한국환경과학회지 제16권(제1호), 9~19, 2007
Journal of the Environmental Sciences

The Role of (Chloro-) Phenols in the Formation of Polychlorinated Dibenzofurans in Municipal Waste Incinerators

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(Manuscript received 25 September, 2006; accepted 10 November, 2006)

Comparing predicted PCDF isomer patterns with those obtained from a municipal waste incinerator assessed the role of two-phenol condensation pathways in the formation of PCDFs. Complete PCDF homologue and isomer distributions were obtained from a Fluidized Bed Incinerator (FBI). Two-phenol condensation model, dependent only on the distributions of phenols, was developed to predict the PCDF congeners produced from phenol precursors. R-squared values from linear correlations are presented for the dichlorinated through hexachlorinated isomer distributions between measured and predicted. They range from 0.003 to 0.1 for the dichlorinated through hexachlorinated isomer sets. Agreement between predicted and measured PCDF isomer distributions was very poor for all homologues. Two-phenol condensation pathways are not likely to be the predominant pathways in the formation of PCDF in a FBI. However, dibenzofuran (DF) is likely to be produced from a condensation of two phenols. This work demonstrates the use of PCDF homologue and isomer patterns for testing PCDF formation mechanism from two-phenol condensation pathways in municipal waste incinerators.

Key Words : Municipal waste incinerator, Thermal process, Combustion, Chlorophenols, Polychlorinated Dibenzofurans (PCDFs), PCDF Prediction model, Fluidized bed incinerator

1. Introduction

In combustion processes, polychlorinated dibenzofuran (PCDF) byproducts are known to be formed by two general formation pathways, which are precursor pathway and so-called '*de novo*' synthesis. The precursor pathway is the formation of PCDFs via similar structures, especially chlorinated phenols[1~3]. This pathway occurs through two different temperature windows: high temperature gas-phase formation around 650°C[4] and low temperature heterogeneous formation catalytically with the fly ash surface[5] between 200 and 500°C. The *de novo* synthesis is the formation of PCDFs between 200 and 500°C from carbonaceous material in soot, which releases PCDFs in the presence of oxygen and catalyst without the gas-phase precursors[6,7]. The mechanisms of PCDF formation have been studied extensively, including gas-phase condensation of phenoxy radicals[8] and flyash-mediated, metal-catalyzed formation from phenols,[9] polycyclic aromatic hydrocarbons[10], and graphitic carbon[11]. Nonetheless, there remains much uncertainty about the predominant pathway of PCDF formation in combustion systems.

To be used most effectively as a characteristic pattern, or fingerprint of PCDF formation mechanism, the complete distributions PCDF congeners are needed, not just the distributions of most toxic 2,3,7,8 congeners. Isomer patterns are independent of combustion conditions such as temperature, gas velocity etc[12~17]. The dominating congener patterns are controlled by specific formation mechanisms. The complete distributions of PCDF congeners provide a rich fingerprint that can be used to identify the formation

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mechanism.

A simple and algebraic model was developed to predict PCDF homologue and isomer distributions, based on two-phenol condensation reactions, using relative rates of PCDF products from phenols. The model can predict 9 PCDF homologue with DF and 135 congener distributions with reasonable accuracy from measurement of the distributions of phenols. This was already validated experimentally in a previous study[18]. Models are needed to help identify PCDF formation pathways in combustion systems and to develop more effective control strategies. In addition, the development of a predictive model might help to reduce the number of measurements necessary to characterize PCDF emissions. Extensive field monitoring of such a large number of congeners present in very low concentration is extremely time-consuming and expensive.

A model can be used to qualitatively assess the role of alternative PCDF formation mechanisms from phenols. In this study, we present a model in which PCDF homologue and isomer distributions are predicted from the distributions of phenols obtained in a municipal waste incinerator, based on relative rates of PCDF products from phenols. We use predicted homologue and isomer patterns to assess the role of two-phenol condensation pathways on PCDF formation by comparing PCDF homologue and isomer patterns obtained in a municipal waste incinerator. This approach would be likely to provide valuable information on complete PCDF congener patterns formed by two-phenol condensation pathways from phenols in municipal waste incinerators.

