

Polychlorinated Naphthalene (PCNs) behavior in the thermal destruction process of wastes containing PCNs

Yukio Noma¹, Robert Giraud², Shin-ichi Sakai¹

¹National Institute for Environmental Studies, 16-2, Onogawa, Tsukuba, Ibaraki 305-8506, Japan

²DuPont Engineering Technology Wilmington, DE 19898, USA,

Introduction

Polychlorinated naphthalenes (PCNs) can compose a mixture of up to 75 congeners and eight CN homologue groups. The large-scale manufacture of PCNs and their main use from 1910 to 1980 as popular industrial compounds become a main source of environmental pollution¹⁻³. The production and use of PCNs were phased out in the US and Europe in the 1980s due to their toxicity and environmental persistence. Although PCNs were also banned for import and manufacture from the year 1979 in Japan, PCN wax was accidentally imported during 1998-2000 to manufacture Neoprene FB polymer, which is a special grade of synthetic rubber product⁴. Rubber belts (FB belts) were made from Neoprene FB and used for the domestic market during 1999-2001. Large efforts recalled all FB polymer as well as finished products containing FB polymer from distribution channels. Most of the remaining finished products in the marketplace will probably be incinerated as wastes after usage in the near future. Therefore, testing was conducted using the thermal testing plant equipment in order to evaluate the emissions from thermal destruction of FB belts containing PCNs, determining TEQ emissions, studying PCNs behavior, considering the mixture effect of FB belts co-incinerated with municipal solid waste (MSW) and examining the effect of two-stage combustion and post-combustion controls. Material balances were analyzed to grasp input and output of PCNs and the destruction behaviors are examined by congener specific analysis of PCNs.

Materials and Methods

Figure 1 shows process flow of the destruction experiment equipment. The system is composed of a rotary kiln primary combustion (with electrical heating), an electrically heated vertical secondary combustion chamber, a gas cooling zone, a bag filter, an activated carbon adsorption tower and a scrubber as a flue gas treatment equipment. Sodium hydrogen carbonate was utilized for neutralizing acid gas. Table 1 shows the conditions of the experiments. The experiments were conducted with three different feed conditions as follows: (1) simulated MSW sample (as a blank), (2) 5mg/kg of FB belts added to MSW (as expected typical level in MSW) and (3) 150mg/kg of FB belts added to MSW (as a high level). Feed materials with particle size of 5 - 10mm were used as crushed MSW. Continuous monitoring was conducted for temperature, O₂, CO and NO_x. A screw-type feeder was used to feed materials at a regular rate (2.5 kg/h). After the measured values of gas concentration by continuous analyzer came to the steady states, sampling for PCNs was started. Flue gases were obtained at 4 sampling points (kiln exit, bag filter entry, bag filter exit and final emission). Bottom ash and fly ash were sampled after the end of the experiments (Figure1).

The solid samples were extracted in toluene by soxhlet and liquid samples were extracted in dichloromethane by shaking. The solution was spiked with isotope-labeled internal standards

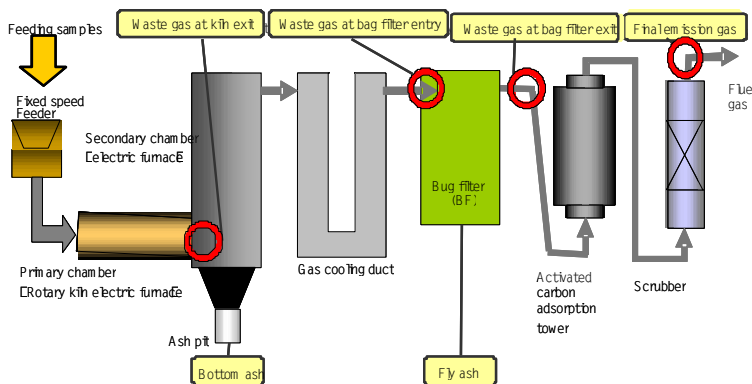


Figure 1 Flow of destruction experiment equipment and flue gas sampling points

solution and then cleaned up by passing through a multi-layer silica gel column chromatograph. At the further clean-up step, the elute was passed through activated carbon column. HRGC/HRMS measurements were carried out with an Agilent Model 6890 gas chromatograph coupled with a JEOL JMS-700 mass spectrometer. An Agilent Ultra 2 capillary column (25 m x 0.2 mm i.d., df=0.33 μm) was used. Peaks were identified using information from Nakano et. al and quantified by isotope dilution⁵. The analytical method used was described in details elsewhere⁶.

