

# CHARACTERISTIC HOMOLOGUE AND ISOMER PATTERNS OF POLYCHLORIATED DIBENZOFURANS FROM PHENOL PRECURSORS

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## *Introduction*

In municipal waste incinerators, polychlorinated dibenzofuran (PCDF) byproducts are formed by two general pathways: homogeneous, gas-phase reactions, and heterogeneous, particle-mediated reactions. The former route, which is observed in post-combustion gas at temperatures between 500 and 700°C, occurs via precursors and strongly favors the formation of dibenzofuran and less chlorinated PCDF congeners<sup>1</sup>. The latter route, which is observed in particle collection devices at temperatures between 250 and 400°C, may involve precursors of similar structure or particulate carbon.

PCDF isomer patterns may provide fingerprints of formation mechanism<sup>2</sup>. For example, PCDF isomer patterns produced from polycyclic aromatic hydrocarbons on fly-ash have been compared to emissions from a fluidized bed incinerator<sup>3</sup>. In addition to the mechanisms described above, chlorination of less chlorinated congeners produced in the gas phase<sup>4</sup> and dechlorination of highly chlorinated congeners produced by *de novo* synthesis<sup>5</sup> have been proposed as factors that might control PCDF isomer distributions. Chlorination on catalytic surfaces has been found to occur dominantly at the 2,3,7,8 positions and they have shown broad PCDF distributions from DF chlorination<sup>6</sup>. PCDF congeners also can be controlled by chlorination patterns in stoker-type municipal waste incinerator<sup>7</sup>.

While PCDF distributions produced from individual precursor combinations have been studied<sup>8, 9</sup>, little is known about distributions from chlorinated phenol mixtures of typical incinerator exhaust gas. Only gas-phase PCDF congener patterns from all 20 phenols are available<sup>10</sup>. In this paper, we investigate and compare PCDF congener patterns on both gas-phase and particle-mediated reaction with CuCl<sub>2</sub>, presenting results using a distribution of phenol reactants of typical incinerator emissions.

## **Methods and Materials**

Experiments were conducted in an electrically heated, quartz tube flow reactor, 40 cm in length and 1.7 cm in diameter. A mixture of all 20 phenols dissolved in benzene was prepared to perform this study. Experimental conditions are shown in Table 1. For particle-mediated formation experiments, a 1 g particle bed of 1 cm height, consisting of silicon dioxide (SiO<sub>2</sub>, 99.6% purity, 325 mesh) and

0.5% (Cu mass) copper chloride ( $\text{CuCl}_2$ , anhydrous, 99.999+% purity) was prepared by mechanical mixing and was located at the center of the reactor. Experiments were conducted at 400°C and experimental durations were 100 and 240 minutes at two different concentration.

For gas-phase PCDF formation study (exp. no. 3,4, and 5), experiments were performed at three different temperatures 600, 650 and 700°C and experimental duration was 240 minutes.  $\text{N}_2$  and  $\text{O}_2$  were used as carrier gas for both gas-phase and particle-mediated reaction studies. Molar ratio of all 20 phenol mixture was obtained from published paper<sup>3</sup> in which they measured all phenol distributions from municipal waste incinerator. The distribution is shown in Figure 1.

**TABLE 1. Experimental Setting Used in Experiments in This Study**

exp. no.	condition	temp.(°C)	concentration (mol/min)		runs	duration (min)	
			organics*	$\text{N}_2$	$\text{O}_2$		
1	$\text{CuCl}_2\text{-SiO}_2\text{-N}_2\text{-O}_2$	400	1.20E-04	5.25E-03	4.56E-04	3	100
2	$\text{CuCl}_2\text{-SiO}_2\text{-N}_2\text{-O}_2$	400	5.00E-05	5.25E-03	4.56E-04	1	240
3	$\text{N}_2\text{-O}_2$	600	5.00E-05	4.22E-03	5.75E-04	1	240
4	$\text{N}_2\text{-O}_2$	650	5.00E-05	4.22E-03	5.75E-04	1	240
5	$\text{N}_2\text{-O}_2$	700	5.00E-05	4.22E-03	5.75E-04	1	240

