



Experimental and modeling study of de novo formation of PCDD/PCDF on MSW fly ash

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Abstract

The effect of sulfur dioxide (SO₂) on the formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) has been studied in an entrained-flow reactor (EFR) under simulated waste combustion conditions. A chlorination model based on conditional probability was employed to evaluate the homologue patterns of PCDDs and PCDFs. Results revealed that the presence of SO₂ did not alter the formation pathway although SO₂ suppressed PCDD/F formation. The prediction model of PCDF showed good agreement with the experimental data ($R=0.95$), whereas the prediction for PCDDs did not correlate well with the experimental data. This may be explained because potential chlorination pathways play a significant role in PCDF formation, whereas PCDDs are mainly formed through condensation reactions. Furthermore, the result indicated that the steric hindrance during formation has more effects on PCDD than on PCDF due to the symmetric molecular structures of PCDDs.

Key words: PCDDs; PCDFs; de novo synthesis formation; chlorination model; sulfur dioxide; air pollution; waste; combustion

Introduction

Municipal solid waste (MSW) incineration has been considered as one of the major sources of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs). PCDDs/Fs can be formed via both homogeneous and heterogeneous reaction pathways. The heterogeneous de novo synthesis formation may play a very important role in determining the final yield of PCDDs/Fs (Huang and Buekens, 1995; Stanmore, 2004; Vogg *et al.*, 1987).

For the de novo synthesis formation of PCDDs/Fs, chlorination is essential (Buekens *et al.*, 1998; Stieglitz *et al.*, 1991). In the presence of particular metal ion catalysts, C–Cl bonds can be formed by direct combination of molecular chlorine and carbon, or by combination of chlorine ion and carbon. The dechlorination from OCDD/F is also a potential pathway for the formation of higher chlorinated congeners (Iino *et al.*, 2001); however, the chlorination of MoCDDs/Fs may also account for the formation of some congeners of higher chlorinated homologue groups (Webber *et al.*, 2001).

Models for predicting PCDD/F formation still need further development because of the lack of understanding of the key reactions and factors involved. Research

has indicated that the condensation of two phenol radicals might be the major pathway of PCDD formation (Louw and Ahonkahai, 2002), whereas the condensation of aromatic precursors was of minor importance in the formation of PCDF (Hell *et al.*, 2001). A dechlorination model was developed to predict the homologue profile of PCDD/F (Iino *et al.*, 2001). This model showed good performance in predicting higher chlorinated homologues, but was less satisfactory when applied to lower chlorinated homologues.

It is important to further understand the mechanisms and pathways of PCDD/F formation through both modeling studies and experimental investigations. Such an understanding is vital to improve the design and operation of combustion processes such as MSW incineration as well as to develop models to predict the formation during online monitoring.

In this article, a series of experiments was conducted using an entrained-flow reactor (EFR) system to investigate the effect of sulfur dioxide (SO₂) on PCDD/F formation. Results from these experiments and model predictions were compared, and the mechanisms of PCDD/F formation were discussed. The modeling study may provide the correlation for low chlorinated congeners, the homologue profile of PCDDs/Fs, and values of the toxicity measure, or Toxic Equivalence (TEQ).

1 Model and experiment

1.1 Chlorination model

A chlorination model (Ryu, 2004) developed recently is used in this study. Both dibenzo-*p*-dioxins (DD) and dibenzofurans (DF) can be chlorinated at eight sites to form PCDDs and PCDFs, as illustrated in Fig.1.

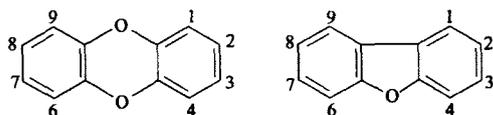


Fig. 1 Dibenzo-*p*-dioxin and dibenzofuran.

Because of the symmetry in the molecular structures of DD, the probabilities of chlorinating the 1, 4, 6, 9 carbon sites, $P(1)$, $P(4)$, $P(6)$, and $P(9)$, are the same; similarly, the probabilities of chlorinating the 2, 3, 7, and 8 positions, $P(2)$, $P(3)$, $P(7)$, and $P(8)$, are also equivalent. The probability of chlorinating the one carbon site, $P(1)$ is defined as A for DD, and $P(2)$ is B , which is equal to $0.25 \times (1-A)$. Similarly, we define the probability of chlorinating 1, 2, and 3 carbon sites for DF, $P(1)$, $P(2)$, and $P(3)$, as X , Y , and Z , respectively, and $P(4)$ as W . Therefore, W is equal to $0.5 \times (1-X-Y-Z)$ (Ryu *et al.*, 2004). For this model, it is assumed that the probability of chlorinating a specific carbon atom is not affected by the chlorination of other sites. This means that the steric hindrance effect is neglected in this chlorination model. Such an assumption has its limitations when practically applied, which will be addressed in the Section 2.

