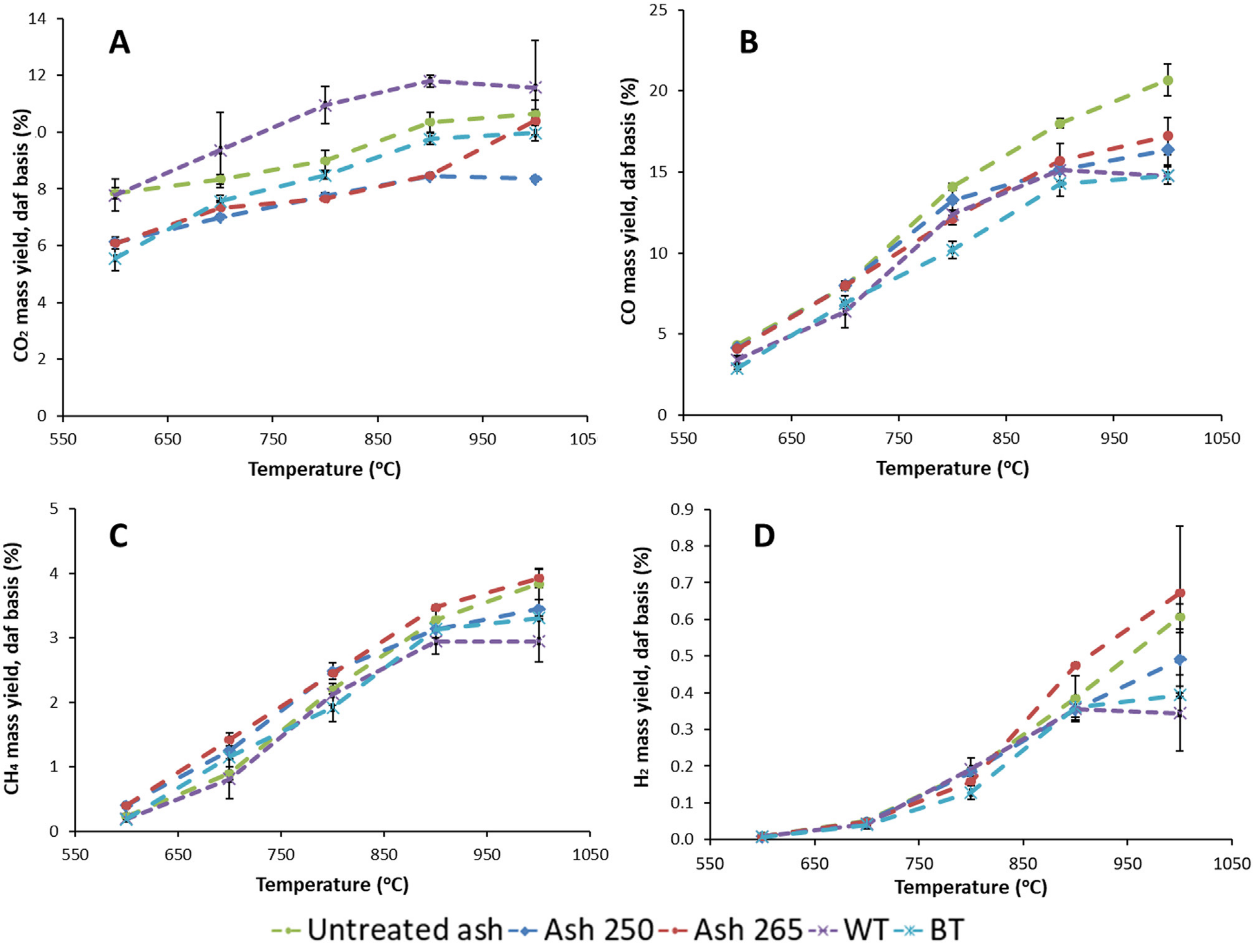

Fig. 5. A: CO_2 yield versus temperature during fast pyrolysis. B: CO yield versus temperature during fast pyrolysis. C: CH_4 yield versus temperature during fast pyrolysis. D: H_2 yield versus temperature during fast pyrolysis.

