PARTICLE-MEDIATED FORMATION OF POLYCHLORINATED NAPHTHALENES IN THERMAL PROCESS

Ryu JY[1], Mulholland JA[2], Choi, CY[1], Lee MJ[1], Jung IH[1]

[1]Radiation Research Division for Industry & Environment, Korea Atomic Energy Research Institute (KAERI), 1266 Sinjeong-dong, Jeongeup-si, Jeollabuk-do, 580-185, Republic of Korea

[2]Environmental Engineering, Civil and Environmental Engineering, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30332, USA

Introduction

Formation of naphthalene at high temperatures in flames has largely been attributed to the hydrogen-abstraction/acetylene-addition (HACA). In post-combustion gas, however, under conditions in which PCDDs and PCDFs are formed from chlorinated phenols, PCNs may be formed directly from coupling of chlorinated phenoxy radicals. In previous studies in this laboratory1), formation of PCNs with PCDDs/PCDFs was observed in gas-phase pyrolysis and oxidation of chlorinated phenols. Today PCNs are mainly unintentionally formed and released through industrial processes like municipal solid waste incineration. In municipal waste incinerators, chlorination of naphthalene (N) could be a significant source of PCNs, due to the high concentration of unsubstituted N in the flue gas. Therefore, chlorination reaction may also affect the distribution of PCN congeners. Chlorination can occur by metal catalysis, and, in particular, by copper (II) chloride ($CuCl_2$). The Deacon process can convert HCl to Cl_2, which then can lead to gas-phase N chlorination. The overall Deacon reaction is as follows.

$$4\ HCl + O_2 \rightarrow 2\ Cl_2 + 2\ H_2O \tag{1}$$

Alternatively, direct chlorination of an aromatic molecule such as Naphthalene by $CuCl_2$ can occur by the following transfer mechanism. 2)

$$ArH + CuCl_2 \rightarrow ArHCl^* + CuCl \tag{2}$$
$$ArHCl^* + CuCl_2 \rightarrow ArCl + CuCl + HCl \tag{3}$$

In this paper, distributions of PCN products formed by $CuCl_2$-catalyzed chlorination of naphthalene are presented. This work shows the distribution of chlorinated congeners and the dependence of naphthalene chlorination on temperature and gas velocity. Especially, this study represents homologue and isomer distributions of lower chlorinated naphthalenes which needs to be filled to acquire comprehensive understanding of PCN formation during thermal processes.

Materials and methods

Reactor System and Operating Conditions

Experiments were conducted in an electrically heated, quartz tube flow reactor, 40 cm in length and 1.7 cm in diameter. High purity naphthalene reactant (40 mg, nominal) was placed in a glass vessel and heated. Reactant vapor was transported to the reactor by 92% nitrogen and 8% oxygen gas stream. The resulting gas stream, containing 0.1% reactant vapor, was introduced to the isothermal reactor. A 1 g particle bed consisting of silicon dioxide (SiO_2) with 0.5% (mass) copper (II) chloride ($CuCl_2$) was located at the center of the reactor. The bed height was 1 cm. Naphthalene chlorination was studied and temperatures ranging from 100 to 400°C, in 50°C increments for gas velocities of 2.7 cm/s and at 300°C for gas velocities of 0.32 cm/s. Temperature profiles inside the quartz tube reactor were measured using a thermocouple for different temperature settings and a gas flow rate of 200 standard ml/min.