The chlorination model (Ryu *et al.*, 2004) can be expressed as:

$$F(i) = S(i)P(i) \quad (1)$$

$$P(i) = \sum_{j=1}^n P(j)P(i|j) \quad (2)$$

Here, $F(i)$ is the isomer fraction within the congeners and $S(i)$ is the number of expressions for the same isomer. For example, 1,2-, 3,4-, 5,6-, 7,8-DiCDDs have actually the same expression as 1,2-DiCDD although they are produced via different pathways of chlorination; thus $S(12)=4$. $P(i)$ is the probability of forming the i th isomer by chlorinating one additional carbon, where $1 \leq i \leq 8$.

1.2 Experiment

The experiments were conducted using an entrained flow reactor, EFR, as illustrated in Fig.2. The system included two major parts: (1) a horizontal reactor, which was composed of an inner and outer quartz tube for preheating gases; and (2) a vertical reactor, also with concentric tubes, into which fly ash was fed by a mechanical vibrating device. The reacting gas was introduced into the system from Ports A or B, as illustrated in Fig.2, depending upon the desired study temperature. The residence time in the horizontal reactor for gas flow was approximately 0.5 s, and the temperature was controlled at 1000°C. The residence time in vertical reactor was about 1.3 s, and the temperature was 400°C. The fly ash used for this study was originally collected from the electrostatic precipitator of a MSW incinerator located in USA. This fly ash was pre-extracted with toluene in a Soxhlet extractor for 24 h and dried at 500°C in a flow of nitrogen. This fly ash has been used in extensive studies of PCDD/F formation in the EFR by Wikström *et al.*, (2003a, b, 2004a, b). The properties of the fly ash are shown in Table 1.

The sampling for PCDDs/Fs from the exit of the EFR was conducted according to a modified version of US EPA Method 23, and the analysis was carried out according to Method 8280B using a high-resolution gas chromatograph/low resolution mass spectrometer (HRGC/LRMS). A detailed description of the method can be found in Wikstrom *et al.* (2003a).

The experimental matrix is shown in Table 2. SO_2 and chlorine (Cl_2) were both added at Port B, into the annulus of the vertical reactor where the gas was preheated to 400°C before mixing with the combustion gas and fly ash at the top of 400°C region. The total sampling time for each run was 120 min, and fly ash was fed at a rate of 1 g/h throughout the experiment.

2 Results and discussion

2.1 SO_2 effect on PCDD/F formation

PCDD/F formation results are shown in Fig.3. Run No.3 (109 ppm SO_2) was conducted thrice to determine the reproducibility of the experiments, and the maximum plus-minus standard derivation is graphically shown in Fig.4. The formation of PCDFs was favored over PCDDs, likely indicating that de novo synthesis formation might be the major pathway. The overall inhibition of PCDD/F

Table 1 Fly ash properties (wt %)

Surface area, m ² /g	Cu	Fe	Mg	Ca	Si	Pb	Al	S	Zn
4.24	0.17	0.93	0.41	4.01	8.54	1.51	2.67	0.00064	4.98

Table 2 Experimental matrix

Run No.	SO_2 (ppm)	Cl_2 (ppm)	Flame	Vertical reactor temp. (°C)	Horizontal reactor temp. (°C)
1	0	109	No Soot	400	1000
2	55	109	No Soot	400	1000
3	109	109	No Soot	400	1000
4	226	109	No Soot	400	1000

