한국환경과학회지 제21권(제8호), 891～899, 2012
Journal of the Environmental Sciences
http://dx.doi.org/10.5322/JES.2012.21.8.891

Homologue Patterns of Polychlorinated Naphthalenes (PCNs) formed via Chlorination in Thermal Process

Jae-Yong Ryu*, Do-Hyong Kim[1)], James A. Mulholland[2)],
Seong-Ho Jang[3)], Chang-Yong Choi, Jong-Bum Kim

Division for Industrial & Environmental Research, Korea Atomic Energy Research Institute (KAERI), Jeollabuk-do 580-185, Korea
[1)]*Land Protection Branch, Georgia Environmental Protection Division, Atlanta, Georgia, USA*
[2)]*School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia, USA*
[3)]*Department of Bioenvironmental Energy, Pusan National University, Miryang 627-706, Korea*
(Manuscript received 12 June, 2012; revised 2 July, 2012; accepted 10 August, 2012)

Abstract

The chlorination pattern of naphthalene vapor when passed through a 1 cm particle bed of 0.5% (mass) copper (II) chloride ($CuCl_2$) mixed with silicon dioxide (SiO_2) was studied. Gas streams consisting of 92% (molar) N_2, 8% O_2 and 0.1% naphthalene vapor were introduced to an isothermal flow reactor containing the $CuCl_2/SiO_2$ particle bed. Chlorination of naphthalene was studied from 100 to 400 °C at a gas velocity of 2.7 cm/s. Mono through hexachlorinated naphthalene congeners were observed at 250 °C whereas a broader distribution of polychlorinated naphthalenes (PCNs) including hepta and octachlorinated naphthalenes was observed at 300 °C. PCN production was peak at 250 °C with 3.07% (molar) yield, and monochloronaphthalene (MCN) congeners were the major products at two different temperatures. In order to assess the effect of a residence time on naphthalene chlorination, an experiment was also conducted at 300 °C with a gas velocity of 0.32 cm/s. The degree of naphthalene chlorination increased as a gas velocity decreased.

Key Words : PCN (polychlorinated naphthalene), Chlorination, Copper (II) chloride, Homologue distribution

1. Introduction

Formation of polychlorinated naphthalenes (PCNs) along with other halogenated aromatics compounds, such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), has been observed to occur in combustion exhaust gas(Imagawa and Takeuch, 1995). There are 75 PCN congeners containing one to eight chlorine atoms. Although data on the toxicity of individual PCNs are very limited, some PCNs are known to strongly bioaccumulate and to exhibit dioxin-like toxicity(Falandysz, 1998).Besides, it has been reported that the amount of PCNs formed from a pilot-scale solid waste incinerator was the same order of magnitude as PCDD/F yields(Sakai et al., 1996). While substantial improvements in the understanding of thermal PCDDs/PCDF formation process have resulted from extensive laboratory study, much less fundamental study of PCN formation has been conducted.

Formation of naphthalene at high temperatures in flames has largely been attributed to the hydrogen-abstraction/acetylene-addition (HACA) mechanism (Frenklach et al., 1984; Frenklach, 1987; McEnally and Pfefferle, 2000). In post-combustion gas, however,

*Corresponding author : Jae-Yong Ryu, Division for Industrial & Environmental Research, Korea Atomic Energy Research Institute (KAERI), Jeollabuk-do 580-185, Korea
Phone: +82-63-570-3345
E-mail: jyryu@kaeri.re.kr; jaeyong03@gmail.com

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 laboratory, formation of PCNs with PCDDs/PCDFs was observed in gas-phase pyrolysis(Akki and Mulholland, 1997) and oxidation(Yang et al., 1998) of chlorinated phenols.