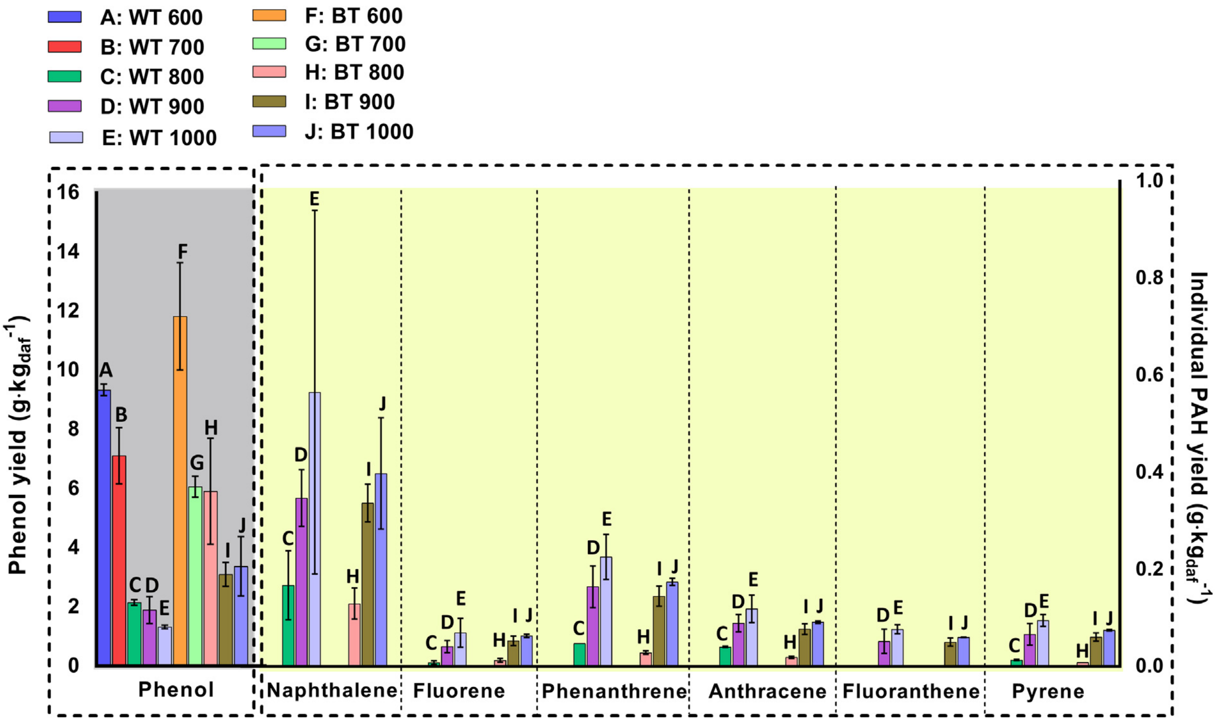

Fig. 6. Phenol and PAH species yields of Torrcoal wood samples during fast pyrolysis.

Table 4
Analyzed organic species yield of WT and BT samples based on GCxGC-FID (for pyroprobe devolatilization tests at 900 °C).

Components	WT900 (g/kg$_{daf}$)	BT900 (g/kg$_{daf}$)
Aromatics[a]	14.97	15.96
Cycloalkanes	1.69	0.14
Dihydroxybenzene	29.37	5.55
Hydrocarbons	32.47	35.68
Ketones	4.09	1.11
Methoxyphenol	5.79	4.16
Naphthalene	21.60	1.80
Phenols	154.46	31.10
Volatile fatty acids	41.79	24.02
Total volatile fraction	306.38	119.53

[a] The aromatics group contains benzene, toluene, ethylbenzene, and xylenes.

Table 5
Detailed analysis of phenols and aromatics yields of WT and BT samples based on GCxGC-FID (for pyroprobe devolatilization tests at 900 °C).

Components	WT900 (g/kg$_{daf}$)	BT900 (g/kg$_{daf}$)
Phenol	4.09	3.75
Phenol, 2-methyl-	1.13	0.97
Phenol, 3-methyl-	3.25	1.39
Phenol, 4-methyl-	2.96	2.08
Phenol, 2,4-dimethyl-	2.40	0.97
Phenol, 3-ethyl-	2.40	0.69
Phenol, 4-ethyl-	4.52	1.11
Phenol, 4-propyl-	13.84	3.19
Toluene	2.40	2.64
Ethylbenzene	0.14	b.i.l.[a]
Undecane	5.93	5.00
Tridecane	5.79	7.36
Pentadecane	3.39	5.00
Heptadecane	b.i.l.	3.33
Nonadecane	b.i.l.	2.92

[a] b.i.l. stands for below identification limit.

the ratio of phenol to PAH species and temperature increase. There is a decreasing trend, showing that phenol is converted to PAH. However, upon torrefaction and at 900 °C this ratio of phenol to PAH stabilizes.