Results and Discussion

Table 2 and Figure 2 show the results of the destruction experiments. Figure 3 shows the homologue patterns of typical samples. The combustion gas

Table 1. Conditions of destruction experiments

Combustion sample		MSW	FB belt additive 5mg/kg	FB belt additive 150mg/kg
Acid gas treatment		NaHCO ₃	NaHCO ₃	NaHCO ₃
Total MSW volume (g)		18750	20000	13750
Temperature (□)	Primary combustion	840	840	838
	Secondary	900	900	900
	Outlet of secondary combustion	764	748	755
Gas flow rate (m ³ N/h)		40	40	40
Air flow rate (m ³ /h)		22	22	22
Flue gas at bag exit	O ₂ (%)	10.3	10.5	10.3
	CO (ppm)	0	0	0
	NOx (ppm)	43	43	47
	Bottom ash	1778.0	1886.5	1336.4
Volume (g)	Fly ash	81.6	91.2	138.8
	MSW size (mm)	φ8 x 25	φ8 x 25	φ8 x 25
MSW feed rate (kg/h)		2.5	2.5	2.5
FB belt size (mm)			3 x 1.5	3 x 1.5
FB belt additive in MSW (mg/kg)			5	150
Assumed PCNs conc. (ng/g)		34	48	454
CO,NOx at O ₂ :12%				

and residues have most congeners of all 75 possible chlorinated naphthalenes, while MSW and FB belt were much simpler.

(1) 1st experiment (MSW only)

PCNs concentration in MSW was 34 ng/g, and total input PCNs amount was 340,000 ng in the 4hrs-sampling time, when total MSW was 10kg. PCNs concentration in flue gas at kiln exit was 83,000 ng/m³, and PCNs amount there was 11,600,000 ng. PCNs were formed as by-product at the kiln by combustion, because the ratio of the PCNs amount in the flue gas at kiln exit to input PCNs amount was 34.2. Most of PCNs were destroyed by the secondary combustion, and the concentration was reduced to 23 ng/m³. After the flue gas treatment, almost all PCNs were removed. PCNs concentration and emissions to air are 2.7 ng/m³ and 432 ng, those to fly ash are 0.96 ng/g and 257 ng, and those to bottom ash are 1.7 ng/g and 1,610 ng. The results show the overall destruction efficiency is 99.32%.

(2) 2nd experiment (Typical level, FB belt 5mg/kg)

PCNs concentration in FB belt was 2,800 ug/g. Total input PCNs amount added on MSW was 480,000 ng in the 4hrs-sampling time, because 0.05g of FB belt was added to MSW. PCNs concentration in flue gas at kiln exit was 63,000 ng/m³, and PCNs amount was 8,820,000 ng. PCNs were formed as by-product at the kiln by combustion, because the ratio of the PCNs amount in the flue gas at kiln exit to input PCNs amount was 18.4. Most of PCNs were destroyed by the secondary combustion, and the concentration was reduced to

100 ng/m³. After the flue gas treatment, almost all PCNs were removed. PCNs concentration and emissions to air are 7.9 ng/m³ and 1,260 ng, those to fly ash are 0.48 ng/g and 123 ng, and those to bottom ash are 0.95 ng/g and 896 ng. The results show the overall destruction efficiency is 99.53%. It seemed that the influences on the emissions to the environment did not appear in the 2nd experiment added on FB belt with 5mg/kg. Like the MSW only experiment, the WHO-TEQ emission for this experiment was less than the 0.1 ng/m³N standard⁷. FB belt addition at 5 mg/kg did not influence thermal treatment emissions to the environment.

(3) 3rd experiment (High level, FB belt 150 mg/kg)

PCNs concentration in FB belt was 2,800 ug/g. Total input PCNs amount added on MSW was 4,540,000 ng in the 4hrs-sampling time, because 1.5g of FB belt was added to MSW. PCNs concentration in flue gas at kiln exit was 66,000 ng/m³, and PCNs amount was 8,980,000 ng. It is not clear from total PCN results whether PCNs were formed at the kiln by combustion or not, because the ratio of the PCNs amount in the flue gas at kiln exit to input PCNs amount was only 1.98. See next section for combustion by-product discussion based on congener specific analysis. Most of PCNs were destroyed by the secondary combustion, and the concentration was reduced to 47 ng/m³. After the flue gas treatment, almost all PCNs were removed. PCNs concentration and emissions to air are 3.3 ng/m³ and 528 ng, those to fly ash are 0.17 ng/g and 61.4ng, and those to bottom ash are 1.2 ng/g and 1,170 ng. The results show the overall destruction efficiency is 99.96%. Like the MSW only experiment, the WHO-TEQ emission for this experiment was less than the 0.1 ng/m³N standard⁷. FB belt addition at 150 mg/kg did not influence thermal treatment emissions to the environment.

