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Mechanistic evaluation of polychlorinated dibenzo-p-dioxin, dibenzofuran and naphthalene isomer fingerprints in microwave pyrolysis of biomass

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HIGHLIGHTS

- Isomer patterns in MAP are more selective than those in combustion.
- Formation pathways involve (chloro)phenol precursors followed by chlorination.
- Isomers with low thermal stability were highly abundant.
- Kinetic factors are important in formation of dioxins in low temperature MAP.

ABSTRACT

Isomer distribution patterns of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and naphthalenes (PCNs) were investigated in microwave-assisted pyrolysis (MAP) products of woody biomass. The feedstocks included bark and impregnated wood. The results indicated that isomer distributions in MAP are more selective compared to those reported from wood burning and waste incineration. Favored formation of 4-MoCDF and highly selective chlorine substitution at the 2,4-position observed during MAP suggested a preferred formation pathway of PCDFs involving (chloro)phenol precursors followed by subsequent chlorination. The PCDD distribution was dominated by isomers typically formed from chlorophenol condensation at relatively low temperature. The PCN isomer distributions showed a tendency for sequential chlorination from non-substituted naphthalene at successive positions. The presence of isomers such as 1-MoCDD, 4-MoCDF, 1,2,3-TriCN with low thermodynamic stability indicates that kinetic factors may be important in the MAP process. © 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Thermochemical conversion of lignocellulosic biomass for renewable energy production has gained an increasing interest over recent years. Microwave-assisted pyrolysis (MAP), characterized by rapid heating of a feedstock under oxygen-deficient conditions at moderate temperature, is one of the most promising technologies for bio-fuel production (Yin, 2012). Contrary to conventional heating, where energy is transferred by thermal gradient, microwave irradiation converts electromagnetic energy directly into molecular kinetic energy. The interaction of biomass feedstocks with microwave dielectric heating enables biomass decomposition at lower temperature (around 200 °C) than those required under conventional pyrolysis (around 300 °C) (Budarin et al., 2010). In conjunction with biomass thermal decomposition, aromatic organic pollutants may be formed as by-products. The latter may include persistent organic pollutants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), commonly known as dioxins, which are of great environmental concern owing to their toxicity and persistence in the environment.
environment (Van den Berg et al., 2006). Polychlorinated naphthalenes (PCNs) may also be formed alongside PCDDs and PCDFs and are considered to be “dioxin-like” owing to their similar chemical structures, formation mechanisms and toxicities (Hanberg et al., 1990).

It is well known that PCDDs, PCDFs and PCNs may be formed as trace compounds in thermal processes in the presence of chlorine. The formation pathways are very complex and largely depend on the particular thermal treatment conditions as well as the feedstock. Two main pathways have been identified and debated: heterogeneous de novo synthesis from a carbonaceous matrix and formation via low-molecular weight precursors (e.g., chlorophenols) by condensation reactions in the gas-phase and/or on particle or boiler surfaces (Born et al., 1993; Schneider et al., 1998; Stiegitz, 1998). Different formation pathways each favor specific distributions of PCDDs, PCDFs and PCNs, resulting in different degrees of chlorination and isomer distribution (Ryu et al., 2006b).

Numerous attempts have been made to unravel the formation mechanisms using isomer-specific information-based on field observations, experimental data and theoretical predictions (Iino et al., 1999, 2001; Ryu et al., 2006b). De novo synthesis has been shown to generate “fingerprints” with dominant presence of highly chlorinated PCDDs and PCDFs, similar to MSWI flue gas, in which 1,4,6,9-substituted isomers are favored (Iino et al., 2000; Everaert and Baeyens, 2002). On the other hand, precursor mechanisms give rise to isomer distributions that are highly dependent on the structure of the precursor compounds, as well as their concentration and nature of species used concurrently in the study (Mulholland et al., 2001). Gas phase formation and subsequent chlorination can lead to a broad distribution of isomers in which 2,3,7,8-substituted isomers are favored (Ryu et al., 2004b). Formations involving chlorination/dechlorination can be identified by careful examination of typical isomer distributions (Iino et al., 2001).