Table 4 presents the GCxGC-FID results of bio-oil derived from WT and BT pyrolysis at 900 °C and Table 5 presents an extensive analysis of grouped species of Table 4, such as phenols. In addition, as the total phenols species yield is much larger than the sum of the specific species of Table 5, it is expected that more unidentified phenols are formed during our tests. These results are in qualitative agreement with the HPLC results in Fig. 3. The GCxGC-FID results also show that the total trapped species reduced upon torrefaction. This reduction derives mainly from phenols, volatile fatty acids and dihydroxybenzene. Based on the phenol species and aromatics of Table 4, the phenol species reduction upon torrefaction is due to methyl-, ethyl-, dimethyl- and propyl-substituted phenol species, as the difference between phenol formation of WT and BT at 900 °C is not significant. In addition, the naphthalene yields are different; however, the naphthalene concentration in both samples was low and it resulted in a minor difference in background noise. Thus, the naphthalene yield of WT900 appears to be significantly larger. These results indicate that torrefaction resulted in increasing slightly only the aromatics and hydrocarbons yields. On the other hand, the other identified species yields were reduced upon torrefaction. These results are in agreement with Srinivasan et al. [3,15] and Neupane et al. [13].

Torrefaction resulted in affecting the untreated ash in a similar way as the WT for phenol; it led to an increase of phenol mass yield and it did not affect the PAH compounds, as shown in Fig. 7. Similar to WT, phenol yield decreases with increasing temperature, whereas, the other analyzed organic compounds increase. The only quantitative difference between ash wood samples is that ash 250 shows a slightly larger phenol yield than ash 265 at 600 °C, and naphthalene yield decreases from 900 °C to 1000 °C for ash 265. While the former can be explained by the effect of torrefaction on the chemical composition of ash 250 and ash 265, the latter cannot. Nanou et al. [38] performed the torrefaction of the untreated ash and these authors reported that the torrefaction gas of ash 265 contained a higher mass fraction of phenol than the torrefaction gas of ash 250; this shows that more lignin was converted. Therefore, it may be said that until phenols starts decreasing (i.e. converting) in the pyroprobe, its quantified yield derived mainly from primary reactions. On the other hand, regarding the naphthalene yield at 1000 °C, Zhou et al. [22] tested lignin and these authors reported that the presence of CO_2 reduced the mass yield of naphthalene while the CO yield increased, similarly to our results. These authors did not provide an explanation for their observation but CO_2 and H_2O may accelerate the decomposition of tars [39], favouring reaction pathways that do not lead to naphthalene formation. In addition Fig. 8 shows the relation between the ratio of phenol to PAH species and temperature increase. There is a decreasing trend, showing that phenol is converted to PAH.

3.3. Analyzed non-condensable gases, phenol and PAH behavior in the CFB gasifier

The non-condensable gases, phenol and PAH species formed in the pyroprobe are considered compounds that are formed when biomass is fed to a thermochemical reactor, such as a gasifier. Therefore, these results are compared with gasification results from O_2-steam blown CFB gasification with the same feedstocks. The gasification experiments were performed with an equivalence ratio (ER) = 0.36 and a steam-to-biomass ratio (SBR) = 0.85 for Torrcoal wood samples, and ER = 0.3 and SBR = 1.0 for ash wood samples. Due to the fact that the CFB gasification tests were carried out at 850 °C, the arithmetic mean of the pyroprobe results of tests at 800 °C and 900 °C was used.

Almost all gases show an increasing trend from pyrolysis to gasification (see Figs. 9 and 10) as pyrolysis concerns only the feedstock as reactant, whereas, in gasification steam and O_2 were fed in the reactor. However, CO yield decreases for ash wood samples, CO increases for BT and CH_4 does not show any change for all tested feedstocks in the gasifier. The increase in CO is attributed partly to reforming of hydrocarbons and partial oxidation in the gasifier due to the high ER. Contrary to Torrcoal samples, the CO yield from all ash wood samples decreases in the gasifier. However, a lower ER is used and in [25] it is concluded that torrefaction of ash wood resulted in increasing the tars in the gasifier; therefore a relation between the CO and tar yields exists [33], i.e. a tar reduction results in a CO increase. Lastly, it is evident that the CH_4 formed during pyrolysis is not as reactive as other existing species, resulting in no change in the gasifier.

Fig. 11 presents the results of analyzed organic species of Torrcoal woods in the gasifier and pyroprobe. Given the reduction in the phenol yield and the increase of the PAH species, one can conclude that tars, such as phenols, were converted to heavier aromatics in the gasifier, such as naphthalene for both WT and BT, and toluene, phenanthrene and pyrene for WT. Contrary to the pyroprobe results, this increase in the naphthalene mass yield during gasification is larger than phenol reduction, so other species are contributing as naphthalene is a stable aromatic species and product of tar growth mechanisms [33]. In addition, traces of phenol are still quantified in the gasifier only for WT. As torrefaction affected mainly the cellulose and hemicellulose content of WT, the pathway of phenol formation exists via species of hemicellulose and cellulose decomposition.