2. METHODS

2.1. PCDF Formation Mechanism from (Chloro-) Phenols

Born *et al.* first proposed a detailed chemical mechanism of gas-phase PCDF formation by condensation of two phenols[8]. We do not address the detailed formation mechanism on metal-mediated phase, which involves adsorption, reaction, and desorption; other researchers have proposed reaction mechanisms analogous to the Ullmann II reaction[19]. Recently, a metal-catalyzed PCDF formation mechanism from two phenols is proposed[20]. They have shown that the major PCDF products from chlorinated phenols on CuO/Silica surface are the same as those predicted and observed for the gas-phase reaction. To give better understanding of PCDF formation pathways, gas-phase PCDF formation pathways from two 3-monochlorophenol are shown in Fig. 1. Carbon-carbon coupling of phenoxy radicals at unchlorinated *ortho* sites followed by enolization results in the formation of a *o,o*-dihydroxybiphenyl (DOHB) intermediate. Subsequent elimination of water leads to the PCDF products. This reaction occurs with no loss of chlorine. All direct PCDF products from condensation of two phenols are shown in Table 1. Note that 2,6 chlorinated phenol precursors (*ortho*-positions are fully occupied with chlorine) are not included as these do not directly produce PCDF products. Dibenzofuran and each of the 135 PCDFs are produced by a unique coupling of a phenoxy radical pair (Note: In this paper, PCDF refers to all chlorinated dibenzofurans, from mono- through octa-).

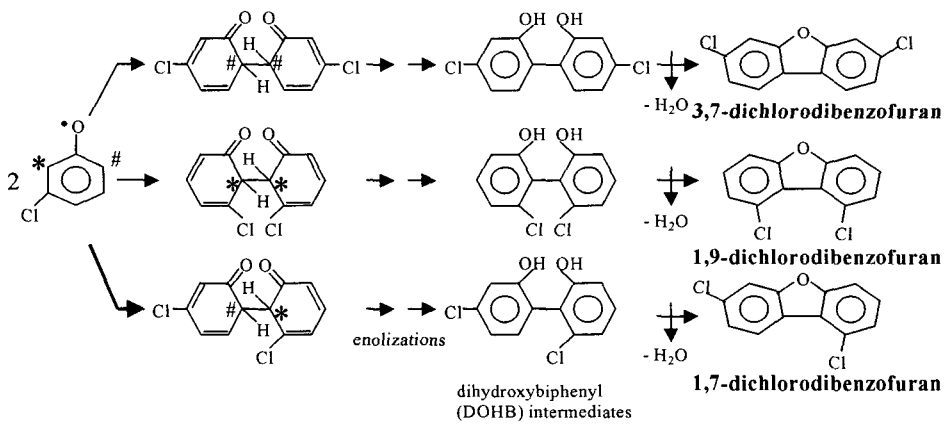

Fig. 1. PCDF formation pathways from two 3-monochlorophenols.

Table 1. PCDF Congeners from Two-Phenol Condensation Pathways [a]

	ph	2-CP	3-CP	4-CP	23-DCP	24-DCP	25-DCP	34-DCP	35-DCP	234-T_3CP	235-T_3CP	245-T_3CP	345-T_3CP	2345-T_4CP
phenol	DF													
2-CP	4	46												
3-CP	1, 3	16, 36	17, 19, 37											
4-CP	2	26	18, 27	28										
23-DCP	34	346	347, 349	348	3467									
24-DCP	24	246	247, 249	248	2467	2468								
25-DCP	14	146	147, 149	148	1467	1468	1469							
34-DCP	12, 23	126, 236	127, 129, 237, 239	128, 238	1267, 2367	1268, 2368	1269, 1478	1278, 1289, 2378						
35-DCP	13	136	137, 139	138	1367	1368	1369	1279, 1378	1379					
234-T_3CP	234	2346	2347, 2349	2348	23467	23468	23469	23478, 23489	23479	234678				
235-T_3CP	134	1346	1347, 1349	1348	13467	13468	13469	13478, 13489	13479	134678	134679			
245-T_3CP	124	1246	1247, 1249	1248	12467	12468	12469	12478, 12489	12479	124678	124679	124689		
345-T_3CP	123	1236	1237, 1239	1238	12367	12368	12369	12378, 12389	12379	123678	123679	123689	123789	
2345-T_4CP	1234	12346	12347, 12349	12348	123467	123468	123469	123478, 123489	123479	1234678	1234679	1234689	1234789	OCDF

[a] Phenols with both *ortho* sites chlorinated do not produce PCDF congeners.

2.2. A PCDF Prediction Model from Two-Phenol Condensation Pathways

The formation of dibenzofuran (DF) from phenol (Ph) in combustion gas exhaust is summarized by the following set of reactions.

