# EMISSION CHARACTERISTICS AND FORMATION PATHWAYS OF DIOXINS FROM CO-COMBUSTION OF MUNICIPAL SOLID WASTE IN A COAL-FIRED POWER PLANT

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# 1. Introduction

For the past decades, coal-fired incinerators have developed to a saturated state in China, with an installed capacity of 1.1 billion kW and an electricity generation fraction of 72.18% in 2019.<sup>1</sup> The government has been formulating policies "encourage large projects and discourage small energy-inefficient power plants" on tackling industrial overcapacity and achieving ultra-low emissions of coal-fired power plants, to optimize and upgrade the national energy structure.<sup>2,3</sup> As Municipal solid waste (MSW) amount grows at a mean rate of 2.7% per year and reached 228 million tons by the end of 2018,<sup>4</sup> co-combustion of MSW in conventional coal-fired incinerators could improve the availability of power plants, gain economic subsidies for waste disposal, and alleviate MSW accumulation.<sup>5</sup> In recent years, the government also promote co-combust wastes in coal-fired power plants from the policy level.<sup>6</sup> However, input wastes status and emission characteristics of industrial coal incinerator co-disposal MSW are still not reported yet.

The largest components of MSW in China are an organic fraction (55.9%–61.2%), plastics and rubber (8.0%–11.2%), and paper (8.5%–10.0%), respectively.<sup>7,8</sup> And the MSW contains higher chlorine, nitrogen, heavy metals, and lower sulfur than coal. Muthuraman et al.<sup>9</sup> studied thermal behavior and characteristic in the combustion of coal and hydrothermally treated MSW. However, the interaction of MSW and coal in the chamber might have a conspicuous influence on the co-combustion emission of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), NO<sub>x</sub>, and SO<sub>2</sub>. Among generated persistent organic pollutants and major air pollutants, PCDD/Fs, which usually form through low-temperature heterogeneous reaction (200–400 °C) and high-temperature homogeneous reaction (500–800 °C), have attracted great attention in public due to their high toxicity and generation in waste incineration facilities. Large-scale coal incinerators are equipped with an advanced flue gas cleaning system, including a selective catalytic reduction (SCR) system and wet scrubbing to achieve ultra-low emission. It should be mentioned that SCR and wet scrubbing could significantly minimize the pollutant concentration including PCDD/Fs, by physical and chemical absorption. However, few studies have been published on PCDD/Fs removal characteristics and mechanisms in large-scale coal-fired power plants co-combusting MSW.

In this paper, the estimation of PCDD/Fs and other major air pollutant concentrations are conducted in the normal operation condition (i.e., pure pulverized coal combustion) and MSW co-combustion tests. And the removal efficiency of PCDD/Fs before and after the flue gas cleaning system is also calculated for background and testing cases. The emission characteristics, isomer distribution, emission factors and amounts, and correlations with other major air pollutants of PCDD/Fs are analyzed and demonstrated to reveal the effects and identify potential environmental pollution from MSW co-disposal coal for engineering application.

# 2. Materials and methods

2.1 Overview of the coal-fired power plant

As shown in Figure 1, the studied 1200 MW coal-fired power plant (4 boilers, 300 MW each) in eastern China mainly comprises the boiler, facilities of selective catalytic reduction (SCR), semi-dry desulfurization, bag-filter, wet scrubbing, and chimney. Positions with red stars are sampling points for the extracted flue gas. The integral power plant includes four boilers, where co-combustion tests are conducted in boiler system #3. In terms of the coal-fired power plant's input fuel, this boiler combusts Shenmu coal with a mixing mass fraction of about 2% MSW (includes kitchen residue, rubber, paper, textile, plastics, etc.) in the test.



Figure 1. Schematic Diagram of the Coal-fired Power Plant Co-combusting MSW

### 2.2 Test condition

Before the tests, ash-blowing of the boiler is conducted. There is no ash-blowing and steam release during the tests to ensure steady operation. The co-combustion tests are carried in two days, with a mean MSW input mass of 2.12 tonnes/hour, in contrast to the mean Shenmu coal input mass of 106.36 tonnes/hour. And the fuel is prepared in advance to ensure the stability of coal quality. Furthermore, the total duration of the MSW co-combustion test in the large-scale coal-fired power plant is 7.5 hours.