Table2 Behavior of PCN destruction and generation in thermal destructive test using Waste containing PCN

No.1 Simulated samples of municipal solid wastes as blank condition

Item	Initial materials		Gas				Fly ash	Bottom ash
	MSW	FB belt	Flue gas at kiln exit	Flue gas at bag entry	Flue gas at bag exit	Flue gas at the final exit		
Concentration PCN	34 ng/g	2,800,000 ng/g	83,000 ng/m ³ N	23 ng/m ³ N	22 ng/m ³ N	2.7 ng/m ³ N	0.96 ng/g	1.7 ng/g
PCN volume PCN	340,000 ng	0 ng	11,600,000 ng	3,220 ng	3,170 ng	432 ng	257 ng	1,610 ng
Sample volume	10,000 g	0 g	140 m ³ N	140 m ³ N	144 m ³ N	160 m ³ N	267 g	948 g
Destruction efficiency	99.3235 %							
Ratio	1		34.2	0.00947	0.00932	0.00127	0.000754	0.00474

No.2 Simulated sample ☐FB belt (FB belt 5mg/kg☐MSW☐

Item	Initial materials		Gas				Fly ash	Bottom ash
	MSW	FB belt	Flue gas at kiln exit	Flue gas at bag entry	Flue gas at bag exit	Flue gas at the final exit		
Concentration PCN	34 ng/g	2,800,000 ng/g	63,000 ng/m ³ N	100 ng/m ³ N	17 ng/m ³ N	7.9 ng/m ³ N	0.48 ng/g	0.95 ng/g
PCN volume PCN	340,000 ng	140,000 ng	8,820,000 ng	14,000 ng	2,450 ng	1,260 ng	123 ng	896 ng
Sample volume	10,000 g	0.05 g	140 m ³ N	140 m ³ N	144 m ³ N	160 m ³ N	257 g	943 g
Destruction efficiency	99.5251 %							
Ratio	1		18.4	0.0292	0.00510	0.00263	0.000257	0.00187

No.3 Simulated sample ☐FB belt (FB belt 150mg/kg☐MSW☐

Item	Initial materials		Gas				Fly ash	Bottom ash
	MSW	FB belt	Flue gas at kiln exit	Flue gas at bag entry	Flue gas at bag exit	Flue gas at the final exit		
Concentration PCN	34 ng/g	2,800,000 ng/g	66,000 ng/m ³ N	47 ng/m ³ N	39 ng/m ³ N	3.3 ng/m ³ N	0.17 ng/g	1.2 ng/g
PCN volume PCN	340,000 ng	4,200,000 ng	8,980,000 ng	6,390 ng	5,620 ng	528 ng	61.4 ng	1,170 ng
Sample volume	10,000 g	1.5 g	136 m ³ N	136 m ³ N	144 m ³ N	160 m ³ N	361 g	972 g
Destruction efficiency	99.9612 %							
Ratio	1		1.98	0.00141	0.00124	0.000116	0.0000135	0.000258

(4) Congener specific analysis of PCNs

The PCNs congeners that are trace or absent in the FB belt or Halowaxes and the significant dominant PCNs congeners in fly ashes and emission gas from incinerations are #29, 44, 66, 67, 70.

They can be the combustion mark congeners⁸⁻⁹.

The major congeners in FB belt were #38/40 (17.1%), #21/24 (14.3%), #37/33/34 (13.2%). They can be the input mark congeners. We focused on these congeners for discussion of the influence of adding FB belt at kiln on combustion emissions. Figure 4 shows the transition of the mark congeners in 3 experiments. As for the combustion mark congeners, the ratio of total amount at kiln exit to input shows 107-161 (#44), 150-231 (#29), 145-223 (#66/67), and 2.45-3.55 (#70) respectively. The combustion mark congeners were clearly formed as by-product at the kiln by combustion. They were destroyed by the secondary combustion, and removed by the flue gas treatment. As for the input mark congeners (major congeners in FB belt), the ratio of total amount at kiln exit to input was largely changed among three experiments. In the 1st experiment, the ratio increased in 3 congener groups, 38/40, 21/24, 37/33/34, and therefore these congeners might be formed to some extent. In the 3rd experiment, the ratio decreased in 3 congener groups and therefore they were clearly destroyed by the kiln combustion. The bag filter and the activated carbon treatment also removed them. The results of congener specific analysis clearly showed that PCN congeners contained in FB belt were both destroyed and formed at the kiln by combustion.

