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PCDDs, PCDFs and PCNs in products of microwave-assisted pyrolysis of woody biomass – Distribution among solid, liquid and gaseous phases and effects of material composition

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HIGHLIGHTS

- Dioxins were predominantly retained in pyrolysis oils, but little in gaseous phases.
- MAP of bark produced more dioxins than bark-free softwood.
- Less chlorinated homologues dominated the dioxin profiles.
- Degrees of chlorination is higher in MAP chars compared to oil products.

GRAPHICAL ABSTRACT
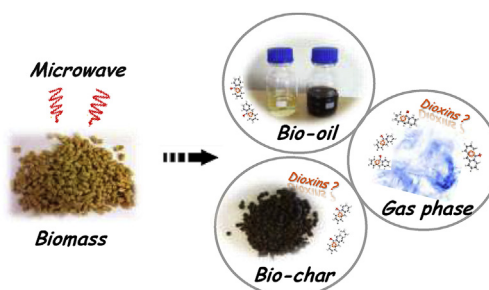
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ABSTRACT

Microwave-assisted pyrolysis (MAP) of lignocellulosic biomass is a technique that could potentially be used to produce and upgrade renewable energy carriers. However, there is no available information about the formation of dioxins and other organic pollutants in MAP treatment of woody biomass. In this study, MAP experiments were conducted in lab-scale using virgin softwood, bark, and impregnated wood as feedstocks. The non-condensable gas, liquid (fractionated into aqueous and oil phases), and char fractions generated during pyrolysis were collected and analysed for polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and naphthalenes (PCNs). The concentrations of PCDDs, PCDFs and PCNs in the pyrolysis products ranged from 0.52 to 43.7 ng kg^{-1}. All investigated compound groups were most abundant in the oil fraction, accounting for up to 68% (w/w) of the total concentrations. The highest PCDD, PCDF and PCN concentrations were found from the pyrolysis of bark, which has relatively high contents of chlorine and mineral matter, followed by impregnated wood, which contains organic and metal-based preservatives. The homologue profiles of all three compound groups were dominated by the less chlorinated homologues. The homologue abundance decreased as the degree of chlorination increased. This trend was observed for all three feedstocks.

1. Introduction

The use of renewable lignocellulosic biomass as replacements of

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fossil fuels is important in the transition to sustainable energy production. Considerable effort has been made to improve the energy efficiency and to increase the yield of the fuel products. Microwave-assisted pyrolysis (MAP) is a promising technique for converting biomass into biofuel, and is becoming increasingly accessible at both pilot and industrial scales (Yin, 2012). MAP is advantageous because it heats the feedstock homogeneously and efficiently by exploiting the dielectric heating effect. Unlike conventional pyrolysis, where heat is transferred from the surface to the core of the treated material by conduction/convection, microwave irradiation generates in-core volumetric heating by direct coupling of microwave energy with exposed biomass. It has recently been shown that the mechanism of microwave-assisted biomass activation differs significantly from the activation mechanism induced by conventional heating (Fan et al., 2013). Notably, the temperature at which biomass decomposes during MAP is lower than in conventional pyrolysis, due to energy redistribution over the feeding material by water vaporisation (Budarin et al., 2009). Low temperature pyrolysis is a process of partial oxidation that primarily favours formation of a broad spectrum of volatile organic compounds (known as tars), some of which are aromatic (Evans and Milne, 1987). These compounds are released quickly due to the rapid heating achieved during microwave pyrolysis which may influence the mechanism of pyrolysis. Because it is not clear how these factors might affect the production of persistent organic pollutants, there is a need to investigate the formation of such compounds including dioxins during MAP of biomass.

Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) are by-products of thermochemical processes. They are among the persistent organic pollutants (POPs) included in the Stockholm Convention (Van den Berg et al., 2006). Polychlorinated naphthalenes (PCN) can be formed along with PCDD and PCDF, and are considered to be "dioxin-like" due to their similar chemical structures, mechanisms of formation, and toxicological properties (Van den Berg et al., 2006). Their formation has been studied extensively; while the full details of the underlying mechanisms remain unclear. The proposed formation mechanisms involve both the degradation of larger aromatic structures ('de novo' synthesis) and the recombination of lighter molecular weight (aromatic) compounds in particular phenolic species ('precursor' mechanisms) (Born et al., 1993; Stieglitz, 1998). Whatever the mechanism, the combination of an inadequate processing temperature and insufficient oxygen supply allows the formation and survival of chlorinated aromatics in the presence of chlorine and metal catalysts (Altarawneh et al., 2009). Given the fact that: 1) the temperatures employed in pyrolysis (around 300–650 °C) are within the range that typically favours the formation of polychlorinated aromatics; 2) phenolics, which are key precursors of these compounds, are among the most abundant components of biomass pyrolysis products; and 3) in the presence of various chlorine sources (inorganic and organic) in many biomass feedstock types, formation of PCDDs, PCDFs and PCNs in biomass pyrolysis is likely to occur, at least under certain operating conditions. The question arises whether or not pyrolysis of biomass at relative low temperature produces similar POP profiles to those generated during e.g. wood combustion and waste incineration. Studies on wood combustion have shown that the formation of PCDD, PCDF and PCN depends on both the combustion conditions and the type or composition of the fuel (Lavric et al., 2004; Tame et al., 2007). Inefficient combustion is believed to favour the formation of chlorinated aromatics, and the burning of waste wood may lead to significantly more extensive formation of chlorinated aromatics than is observed with virgin wood. Studies on pyrolysis-driven processes for municipal solid waste and auto shredder residues have shown that yields of PCDFs are more dependent on operating

conditions and input composition compared to PCDDs (Mohr et al., 1997; Weber and Sakurai, 2001). Recent study on MAP of sewage have investigated the formation of PCDDs and PCDFs in the pyrolysis products (Dai et al., 2013). However, results obtained by pyrolysis of waste materials are unlikely to be representative of those achieved with lignocellulosic biomass. To our knowledge, there has only been one attempt to quantify PCDDs and PCDFs in char products generated by the conventional pyrolysis of grass and hardwood (Hale et al., 2012). Unfortunately, that study did not examine PCDD/Fs in pyrolysis oils despite their importance.

Given the environmental importance of PCDDs, PCDFs, and PCNs, the lack of data on the concentrations, profiles and occurrence of these compounds in the products of woody biomass pyrolysis represents a serious knowledge gap. In this study, we have conducted a series of laboratory-scale MAP experiments using three feedstocks: pelletized virgin softwood from pine and spruce; pelletized virgin bark from spruce; and chipped impregnated wood. Pyrolysis products including non-condensable gases, liquids (fractionated into water- and organic-soluble phases) and char products were collected for determination of PCDDs, PCDFs and PCNs. The main aims of the study were to quantify the formation of PCDD, PCDF and PCN during MAP treatment of biomass; to investigate the influence of the biomass feedstock's chemical composition (particularly with respect to its contents of chlorine and metals) on the formation of these compounds; and to determine the distribution of these organic pollutants within the different pyrolysis product fractions (gas, liquid, and char). In addition, the homologue profiles of PCDD, PCDF and PCN were examined. The resulting knowledge provides useful insights into the formation of chlorinated organics during MAP of biomass, which will support the development of environmentally safe MAP strategies.

2. Materials and methods

2.1. Feedstocks

Three types of woody biomass were selected as feedstocks for the MAP experiments: 1) commercial (virgin) soft wood pellets (Ø 8 mm, 10–20 mm in length) made of spruce and pine (mixed in unknown proportion); 2) spruce bark pellets (Ø 8 mm, 10–20 mm in length); and 3) wood impregnated with organic and metal-based preservatives (shredded to an average particle size of 1 mm). The impregnated wood sample was taken from a discarded telephone pole whose origin, age and geographical location during use was not known to us. Details on the measurement of biomass chemical properties were described in Supporting Information (SI). The feedstocks were not subjected to any pre-treatment other than comminution.