Sample Collection and PCN Analysis

The entire product gas stream was rapidly quenched at the bottom of the reactor by blowing room temperature air to facilitate product collection. Aromatic samples were collected in a dual ice-cooled dichloromethane (DCM) trap. After each experiment, the quartz tube (reactor), all fittings, and collection trap were also rinsed with DCM to remove any products deposited on the surface. Rinsed DCM was combined with the DCM in the collection trap. Sample and rinsed solutions were filtered with polytetrafluorothylene (PTFE) membrane filter of 0.25µl pore diameter by vacuum filtration to remove soot, defined as the DCM-insoluble fraction. Analysis of PCN congeners was accomplished with a Hewlett-Packard 6890 series gas chromatography with HP-5MS column (30m, 0.25 mm i.d., 0.25 µm film thickness) coupled to a Hewlett-Packard 5973 mass spectrometer. The column oven temperature was programmed as follows: 38 to 80°C at a rate of 3°C/min, 180 to 250°C at a rate of 5°C/min, 250 to 280°C at a rate of 6°C/min, and a final hold time of 3 min. For quantification, the mass spectrometer was operated in selective ion mode at the two most intensive and characteristic ion masses. PCN congeners were identified based on the published relative retention time and elution order of PCNs in Halowax 1001, 1014, and 1051.[3)] Unchlorinated naphthalene was used as universal response factors to estimate yields of PCN products. Due to the lack of standards of individual PCN congeners, Halowax 1001, 1014, and 1051, commercially manufactured PCN mixtures were used as PCN standards. Unchlorinated naphthalene was used as a universal response factor for PCN products. Preliminary identification of PCN products was done according to published reports.[3)] Elution orders of congeners not identified in our analytic system are also listed in accordance with the published reports.

Results and discussion:

PCNs Yields

The average yields of PCNs over the temperature range of 100-400°C at a gas velocity of 2.7cm/sec (gas-particle contact time of 0.3sec) from particle-mediated experiment are presented in Figure 1, expressed in units of total naphthalene (N) conversion to PCNs. The average and ± one standard deviation are shown from replicated experiments. As temperature increased PCNs yields were also increased and observed to peak at 3.07% (percent of N input, carbon basis) at 250°C. Above this temperature, PCNs yields decreased. Not shown here, at all temperatures, MCN yields were greatest. Similar observation is obtained from another study.[4)] They found PCDD/Fs yields from dibenzo-p-dioxin (DD) and dibenzofuran (DF) chlorination by copper (II) chloride was greatest at the range of 225-250°C.

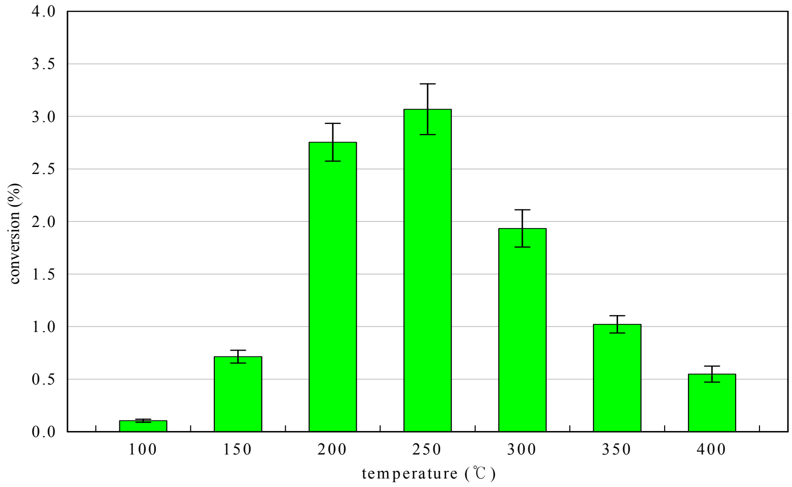

Figure 1. Average PCNs Yields at a gas velocity of 2.7cm/sec

PCNs Homologue Patterns

Figure 2 shows the homologue distributions formed from naphthalene chlorination via particle-mediated reaction. The average and ± one standard deviation are shown from replicated experiments. Completed homologue yields were not observed at a gas velocity of 2.7cm/sec, but at a gas velocity of 0.32cm/sec. PCNs homologue distributions are similar for the two different gas velocities at 300°C. In two cases the homologue patterns were clearly dominated by the lower chlorinated homologues. MCN fraction was approximately 0.6 and 0.55 of the