Fig. 12 presents the results of analyzed organic species of ash woods experiments in the gasifier and pyroprobe. The evolution of analyzed species is similar to Torrcoal wood samples, except for species heavier than phenanthrene which remained the same after the pyrolysis step in the gasifier. This shows that phenol was converted to naphthalene but also to other species in the gasifier, such as benzene and CO_2 [37].

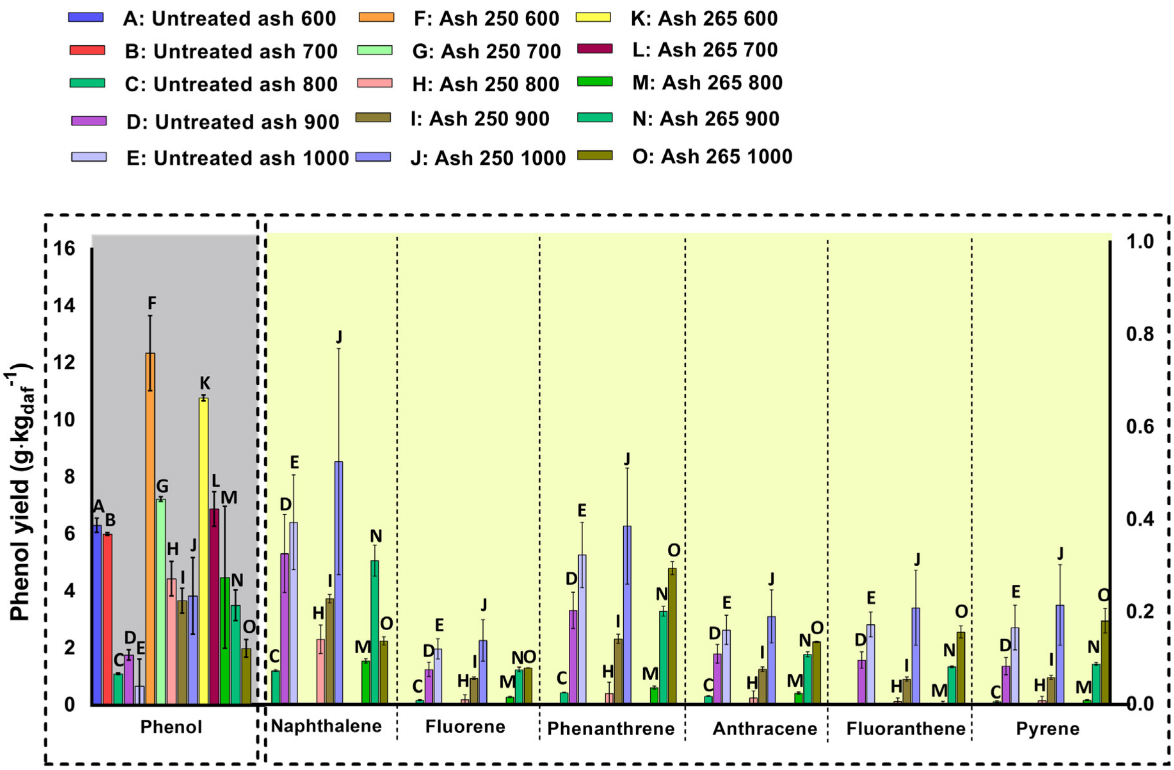

Fig. 7. Phenol and PAH species yields of ash wood samples during fast pyrolysis.

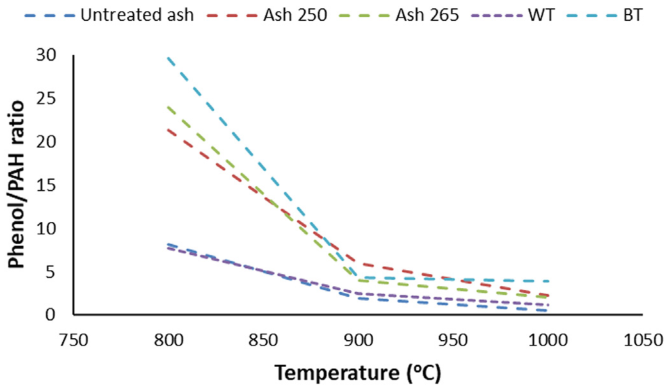

Fig. 8. Phenol to PAH ratio of the investigated wood feedstock.