2.2. Microwave-assisted pyrolysis

The MAP system used in this study consisted of a microwave reactor (Milestone ROTO SYNTH, Srl., Italy) fitted with a vacuum module and two cooling traps for collecting liquid condensate. A schematic of the MAP sample collection is shown in Fig. 1. The MAP system is described in detail elsewhere (Gronnow et al., 2013). A partial vacuum with an initial pressure of 60 ± 5 mbar was applied during pyrolysis to maintain a low oxygen atmosphere and to facilitate collection of volatile products. A 300 g batch of feedstock was pyrolysed in each experimental run. The materials were heated at a maximum rate of 16 °C min^{-1} to 200 °C, at a constant microwave generator power (Maximum 1200 W). The choice of temperature was based on previous studies, in which MAP of biomass (and generation of volatile organic compounds) typically takes place in the temperature range 100–200 °C (Budarin et al., 2010,
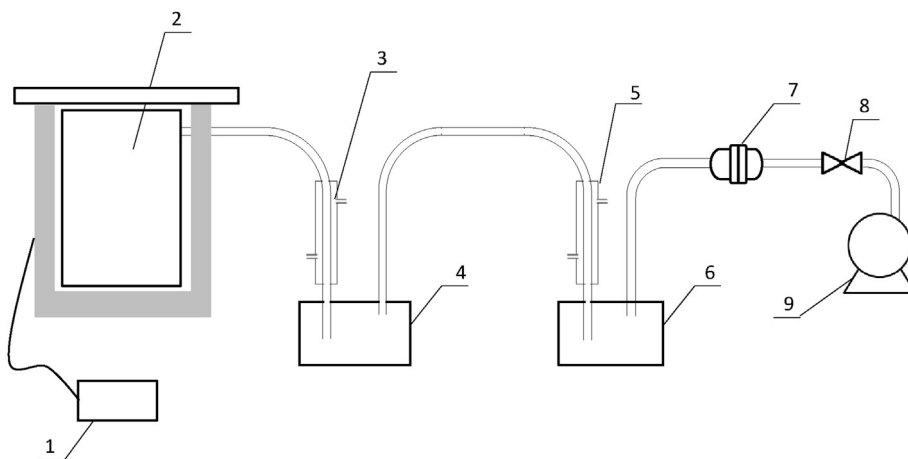
Fig. 1. Schematic of the experimental microwave-assisted pyrolysis and sampling apparatus. 1- System controller and monitoring console; 2- Microwave reactor; 3- Air-cooled (approx. 20 °C) condenser; 4- Liquid collector for the organic fraction of the liquid pyrolysis products; 5- Water-cooled (0 °C) condenser; 6- Liquid collector for the aqueous fraction of the liquid pyrolysis products; 7- Gas sampling point with a glass fibre filter and a polyurethane foam plug; 8- Electromagnetic valve; 9- Vacuum pump.

2012). The sample temperature was measured using an infrared detector within the reactor chamber. Liquid products were collected using two condensers connected in series. The first of these was an air-cooled condenser used to collect organic liquids (i.e. the oil fraction) while the second was a water-cooled condenser with cooling water at a temperature of around 0 °C that was used to collect the water-soluble liquid fraction. Non-condensable gases were collected on a glass fibre filter and a polyurethane foam plug (PUF). All experiments were run in triplicate. A field blank was prepared in duplo.

2.3. Sample extraction and clean-up

Gas samples trapped on the PUFs and filters were extracted using a Soxhlet apparatus. Pyrolysis oils were subjected to liquid––liquid extraction with hexane. Char samples were extracted by pressurized liquid extraction (PLE) (ASE 350, Dionex, Sunnyvale, CA) in accordance with the method described by Gao et al. (Gao et al., 2015). Prior to extraction, ^{13}C-labelled internal standards (IS) were added to the samples (Liljelind et al., 2003; Jansson et al., 2008). The extracts were then subjected to a multilayer silica column clean-up, followed by fractionation using an AX21 carbon/celite column. ^{13}C-labelled recovery standards (Cambridge Isotope Laboratories) were added to the final extracts before instrumental analysis (Liljelind et al., 2003).