#### 2.3 Sample and analysis

Parallel flue gas samples are collected by flue gas sampler equipment (M5, KNJ Engineering, Japan) in two positions, before SCR (i.e., also after the outlet of boiler) and in the chimney for 1 hour for each testing time. In total, 19 PCDD/F gas samples, 4 gas samples of major air pollutants, and 3 fly ash samples are extracted, respectively. The flue gas sample analysis follows the U.S.EPA. Method 23, and fly ash samples follow the U.S.EPA Method 1613B. After the pre-treatment procedure, the PCDD/Fs in the samples are analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (JMS-800D, JEOL, Japan) with a DB-5MS column (60 m length × 0.25 mm internal diameter × 0.25  $\mu$ m film thickness) column. The recovery rates of the PCDD/Fs are estimated by <sup>13</sup>C<sub>12</sub>-PCDD/F surrogates and range from 61.90% to 115.2%, which satisfies the corresponding requirement of standards The concentrations of PCDD/Fs are normalized to 100 kPa, 273.15K, and dry air containing 11% O<sub>2</sub> (GB 18485-2014).

#### 3. Results and discussion

### 3.1 Emission characteristics of major air pollutants and PCDD/Fs

Concentrations of heterogeneous major air pollutants, including PM, HCl, SO<sub>2</sub>, NO<sub>x</sub>, and heavy metal, are estimated before the SCR and inside the chimney during the CCT process. The mean concentrations of specified pollutants (standard conditions, dry,  $11\%O_2$ ) are  $1.10\pm0.14$  mg/Nm<sup>3</sup> for PM,  $2.92\pm0.03$  mg/Nm<sup>3</sup> for HCl,  $6.70\pm0.33$  mg/Nm<sup>3</sup> for SO<sub>2</sub>,  $8.93\pm0.38$  mg/Nm<sup>3</sup> for NO<sub>x</sub>,  $1.06\pm0.04$  µg/Nm<sup>3</sup> for Hg and its compounds,  $0.40\pm0.34$  µg/Nm<sup>3</sup> for Cd and Ti,  $0.024\pm0.017$  mg/Nm<sup>3</sup> for As, Pb, Cu, Cr, Ni, Mn, Sb, Ni, and V. All these pollutants are satisfied within the limit values of national standard EU Directive 2010 and GB 18485-2014. As a result, the emission factors of gaseous pollutants are  $10.71\pm1.38$  g/ton fuel,  $28.43\pm0.28$  g/ton fuel,  $65.24\pm3.21$  g/ton fuel,  $86.99\pm3.67$  g/ton fuel,  $10.28\pm0.41$  mg/ton fuel,  $38.62\pm33.51$  mg/ton fuel, and  $0.2350\pm0.1665$  g/ton fuel for PM, HCl, SO<sub>2</sub>, NO<sub>x</sub>, Hg, Cd and Ti, and As-V, respectively.

The emission factor and annual emission amount of the toxic 2,3,7,8-PCCD/Fs during CCT are  $6.273\pm3.589$  µg/ton fuel and  $4.620\pm2.643$  g/year on the mass concentration level, and  $0.5217\pm0.3015$  µg TEQ/ton fuel and  $0.3842\pm0.2220$  g/year on the TEQ level, respectively. Following this, the emission factor and annual emission amount of the coal-fired power plant in NOC are  $4.555\pm2.846$  µg/ ton fuel and  $3.355\pm2.096$  g/year on the mass concentration level, and  $0.4825\pm0.4616$  µg TEQ/ton fuel and  $0.3554\pm0.3400$  g/year on the TEQ level, respectively. As Figure 2 indicates, the mixing of 2% MSW within the coal does not seriously affect the grand proportion and concentration in CCT. Last but not least, the PCDD/F concentration in the flue gas and fly ash, as 53.58 pg TEQ/Nm<sup>3</sup> and 1.830 ng TEQ/kg for CCT, and 49.55 pg TEQ/Nm<sup>3</sup> and 1.867 ng TEQ/kg for NOC, are all permissive under the limit values of national standards.