To date, research on detail isomer-specific analyses (with all 75 PCDDs and 135 PCDFs included) and formation mechanisms has mainly focused on combustion processes under oxidative conditions (Bacher et al., 1992; Ryu et al., 2006b). In fact, such studies have mainly focused on zones where flue gas (including products of incomplete combustion, water and minor inorganic combustion by-products like HCl) and solid combustion residues are in contact with residual combustion air. However, it is still unclear whether a similar formation pathway occurs during pyrolysis-driven processes. The formation pathway of PCDDs and PCDFs under pyrolysis conditions has been investigated using industrial waste (i.e., automobile shredder residues) as feedstocks (Weber and Sakurai, 2001; Joung et al., 2009) as well as using model chlorophenols as precursor compounds (Born et al., 1989). However, the temperatures employed in the conventional pyrolysis process were generally high (400–600 °C) compared to low temperature MAP (<350 °C). Moreover, studies on isomer patterns focused only on the 17 toxic congeners (2,3,7,8-substituted) and no complete isomer distributions were shown, and thus it is difficult to deduce a dominant formation pathway.

We have previously reported the occurrence of PCDDs, PCDFs and PCNs during the microwave pyrolysis of woody biomass (Gao et al., 2016). Our results showed that the concentrations of polychlorinated organics largely depend on the type and chemical composition of feedstocks. Homologue profiles were found to be generally dominated by low chlorinated compounds. However, we did not show full isomer distribution patterns of PCDDs, PCDFs and PCNs, which would be valuable for unraveling the prevailing pathways of formation of these compound groups in the MAP process. To the best of our knowledge, no full isomer distributions of PCDDs, PCDFs and PCNs in pyrolysis conditions have been reported.

Thus, the present study is a follow-up to our previous MAP study aimed at evaluating the isomer distributions and identifying possible formation pathways. Pyrolysis products obtained in our previous study using bark and impregnated wood as feedstocks were used for this evaluation. The knowledge gained was anticipated to aid mechanistic understanding and development of strategies for the control of organic pollutants in biomass pyrolysis processes.

2. Materials and methods

2.1. Materials

Woody biomass used as feedstocks in the MAP experiments were as follows: bark pellets from spruce; and impregnated wood with organic and metal-based preservatives from a discarded telephone pole. The chlorine contents in the impregnated wood and bark pellets were 118.7 mg kg⁻¹ and 202.5 mg kg⁻¹, respectively. The bark and impregnated wood contained comparable amounts of copper (3.4 mg kg⁻¹). Additionally, the impregnated wood contained various heavy metals, such as As, Cr, Cd and Zn. Further details of the biomass feedstocks are given in our previous paper (Gao et al., 2016).

2.2. Microwave-assisted pyrolysis

The MAP experiments were conducted using a bench-scale microwave reactor (Milestone ROTO SYNTH, Srl, Italy) fitted with a vacuum module and two cooling traps for collecting liquid condensate. A vacuum was applied to maintain a low oxygen atmosphere and collect volatile fractions. The materials were heated at a maximum rate of 16 °C min⁻¹ to 200 °C using constant microwave generator power (maximum 1200 W). The sample temperature was measured via an infrared detector within the reactor chamber. Details of the MAP set-up and sample collection, extraction and clean-up are described elsewhere (Gao et al., 2016). All experiments were run in triplicate.

2.3. Instrumental analysis and identification of isomers

Analyses of PCDDs, PCDFs and PCNs were carried out using a gas chromatography/high resolution mass spectrometry (GC/HRMS) comprising a Hewlett-Packard 5890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled to an Autospec Ultima mass spectrometer (Waters Corporation, Milford, MA, USA). Separation of PCDDs and PCDFs was performed on a J&W fused silica capillary column DB5-ms (60 m × 0.25 mm i. d. × 0.25 μm film thickness, J&W Scientific, Folsom, CA, USA). Samples were re-injected onto a SP 2331 column (60 m × 0.25 mm i. d. × 0.25 μm film thickness, Supelco) to resolve isomers co-eluting on the DB5-ms column. Separation of PCNs was performed on a J&W fused silica capillary column DB5 (60 m × 0.25 mm i. d. × 0.35 μm film thickness, J&W Scientific, Folsom, CA, USA). The MS was tuned to a resolution of >10 000 and operated using electron ionization and selected ion monitoring. Details of the operating conditions of the GC/MS are given elsewhere (Jansson et al., 2008). Positive identification was considered for a signal-to-noise ratio (S/N) above three and isotope ratio of ±20% from theoretical values. Individual congeners were identified by comparing their relative retention times with those of quantification standards and retention data previously reported for similar columns (Ryan et al., 1991; Bacher et al., 1992; Takeshi and Roland, 2000; Jansson et al., 2008). Methods of sample cleanup and instrumental analysis of polychlorophenols (PCPhs) are given in Supporting Information.
3. Results and discussion