\* organics = phenols + benzene

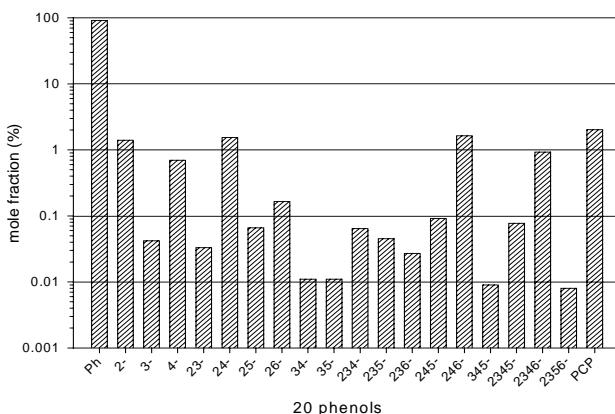


Figure 1. Distribution of phenol and 19 chlorinated phenols used in this study.

The entire product gas stream was rapidly quenched and samples were collected in an ice-cooled dichloromethane (DCM) trap. For particle-mediated formation study (exp. no. 1 and 2) the particles were thoroughly rinsed after each catalytic reaction experiment. Gas and rinse solutions were combined. For gas-phase reaction experiments, gas solution was directly obtained from

DCM. Sample solutions then were filtered and then analyzed by GC/MS (HP 6890 series gas chromatograph with model 5973 mass selective detector-EI type) with auto-sampler equipped with a HP-5MS capillary column with length 30m, i.d. 0.25mm and phase 0.25 $\mu$ m film of cross-linked 5% PH ME siloxane (J&W Scientific, CA). For identification the mass spectrometer was operated in the scan mode and in selected ion mode (SIM) for quantification.

## Results and Discussion

### PCDD and PCDF Formation

Total PCDD and PCDF yields from each experiment are given in Table 2, expressed in units of total phenol % conversion to PCDD/Fs during each experiment. Exp. no. 1 and 2 were conducted in particle-mediated environment with two different concentrations at 400°C, and exp. 3,4 and 5 were performed in homogeneous (gas-phase) environment without particle at three different temperatures of 600, 650 and 700°C.

TABLE 2. Yields of PCDD and PCDF (unit: % phenol conversion)

exp. no.	DF	MCDF	DCDF	T <sub>3</sub> CDF	T <sub>4</sub> CDF	P <sub>3</sub> CDF	H <sub>6</sub> CDF	H <sub>7</sub> CDF	OCDF	Total
1	0.877 $\pm$ 0.172	0.053 $\pm$ 0.005	0.024 $\pm$ 0.002	0.014 $\pm$ 0.002	0.009 $\pm$ 0.001	1.6E-4 $\pm$ 8.9E-5	3.6E-5 $\pm$ 2.3E-5	9.5E-6 $\pm$ 5.4E-6	4.8E-6 $\pm$ 3.3E-6	0.977 $\pm$ 0.177
2	0.323	0.013	0.005	0.002	0.001	4.00E-05	7.42E-06	1.85E-06	3.38E-07	0.344
3	2.370	0.066	0.043	0.013	0.008	1.00E-04	1.63E-05	nd*	nd	2.500
4	1.442	0.061	0.042	0.013	0.005	7.70E-05	9.34E-06	nd	nd	1.563
5	0.046	0.002	0.001	3.00E-04	2.78E-05	5.73E-07	nd	nd	nd	0.049
exp. no.	DD	MCDD	DCDD	T <sub>3</sub> CDD	T <sub>4</sub> CDD	P <sub>3</sub> CDD	H <sub>6</sub> CDD	H <sub>7</sub> CDD	OCDD	Total
1	0.031 $\pm$ 0.006	0.011 $\pm$ 0.002	0.008 $\pm$ 0.001	0.006 $\pm$ 0.001	0.008 $\pm$ 0.001	9.7E-4 $\pm$ 2.7E-4	4.4E-4 $\pm$ 1.5E-4	1.8E-4 $\pm$ 1.1E-4	3.2E-4 $\pm$ 3.8E-4	0.066 $\pm$ 0.009
2	0.024	0.009	0.005	0.003	0.004	2.90E-04	1.60E-04	1.50E-04	2.20E-04	0.046
3	3.77E-05	4.68E-05	nd	1.35E-04	1.04E-04	nd	nd	nd	nd	0.00032
4,5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
exp. no.	Ratio of DD+PCDD/DF+PCDF									
1	0.03535	0.20755	0.33333	0.42857	0.88889	6.06250	12.05479	18.94737	66.66667	0.06755
2	0.07430	0.69231	1.00000	1.50000	4.00000	7.25000	21.56334	81.08108	650.88757	0.13318
3	0.00002	0.00071		0.01038	0.01300					0.00013