(1) Ph → PhR + H

(2) Ph + X → PhR + HX where X = H, OH, Cl, ...

(3) PhR → decomposition products

(4) PhR + PhR ⇆ PhR-PhR → → DOHB → DF + H_2O

Phenoxy radicals (PhR) produced by reactions (1) and (2) can either be consumed by decomposition (reaction 3), such as CO elimination, or by dimerization which leads to the formation of DF via the o,o-dihydroxybiphenyl intermediate (reaction sequence 4).

Assuming pseudo-steady state concentrations of intermediates in reaction sequence 4, the rate of DF formation (R_{DF}) is given as follows.

(5) $R_{DF} = k_{4,eff}\,[PhR]^2$

The overall rate of DF formation from phenol is defined as follows.

(6) $R_{DF} = k_{eff}\,[Ph]^n$

Here, k_{eff} is an effective rate constant and n is the order of reaction with respect to phenol. The value of n is expected to lie between 1 and 2, as discussed below.

In the limit that phenoxy radical is consumed pre-

dominantly by reaction (3), the pseudo-steady state approximation for PhR yields the following.

(7) $d[PhR]/dt = 0 = R_1 + R_2 - R_3$

(8) $[PhR] = \{(k_1+k_2)/k_3\}\ [Ph]$

Plugging equation 8 into equation 5, the order with respect to phenol (n) is found to be 2. In the other limit in which the predominant phenoxy radical consumption pathway is reaction (4), the pseudo-steady state approximation for PhR yields the following.

(9) $d[PhR]/dt = 0 = R_1 + R_2 - 2\ R_{4,eff}$

(10) $[PhR] = \{½(k_1+k_2)/k_{4,eff}\}^{½}\ [Ph]^{½}$

Plugging equation 10 into equation 5, the order with respect to phenol (n) is found to be 1.

Extending equation 6 to any of the 135 PCDF congeners, the overall rate of formation of PCDF congener i is written as follows.

(11) $R_i = k_{eff,i}\ [Ph1_i]^{n/2}\ [Ph2_i]^{n/2}$

Here, Ph1 and Ph2 are the pair of phenol precursors. For simplicity, we assume that the order with respect to each phenol reactant is the same (n/2). Without this simplification, 270 values of n would be needed; the validity of this assumption was evaluated elsewhere[18].

The relative rate of formation of PCDF congener i to PCDF congener j is given as follows.

(12) $R_{rel,i/j} = [PCDF_i] / [PCDF_j] = k_{rel,i/j}\ \{[Ph1_i]\ [Ph2_i] / ([Ph1_j]\ [Ph2_j])\}^{n/2}$

Each PCDF congener is formed from only one pair of phenol precursors. To calculate the distribution of PCDF congeners produced from the distributions of phenol reactants, 135 relative rate constants, $k_{rel,i/j}$, and the reaction order, n, are needed. Gas-phase PCDF prediction model with relative rate constants and average reaction order from phenol precursors is well described elsewhere[18]. The prediction of total PCDF yield was not discussed at this stage, but the addition of one absolute rate constant would allow for total PCDF yield to be calculated.

PCDF prediction model can be applied to PCDF congener distributions from phenol precursors on metal-mediated phase. The total PCDF yield was different between gas-phase and metal-mediated formations. However, PCDF homologue and isomer distributions from the experiments with phenols have shown remarkably similar distributions[21]. For this model to be run, the distributions of all phenols as model inputs are needed, and PCDF congener distributions in MWI are also needed for comparison with predicted PCDF congeners. This will be discussed in the following section.

2.3. Municipal Waste Incinerator Data.

To assess the potential role of two-phenol condensation pathways in PCDF formation, using two-phenol condensation model, distributions of all phenols as model inputs are needed for running this model. In addition, PCDF homologue and isomer distributions are also needed to compare with predicted PCDF homologue and isomer distributions. Available municipal waste incinerator emission data that include a complete characterization of PCDF congeners (mono through octachlorinated-) and distributions of phenols together are very limited. Therefore, published data[22,23] were used for taking model inputs and PCDF congeners in MWIs. Weber and Hagenmaier[22] measured all phenol distributions at four sampling points of furnace-out, electrostatic precipitator-inlet, electrostatic precipitator-outlet and fly-ash from a fluidized bed incinerator (MWI-A). Zimmermann *et al.* also have shown most of phenol distributions in a municipal waste incinerator (MWI-B)[23]. They measured phenols at post-combustion region at three different operating conditions of normal, malfunction, and 1 hour-after malfunction. Molar distributions of phenols measured in MWI-A and MWI-B are shown in Fig. 2, respectively. The concentrations of chlorinated phenols at each point and operating condition varied considerably, but most abundant chlorinated phenols were largely constant. For instance, high concentrations of