2.4. Instrumental analysis

Analyses of PCDD, PCDF and PCN were performed by GC/high resolution MS. The GC/MS apparatus consisted of a Hewlett––Packard 5890 gas chromatograph (Agilent Technologies, Palo Alto, CA) coupled to an Autospec Ultima mass spectrometer (Waters Corporation, Milford, MA). Separation was performed on a DB5-ms J&W fused silica capillary column (60 m × 0.25 mm i.d. × 0.25 μm film thickness). The mass spectrometer was tuned to a resolution of >10 000 and was operated using electron ionization and selected ion monitoring. Details on the operating condition of the GC/MS are given elsewhere (Liljelind et al., 2003; Jansson et al., 2008). Quantification was performed using the isotope dilution method. Positive identification was considered with S/N > 3 and the isotope ratio within 20% of the appropriate theoretical values. Field and laboratory blanks were subjected to the same extraction and

clean-up procedures applied to the samples. Data with recoveries outside of the acceptable range of the EN 1948 standard method (ECS, 1997) were excluded.

3. Results and discussion

3.1. Feedstock characterisation

Table 1 lists the chemical properties of the softwood, bark and impregnated wood. The chlorine contents of softwood and impregnated wood were 98.6 mg kg^{-1} and 118.7 mg kg^{-1}, respectively, while that of bark was the highest (202.5 mg kg^{-1}). Bark and impregnated wood contained comparable amounts of copper (3.4 mg kg^{-1}) while softwood had much lower concentrations of this element (1.0 mg kg^{-1}). Fe content was the highest in bark (0.04%), followed by impregnated wood (0.007%) and softwood (0.001%). The impregnated wood contained various heavy metals including Cr (35.9 mg kg^{-1}), As (362 mg kg^{-1}), Cd (1.6 mg kg^{-1}) and Zn (590 mg kg^{-1}). Although the origin and treatment history of the telephone pole could not be confirmed, the treatment of utility poles in Sweden was commonly performed by use of creosote oils or metal-based preservatives such as chromated copper arsenate (CCA), or a mixture of both (Sundqvist, 2009). The characteristic tar smell of the wood material in combination with the analysis results confirming presence of Cr, Cu and As indicated that treatment was conducted using both creosote oil and CCA. Measurements of the PCDD, PCDF and PCN concentrations in the feedstock materials (Table 1) resulted in concentrations within the range reported for woody biomass from unpolluted areas (Lavric et al., 2004).

3.2. Yields of MAP products

The MAP setup under vacuum facilitates the continuous extraction of volatile products while maintaining a uniform distribution of microwave heating within the biomass. The use of two cooling traps connected in series with different coolant temperatures allows the liquid pyrolysis products to be fractionated into aqueous and organic phases. The release/formation of water vapour during pyrolysis occurred at around 50 °C, whereas organic volatiles with low water content were released at approximately 90 °C. At temperatures above 180 °C release of volatiles was not observed,

Table 1
Chemical characteristics, MAP product yields and PCDD/PCDF/PCN concentrations in softwood, impregnated wood and bark (wt. % ± 1SD).

Parameters	Unit	Softwood (virgin)	Impregnated wood	Bark
Gross calorific value	MJ kg^{-1}	20.6	20.7	21.0
Ash	% of dry matter	0.4	0.5	3.9
Moisture	% as received	7.3	12.8	7.0
Volatile matter	%	85.2	84.3	72.6
C	%	51.2	51.3	53.0
H	%	6.2	6.2	5.8
N	%	0.1	0.1	0.4
O	%	42.1	41.9	36.9
S	%	0.03	0.02	n.a.[a]
Cl	mg/kg	98.6	118.7	202.5
Fe	%	0.001	0.007	0.04
Cu	mg/kg	0.97	3.38	3.39
Zn	mg/kg	8.6	590	88
As	mg/kg	<0.1	362	<0.1
Cd	mg/kg	0.08	1.56	0.48
Cr	mg/kg	0.1	35.9	4.9
Cellulose	% w/w	26.6 ± 2.1	36.8 ± 3.4	19.2 ± 5.0
Lignin	% w/w	26.0 ± 2.2	26.4 ± 3.0	36.8 ± 1.5
Product yields	% w/w initial weight			
Gas[b]		18.2 ± 1.4	24.7 ± 1.1	19.8 ± 3.1
Organic		16.7 ± 3.3	17.3 ± 2.7	9.4 ± 1.2
Aqueous		30.1 ± 0.6	22.2 ± 1.2	24.5 ± 2.8
Char		35.1 ± 1.9	35.9 ± 0.9	46.3 ± 1.5
PCDD	ng/kg	4.39 ± 0.30	5.34 ± 8.62	7.67 ± 0.31
PCDF	ng/kg	9.34 ± 0.69	7.79 ± 0.88	29.96 ± 2.42
PCN	ng/kg	1.41 ± 0.23	18.16 ± 0.57	13.67 ± 1.19