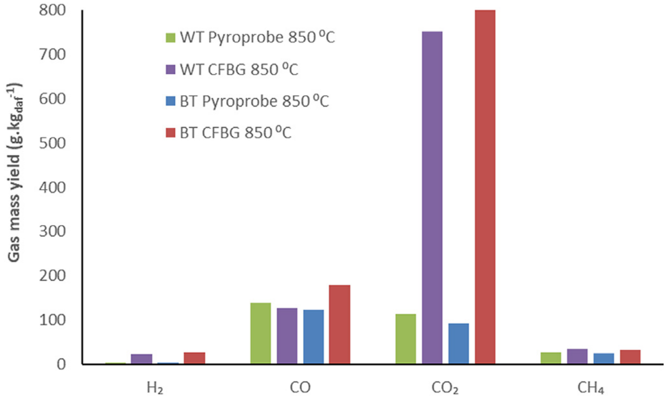

Fig. 9. Gas mass yields in fast pyrolysis and CFB gasification [24] (850 °C, ER = 0.3 and SBR = 1.0) of Torrcoal wood samples.

4. Conclusions

In this paper we investigated the impact of wood torrefaction on fast pyrolysis using a pyroprobe. Fast pyrolysis is the first chemical conversion step of many thermochemical conversion technologies. Therefore, the pyrolysis products were considered as primary products formed in a CFB gasifier, and here we compared their yields with experimental results of CFB gasification with exactly the same feedstocks. The chemical analysis results show that torrefaction temperature affects different types of wood differently regarding the hemicellulose, cellulose and lignin contents. In addition, the torrefaction residence time can be an important factor when processing biomass. An increased residence time results in increasing the torrefaction degree to similar values as torrefaction temperature would. The fast pyrolysis experiments showed that torrefaction decreased the bio-oil and gas mass yields, increased the char and phenol mass yields and did not show a significant effect on the PAH mass yield. However, torrefaction did not affect the increasing or decreasing trends with increasing temperature in the pyroprobe. The analyzed species formed during pyrolysis show different behaviors in the CFB gasifier. H_2 and CO_2 mass yields increased due to the oxidation agents, CH_4 that is formed during pyrolysis is rather unreactive in the gasifier, and CO is depended on tar conversion and gasification conditions. Lastly, even though phenol and naphthalene that are formed during pyrolysis are decreased and increased, respectively, they do not necessarily convert to heavy PAH. The latter are produced during pyrolysis and remain relatively constant. Therefore, a method that would reduce heavy PAH in the pyrolysis step would result in reducing them in the gasification step too.

Comparing pyroprobe tests with tests at thermochemical reactors which include a pyrolysis step show that secondary reactions are indeed minimized in the pyroprobe. Therefore, such a comparison is promising. It is suggested that the same species are quantified in the pyroprobe and the thermochemical reactor, but additional species should be considered, such as benzene. This way reaction pathways of organic species can be distinguished.

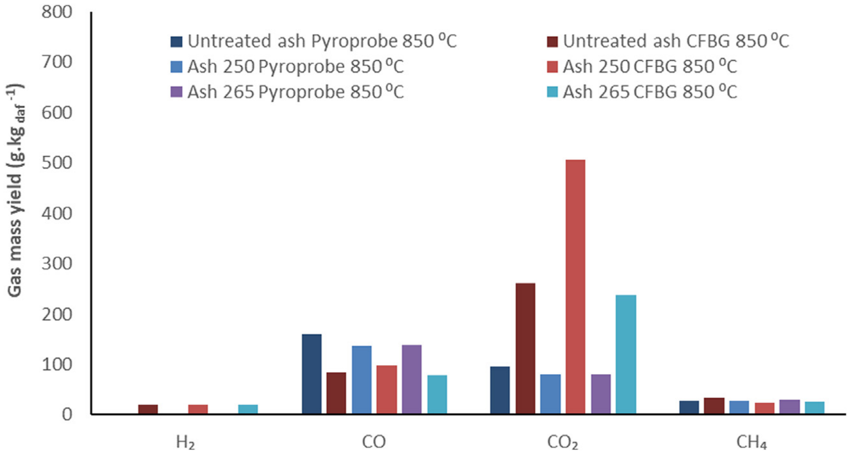

Fig. 10. Gas mass yields in fast pyrolysis and CFB gasification [25] (850 °C, ER = 0.3 and SBR = 1.0) of ash wood samples.