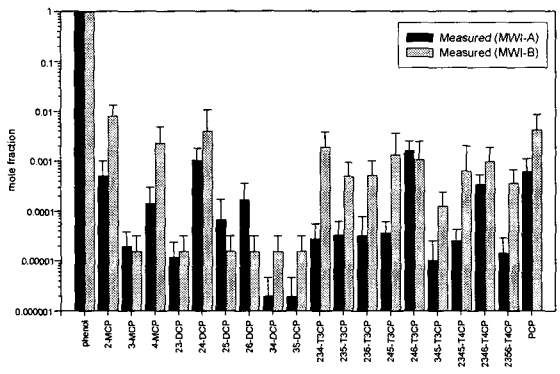

Fig. 2. Molar distributions of 20 phenols obtained in two municipal waste incinerators (MWI-A and B). Error bars represent ± one standard deviation.

phenols were 2-CP, 4-CP, 2,4-DCP, 2,4,6-T_3CP, 2,3,4, 6-T_4CP and PCP, although the concentration of 2,3,4- and 2,4,5-T_3CP were higher than 2,4,6-T_3CP in MWI (B). Similar phenol distributions are found in studies of other researchers from MSW combustion[24,25]. In the phenol measurements (MWI-B), 3- MCP, 2,3-, 2,5-, 2,6-, 3,4-, and 3,5-DCP were not detected, which were assumed as one-order lower values than minimum detected. For example, one- order lower values are given to 3-MCP, 2,3-, 2,5-, 2,6-, 3,4-, and 3,5-DCP than 3,4,5-T_3CP, which was detected at the lowest amount. Operating conditions, sampling, and analytical methods are described in detail elsewhere[22,23].

3. RESULTS AND DISCUSSION

3.1. Measured and Predicted PCDF Homologue Distributions.

Measured and predicted PCDF homologue distributions are presented for two municipal waste incinerators in the top (MWI-A) and bottom (MWI-B) of Fig. 3. In a MWI-A, sampling was performed at before and after electrostatic precipitator at low temperature around 300°C. The average PCDF homologue distributions are given here. Predicted PCDF homologue distributions were obtained from PCDF prediction model using four formulations of phenols measured at furnace-out, electrostatic precipitator-inlet, electrostatic precipitator-outlet and fly ash sample. Average and ± one standard deviations are given for four predicted PCDF homologue distributions. Predicted homologue distributions are almost constant. Predicted PCDF homologue fractions decreased drastically with increasing the number of chlorine substituents, whereas measured PCDF fractions slightly increased. In the case of OCDD molar fraction, seven orders of difference are shown between measured and predicted.

In a MWI-B, sampling was conducted at the outlet of the post-combustion chamber at temperatures between 650 and 880°C prior to any emission reduction devices. Predicted PCDF homologue distributions were calculated based on five measurements of phenol distributions obtained at the same sampling point. Sampling was performed at three different operating conditions (normal condition-three times, malfunction condition-once, and 1 hour after malfunction-once). Average and ± one standard deviations are given for five predicted PCDF homologue

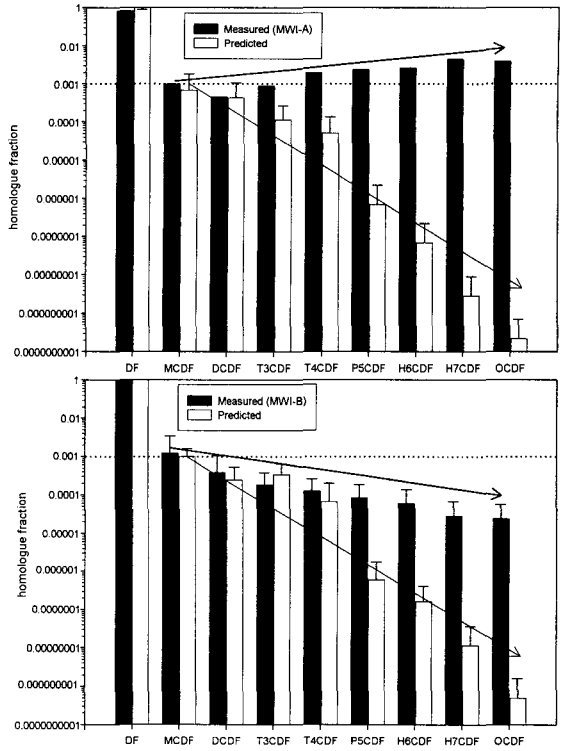

Fig. 3. PCDF homologue patterns measured in two municipal waste incinerators and predicted by model (black: measured; white: predicted). Error bars represent ± one standard deviation.