[a] Not available.
[b] Estimated as the difference between the sum of all of collected liquid and char and the amount of biomass initially input in the system, based on an assumption that all condensable matters were collected completely into organic and aqueous fractions.

indicating that the pyrolysis reaction had been terminated at this temperature. It took around 9 min for the entire pyrolysis process to complete. The temperature profile over the duration of the MAP process varied slightly with the feedstock used (Fig. S1 in SI). These differences are probably due to the variation in the composition of the feedstocks, including ash and water contents as well as contents of major structural components such as cellulose, hemicellulose and lignin. The pyrolysis of the three feedstocks under these conditions yielded organic fractions amounting to 9.4–17.3% of the original feedstock mass (Table 1), which is consistent with the results of previous MAP studies using wood and agricultural biomass as feedstocks at comparable temperatures (Budarin et al., 2009; Robinson et al., 2010).

3.3. Concentrations of PCDF, PCDD and PCN and their distributions in MAP products

Concentrations of PCDD, PCDF and PCN in the different pyrolysis products varied over two orders of magnitude, ranging from 0.5 to 43.7 ng kg^{-1} (based on feedstock load) depending on the feedstock, product and compound group under consideration (Fig. 2). The highest and second highest total PCDD, PCDF, and PCN concentrations (i.e. the summed concentrations in the gases, liquids, and char) were found from the pyrolysis of bark and impregnated wood, respectively. The PCDD, PCDF, and PCN concentrations in the char products ranged from 3.6 to 31.5 ng kg$_{CHAR}^{-1}$, 7.5–49.0 ng kg$_{CHAR}^{-1}$, and 7.3–34.0 ng kg$_{CHAR}^{-1}$, respectively. These values are based on char weight to facilitate comparison of the results with literature data, in contrast to the data in Fig. 2 which is based on feedstock load. The concentrations of tetra-to octa- PCDDs and PCDFs in the MAP chars (2.3–19.1 ng kg^{-1} and 0.2–15.4 ng kg^{-1}, respectively) were significantly lower than those reported for biochar from pine wood (91.5 ng kg^{-1}) (Hale et al., 2012); this comparison excludes mono-, di-, and tri-chlorinated congeners because no data for the concentrations of these compounds in pine wood biochar were

presented. Microwave-assisted pyrolysis products are more aliphatic in nature and contain less aromatic compounds compared to conventional heating at similar temperatures (Dai et al., 2013). This is probably because the direct heating induced by MAP reduces the extent of secondary cracking of the carbonaceous matrix. The heterogeneous formation of chlorinated organics is generally believed to occur on particle surfaces at temperatures of 200–400 °C. The low temperatures used during MAP (up to 200 °C) are probably too low to support extensive "de novo" synthesis. The temperature range for microwave pyrolysis was significantly lower than the temperature of conventional pyrolysis and even torrefaction. A previous study has shown that microwave irradiation can dramatically increase the decomposition rate of feedstock materials (i.e., cellulose), and generate products which would require much higher temperatures (100 °C higher) to form under conventional conditions (Budarin et al., 2010). The fact that we observed PCDD, PCDF and PCN in MAP products indicated that formation of MAP by-products including chlorinated organics and other POPs could also take place at relatively low temperature.