No attempt was made to elucidate the detailed mechanism of PCN formation because many of the PCN congeners had not been identified. It has been suggested that naphthalene formation from phenol in flames can occur by combination of cyclopentadienyl (CPDyl) radicals, produced from the decomposition of phenoxy radical via loss of CO(Manion and Louw, 1989; Castaldi et al., 1996; Marinov et al., 1997). Melius and coworkers(Melius et al., 1996) performed quantum chemical modeling on naphthalene formation from dihydrofulvalene, proposing that the recombination of CPDyl radicals produces dihydrofulvalene which then undergoes intramolecular rearrangements via resonance-stabilized radicals. Three-member ring closure and opening results in fusion of the bi-cyclic dihydrofulvalene intermediate to form naphthalene. Recently, we have studied the slow oxidation of monochlorophenols (MCPs) and proposed PCN formation pathways based on the published mechanisms of PCDF formation from chlorinated phenols and naphthalene formation from dihydrofulvalene (Kim et al., 2007; Ryu et al., 2006a, 2006b; Kim et al., 2005, 2007).

Nowadays, PCNs are mainly unintentionally formed and released through industrial processes like municipal solid waste incineration(Abad et al., 1999). In municipal waste incinerators, chlorination of naphthalene (N) is considered to be a significant route of PCN production, due to the presence of the large amount of unsubstituted N in the flue gas. In addition, chlorination reaction would 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.

$$4\ HCl + O_2 \rightarrow 2\ Cl_2 + 2\ H_2O \quad (1)$$

Alternatively, direct chlorination of an aromatic molecule such as naphthalene by $CuCl_2$ can occur by the following transfer mechanism(Hoffman et al., 1990; Stieglitz et al., 1990).

$$ArH + CuCl_2 \rightarrow ArHCl^* + CuCl \quad (2)$$

$$ArHCl^* + CuCl_2 \rightarrow ArCl + CuCl + HCl \quad (3)$$

In this paper, PCN product distributions via $CuCl_2$-catalyzed chlorination of naphthalene are presented. The observed homologue distributions of PCN products would provide a better understanding of PCN formation in thermal processes.

2. Materials and Methods

2.1. Reactor System and Operating Conditions

The experimental apparatus is shown in Figure 1. 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