distributions. PCDF homologue distributions between measured and predicted are constant. Predicted PCDF homologue distributions decreased with increasing the number of chlorine substituents, as in MWI-A, and measured PCDF homologue distribution steadily decreased, too. Homologue distribution patterns between measured and predicted are very similar in a MWI-B.

From two municipal waste incinerators, predicted DF was most abundant and less chlorinated PCDF congeners were favored over higher chlorinated congeners. Two measured PCDF homologue patterns (MWI-A and MWI-B) clearly show that dominant PCDF formation pathways are considerably different. Comparison of homologue patterns between measured and predicted shows that model predicts reasonably for DF and lower chlorinated PCDF (DF through DCDF for MWI-A and DF through T_4CDF for MWI-B). Especially, DF fraction between predicted and measured very well matched, showing 1,000 times higher than other total PCDF concentration in

municipal waste incinerators[22,23]. Similar observation was obtained from another study. Wikstrom and Marklund[13] have also shown DF fraction was 99.9% and 99% at before and after convector from a municipal waste combustion. DF is likely to be formed from the condensation of two unchlorinated phenols. Many PCDF formation mechanisms have been proposed, but no evidence have been reported on DF formation except for phenol condensation. Recently, Wikstrom *et al.* performed experiments with soot deposit as a carbon source for PCDF formation (*de novo* synthesis), but DF was below detection limit[26]. This is not agreeing to the truth, which DF concentration is very high from municipal waste incinerator exhaust gases, as shown above. An important point to emphasize here is unchlorinated phenol, at least, plays a major role in the formation of DF, which is not formed from carbon matrix by *de novo* synthesis. However, it is hard to conclude, at this stage, that lower chlorinated PCDFs are produced from phenol condensation pathways before looking at PCDF isomer distributions. Homologue patterns can be easily changed by combustion conditions, such as a chlorine/hydrogen ratio and temperature[27]. Predicted homologue patterns here can be used as a PCDF characteristic or fingerprint of formation by two-phenol condensation pathways from phenols in the combustion processes, either in high temperature or low temperature regions.

3.2. Predicted PCDF Isomer Distributions in MWI-A and MWI-B

Predicted PCDF isomer distributions from MWI-A and MWI-B were presented in Fig. 4. All PCDF isomer distributions were calculated based on phenol distributions measured in both MWI-A and MWI-B. Phenol distributions used for calculations are shown in Fig. 1. PCDF prediction model was run with phenol distributions of four measurements for MWI-A, and run with phenol distributions of five measurements for MWI-B for three different operating conditions. Average isomer fractions are shown with ± one standard deviations. Predicted PCDF isomer distributions by two-phenol condensation pathways are highly similar to each other (MWI-A and MWI-B), though measured phenol distributions are slightly different. PCDF major congeners are always constant, except for H_6CDF. 1,2,3,4,6,8-H_6CDF is predicted in the highest isomer in MWI-A, but 2,3,4,6,7,8-H_6CDF is the biggest isomer in MWI-B. 1,2,3,4,6,8-H_6CDF is formed from a condensation of 2,4-DCP and 2,3,4,5-T_4CP, and 2,3,4,6,7,8-H_6CDF is formed from a condensation of two 2,3,4-T_3CP. As shown Fig. 1, 2,3,4-T_3CP is much higher than 2,4-DCP and 2,3,4,5-T_4CP in MWI-B. This result shows that predicted PCDF isomer patterns formed from two-phenol condensation pathway are almost consistent in the two different MWI-A and MWI-B. Although two municipal waste incinerators have two different dominant PCDF formation mechanisms, PCDF congener patterns formed from phenols will show very similar distributions.