As shown in Fig. 2, all three investigated compound groups were most abundant in the oil fractions of the pyrolysis products, which contained up to 68% of the total measured PCDD/PCDF/PCN output from each MAP experiment. The relative abundances of these compounds in the non-condensable gas and aqueous phases were much lower, which could be due to a "wet scrubbing" effect, i.e. physical or chemical trapping of gases in droplets of the liquid products (Zwart et al., 2009). The partitioning of the bulk of the POP content into the oil fraction may be due to its hydrophobicity and the distillation effect, together with wet scrubbing as noted above. Interestingly the distribution of PCN across the different product fractions differed slightly from those of PCDD and PCDF. For example, in the case of both bark and impregnated wood, the relative abundance of PCN of the char products (32.4 and 23.9% for bark and impregnated wood, respectively) was appreciably greater than those of PCDD or PCDF, which were quite similar (26.7–28.9%
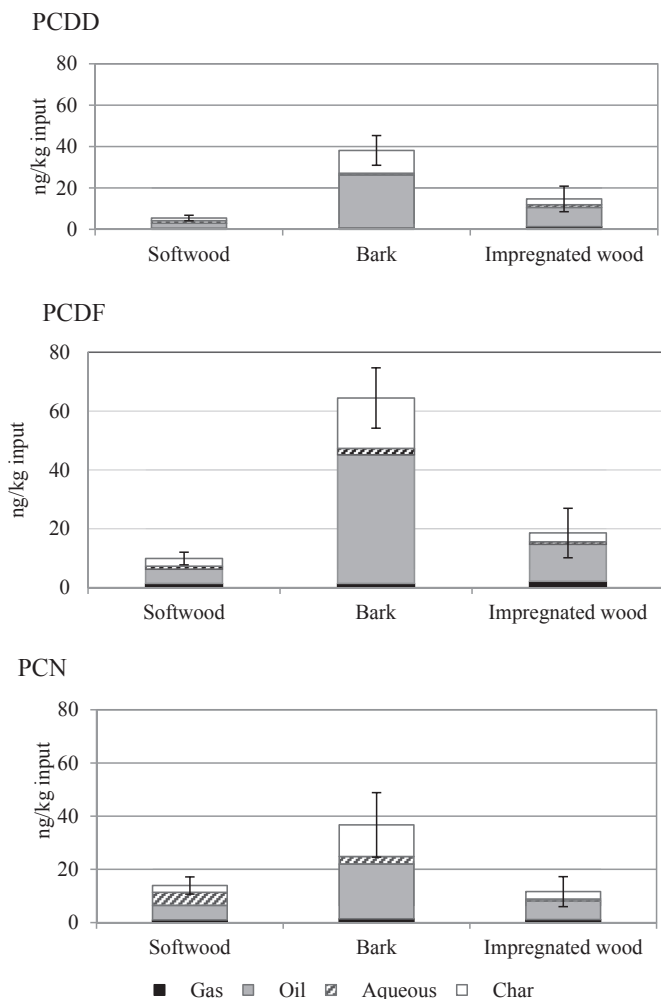
PCDD

PCDF

PCN

■ Gas ▦ Oil ▨ Aqueous □ Char

Fig. 2. Concentrations and distributions of PCDD, PCDF and PCN in MAP products of softwood, bark and impregnated wood (ng kg^{-1}). Error bars represent ±1 SD.

for bark and 16.0–18.9% for impregnated wood). This could be related to differences in the absorption behaviour of these compound classes on the carbon matrix, which may be linked to spatial or steric factors.

The toxicity equivalents (TEQ) in different MAP products were in a range of 0.003–0.19 ng I-TEQ kg$_{FUEL}^{-1}$ (Table S1 in Supporting Information). The highest TEQ concentration was found in MAP oil of bark. MAP oils accounted for 58%, 62% and 54% of the total TEQ for softwood, bark and impregnated wood, respectively. Based on char weight, the TEQ in chars ranged from 0.03 (in softwood) to 0.29 (in bark) ng I-TEQ kg$_{CHAR}^{-1}$, all of which should be considered as quite low. As an example, these TEQ concentrations are substantially lower than the Swedish guideline values for dioxin contamination for sensitive land use (50 pg TEQ g^{-1}) (Elert et al., 1997). Although there is no guideline of TEQ concentrations in bio-oil, compared to wood burning where emission of PCDDs and PCDFs was in the range of 7.3–22.8 ng I-TEQ kg$_{FUEL}^{-1}$ (Lavric et al., 2004) the TEQ concentrations in MAP products were much lower.