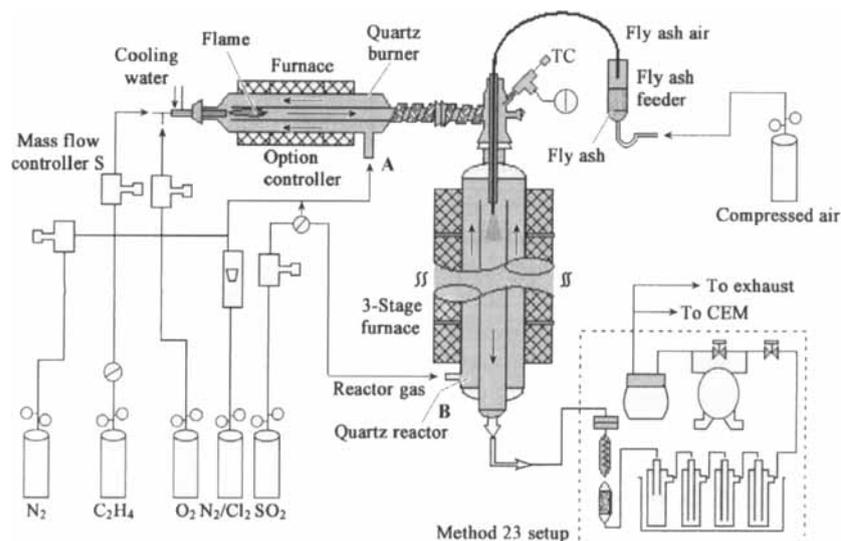


Fig. 2 Entrained flow reactor system (not to scale).

formation could be observed when SO₂ concentration was increased in the reacting atmosphere. In the formation of PCDDs, the most prevalent homologues were PeCDD and HxCDD (Fig.4), whereas DiCDF, TriCDF, and TeCDF comprised the highest percentage of the total PCDFs (Fig.4). More detailed discussion on the effect of SO₂ on PCDD/Fs will be presented elsewhere (Ryan *et al.*, 2006).

Moreover, it can be observed from Fig.4 that the presence of SO₂ in the reacting atmosphere did not produce dramatic shifts in the homologue profiles of PCDDs/Fs within the concentration range of SO₂ used in this study (0–226 ppm). Thus, the inhibition of SO₂ did not change the specific pathways during the formation, but influenced certain overall parameters to decrease the total formation of PCDDs/Fs. This may be due to the conversion of metal chlorides (Me_xCl_y) to metal sulfates (Gullett *et al.*, 1992). However, the inhibition effect of SO₂ on PCDD/F formation is general or nonspecific rather than favorable to certain particular homologues. Thus, it is feasible to employ the chlorination model to investigate the PCDD/F formation.

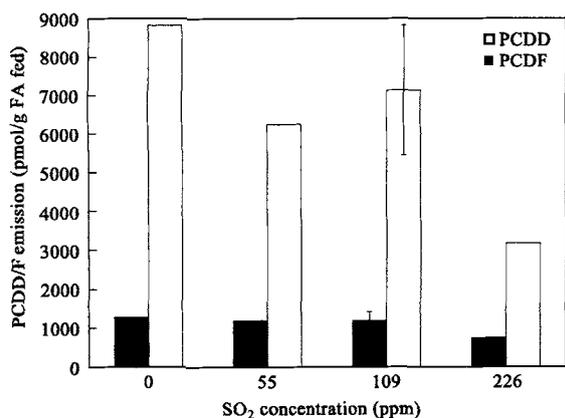


Fig. 3 Effect of SO₂ on total PCDD/F formation.

2.2 Model computation and evaluation

The values of parameters used in the chlorination model were all obtained from the mean experimental values (Table 3).

Table 3 Model parameters and predictions for MCDD/F

Isomer	Model parameter	Fraction in homologue
1-MoCDD	A = 0.034	0.137
2-MoCDD	B = 0.216	0.863
1-MoCDF	X = 0.126	0.253
2-MoCDF	Y = 0.141	0.282
3-MoCDF	Z = 0.189	0.378
4-MoCDF	W = 0.044	0.087

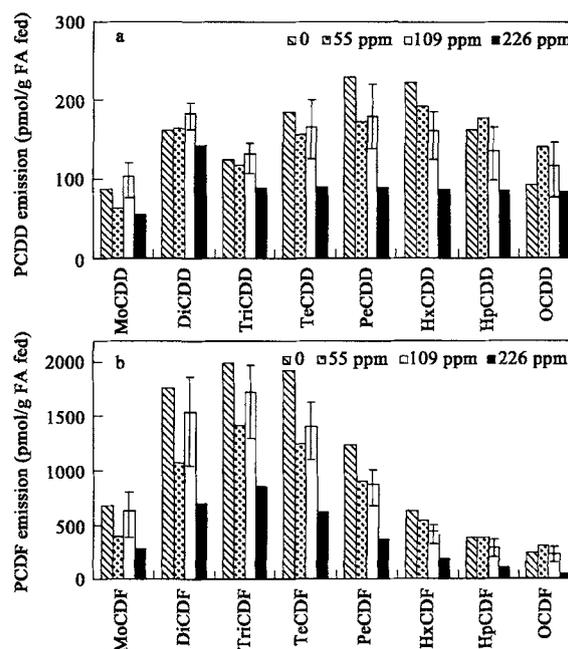


Fig. 4 PCDD (a) and PCDF (b) homologue profiles with changes in SO₂ concentration.