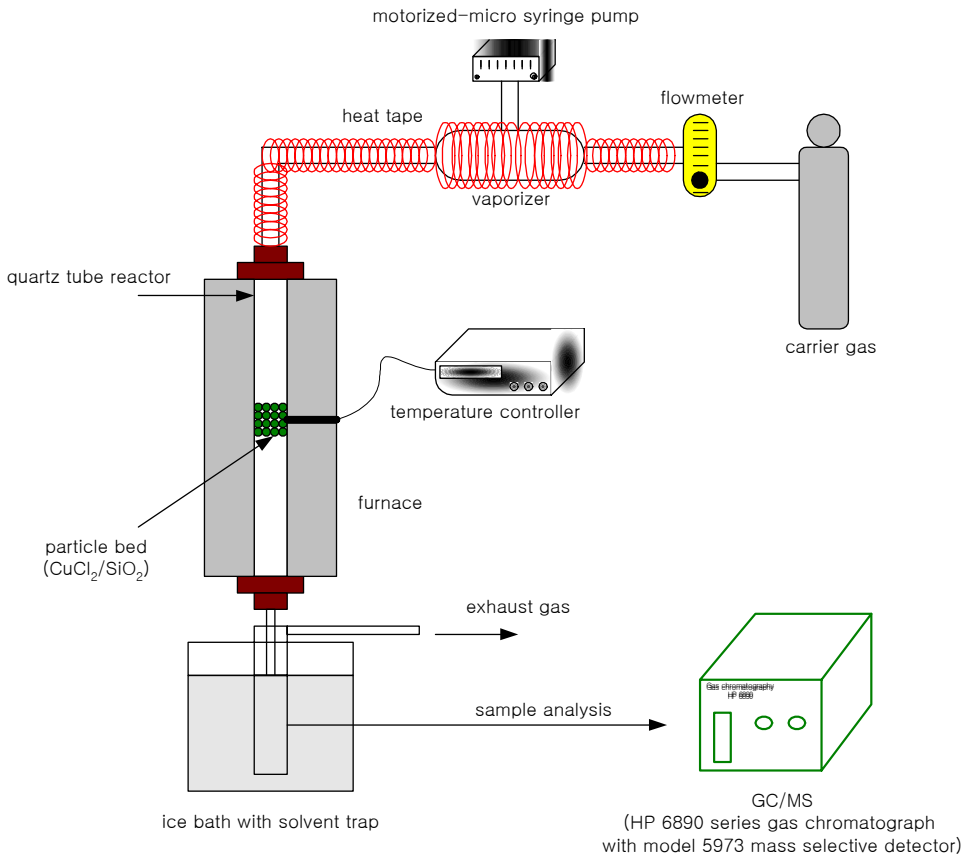

Fig. 1. Experimental Apparatus.

were measured using a thermocouple for different temperature settings and a gas flow rate of 200 standard ml/min. These are shown in Figure 2. Measurements of the reactor temperature profiles indicate that temperatures at the top 8 cm and bottom 9 cm of the quartz tube are lower than the set value. The gas temperatures in the remaining 31 cm of the reactor, defined as a reaction zone, are approximately constant within $\pm$ 10 ^{o}C of the set value. Radial variation of temperature was assumed to be negligible due to small tube diameter.

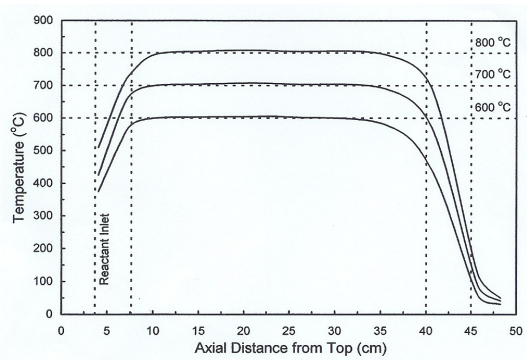

Fig. 2. The axial temperature profile of the quartz tube reactor(Yang et al., 1998).

2.2. Product 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 products 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 a polytetrafluorothylene (PTFE) membrane filter of 0.25 μl 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 a HP-5MS column (30 m, 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(Järnberg et al., 1994; Schneider et al., 1998). 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. The analytical results of Halowaxes used for this study are summarized in Table 1. Unchlorinated naphthalene was used as a universal response factor for PCN products.

Table 1. Composition of Halowax Standards

Halowax	Cl-content	Chlorinated degree Cl_xN	Concentration
1000	26%	x=1,2	100 μg/ml in MeOH
1001	50%	x=(1,2)3,4,(5)	100 μg/ml in MeOH
1014	62%	x=(3) 4,5,6,(7)	100 μg/ml in MeOH
1051	70%	x=7,8	100 μg/ml in MeOH

A preliminary identification of PCN products was done according to published reports(Järnberg et al., 1994; Schneider et al., 1998). The HP-5MS column provided the following separation of PCN isomer peaks: 2 peaks/2 monochloronaphthalene (MCN) isomers, 7 peaks/10 dichloronaphthalene (DCN) isomers, 8 peaks/14 trichloronaphthalene (T_3CN) isomers, 13 peaks/ 22 tetrachlronaphthalene (T_4CN) isomers, 12 peaks/14 pentachloronaphthalene (P_5CN) isomers, 6 peaks/ 10 hexachloronaphthalene (H_6CN) isomers, 2 peaks/2 heptachloronaphthalene (H_7CN) isomers. The GC temperature program for PCN product identification is shown in Table 2. For quantification, the mass spectrometer was operated in selective ion mode at the two most intensive and characteristic ion masses. Mass spectral information on PCN is provided in Table 3.