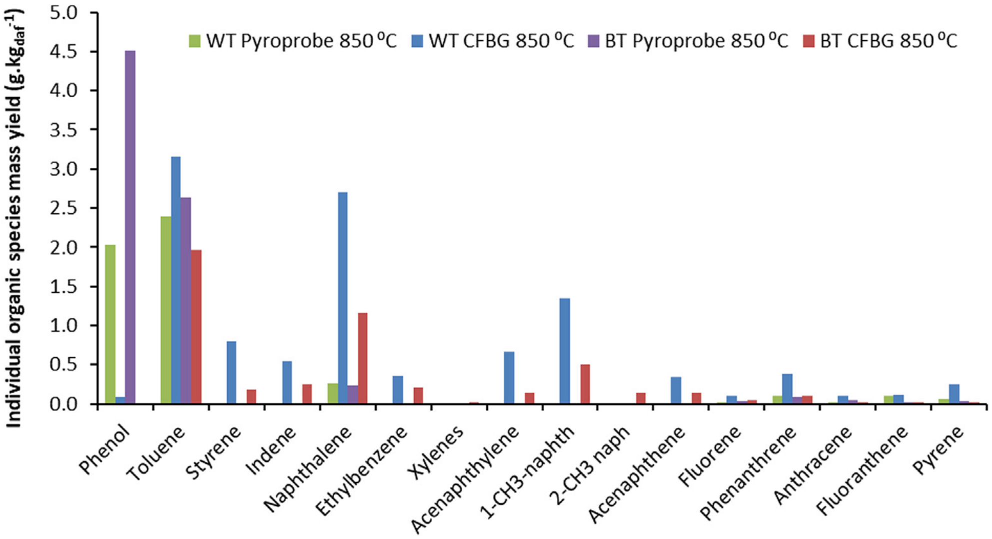

Fig. 11. Individual organic species mass yield in fast pyrolysis and CFB gasification [24] (850 °C, ER = 0.3 and SBR = 1.0) of Torrcoal wood samples.

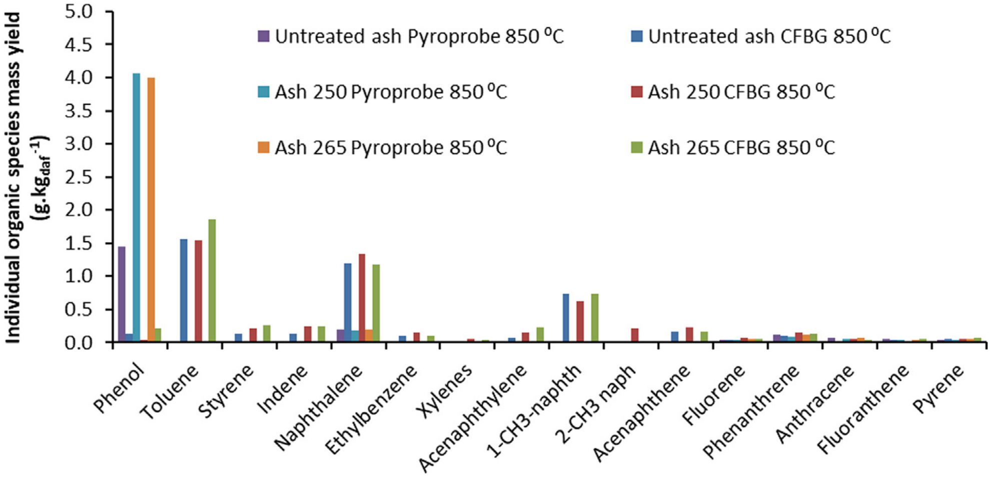

Fig. 12. Individual organic species mass yields in fast pyrolysis and CFB gasification [25] (850 °C, ER = 0.3 and SBR = 1.0) of ash wood samples.

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References

[1] M.J.C. van der Stelt, H. Gerhauser, J.H.A. Kiel, K.J. Ptasinski, Biomass upgrading by torrefaction for the production of biofuels: a review, Biomass Bioenergy 35 (2011) 3748–3762, http://dx.doi.org/10.1016/j.biombioe.2011.06.023.

[2] G.-A. Tsalidis, Y. Joshi, G. Korevaar, W. de Jong, Life cycle assessment of direct co-firing of torrefied and/or pelletised woody biomass with coal in The Netherlands, J. Clean. Prod. 81 (2014) 168–177, http://dx.doi.org/10.1016/j.jclepro.2014.06.049.

[3] V. Srinivasan, S. Adhikari, S.A. Chattanathan, S. Park, Catalytic pyrolysis of torrefied biomass for hydrocarbons production, Energy Fuel 26 (2012) 7347–7353, http://dx.doi.org/10.1021/ef301469t.

[4] J. Meng, J. Park, D. Tilotta, S. Park, The effect of torrefaction on the chemistry of fast-pyrolysis bio-oil, Bioresour. Technol. 111 (2012) 439–446, http://dx.doi.org/10.1016/j.biortech.2012.01.159.