Figure 2. Mass and TEQ Concentration of PCDD/Fs in the SCRI, CHIM, and FA during CCT and NOC

3.2 Emission characteristics of major air pollutants and PCDD/Fs

3.2.1 Isomer distribution of 136 PCDD/Fs

The isomer distribution of 136 PCDD/Fs represents the ratio of certain isomer (2,3,7,8-TCDD) and its corresponding homologue (TCDDs in 136PCDD/Fs), which provides information on PCDD/F formation pathway and mechanism. The distribution profile of PCDD/Fs (P=4-8) are shown as Figure 3. In fact, even though there is huge gap in the quantity of PCDD/Fs, but the variation in the overall distribution pattern is finite. For TCDDs in the gas and solid phase, 1,3,6,8 and 1,3,7,9-TCDD were the main contributor, reaching above 20% and 40% (for flue gas), 10% and 20% (for fly ash) percentage, respectively. Overall, 1,2,4,7,9/1,2,4,6,8- and 1,2,3,6,8- PeCDDs, 1,2,3,4,6,8-HxCDD, 1,2,4,7/1,3,4,7/1,3,4,8/1,3,4,6/1,2,4,6- and 1,2,3,8/1,2,3,6/1,4,6,9/1,6,7,8/1,2,3,4/2,3,6,8-

TCDFs, 1,2,3,4,6- and 1,2,3,6,9/2,3,4,6,7- PeCDFs, and 1,3,4,6,7,8/1,2,4,6,7,8- HxCDF occupy most, respectively.



Figure 3. Distribution of PCDD/F Congeners (%) in the Flue Gas and Fly Ash on the Mass Concentration Level

#### 3.2.2 CP-route synthesis

The ratios of integrated PCDD to PCDF in the flue gas (and fly ash) are 1.167 (1.074) and 0.3401 (0.537) for CCT and NOC, respectively, which suggests that precursor synthesis is leading during CCT, while *de novo* synthesis is dominant in PCDD/F formation during NOC. CP is the most direct precursor for PCDD/F formation, among which 2,4,6-TrCP, 2,3,4,6-TeCP, and PCP usually exist in the furnace. Afterwards these CPs generate 1,3,6,8-, 1,3,7,9-TCDD, 1,2,4,6,8-, 1,2,4,7,9-, 1,2,3,6,8-, 1,2,3,7,9-PeCDD, and 1,2,3,4,6,8-HxCDD of 136 PCDD/Fs. Principal component analysis (PCA) is conducted. As Fig. 5 shows, the PCA results subdivide the PCDD-congeners into two clusters. The higher left quadrant harbors those congeners derived from CP precursors: 1,3,6,8- and 1,3,7,9-TCDD (Figure 5a), 1,2,4,6,8/1,2,4,7,9-PeCDD (Figure 5b), and 1,2,3,4,6,8-HxCDD (Figure 5c), following a logical chlorination sequence in similar graph position. The similarly distributed clusters suggest a different formation route of these isomers from others, which suggests the CP-route chlorinates these PCDDs. But Figure 5d suggests that the above clusters reunite with each other, locating in close-knit positions, meaning that few of these PCDFs are generated by the CP route.



Figure 4. PCA of Congener Profiles within TCDD, PeCDD, HxCDD, and TCDF in CCT

#### 3.2.3 Chlorination of DD or DF

To further evaluate the level of chlorination of DD in CCT, the signal intensity summarization of 2,3,7,8-substituted congeners is calculated (Table 1). Usually, the chlorination of DD and chlorination of dibenzofurans (DF) follow the sequence of  $2\rightarrow 8\rightarrow 3\rightarrow 7\rightarrow 1\rightarrow 4\rightarrow 6\rightarrow 9$ , which is competitive to the 1,3,7,9- and 1,3,6,8- TCDD

formation of CP-route with the electrophilic aromatic mechanism. The average signal intensity of 2,3,7,8-PCDD, PCDF, and PCDD/F in flue gas (and fly ash) from CCT are 10.63 (2.546), 23.66 (2.865), and 16.65 (2.720), respectively, indicating that DD chlorination is not the major formation pathway in CCT. In a word, CP-route is the main reason for precursor synthesis for PCDD/F formation in CCT.