Table 2. GC temperature program for PCN analysis

Start (°C)	End (°C)	Rate (°C/min)	Time (min)
38	38	0	2
38	180	3	47.33
180	180	0	2
180	250	5	14
250	250	0	5
250	280	6	5
280	280	0	3
280	300	2	10

Table 3. Selected Ion for PCN analysis

Compounds	M+	M+2	Ion ratio
MCNs	162.02	164.02	3.07
DCNs	195.98	197.98	1.55
T_3CNs	229.95	231.94	1.04
T_4CNs	263.61	265.90	0.78
P_5CNs	299.86	301.86	1.55
H_6CNs	333.83	335.82	1.24
H_7CNs	367.79	369.78	1.04
OCN	401.75	403.75	0.89

Seventy-four of 76 PCN congeners including unchlorinated naphthalene have been identified, and the elution order of identified PCNs is shown in Table 4. Elution orders of congeners not identified in our analytic system are also listed in accordance with the published reports. Co-eluted congeners are shown in bold boxes.

3. Results and Discussion

3.1. PCNs Yields

The average yields of PCNs over the temperature range of 100-400°C at a gas velocity of 2.7 cm/sec with a gas-particle contact time of 0.3 sec from particle-mediated experiments are presented in Figure 3, 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 also increased,

Table 4. Elution order of PCNs on HP-5ms column

N	MCN	DCN	T_3CN	T_4CN	P_5CN	H_6CN	H_7CN	OCN
naphthalene	2-(29.37)	13-(36.06)	136-(42.49)	1357-(47.47)	12357-(54.84)	123467-(60.19)	1234567-(64.98)	12345678-
(20.93)	1-(29.63)	14-(36.57)	135-(42.49)	1257-(48.62)	12467-(54.84)	123567-(60.19)	1234568-(65.08)	(73.50)
		15-(36.73)	137-(42.94)	1246-(48.62)	12457-(55.44)	123457-(60.73)		
		16-(36.73)	146-(42.94)	1247-(48.62)	12468-(55.69)	123568-(60.73)		
		17-(36.73)	124-(43.35)	1367-(49.02)	12346-(55.86)	123578-(60.94)		
		26-(37.07)	125-(43.62)	1467-(49.39)	12356-(55.97)	124568-(61.16)		
		27-(37.07)	126-(43.90)	1368-(49.92)	12367-(56.70)	124578-(61.16)		
		12-(37.42)	127-(44.23)	1256-(49.92)	12456-(56.84)	123456-(61.89)		
		23-(37.66)	167-(44.55)	1235-(50.23)	12478-(57.07)	123458-(62.31)		
		18-(39.68)	236-(44.55)	1358-(50.23)	12358-(57.25)	123678-(62.75)		
			123-(44.80)	1237-(50.62)	12368-(57.25)			
			138-(45.21)	1234-(50.70)	12458-(57.69)			
			145-(45.45)	1267-(50.86)	12345-(57.93)			
			128-(46.87)	1245-(51.14)	12378-(58.77)			
				2367-(51.27)				
				1248-(51.43)				
				1258-(51.94)				
				1268-(51.94)				
				1458-(53.12)				
				1238-(53.48)				
				1278-(53.88)				

* note: elution time of each congener is written in parenthesis, and congeners shown in boxes co-elute; the order of congeners without elution times is based on literature elution order using similar columns.

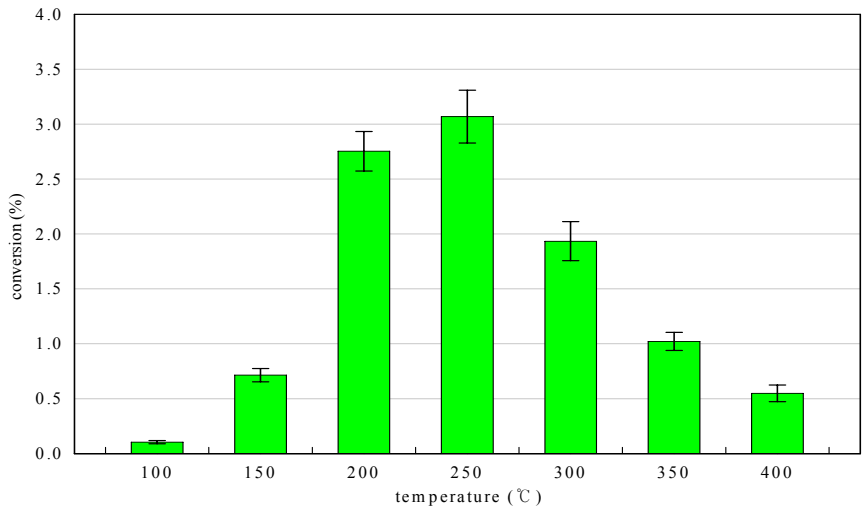

Fig. 3. Average PCNs Yields at a gas velocity of 2.7 cm/sec.