3.3. Predicted and Measured PCDF Isomer Distributions in a MWI-A

Fig. 5 presents PCDF congener distributions between measured in MWI-A and predicted with phenol distributions obtained at the same incinerator. PCDF congener patterns are not available in the MWI-B. Measured PCDF congeners are obtained as an average of two measurements at before and after electrostatic precipitator in the incinerator. Again, predicted PCDF isomers were calculated based on phenol distributions of four measurements in MWI-A. Error bars represent ± one standard deviations for four predicted PCDF isomers. Distinct differences between measured and predicted are observed for seven homologue groups, to a lesser extent, MCDF isomer distributions appear to be predicted by this model. For example, model predicted higher yields of 2,4-DCDF, 1,3,4-/2,4,9-T_3CDF, 1,2,3,4-/2,3,4,9-T_4CDF, 1,2,3,4,8-P_5CDF, 1,2,3,4,6,8-H_6CDF, and 1,2,3,4,6,7,8-H_7CDF congeners. However, 2,3-DCDF, 1,2,3-/2,4,7-/3,4,6-T_3CDF, 2,4,6,7-/2,3,4,6-/3,4,6,7-T_4CDF, 2,3,4,6,8-/2,3,4,6,7-H_5CDF, 2,3,4,6,7,8-H_6CDF, 1,2,3,4,6,8,9-H_7CDF were found to be in the highest amount from a municipal waste incinerator. These congeners are found to be in high amount in another study with fluidized bed combustion[28]. This tells us fluidized bed incinerators have very similar PCDF formation mechanisms.

Correlation coefficients were computed to quantify the degree of agreement between measured PCDF isomer distributions in MWI-A and those predicted by the model with four different phenol distributions obtained in MWI-A. In Table 2, R-squared values from linear correlations are presented for the dichlorinated