Equally important, PCDF is mainly formed by condensation of precursors such as CB and CP, DF chlorination, and *de novo* synthesis. Usually, *de novo* synthesis and DF is both preferred to form PCDF than PCDD, and the amount of DF is tens of times higher than that of the total CP in the MSW incinerator. However, consensus on the distribution of isomers generated by the CP pathway in PCDF has not been achieved. It is believed that the CProute is supposedly supported by 1,2,3,8-/1,2,3,6-/1,4,6,9-/1,6,7,8-/1,2,3,4-/2,3,6,8-TCDF and 2,4,6,8-TCDF, which were the only known PCDFs generated by precursor synthesis. The mutual R<sup>2</sup> between 1,2,3,8-/1,2,3,6-/1,4,6,9-/1,6,7,8-/1,2,3,4-/2,3,6,8-TCDF and 2,4,6,8-TCDF is 0.4968, which is poorly related; while their correlation with other PCDF congeners is strong, suggesting similar formation pathways for those congeners and precursor route could be excluded from the PCDD/F formation in NOC. Furthermore, to investigate the proportion of DF chlorination route, the average signal intensity of 2,3,7,8-PCDD, PCDF, and PCDD/F in flue gas (and fly ash) from NOC are calculated as 56.69 (10.67), 31.72 (12.68), and 38.85 (11.63), respectively. These values increased compared to those from CCT, indicating that DD/F chlorination is relatively accounting for the PCDD/PCDF formation in NOC. In brief, de novo synthesis and DF chlorination are major formation pathways for NOC, and the potential reason is that coal incinerator generates abundant carbon in fly ash, which is the direct source for de novo synthesis.

Table 1. Hagenmaier Profiles of the 17 toxic PCDD/F Isomers during CCT and NOC

2,3,7,8-PCDD/F isomers	SCRI-CCT	SCRI-NOC	CHIM-CCT	CHIM-NOC	FA-CCT	FA-NOC
2,3,7,8-TCDD	0.1945	1.058	0.5420	0.1380	4.909	7.736
1,2,3,7,8-PeCDD	2.366	3.302	2.219	1.047	9.936	15.07
1,2,3,4,7,8-HxCDD	2.674	2.587	2.458	1.097	3.571	4.924
1,2,3,6,7,8-HxCDD	5.033	4.938	4.651	1.872	8.003	8.793
1,2,3,7,8,9-HxCDD	3.103	2.766	2.965	1.211	6.446	7.083
1,2,3,4,6,7,8-HpCDD	42.76	49.14	44.41	37.91	41.57	43.46
OCDD	2.821	4.189	5.921	1.274	13.81	15.82
Average of PCDD	10.63	56.69	52.04	9.718	2.546	10.67
2,3,7,8-TCDF	0.8662	1.213	1.426	0.5735	2.497	2.446
1,2,3,7,8-PeCDF	4.646	2.543	4.225	2.209	6.032	4.682
2,3,4,7,8- PeCDF	10.56	7.043	10.73	4.692	8.181	6.350
1,2,3,4,7,8-HxCDF	8.088	6.878	8.153	4.999	12.12	9.773
1,2,3,6,7,8- HxCDF	7.288	8.819	8.350	6.349	6.416	5.172
1,2,3,7,8,9- HxCDF	15.97	13.12	15.58	11.56	2.417	1.948
2,3,4,6,7,8- HxCDF	5.138	6.572	5.285	4.576	4.279	7.218
1,2,3,4,6,7,8-HpCDF	46.69	50.85	48.13	47.52	56.99	49.66
1,2,3,4,7,8,9- HpCDF	11.87	13.36	12.14	9.753	10.93	26.32
OCDF	1.330	1.453	1.793	1.056	9.325	8.513
Average of PCDF	23.66	31.72	47.11	15.67	2.865	12.68
Average of PCDD/F	16.65	38.05	48.74	13.08	2.720	11.63

\* Hagenmaier values of PCDD/Fs is calculated as follows:

 $Hagenmaier \ values = \frac{2,3,7,8 - substituted \ PCDD / F \ (e.g. \ 2,3,7,8 - TCDD)}{\sum Corresponding \ PCDD / F \ isomer \ (e.g. \ \sum TCDDs)}$ 

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