For high reactant loading at 400°C (exp. no. 1), the average and standard deviation are shown. For both conditions of gas- phase and particle-mediated reaction, PCDD/Fs are observed. PCDF formation at gas-phase reaction (600 and 650°C) was 4.5-7.3 times higher than particle-mediated phase reaction (400°C) at the same concentration of phenol precursor and experimental duration. Even in the high concentration at 400°C, PCDF yield was 1.6-2.6 times lower than gas-phase condition (600 and 650°C). At high precursor concentration (exp. no. 1) at particle-mediated reaction experiment, more PCDF was produced over from low concentration (exp. no. 2). At 700°C, however, gas-phase PCDF formation was very low. This result shows that gas-phase PCDF formation (600 and 650°C) was favored over PCDF formation at particle-mediated reaction (400°C). DF was most favored from all experimental conditions. Other researchers also reported DF was found in most abundant amount from municipal waste combustion <sup>3, 4</sup>. Total PCDD

formation at particle-mediated phase at 400°C (exp. no. 1 and 2) was 144-206 times higher than gas-phase experiments at 600°C.

At gas-phase experiments of 650 and 700°C, no PCDD was detected from these experimental conditions. The ratio of PCDD(DD)/PCDF(DF) is also shown (last three rows of Table 2). At the particle-mediated phase experiments, ratio increased when chlorine substituents increased. The ratio of total PCDD(DD)/PCDF(DF) at particle-mediated phase experiments was 520-1025 times higher than gas-phase experiments. This results show that PCDD mostly formed from particle-mediated phase while PCDF are produced from both gas-phase and particle-mediated phases. Here we are focus on the PCDF homologue and isomer distributions formed from both gas-phase and particle-mediated experiments.

## PCDF Homologue Distributions

Figure 2 shows each homologue fraction of PCDF from different experimental conditions. As shown, PCDF homologue distribution was almost similar for all experimental conditions. The most abundant PCDF product was DF. The average of DF homologue fraction was 0.90 and 0.95 for particle-mediated and gas-phase reactions, respectively. Gas-phase DF formation was slightly higher than particle-mediated reaction. High yield of PCDF congeners with few chlorine substituents was also observed. This homologue distribution is also found in the municipal waste incinerator<sup>1</sup>. They observed that DF formation was most abundant and less chlorinated congeners were favored from municipal waste incinerator at all combustion conditions such as normal operation, at malfunction and after malfunction. DF and less chlorinated PCDF are formed from combination of two unchlorinated phenols and unchlorinated phenol and other chlorinated phenol. Next, the potential for using isomer patterns as PCDF characteristic or fingerprint of formation by phenol precursor mechanism is also considered.

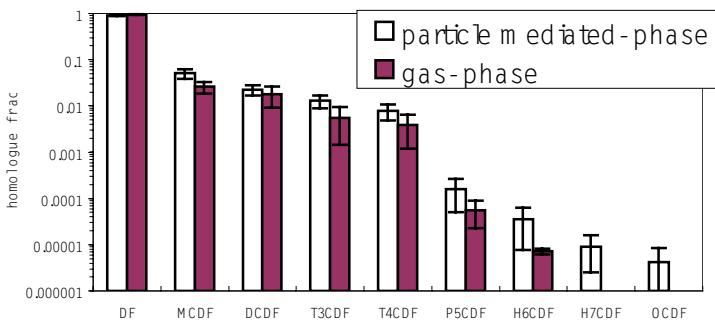


Figure 2. PCDF Homologue Fraction.