PCNs at a gas velocity of 2.7cm/sec and 0.32cm/sec. DCN fraction was approximately 0.27 and 0.28 of the PCNs at a gas velocity of 2.7cm/sec and 0.32cm/sec, respectively. The T_3CN and T_4CN were also abundant. The PCNs homologue fraction decreased with increasing number of chlorine substituents in two different gas velocities. H_6CN through O_8CN were not detected or close to the quantification limit at a gas velocity of 2.7cm/sec and 0.0005% of H_6CN through O_8CN were formed at a gas velocity of 0.32cm/sec. These homologue distributions are consistent with the result by Jansson et al. 5) Recently, they performed experiments to investigate PCN formation and chlorination in the post-combustion zone during municipal solid waste (MSW) combustion. They found that lower chlorinated PCNs were clearly dominated and MCN was about 50% of PCNs from all experimental conditions and the O_8CN was not detected, resulting in low and highly uncertain concentrations. This result is also similar to the previous study. 6) In the particle-mediated dibenzofuran (DF) chlorination experiment, lower chlorinated dibenzofurans were clearly dominated. MCDF was most abundant and homologue fractions decreased with increasing number of chlorine substituents. Jansson et al.5) have speculated that PCN homologue patterns, massive domination of the least-chlorinated PCN homologue, may be attributed to a PCN formation route involving successive chlorination of the naphthalene backbone. This is in agreement with the previous studies. 6) PCDF and PCN homologues were closely related, and that the main PCDF and PCN formation mechanisms were likely related to chlorination and/or dechlorination.

However, PCN homologue fraction decreased with with increasing number of chlorine substituents in the municipal waste incinerator fly samples. 3) At 300°C, broad homologue distributions were obtained as shown in Figure 4. The homologue distributions for gas velocities of 2.7cm/sec and 0.32cm/sec, corresponding to gas-particle contact times of 0.3 and 2.5 s, were similar, although the total PCN yields was higher for the latter. Total average PCNs yields were 2.74% and 1.93% at 0.32cm/sec and 2.7cm/sec, respectively.

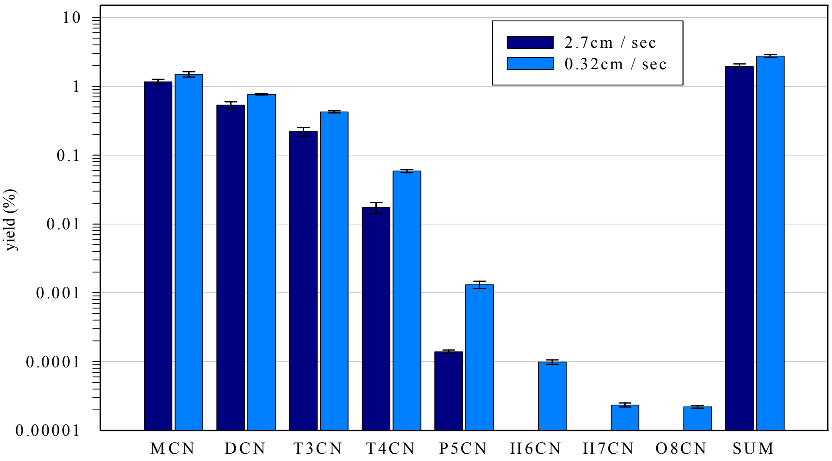

Figure 2. Average PCNs Homologue yields at two different gas velocities of 2.7 and 0.32cm/sec at 300°C.

PCNs Isomer Patterns

To further assess the role of N chlorination in PCNs formation, PCNs isomer distributions are investigated. Broader isomer distributions were obtained from the experiment at a gas velocity of 0.32cm/sec. Figure 3 shows PCNs isomer distributions formed from N chlorination at 300°C. Isomer distributions are much less variable than homologue distributions with varying combustion conditions. PCN, written as $C_{10}H_8$-xClx or in short term ClxN, build up a class of 75 possible congeners similar to the polychlorinated dibenzo-p-dioxin (PCDD). Isomer groupings were developed on the basis of combinations of coeluting PCN isomers. Means and standard deviations are given for three measurements of formation via particle-mediated naphthalene chlorination. All major PCN products yields peaked between 200°C and 300°C. The predominant N chlorination pathways leading to the 1,4 PCN congeners are shown below. These are 1-MCN, 1,4-DCN, 1,4,6-T_3CN, 1,2,5,7-/1,2,4,6-/1,2,4,7-T_4CN, 1,2,4,6,8-P_5CN, 1,2,4,5,6,8-/1,2,4,5,7,8-H_6CN, 1,2,3,5,7,8-H_6CN and 12,3,4,5,6,8-H_7CN. As shown in Figure 4, little variation in the PCN isomer distributions was observed, even though the total PCN yield did vary significantly. This is also evidenced by the small standard deviation in isomer fractions for the three experiments.