3.4. Influence of the fuel composition

As mentioned above, the highest concentrations of investigated compounds were generated during the MAP of bark – about three times those for impregnated wood. Several potential explanations exist for the relatively substantial POP formation during bark MAP. First, the content of chlorine and transition metals (i.e. Cu and Fe) in the feedstock is important for the formation of chlorinated aromatics. Although the chlorine contents in all feedstocks were present in trace amounts, in contrast to chlorine levels in e.g. waste materials, the relatively high amounts of PCDD/PCDF/PCN in bark MAP suggested that the crucial role of chlorine in the formation of chlorinated organics could be the same. In addition, bark generally has substantially higher concentrations of phenolic extractives than softwood, regardless of the tree species from which the wood is taken (Vassilev et al., 2010). Also, pyrolysis of lignin components has been shown to produce high levels of phenolics (Fu et al., 2014). Whether or not these phenolics are single (chloro) phenol molecules directly produced during lignin matrix break down, or associated with other aromatic compounds cannot be determined based on this study. However, in any case these phenolic compounds may certainly play a role in dioxins and PCN formation in the considered system.

The pyrolysis of impregnated wood yielded higher concentrations of PCDD, PCDF and PCN than were observed for softwood pyrolysis, which could potentially be associated to a number of factors. First, the presence of chlorine and transition metals in impregnated wood is important as discussed above. Additionally, the presence of metal-based preservatives could alter the thermal degradation behaviour of biomass, for example by enabling sustained smouldering during pyrolysis. This may enhance the formation of polychlorinated compounds, as was observed in a study on the pyrolysis of CCA-treated wood (Tame et al., 2007). With regards to the presence of creosote in the impregnated wood, it has been shown in co-combustion tests using creosote treated wood that the effect of creosote on formation of dioxins was unnoticeable (Freeman et al., 2000).

Although the concentrations of PCDDs, PCDFs and PCNs in MAP products varied depending on the chemical composition of biomass, the patterns of their relative distributions in various phases (i.e., dominant in oil fractions and insignificant in aqueous and gas phases) remained the same, regardless the feedstocks used. This indicated that the factors that govern the partitioning of POPs between different phases, i.e. the distillation effect and wet scrubbing as mentioned above, are not influenced substantially by the composition of the feedstock. Instead, the hydrophobicity of the chlorinated organic compounds could be mainly responsible for the observed results. This is supported by the previous pyrolysis studies using municipal and industrial waste as feedstock (Mohr et al., 1997; Joung et al., 2009), where a dominance of PCDD/Fs in pyrolysis oils was also observed, although the feedstocks used in their studies were far different from woody biomass in terms of chemical composition.