Isomer distributions of low chlorinated PCDFs (mono-to tetra-), PCDDs (mono-to tetra-) and PCNs (di-to tetra-) are shown in Figs. 1–3, respectively. The results are presented as total concentrations (sum of gas, liquid and char) after subtraction of the concentrations from raw feedstocks. The concentrations of PCDDs, PCDFs and PCNs in the MAP of bark were generally higher than those from impregnated wood. High chlorinated compounds (Fig. S1–S3 in SI) were less prevalent than the low chlorinated groups, i.e., there was a general trend of decreasing concentrations with increasing degree of chlorination. Results of isomer distributions from gas, oil and char products are given in Fig. S4–12 of SI. There are no substantial differences regarding isomer patterns among the three phases (gas, oil and char) for both bark and impregnated wood.

3.1. PCDF isomer distribution

PCDF isomer distributions obtained from the MAP of bark and impregnated wood resembled each other with respect to relative abundance, although the absolute concentrations in bark were generally higher than those in impregnated wood (Fig. 1). The less...
chlorinated homologues (mono-to tetra-substituted) were dominated by only a few specific isomers, namely 2-MoCDF, 4-MoCDF, 2,4-DiCDF, 2,4,6-TriCDF, 2,4,8-TriCDF, and 1,2,4,6-TeCDF. Concentrations of PeCDF, HxCDF and HpCDF were generally low (some were close to the limit of quantification, Fig. S1 in SI), which makes it difficult to identify a specific isomer pattern. The isomer distributions in our MAP study, showing highly selective chlorine substitution, differed considerably from those reported in wood burning (soot deposit) (Bacher et al., 1992) and waste incineration (in flue gas) (Ryu et al., 2006b), where formation of many isomers at comparable concentrations was normally observed. It has been proposed that one of the major pathways for PCDF formation in combustion processes is chlorination from non- or low-substituted precursors (Wikström et al., 1999). Non-chlorinated dibenzofuran (DF) has been shown to be important for subsequent formation of highly chlorinated PCDF (Wikström and Marklund, 2000; Altarawneh et al., 2009). We did not conduct analysis of non-chlorinated DF unfortunately and therefore its concentration in MAP product was unavailable. Nevertheless, the pathway of chlorination initiated from unsubstituted DF often shows a typical MoCDF signature with dominant 2-MoCDF and 3-MoCDF at comparable abundance, as observed in most field studies of combustion (Ryu et al., 2004a, 2006b). Unlike the MoCDF signature which was dominated by 2- and 3-MoCDF reported in those combustion studies, 4- and 2-MoCDF were the most abundant MoCDF isomers in our study. This implies that, in contrast to combustion processes,
initial chlorination directly from DF could be less important in MAP.
It is commonly known that DF is formed by gas phase condensation
of unsubstituted phenol and benzene at high temperature
(>650 °C) (Wikström and Marklund, 2000). The temperature
employed in our MAP study (up to 200 °C) is probably insuffi-
cient to support this reaction. Dominant formation of 2- and 4-MoCDF
has been reported in both pyrolysis and oxidation-driven exper-
iments as well as theoretical predictions using various chlorinated
and unsubstituted phenols as precursor compounds (Yang et al.,
1998; Ryu et al., 2005, 2006a). Similar to our MAP results, PCDFs
from (chloro)phenol precursors have been shown to be highly se-
lective with 2-MoCDF, 4-MoCDF, 2,4-DiCDF, 1,2,4-TriCDF and
1,2,3,4-TeCDF being dominant (Ryu et al., 2005, 2006a). Reactions
involving (chloro)phenoxyl radicals as precursors have been pro-
posed to be essential for the formation of particular isomers (Ryu
et al., 2005), as discussed below.

Though the concentrations were relatively low, it is worth
mentioning that higher chlorinated (penta-to octa-) PCDFs (Fig. S1)
were also clearly formed. The presence of these compounds sig-
nifies the possible great complexity of formation pathways. To form
such compounds, beyond the above discussed simple recombi-
nation of reactive (chloro) phenols and derivatives, it would possibly
require a combination of several reactions or a multitude of steps,
I.e., chlorination/dechlorination reactions, also with possible cata-
lytic assistance from the mineral matter in the feedstock.