The model results show that chlorination of the 2 position was favorable for the formation of MCDD, whereas chlorination at the "1", "2", and "3" sites was favored over that at the "4" site in MCDF. This difference between MCDD and MCDF emphasizes that PCDF is not as symmetric as the PCDD molecule. From the molecular structure, the 1st and 4th sites in PCDDs and the 4th site in PCDFs are the sites that are near the oxygen atoms. The reduced occurrence of chlorination in these sites for MCDD and MCDF provides evidence for the steric hindrance effect, which means that existing chlorination may influence subsequent chlorination (Luijk *et al.*, 1994).

The correlations of the predicted results between the experimental and the chlorination model were analyzed using the Pearson coefficient, as indicated in Table 4. In general, the chlorination model showed better performance for predicting PCDFs compared with PCDDs. The Pearson coefficient for total PCDFs is 0.95, indicating that a strong correlation existed between the predicted results and experimental results. This suggests that the lack of steric hindrance effects in the model does not significantly impact the PCDF predictions. The coefficient for total PCDDs is 0.78, inferring that the prediction for PCDDs needs improvement. The relatively high coefficients obtained for DiCDD, TriCDD, and TeCDD suggest that the chlorination model showed good performance for predicting the lower chlorinated congeners. Whereas, the predictions for PeCDD and HxCDD are not as good as those for DiCDD, TriCDD, and TeCDD, thus indicating that this model may not be useful for predicting higher chlorinated congeners. Similarly, for PCDFs, the experimental data for DiCDF, TriCDF, and TeCDF correlated well with model predictions, whereas the correlations are not as good for PeCDF and HxCDF. Thus, it can be concluded that the chlorination model predicts the profile of low chlorinated congeners well, whereas the prediction for higher congeners needs further improvement.

Table 4 Correlation analysis between prediction and experiment

Homologue	Pearson correlation coefficient	Homologue	Pearson correlation coefficient
DiCDD	0.88	DiCDF	0.92
TriCDD	0.92	TriCDF	0.86
TeCDD	0.86	TeCDF	0.82
PeCDD	0.58	PeCDF	0.23
HxCDD	0.54	HxCDF	0.12
Total PCDDs	0.78	Total PCDFs	0.95

The PCDF homologues with maximum (DiCDF) and minimum (HxCDF) correlations and analyzed their isomer profiles were analyzed in this study, as indicated in Figs.5a and 5b. It can be seen that the isomer predictions of DiCDF had a good correlation with experimental data, whereas HxCDF did not show such a positive correlation. The difference between the prediction results and experimental results for HxCDF was mainly attributed to 123789-, 123468-, 134678-, and 124678-HxCDF. The inaccurate prediction may have resulted from the absence of steric hindrance effects in the model, which might

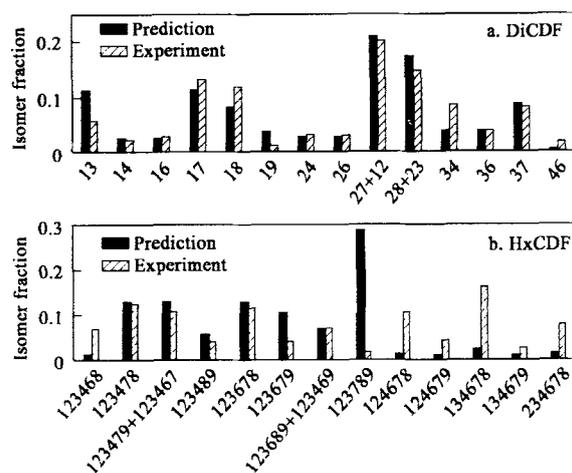


Fig. 5 DiCDF (a) and HxCDF (b) isomer profile.

play an important role in the formation of higher chlorinated homologues. Such hindrances would suggest that formation of the higher chlorinated homologues (i.e., the identified toxic isomers) are not formed predominantly via chlorination of DD or DF. Moreover, for higher chlorinated homologues, dechlorination might be the dominant pathway (Iino *et al.*, 2001). This pathway could result from formation of higher chlorinated congeners (i.e., OCDD and OCDF) via de novo synthesis followed by dechlorination to form the lower chlorinated congeners. The prediction of the chlorination model for PCDFs suggests that dechlorination might dominate the formation of higher chlorinated congeners, whereas chlorination might be the major pathway for the formation of lower chlorinated congeners.