[5] D.K. Shen, S. Gu, A.V. Bridgwater, Study on the pyrolytic behaviour of xylan-based hemicellulose using TG–FTIR and Py–GC–FTIR, J. Anal. Appl. Pyrolysis 87 (2010) 199–206, http://dx.doi.org/10.1016/j.jaap.2009.12.001.

[6] A. Broido, M.A. Nelson, Char yield on pyrolysis of cellulose, Combust. Flame 24 (1975) 263–268, http://dx.doi.org/10.1016/0010-2180(75)90156-X.

[7] Y.F. Liao, S.R. Wang, Z.Y. Luo, Research on cellulose rapid pyrolysis, J. Zhejiang Univ. Eng. Sci. 37 (2003) 582–587.

[8] N. Worasuwannarak, T. Sonobe, W. Tanthapanichakoon, Pyrolysis behaviors of rice straw, rice husk, and corncob by TG-MS technique, J. Anal. Appl. Pyrolysis 78 (2007) 265–271, http://dx.doi.org/10.1016/j.jaap.2006.08.002.

[9] S. Wang, H. Lin, L. Zhang, G. Dai, Y. Zhao, X. Wang, B. Ru, Structural characterization and pyrolysis behavior of cellulose and hemicellulose isolated from softwood *Pinus armandii* Franch, Energy Fuel 30 (2016) 5721–5728, http://dx.doi.org/10.1021/acs.energyfuels.6b00650.

[10] B. Joffres, D. Laurenti, N. Charon, A. Daudin, A. Quignard, C. Geantet, Thermochemical conversion of lignin for fuels and chemicals: a review, Oil Gas Sci. Technol. 68 (2013) 753–763, http://dx.doi.org/10.2516/ogst/2013132.

[11] M. Brebu, C. Vasile, Thermal degradation of lignin – a review, Cellul. Chem. Technol. 44 (2010) 353–363.

[12] D. Ferdous, A.K. Dalai, S.K. Bej, R.W. Thring, Pyrolysis of lignins: experimental and kinetics studies, Energy Fuel 16 (2002) 1405–1412, http://dx.doi.org/10.1021/ef0200323.

[13] S. Neupane, S. Adhikari, Z. Wang, A.J. Ragauskas, Y. Pu, Effect of torrefaction on biomass structure and hydrocarbon production from fast pyrolysis, Green Chem. 17 (2015) 2406–2417, http://dx.doi.org/10.1039/c4gc02383h.

[14] D.K. Ojha, R. Vinu, Fast co-pyrolysis of cellulose and polypropylene using Py-GC/MS and Py-FT-IR, RSC Adv. 5 (2015) 66861–66870, http://dx.doi.org/10.1039/c5ra10820a.

[15] V. Srinivasan, S. Adhikari, S.A. Chattanathan, M. Tu, S. Park, Catalytic pyrolysis of raw and thermally treated cellulose using different acidic zeolites, Bioenergy Res. 7 (2014) 867–875, http://dx.doi.org/10.1007/s12155-014-9426-8.

[16] F. Ateş, M.A. Işıkdağ, Evaluation of the Role of the Pyrolysis Temperature in Straw Biomass Samples and Characterization of the Oils by GC/MS, Energy Fuel 22 (3) (2008) 1936–1943.

[17] S. Thangalazhy-Gopakumar, S. Adhikari, R.B. Gupta, S.D. Fernando, Influence of pyrolysis operating conditions on bio-oil components: a microscale study in a pyroprobe, Energy Fuel 25 (2011) 1191–1199, http://dx.doi.org/10.1021/ef101032s.

[18] S. Wu, D. Shen, J. Hu, H. Zhang, R. Xiao, Cellulose-hemicellulose interactions during fast pyrolysis with different temperatures and mixing methods, Biomass Bioenergy 95 (2016) 55–63, http://dx.doi.org/10.1016/j.biombioe.2016.09.015.

[20] Z. Yang, M. Sarkar, A. Kumar, J.S. Tumuluru, R.L. Huhnke, Effects of torrefaction and densification on switchgrass pyrolysis products, Bioresour. Technol. 174 (2014) 266–273, http://dx.doi.org/10.1016/j.biortech.2014.10.032.

[21] M.A.F. Mazlan, Y. Uemura, N.B. Osman, S. Yusup, Fast pyrolysis of hardwood residues using a fixed bed drop-type pyrolyzer, Energy Convers. Manag. 98 (2015) 208–214, http://dx.doi.org/10.1016/j.enconman.2015.03.102.

[22] H. Zhou, C. Wu, J.A. Onwudili, A. Meng, Y. Zhang, P.T. Williams, Polycyclic aromatic hydrocarbon formation from the pyrolysis/gasification of lignin at different reaction conditions, Energy Fuel 28 (2014) 6371–6379.