## PCDF Isomer Distributions

PCDF isomer distributions from gas- phase and particle-mediated reactions are shown in Figure 3. PCDF isomers that could not be separated are listed in groups. Isomer distributions of MCDF through H<sub>6</sub>CDF from particle-mediated reaction are very similar to those formed from gas-phase experiments. H<sub>7</sub>CDF isomers were not detected from gas-phase experiments. This result shows that PCDF isomer distributions are largely independent of experimental conditions such as temperature and gas-phase or particle-mediated phases even though total PCDF yield varied. This is evidenced by small standard deviation in isomer fraction for all experiments. However, there are a couple of exceptions on the order of isomer fraction between gas-phase and particle-mediated reactions. For T<sub>3</sub>CDFs, 1,2,4-T<sub>3</sub>CDF was most abundant from particle mediated-phase experiments, but 2,3,4-/3,4,7/1,4,9-T<sub>3</sub>CDF was also formed in abundant amount from gas-phase experiments. For P<sub>5</sub>CDFs, 1,2,3,4,8-P<sub>5</sub>CDF was major isomer from particle-mediated reaction experiment; however, in gas-phase experiments, 2,3,4,6,8-/1,2,3,4,7-/1,2,3,4,6- P<sub>5</sub>CDF was major products. As can be seen, PCDF isomers with one bay chlorine (1 or 9-positions) at particle-mediated phase experiments are greater than at gas-phase experiments. This is evidenced by higher isomer fractions of 1-MCDF, 1,3-, 1,4-DCDF, 2,4,9-/1,4,7-/1,3,4-, 1,2,4-, 1,2,7-/2,3,9-T<sub>3</sub>CDF at particle-mediated phase. All major isomer of each homologue group (MCDF – T<sub>4</sub>CDF) was formed from combination with unchlorinated phenol, which is present in very high amount. Unchlorinated phenol plays very important role in the formation of PCDFs from gas-phase and particle-mediated phase experiments. PCDF isomer distributions also show good agreement between gas- phase and particle-mediated formation. This homologue and isomer distribution can be used as a fingerprint or characteristic pattern of PCDFs formed from phenol precursors.

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## References

1. Zimmermann, R., Blumenstock, M., Heger, H.J., Schramm, K.-W., Kettrup, A.; (2001) Environ. Sci. Technol. 35, 1019.
2. Wehrmeier, A., Lenoir, D., Schramm, K.-W., Zimmermann, R., Hahn, K., Henkelmann, B., Kettrup, A.; (1998) Chemosphere 36, 2775.
3. Weber, R. and Hagenmaier, H.; (1999) Chemosphere 38, 529.
4. Wikstrom, E. and Marklund, S.; (2000) Environ. Sci. Technol. 34, 604.
5. Iino, F., Imagawa, T., Gullett, B.; (2000) Environ. Sci. Technol. 34, 3143.
6. Ryu, J.-Y., Mulholland, J.A., Chu, B.; (2003) Chemosphere 51, 1031.
7. Ryu, J.-Y., Mulholland, J.A., Dunn, J.E., Iino, F., Gullett, B.K.; (2004) Environ. Sci. Technol. (Submitted for publication).
8. Ryu, J.-Y. and Mulholland, J.A.; (2002) Proc. Combust. Inst. 29, 2455.
9. Ryu, J.-Y. and Mulholland, J.A.; (2004) Chemosphere (Submitted for publication).
10. Ryu, J.-Y., Mulholland, J.A., Oh, J.-E., Nakahata, D.-T., Kim, D.-H.; (2004) Chemosphere 55, 1447.
11. Blumenstock, M.; (1999) Ph.D. Thesis, Universitat Munchen.