and a peak yield of 3.07% (percent of N input, carbon basis) was observed at 250 °C. Above this temperature, PCNs yields decreased. With respect to homologue distributions, MCN yield was higher than other homologue groups at all temperatures (not shown here). Similar observation is obtained from another study(Ryu et al., 2003). 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 to 250 °C.

Because the previous study on the chlorination of dioxin and dibenzofuran indicated that the degree of chlorination was greater and isomer patterns were broader for the 300 °C with the gas velocity of 0.32 cm/sec experiments(Ryu et al., 2003), PCN homologue distributions via chlorination of naphthalene were also investigated at 300 °C with a gas velocity 0.32 cm/sec.

3.2. PCNs Homologue Distributions

Figure 4 shows the homologue distributions formed from naphthalene chlorination via particle-mediated reaction. The average and ± one standard deviation are shown from replicated experiments. While all of PCN homologue groups were observed at gas velocity of 0.32 cm/s, hexa, hepta, and octa PCN homologue groups were not observed at a gas velocity of 2.7 cm/sec. Relative PCNs homologue distributions are, however, similar for the two different gas velocities at 300 °C. In both 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 2.7 cm/sec and 0.32 cm/sec, respectively. DCN fraction was approximately 0.27 and 0.28 of the PCNs at a gas velocity of 2.7 cm/sec and 0.32 cm/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 observed only at a gas velocity of 0.32cm/sec with their combined yield of 0.0005%. The observed homologue distributions are consistent with the result by Jansson et al.(Jansson et al., 2008). Recently, Jansson and co-workers experimentally investigated PCN formation via chlorination in the post-combustion zone during municipal solid waste (MSW) combustion. Their experimental results

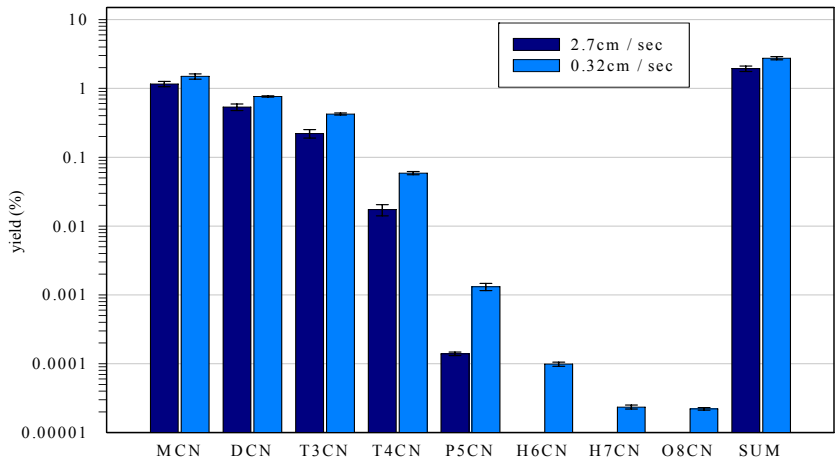

Fig. 4. Average PCNs Homologue yields at two different gas velocities of 2.7 and 0.32cm/sec at 300°C.

indicated that lower chlorinated naphthalenes were clearly dominated products, MCN comprised about 50% of the observed 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(Ryu et al., 2003). 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 and co-workers (Jansson et al., 2008) have speculated that massive domination of the least-chlorinated PCN homologue in PCN homologue patterns may be attributed to a PCN formation via successive chlorination of the naphthalene backbone. This is in agreement with the previous studies on chlorination of dioxin and dibenzofuran(Ryu et al., 2004; Ryu et al., 2005). 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 increasing number of chlorine substituents in the municipal waste incinerator fly samples(Schneider et al., 1998). At 300 °C, broad homologue distributions were obtained as shown in Figure 4. The homologue distributions for gas velocities of 2.7 cm/sec and 0.32 cm/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 0.32 cm/sec and 2.7 cm/sec, respectively. Homologue patterns are sensitive to combustion conditions, such as a chlorine/hydrogen ratio and temperature(Ryu et al., 2003; Ryu et al., 2005; Iino et al., 1999).