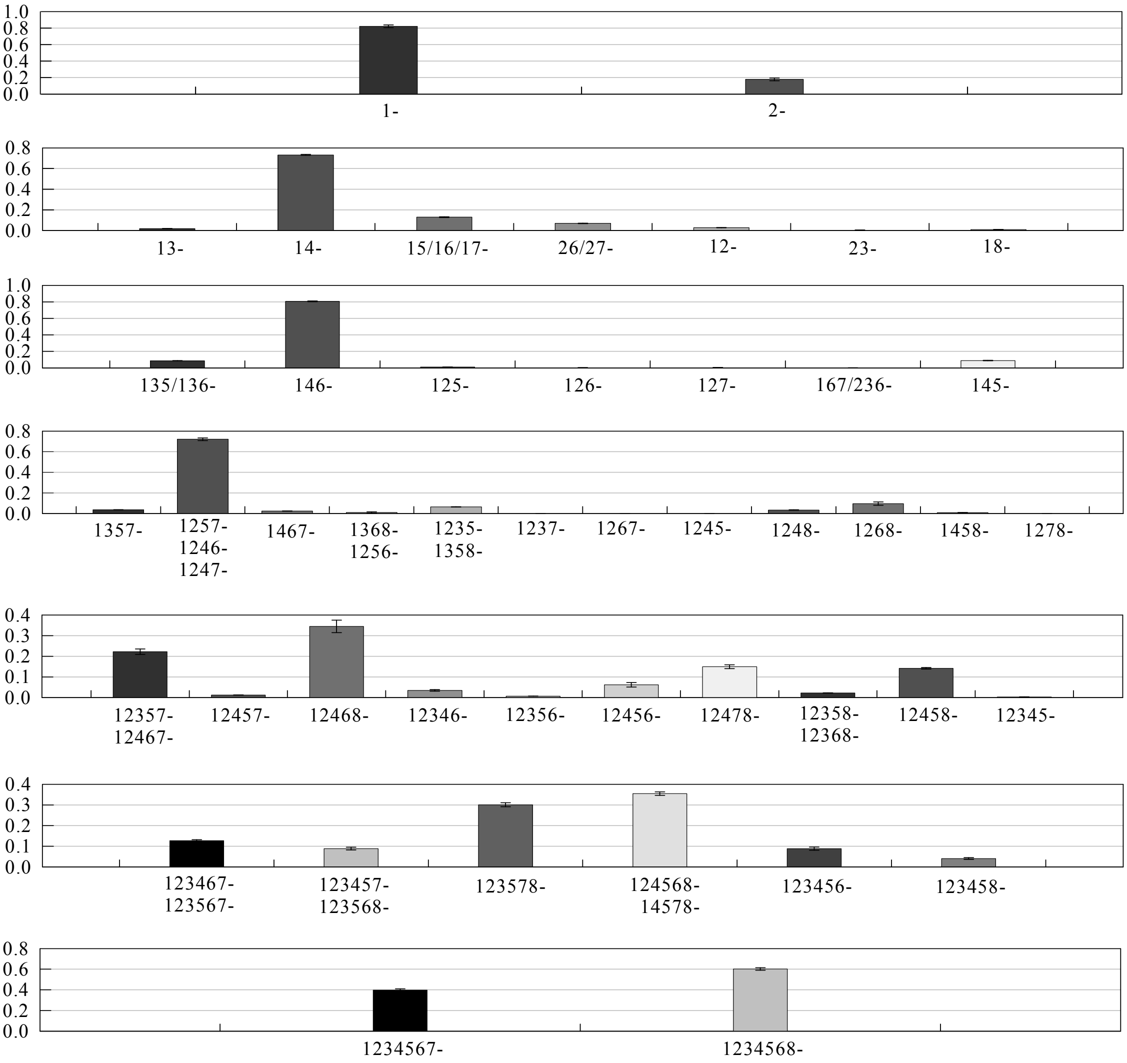

Figure 3. Average PCNs Isomer distributions at 0.32cm/sec at 300°C.

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