3.5. Homologue profiles and degrees of chlorination

The evaluation of the homologue profiles primarily focused on the oil and char products since they accounted for most of the PCDD, PCDF and PCN (83 ± 9%). The homologue profiles were generally dominated by the least chlorinated homologues (Fig. 3), and homologue abundance decreased with increased degree of chlorination. This trend was observed for all three feedstocks. A similar domination of less-chlorinated homologues was observed in earlier pyrolysis studies (Weber and Sakurai, 2001). The oxygen deficient conditions used in pyrolysis were believed to be responsible for the observed results because they are likely to limit the formation of free chlorine via Deacon-type metal-catalysed reactions. This was demonstrated by Pekarek et al. (Pekárek et al., 2001), who observed a dramatic shift towards less chlorinated PCDDs and PCDFs as the oxygen content was reduced from 10%
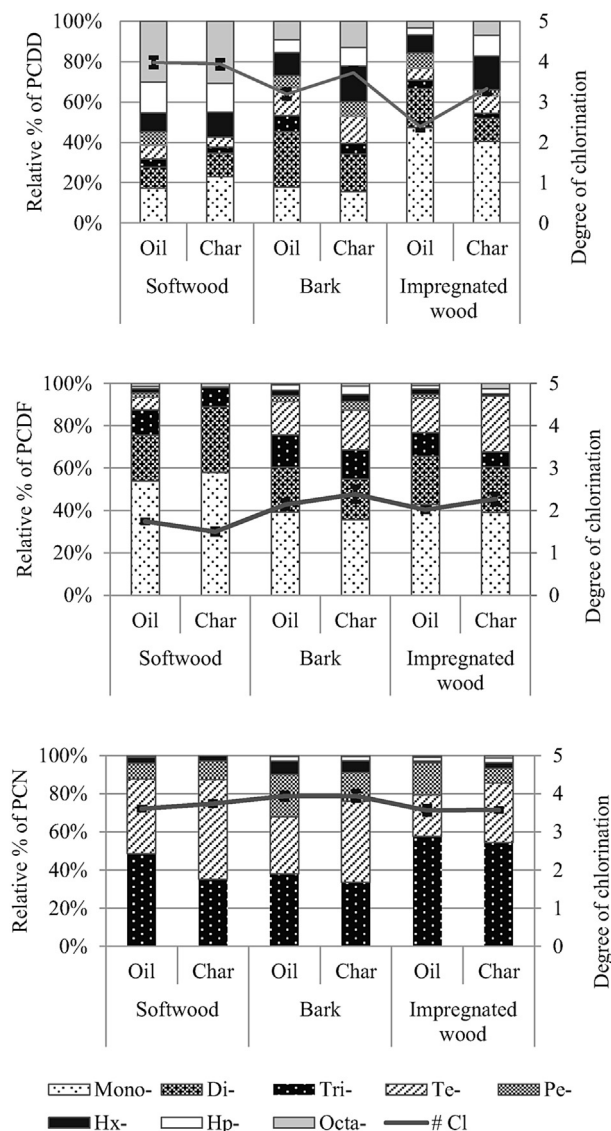
Fig. 3. Degree of chlorination (#Cl) and relative abundance of PCDD (mono-to octa-), PCDF (mono-to octa-) and PCN (tri-to octa-) homologues in pyrolysis oils and chars. Error bars represent ±1 SD. Degree of chlorination is calculated as Σ[(homologue sum/ΣPCXs) × no. of Cl].

to < 0.001%. In addition, less-chlorinated homologues tend to be dominant in the products of (relatively) low-temperature thermochemical processes regardless of the feedstock used (Yasuhara et al., 2003).

The oil fractions have a greater relative abundance of less chlorinated homologues than the chars, as indicated by their lower degrees of chlorination (Fig. 3). The observed differences in homologue profiles between the oil and char products could be related to the different vapour pressures of the low and high chlorinated congeners. The highly chlorinated congeners with low volatility tend to be retained by particles whereas the less chlorinated congeners tend to volatilise into the gas phase. The different homologue profiles from softwood (with lower degree of chlorination in the char) could be partly explained by their generally low concentrations of PCDDs and PCDFs in the char fraction. Thereby, the degrees of chlorination in the softwood char could be underestimated since some congeners in softwood char, particularly those with higher degree of chlorination (including most congeners

in Te- to HpCDF, and PeCDD), were below detection limit. The variation in the degree of chlorination between PCNs and the other compound groups was not evaluated due to analytical limitations resulting in unavailable data on mono- and di-CN.

4. Conclusion

The presence of chlorine and catalytically active metals (mainly Cu and Fe) in the fuel is known to be essential for the chlorination of aromatic hydrocarbons and the subsequent formation of PCDD, PCDF and PCN during thermal processes. The relatively high concentrations of these compounds generated during bark pyrolysis demonstrate the influence of the feedstock's composition (including its chlorine content) on POPs formation. The oxygen deficient conditions and low temperatures applied during MAP, as well as the homogeneous heating of the substrate, all probably have an impact on the characteristics of the investigated compounds. However, detailed examinations of the PCDD, PCDF, and PCN fingerprints (i.e. isomer distributions) will be required to fully understand the mechanisms of POPs formation during MAP. While mechanistic understanding was not the primary objective in this paper, evaluations based on isomer distribution patterns will be provided in coming papers.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2015.11.110.

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