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

Qiuju Gao [a], Mariusz K. Cieplik [b], Vitaliy L. Budarin [c], Mark Gronnow [d], Stina Jansson [a, *]

[a] Department of Chemistry, Umeå University, SE -901 87, Sweden
[b] Energy Research Centre of The Netherlands, ECN Biomass and Energy Efficiency, 1755 ZG Petten, The Netherlands
[c] Green Chemistry Centre of Excellence, Department of Chemistry, University of York, YO10 5DD, UK
[d] Biorenewables Development Centre, York Science Park, York, YO10 5NY, UK

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.

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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.

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

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* Corresponding author.
E-mail address: stina.jansson@umu.se (S. Jansson).

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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; Stieglitz, 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. × 0.25 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 (Liljelind et al., 2003; 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