However, despite a rather complex nature of the final “blend” of
PCDD/Fs it can be notices that some 2,3,7,8-substituted PCDFs (i.e.,
1,2,3,7,8-PeCDF, 1,2,3,6,7,8-HxCDF and 1,2,3,4,8,9/1,2,3,7,8,9-HxCDF)
were presented as dominant congeners. These congeners are highly
toxic and hence should receive proper analytical attention when
scaling up any biomass thermochemical conversion/upgrading
options, including MAP. Nonetheless it should be stressed, that the
overall levels of the 2,3,7,8-substituted PCDFs, toxic congeners
(including PCDD’s) found in the products from the current series of
tests were low, and only in the range between 0.003 and 0.19 ng l-
TEQ/kg products (sum of char/oil/gas-phase). These measured
levels are of no specific safety concern, with regard to handling of
such materials or even direct application of chars in soil (Gao et al.,
2016). However, presuming these upgraded materials will still
undergo further (thermo)chemical processing before their
final application, care should be taken to monitor further fate of these
toxic compounds, particularly in extractive processes, where they
could possibly accumulate in the solvents/leachates streams.

3.2. PCDD isomer distributions

PCDD isomer distributions in MAP products of bark were similar
to those of impregnated wood (Fig. 2). 1-MoCDD and 2-MoCDD
were present at concentrations in the same order of magnitude,
DiCDD and TriCDD homologue included only a few isomers, namely

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Fig. 3. Di-to tetra-CN isomer distributions of MAP products. The results are presented as total concentrations (sum of gas, liquid and char) after subtraction of concentrations in raw feedstocks. Isomers that could not be resolved by GC separation were listed in groups. Isomers below detection limits are not included. Error bars represent ±1 standard deviation (n = 3).
et al., 2008). Furthermore, the short reaction time and high heat process could restrict PCN chlorination to a higher degree, since PCN chlorination is highly temperature-dependent (Jansson et al., 2009). However, the isomers obtained in the latter combustion studies were not observed in MAP, suggesting that gas phase condensation of chlorophenol and/or de novo synthesis could be less important in MAP. It is noteworthy that the dominant isomer 1,2,3-TriCN found in the MAP of bark has been reported to be thermodynamically unfavorable (Zhai and Wang, 2005). However, isomers with higher thermodynamic stability, i.e., substituted at 2,3,6,7-sites, that were commonly favored during MSW, were not observed in our study. It appears that successive chlorination to provide high electrophilic stability is more important than the thermodynamic stability or steric hindrance effect (Zhai and Wang, 2005). The reasons for the differences between the PCN isomer distributions of bark and impregnated wood remain unclear.

### 3.4. Possible formation mechanisms

The isomer distributions of PCDDs, PCDFs and PCNs in MAP generally exhibited a more selective pattern compared to those reported in combustion processes. We propose that de novo synthesis and dechlorination of highly chlorinated compounds, which typically generate a “combustion” pattern without dominance of particular isomers, could be less important in MAP. Incorporation of oxygen as well as a sufficiently high temperature, which are essential for de novo formation, might be a limiting factor in MAP under low temperature (up to 200 °C). Dechlorination of highly chlorinated PCDDs and PCDFs has been shown to occur preferentially at so-called “bay sites” (19-) (Kim and O’Keefe, 2000), followed by lateral sites (2,3,7,8-position), resulting in favored formation of isomers with 4,6 substitution (Ryu et al., 2006b). The absence of such isomers in our study suggests that dechlorination is not a primary route in MAP. This is also supported by the typical “ladder pattern” of homologues (decreasing concentrations with increasing chlorination degrees) as shown in our previous work (Gao et al., 2016). The similar patterns of isomer distributions for bark and impregnated wood suggest that the pathways for PCDD and PCDF formation were not affected substantially by the differences in chemical composition of these materials, although the absolute concentrations of PCDDs and PCDFs in MAP products of bark were higher than those of impregnated wood.