[23] A.C. Louwes, L. Basile, R. Yukananto, J.C. Bhagwandas, E.A. Bramer, G. Brem, Torrefied biomass as feed for fast pyrolysis: an experimental study and chain analysis, Biomass Bioenergy 105 (2017) 116–126, http://dx.doi.org/10.1016/j.biombioe.2017.06.009.

[24] M. Di Marcello, G.A. Tsalidis, G. Spinelli, W. de Jong, J.H.A. Kiel, Pilot scale steam-oxygen CFB gasification of commercial torrefied wood pellets. The effect of torrefaction on the gasification performance, Biomass Bioenergy 105 (2017) 411–420, http://dx.doi.org/10.1016/j.biombioe.2017.08.005.

[25] G.A. Tsalidis, M. Di Marcello, G. Spinelli, W. de Jong, J.H.A. Kiel, The effect of torrefaction on the process performance of oxygen-steam blown CFB gasification of hardwood and softwood, Biomass Bioenergy 106 (2017) 155–165, http://dx.doi.org/10.1016/j.biombioe.2017.09.001.

[26] G.-A. Tsalidis, K. Voulgaris, K. Anastasakis, W. De Jong, J.H.A. Kiel, Influence of torrefaction pretreatment on reactivity and permanent gas formation during devolatilization of spruce, Energy Fuel 29 (2015) 5825–5834, http://dx.doi.org/10.1021/acs.energyfuels.5b01101.

[27] J. Lédé, O. Authier, Temperature and heating rate of solid particles undergoing a thermal decomposition. Which criteria for characterizing fast pyrolysis? J. Anal. Appl. Pyrolysis 113 (2015) 1–14, http://dx.doi.org/10.1016/j.jaap.2014.11.013.

[28] Y. Wang, S. Agarwal, H.J. Heeres, Catalytic liquefaction of humin substances from sugar biorefineries with Pt/C in 2-propanol, ACS Sustain. Chem. Eng. 5 (2017) 469–480, http://dx.doi.org/10.1021/acssuschemeng.6b01834.

[29] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker, Determination of Structural Carbohydrates and Lignin in Biomass, National Renewable Energy Laboratory, Colorado, 2012http://www.nrel.gov/docs/gen/fy13/42618.pdf.

[30] Y. Joshi, M. Di Marcello, W. de Jong, Torrefaction: mechanistic study of constituent transformations in herbaceous biomass, J. Anal. Appl. Pyrolysis 115 (2015) 353–361, http://dx.doi.org/10.1016/j.jaap.2015.08.014.

[31] H. Yu, Z. Zhang, Z. Li, D. Chen, Characteristics of tar formation during cellulose, hemicellulose and lignin gasification, Fuel 118 (2014) 250–256, http://dx.doi.org/10.1016/j.fuel.2013.10.080.

[32] CEN/TS 15439, Biomass Gasification – Tar and Particles in Product Gases – Sampling and Analysis, European Committee for Standardization, Brussels, 2006.

[33] C. Font Palma, Modelling of tar formation and evolution for biomass gasification: a review, Appl. Energy 111 (2013) 129–141, http://dx.doi.org/10.1016/j.apenergy.2013.04.082.

[34] F.J. Goosens, M. Siedlecki, Investigation of the Fate of Tars and Non-condensable Gaseous Compounds. By Means of Biomass Pyrolysis Experiments in a Heated Grid Reactor, Technical University of Delft, Delft, The Netherlands, 2009.

[35] R. Cypres, C. Lejeune, Craque thermique de m-crésol, du bènzene, du toluène et du phénol entre 650 et 850°C, Ann. Mines Belgique. 7–8 (1965) 1091–1109.

[36] Y. Qin, A. Campen, T. Wiltowski, J. Feng, W. Li, The influence of different chemical compositions in biomass on gasification tar formation, Biomass Bioenergy 83 (2015) 77–84, http://dx.doi.org/10.1016/j.biombioe.2015.09.001.

[37] X. Nitsch, J.-M. Commandré, J. Valette, G. Volle, E. Martin, Conversion of phenol-based tars over biomass char under H_2 and H_2O atmospheres, Energy Fuel 28 (2014) 6936–6940, http://dx.doi.org/10.1021/ef500980g.

[38] P. Nanou, M.C. Carbo, J.H.A. Kiel, Detailed mapping of the mass and energy balance of a continuous biomass torrefaction plant, Biomass Bioenergy 89 (2016) 67–77, http://dx.doi.org/10.1016/j.biombioe.2016.02.012.

[39] B.J. Vreugdenhil, R.W.R. Zwart, Tar Formation in Pyrolysis and Gasification, ECN (2009).