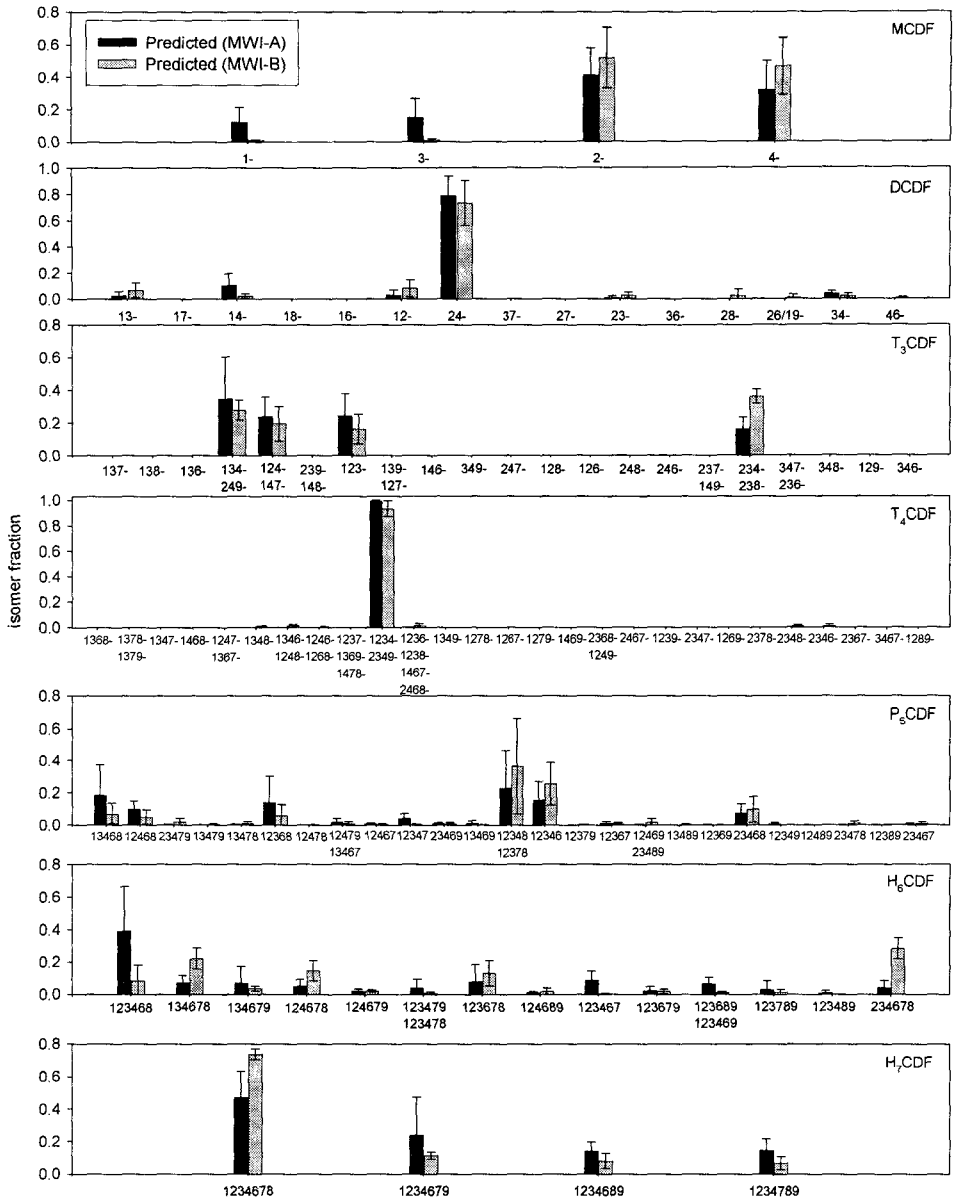

Fig. 4. Comparison of PCDF congeners predicted with 20 phenol distribution measured at MWI (A) and (B). Error bars represent ± one standard deviation.

through hexachlorinated isomer distributions. Analysis of the monochlorinated and heptachlorinated isomer distribution is not included because the number of these isomers is small. It is known that the isomer patterns are independent of combustion conditions even under conditions that provide different homologue distributions. Two-phenol condensation pathways may partly contribute PCDF formation, but this result (isomer comparison) shows it likely to be not a predominant pathway in the formation of PCDFs in a fluidized bed incinerator.

Looking at MCDF and H_7CDF congener patterns measured closely, MCDF isomer patterns are typical chlorination pattern (2,3,7,8-positions favored) and H_7CDF isomer pattern is dechlorination pattern (1,4,6,9-positions favored). Therefore, chlorination of less chlorinated congeners (including DF) produced in the gas phase is probably the main pathway to form PCDF congeners[13,29]. They concluded chlorination reaction from DF and lower chlorinated PCDF isomers