4. Conclusions

MCN through OCN congeners of N chlorination by $CuCl_2$ has been measured as a function of temperature and gas velocity. At a gas velocity of 2.7 cm/s, the maximum PCN yield of 3.07% (molar) from N occurred at 250 °C, with mono- through hexa-congeners observed. MCN was most abundant homologue group, and the homologue distributions decreased with increasing number of chlorine substituents in two different gas velocities. At 300 °

C, maximum conversion of N to PCN of 2.74% occurred at a gas velocity of 0.32 cm/s. To further assess the role of naphthalene chlorination in the formation of PCN, more study is needed to compare PCN isomer distributions formed chlorination and those obtained from MWI fly ash samples.

Acknowledgments

J.-Y. Ryu's work was supported from the United States National Science Foundation (NSF) under grant CTS-0210089 and the Eco-Innovation Project through the Korea Environmental Industry & Technology Institute funded by the Ministry of Environment and by the Nuclear Research and Development Program of Ministry of Education, Science and Technology.

References

Abad, E., Caixach, J., Rivera, J., 1999, Dioxin like compounds from municipal waste incinerator emissions: assessment of the presence of polychlorinated naphthalenes, Chemosphere, 38, 109-120.

Akki, U., Mulholland, J. A., 1997, Gas-phase formation of dioxin and other aromatic products from 2,6-dichlorophenol pyrolysis, Organohalogen Compounds, 31, 475-479.

Castaldi, M. J., Marinov, N. M., Melius, C. F., Huang, J., Senken, S. M., Pitz, W. J., Westbrook, C. K., 1996, Experimental and modeling investigation of aromatic and polycyclic aromatic hydrocarbon formation in a premixed ethylene flame, Proc. Combust. Inst., 26, 693-702.

Falandysz, J., 1998, Polychlorinated naphthalenes: an environmental update, Environmental Pollution 101(1), 77-90.

Frenkalch, M and Warnatz, J., 1987, Detailed modeling of PAH profiles in a sooting low-pressure acetylene flame, Combust. Sci. Technol., 51, 265-283 .

Frenklach, M., Clary, D. W., Cardiner, W. C. and Stein, S. E., 1984, Detailed kinetic modeling of soot formation in shock-tube pyrolysis of acetylene, Proc. Combust. Inst., 20, 887-901.

Hoffman, R. V., Eiceman, G. A., Long, Y. T., Margaret, C. C., Lu, M. Q., 1990, Mechanism of chlorination of aromatic compounds adsorbed on the surface of fly ash from municipal incinerators, Environ. Sci. Technol., 24, 1635-1641

Iino, F., Imagawa, T., Takeuchi, M., Sadakata, M., 1999, De Novo synthesis mechanism of polychlorinated dibenzofurans from polycyclic aromatic hydrocarbons, Environ. Sci. Technol., 33, 1038-1043.

Imagawa, T., Takeuchi, M., 1995, Relation between isomer compositions of polychlorinated naphthalens and congener compositions of PCDDs/PCDFs from incinerators, Organohalogen Compounds, 23, 487-490.

Jansson, S., Fick, J., Marklund, S., 2008, Formation and chlorination of polychlorinated naphthalenes (PCNs) in the post-combustion zone during MSW combustion, Chemosphere, 72, 1138-1144.

Järnberg, U., Asplund, C., Jakobsson, E., 1994, Gas chromatographic retention of polychlorinated naphthalenes on non-polar, polarizable, polar and semectic capillary columns, J. Chromat., 683A, 385-396.