Similarly, TriCDD and HxCDD, which had the maximum and minimum correlations for their predictions, respectively, were chosen in this study to investigate the profile of PCDDs, as indicated in Figs.6a and 6b. Although the correlation of prediction results and experimental results for TriCDD is 0.92, it could be seen from Fig.6a

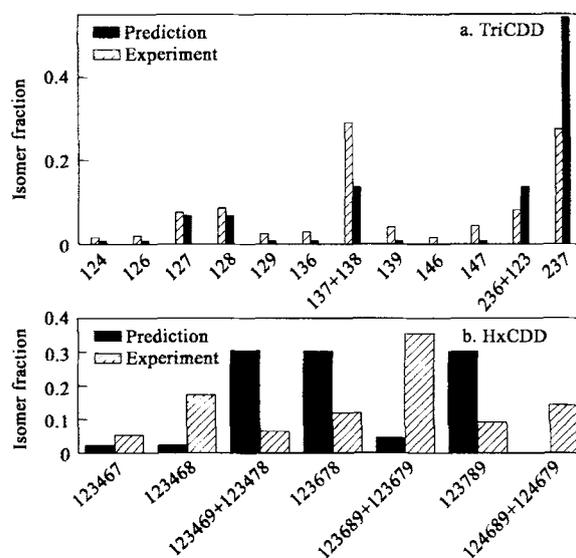


Fig. 6 TriCDD (a) and HxCDD (b) isomer profile.

that the predictions for 237-, 137- and 138-TriCDD need improvement. For HxCDD, three isomers (or inseparable HRGC/LRMS peaks) are predicted to have equivalent propensity to be formed; however, this is not the case in reality. The difference between the predicted and observed isomer patterns for the HxCDD homologue might be due to the symmetric structures of PCDDs; in the model, there are only two sites of different chlorination probability. However, when steric hindrance effects are considered, more than two sites of different probability for chlorination actually exist. Therefore, due to the lack of inclusion of steric hindrance in the model, the predictions for PCDDs do not perform as well as those for PCDFs. The exclusion of steric hindrances also explains why the prediction results are better for lower chlorinated congeners; successive chlorination is of less importance as a pathway for the formation for higher chlorinated PCDDs/Fs (i.e., above di- or tri-chlorinated congeners). Furthermore, condensation might account for a significant portion of PCDD formation at low temperatures; however, the chlorination model does not take this condensation pathway into consideration. It can be seen that although the correlation between prediction results and experimental results for HxCDD is 0.54, which is larger than that for HxCDF (0.12); therefore, the prediction of the HxCDF isomer profile might be better than that for HxCDD. Similar to the case with the higher chlorinated PCDFs, the prediction for higher chlorinated congeners of PCDDs needs further improvement.

From the result it can be inferred that the model may have correlated better for PCDFs than PCDDs. In addition, another potential reason is that Mo-TriCDFs (>50%) make up a significant percentage more of the total PCDFs than do the Mo-TriCDDs (>30%) of the total PCDDs. Thus, if chlorination of DD/DF can explain a good portion of the Mo-TriCDDs/Fs, it would be expected that the correlation would be better for the total PCDFs than for the total PCDDs.

3 Conclusions

Increasing concentrations of SO₂ result in greater inhibition of PCDD/F formation. Throughout this range of SO₂ concentrations, it is possible to predict the relative levels of some PCDD/F homologues (containing less than four chlorine atoms) using a chlorination model. This indicates that the inhibitory effect of SO₂ does not alter the basic mechanism of PCDD/F formation.

Overall, the chlorination model showed better performance in predicting PCDFs compared with PCDDs. Through the Pearson correlation analysis, the correlation value for total PCDFs reached 0.95, indicating a good accuracy for predicting PCDFs. This result is due to the dominance of the lower chlorinated homologues in the total PCDF emissions. Moreover, chlorination may account for the major pathway for the formation of lower chlorinated congeners, whereas dechlorination may be the dominant pathway for higher chlorinated PCDFs.

The chlorination model did not perform well in predicting PCDDs. The reason may be due to the symmetric

structure of the PCDD molecule, as a result of which the steric hindrance effect is not considered for predicting PCDD profiles of the model, the steric hindrance effect being more significant for PCDDs than for PCDFs. Moreover, the condensation pathway may account for a significant portion of PCDD formation, which has not been taken into account in the chlorination model.

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