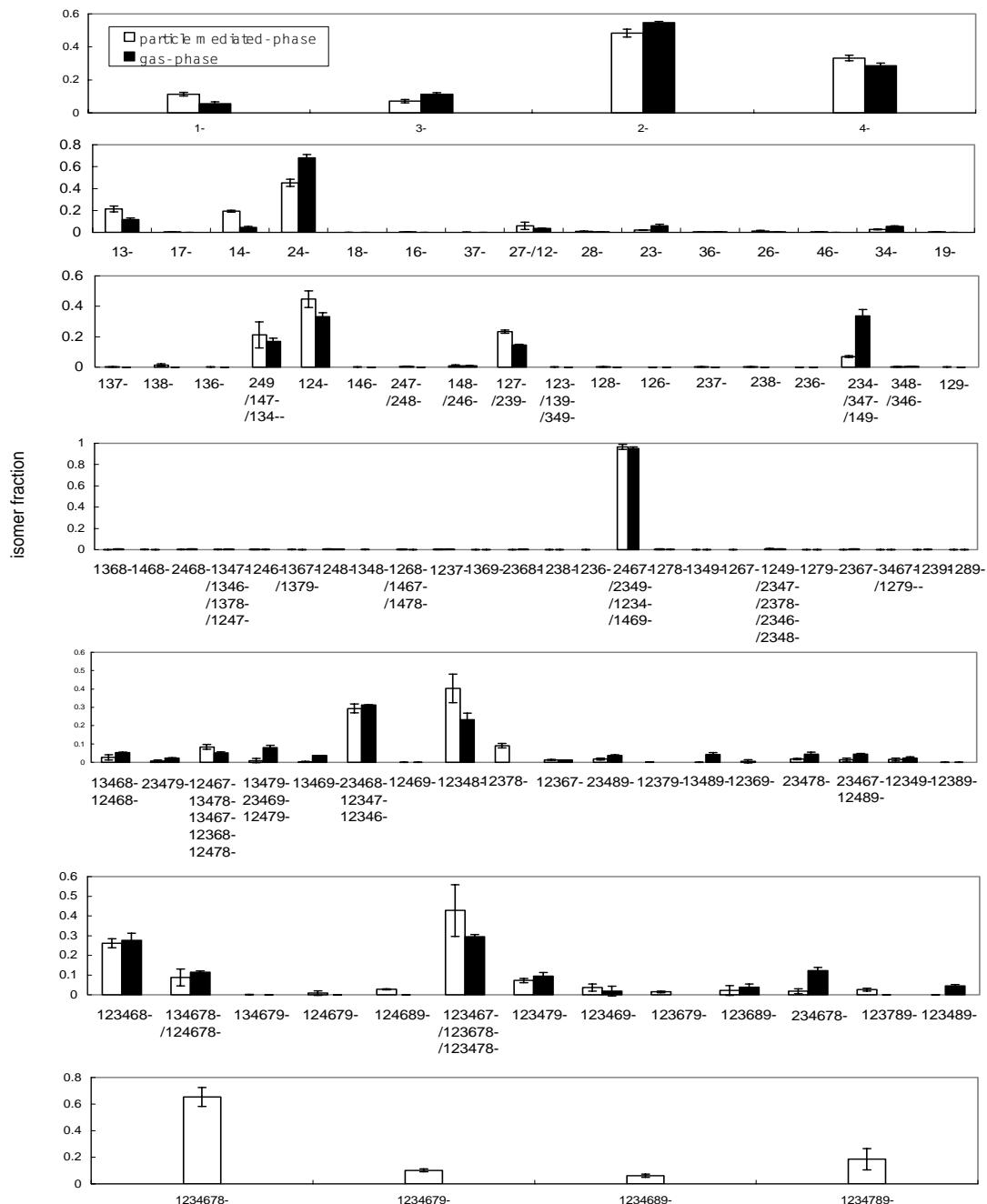


Figure 3. PCDF isomer distribution from gas-phase and particle-mediated phase experiments.