Kim, D. H., Kim, J. K., Jang, S. H., Mulholland, J. A., Ryu, J. Y., 2007, Thermal formation of polycyclic aromatic hydrocarbons from cyclopentadiene (CPD), Environ. Eng. Res., 12(5), 211-217.

Kim, D. H., Mulholland, J. A., Ryu, J, Y., 2007, Chlorinated naphthalene formation from the oxidation of dichlorophenols, Chemosphere 67, S135-S143.

Kim, D. H., Mulholland, J. A., Ryu, J. Y., 2005, Formation of polychlorinated naphthalenes from chlorophenols, Proc. Combust. Inst., 30, 1249-1257.

Manion, J., Louw, R., 1989, Rates, products, and mechanisms in the gas-phase hydrogenolysis of phenol between 922 and 1175 K, J. Phys. Chem., 93, 3563-3574.

Marinov, N. M., Castaldi, M. J., Melius, C. F., Tsang, W., 1997, Aromatic and Polycyclic Aromatic Hydrocarbon Formation in a Premixed Propane Flame, Combust. Sci. Technol., 128, 295-342 .

McEnally, C.S. and Pfefferle, L. D., 2000, The use of carbon-13-labeled fuel dopants for identifying naphthalene formation pathways in non-premixed flames, Proc. Combust. Inst., 28, 2569-2576.

Melius, C. F., Colvin, M. E., Marinov, N. M., Pitz, W. J.,

Senkan, S. M., 1996, Reaction mechanisms in aromatic hydrocarbon formation involving the C_5H_5 cyclopentadienyl moiety, Proc. Combust. Inst., 26, 685-692.

Ryu, J. Y., Kim, D. H., Choi, K. C., Suh, J. M., 2006, Polychlorinated naphthalene(PCN) and dibenzofuran (PCDF) congener patterns from phenol precursors in thermal process: [I] a priori hypothesis of PCN and PCDF formation pathways from monochlorophenols, Environ. Eng. Res., 11(4), 218-232.

Ryu, J. Y., Kim, D. H., Choi, K. C., Suh, J. M., 2006, Polychlorinated naphthalene(PCN) and dibenzofuran (PCDF) congener patterns from phenol precursors in thermal process: [II] experimental results from dichlorophenols (DCPs), Environ. Eng. Res., 11(4), 233-241.

Ryu, J. Y., Mulholland, J. A., Chu, B., 2003, Chlorination of dibenzo-p-dioxin and dibenzofuran vapor by $CuCl_2$, Chemosphere, 51, 1031-1039.

Ryu, J. Y., Mulholland, J. A., Dunn, J. E., Iino, F., Gullett, B. K., 2004, Potential Role of Chlorination Pathways in PCDD/F Formation in a Municipal Waste Incinerator, Environ. Sci. Technol., 38, 5112-5119.

Ryu, J. Y., Mulholland, J. A., Takeuchi, M., Kim, D. H., 2005, Homologue and Isomer Patterns of Polychlorinated Dibenzo-p-dioxin (PCDD) and Dibenzofuran (PCDF) from Phenol Precursors: Comparison with Municipal Waste Incinerator Data, Environ. Sci. Technol., 39, 4398-4406.

Sakai, S., Hiraoka, M., Takeda, N. and Shiozaki, K., 1996, Behavior of coplanar PCNs and PCNs in oxidative conditions of municipal waste incineration, Chemosphere, 32, 79-88.

Schneider, M., Stieglitz, L., Will, R., Zwick, G., 1998, Formation of polychlorinated naphthalenes on fly ash, Chemosphere, 37, 2055-2070.

Stieglitz, L., Vogg, H., Zwick, G., Beckj, J., Bautz, H., 1990, On formation conditions of organohalogen compounds from particulate carbon of fly ash, Chemosphere., 23,1255-1264.

Yang, Y., Mulholland, J. A., Akki, U., 1998, Formation of furans by gas-phase reactions of chlorophenols, Proc. Combust. Inst., 27, 1761-1768.