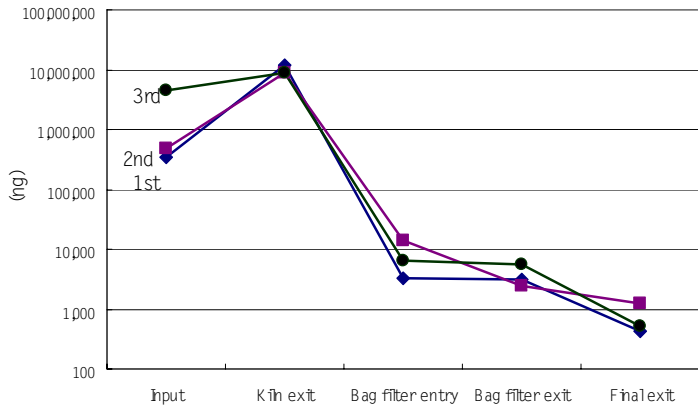
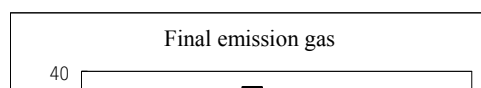
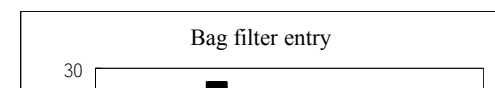
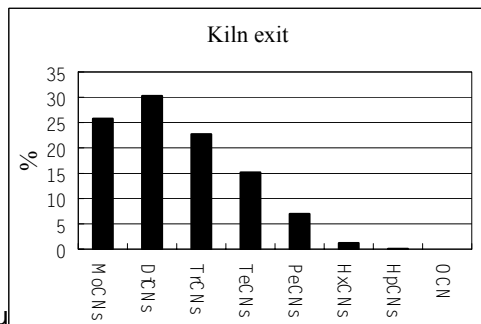
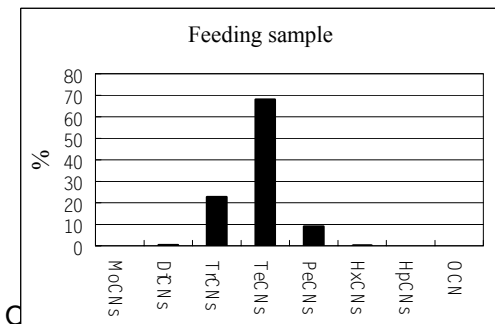


Figure 2 PCNs behavior in thermal process testing



When input PCNs were 340,000–4,540,000 ng in three tests, PCNs formed as by-product at the kiln was more than the input PCNs. Most of PCNs were destroyed by the secondary combustion and almost all PCNs were removed after a flue gas treatment. The destruction efficiencies in this system were calculated as 99.53% and 99.96%, and adding FB belt in two tests did not influence emissions to the environment. As for the major congeners in FB belt, #38/40, #21/24, #37/33/34, the ratio of kiln exit amount to input decreased, which

demonstrated original PCNs in the feed materials

were decomposed by the kiln combustion. Meanwhile, because the combustion mark congeners were largely formed as by-product, thermal treatment of FB finished products should be conducted in modern type of solid waste incinerators meeting current dioxin emission standards to assure acceptable emissions to the environment.

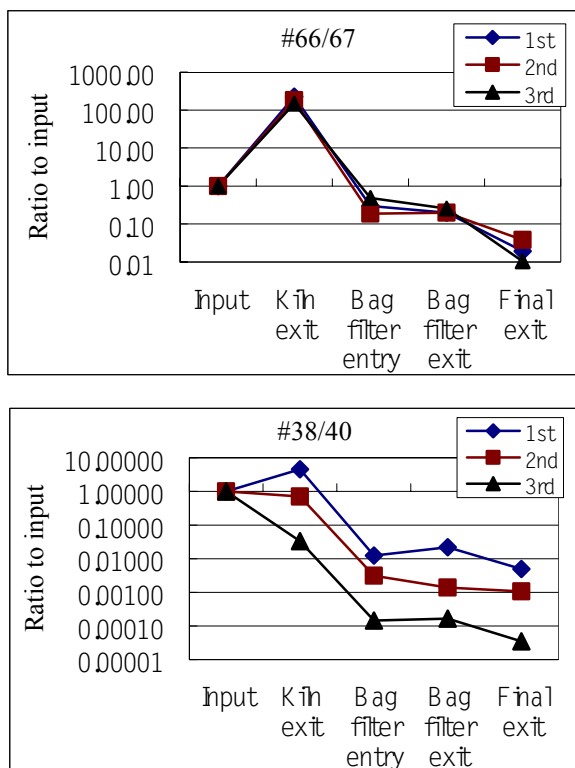


Figure 4 Transition of the mark congeners in 3 experiments

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