#### 3.4.1. Role of (chloro)phenols as precursors

As mentioned above, the PCDF patterns with high selectivity in MAP indicate that the dominant pathway involves (chloro)phenol precursors and subsequent chlorination. The predominant isomer pair of 1,3,6,8- and 1,3,7,9-TriCDD in MAP may also provide some evidence of the importance of (chloro)phenols as precursors. Generally, the degree of chlorination and substitution pattern of the chlorophenol precursors plays an important role on the resulting isomer fingerprint. Phenols chlorinated at both ortho sites (2,6-substituted) produce only PCDDs, whereas those containing only one ortho chloro substituent produce both PCDDs and PCDFs (Ryu and Mulholland, 2005). In our study, the observed chlorophenol isomers were mainly 2-MoCPh, 2,6-DiCPh and 2,4,6-TrICPh, with decreasing abundance with increasing degree of chlorination (i.e., 2-MoCPh > 2,6-DiCPh > 2,4,6-TrICPh) (Table S2 in SI). TeCPh and PeCPh were present in trace amounts close to the detection limit. Formation pathways via 2-MoCPh precursors have been studied both theoretically and experimentally (Born et al., 1989; Evans and Dellinger, 2003; Zhang et al., 2014). Unlike the result from oxidative condition (Born et al., 1989), 4,6-DiCPh as a preferred product of 2-MoCPh precursor in that study was not observed in MAP, which is consistent to the result of a pyrolysis study (Evans and Dellinger, 2003). For low temperature pyrolysis, the relative reaction rate involving formation of radical
intermediates is one of the main factors governing the patterns of isomer distributions. In contrast, the formation during oxidation-driven, and thus either high temperature or much more radical-forming, processes is believed to be largely thermodynamically controlled, whereby isomers with high thermodynamic stability are preferentially formed (Mulholland et al., 2001).

3.4.2. Kinetics and reactivity of (chloro)phenoxyl intermediates in MAP

The presence of isomers with low thermodynamic stability, such as 1-MoCDD, 4-MoCDF, and 1,2,3-TricCN, in MAP indicates that the formation pathways could be governed not only by thermodynamic factors but also kinetic factors and the reactivity of precursor intermediates. This conclusion is supported by a kinetics study of MAP (Dong and Xiong, 2014), which showed that kinetic processes are crucial in MAP with a high heating rate owing to the high efficiency of energy transfer. Phenoxyl radical coupling is a low activation energy process, and only the ortho- and para-sites are reactive sites, which results in greater isomer selectivity in the product distribution. The formation of PCDFs by cross-condensation is more favored than self-condensations of chlorophenoxyls owing to the former’s low energy barrier (Xu et al., 2010). Given the reactivity of intermediate radicals during pyrolysis, we propose that a PCDF formation pathway involving cross-coupling of (chloro)phenoxyl radical intermediates and successive chlorination from Mo- to TeCDF may be important in MAP, as shown in Scheme 1. Following initiated formation of 4-MoCDF by cross-coupling of a phenoxyl and 2-MoCPh radical, chlorine substitution is directed to the same benzene ring at the 2-position, providing high electrophilic stability. Subsequent chlorine substitution may then take place at favorable sites that minimize steric hindrance.

4. Conclusion

The analysis of all isomers, including low chlorinated and less-toxic non-2,3,7,8-substituted congeners, provides PCDD, PCDF, and PCN fingerprints that may be useful for eliciting information on their formation mechanisms. The isomer patterns in this MAP study are more selective compared to those reported from combustion processes. We suggest that a precursor mechanism involving (chloro)phenol and reactive phenoxyl radical intermediates could be important in MAP. The presence of isomers with low thermodynamic stability indicates that a kinetic factor may play a role in the MAP process. We have reported in our previous work (Gao et al., 2016) that biomass chemical compositions (C1, transition metals etc.) have an impact on the concentrations of PCDDs, PCDFs and PCNs in MAP products. However, the relative abundances of PCDD and PCDF isomers are not substantially affected, which indicates that the chemical composition of the feedstocks has less influence on the isomer patterns (except PCN) than the actual concentrations. In our opinion, the typical MAP process conditions, such as low temperature, oxygen deficiency and high heating rate, are likely to be key factors governing the formation pathway of chlorinated organic compounds. This study provides important insights for understanding the formation mechanisms of POPs in MAP and similar pyrolysis processes.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.02.031.

References

Jansson, S., Fick, J., Tysklind, M., Marklund, S., 2009. Post-combustion formation of

Scheme 1. Postulated PCDF formation pathways involving cross-coupling of (chlorinated) phenoxyl radical intermediates.