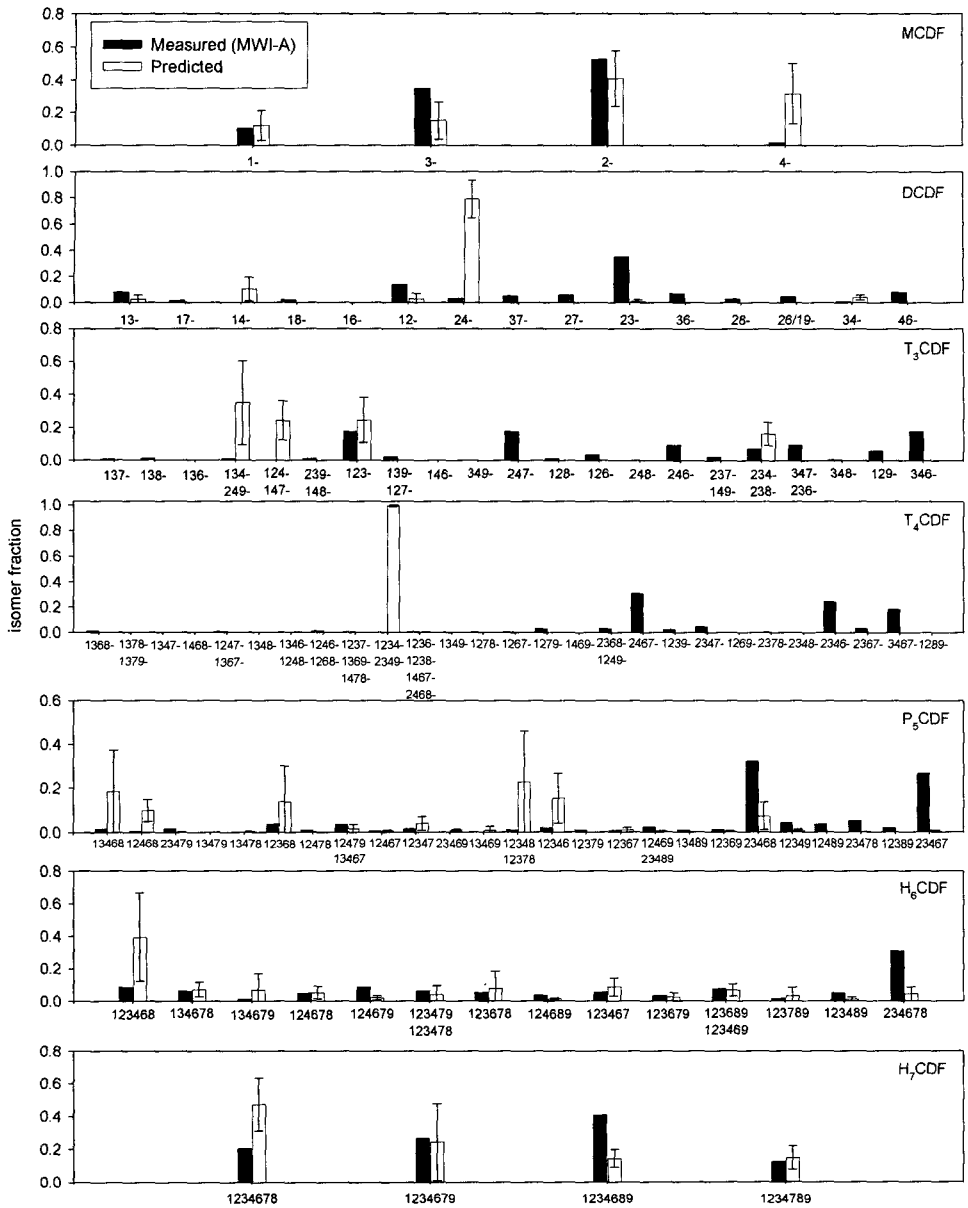

Fig. 5. Comparison of PCDF congeners measured (black) at MWI (A) and predicted (blank). Error bars represent ± one standard deviations.

was a crucial pathway in the formation of PCDF isomers. Recently, Tuppurainen *et al*[30]. also reviewed PCDF formation pathways from MWI and other combustion processes and speculated that chlorination pathway is the main pathway of PCDF formation. Depending on the combustion conditions or chlorine abundance, dechlorination of highly chlorinated congeners produced by *de novo* synthesis could be dominant PCDF formation mechanism[16]. Therefore, chlorination model based on MCDF isomer distribution and dechlorination model based on H_7CDF isomer distribution run to compare PCDF isomer patterns with those predicted, as performed before[16,29]. In Table 2, R-squared values from linear correlations are presented for the dichlorinated through hexachlorinated isomer distributions between measured and predicted by chlorination and dechlorination models. Again, analysis of the monochlorinated and heptachlorinated isomer distributions not included because the number of these isomers is small. The R-squared values show

Table 2. Correlation Results between Mean observed and Predicted Isomer Distributions Figures Represent Linear Correlation R-squared Values

	Two-phenol condensation pathways					Chlorination	Dechlorination
	Furnace-out	ESP-inlet	ESP-outlet	Fly ash	Average		
DCDF	0.0053	0.0267	0.0111	0.0138	0.0135	0.3040	0.1050
T_3CDF	0.0007	0.0063	0.0147	0.0999	0.0083	0.0001	0.0115
T_4CDF	0.0079	0.0080	0.0079	0.0079	0.0079	0.0321	0.0019
P_5CDF	0.0034	0.0037	0.0011	0.0442	0.0003	0.0067	0.0004
H_6CDF	0.0083	0.0121	0.0044	0.0239	0.0029	0.0478	0.0058

PCDF isomer distributions are completely different between measured and predicted. Other municipal waste incinerators also have shown different PCDF isomer patterns formed from two-phenol condensation pathways[16,29].

Results presented here indicate that, based on isomer patterns, two-phenol condensation pathways (precursor) are likely not a predominant pathway of PCDF formation in a fluidized bed incinerator. We can point out that there may be other major pathway(s) of PCDF formation that affect isomer distributions. For example, *de novo* reactions from carbon matrix or formation from precursors other than phenols may contribute directly to the formation of PCDF congeners. Weber and Hagenmaier postulated PCDF could be formed from condensation reactions of phenols and benzenes[22] or *de novo* synthesis from polycyclic aromatic hydrocarbons[31]. In addition, multiple mechanisms may contribute simultaneously to the formation of PCDF congener distributions. Hell *et al*[32]. suggested that 99% of PCDF are directly released from performed structures in the amorphous carbon matrix partly via chlorinated phenols, implying that *de novo* synthesis and precursor pathway may be closely related.

4. CONCLUSIONS

The results presented in this paper provide a means for testing on PCDF formation mechanism from two-phenol condensation pathways in combustion systems. Presented here is a model application that predicts the PCDF congener distributions from distributions of phenols measured in municipal waste incinerators. The role of phenol condensation pathways in the formation of PCDF in a municipal waste incinerator was assessed by comparing predicted PCDF homologue and isomer patterns with those obtained from the incinerator. Two-phenol condensation pathways are not likely to be the predominant pathways in the formation of PCDF in a FBI.

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