

Formation Characteristics of PCDD/Fs in the Co-combustion and Pyrolysis Process of Coal and Sewage Sludge

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ABSTRACT

Co-combustion technology of coal and sewage sludge (SS) was encouraged and recommended in China. Previous studies most focused on its influence on combustion characteristics, migration characteristics of heavy metals in fly ash, and emission of conventional pollutants, etc., but less reported the formation characteristics of polychlorinated- ρ -dibenzodioxins and dibenzofurans (PCDD/Fs). To well reveal it, this study carried out five parallel experiments, including the pyrolysis of SS, the combustion of SS, the co-combustion of coal and SS with the proportion of 0%, 2.5% and 5%, respectively. The emission concentration of PCDD/Fs respectively increased from 0.42 ng g⁻¹ (0.0022 ng I-TEQ g⁻¹) to 0.54 ng g⁻¹ (0.0030 ng I-TEQ g⁻¹) and 1.70 ng g⁻¹ (0.0305 ng I-TEQ g⁻¹) with increasing blending proportion of SS. The dominant part was also changed from PCDF (0.32 ng g⁻¹ in M-0%, 0.38 ng g⁻¹ in M-2.5%) to PCDD (1.11 ng g⁻¹ in M-5%). The formation concentration of PCDD/Fs in the combustion process of SS was about 0.34 ng g⁻¹ (0.0019 ng I-TEQ g⁻¹). In the pyrolysis process of SS, the concentration of PCDD/Fs was 0.59 ng g⁻¹ (0.0037 ng I-TEQ g⁻¹). The de novo synthesis should be the major formation pathway of PCDD/Fs in the co-combustion process of coal and SS. On the basis of sufficient carbon sources, the PCA analysis revealed the chlorine source (Cl) and metal catalyst (Fe) should contribute a lot on the formation of PCDD/Fs. The results paved the way for further optimization on the operation of co-combustion of coal and SS and assist in controlling the PCDD/F emission from co-combustion process.

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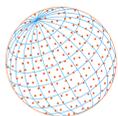
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Keywords: Co-combustion of coal and sewage sludge, Polychlorinated- ρ -dibenzodioxins and dibenzofurans, Pyrolysis of sewage sludge, Formation pathways, Congener distribution

1 INTRODUCTION

With the development of social economy and the improvement of sewage treatment rate, the by-product treatment of sewage sludge (SS) also increased rapidly. Some source reported that the generation amount of municipal sewage sludge and industrial sewage sludge had reached 31 Mt and 8.81 Mt, respectively, in 2018 (Intelligence Research Group, 2019). In addition, the SS treatment methods in China mainly included landfill, composting, natural drying and incineration, which account for 65%, 15%, 6%, and 3%, respectively (Intelligence Research Group, 2019). The huge amount of sludge had become an urgent problem for urban development, and better alternative disposal technology should be actively developed, for instance, co-combustion with coal. The coal fired power plant coupled with biomass power generation was an important development direction to achieve the low carbon transformation of coal-fired power generation and reduce more CO₂ emissions.

Under this background, the co-combustion technology of SS in coal-fired power plant had been



accepted and valued by local governments and plants in China. Relevant national departments had also issued a series of policies to promote the utilization of SS, and carried out the construction of demonstration projects. It was also required to accelerate the research and development, achievement transformation and standard formulation of key technologies of coal-fired coupled biomass power generation. For instance, the highest blending proportion of SS was recommended as 5% in the Emission Standard of Air Pollutants for Coal & Sludge Co-fired Power Plant in Shanghai, China (Shanghai Municipal Bureau of Ecology and Environment, 2021).

Many researches had carried out co-combustion tests of SS and numerical simulation in coal-fired power plant. Most of them mainly focused on the influence on the combustion characteristics of the boiler with different type of SS (Kijo-Kleczkowska *et al.*, 2013; Xia *et al.*, 2021; Zhu *et al.*, 2015), different blending proportions (Kijo-Kleczkowska *et al.*, 2016; Tan *et al.*, 2017; Zhang *et al.*, 2015), and different moisture content of SS (Tan *et al.*, 2017; Zhang *et al.*, 2015), etc., migration characteristics of heavy metals in fly ash (Namkung *et al.*, 2018), and emission of conventional pollutants (Yang *et al.*, 2016). All of which were quite important and basic information for further application of co-combustion technology. The co-combustion of SS also benefited to volume reduction, toxic organics destruction as well as energy recovery (Magdziarz and Werle, 2014; Werle and Wilk, 2010). However, less attention was focused on the emission of organic pollutants in the co-combustion process, especially the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), which was heavily regulated in some industries, such as waste incineration.

PCDD/Fs was mainly generated by the homogeneous reaction in high temperature range (500–800°C) and the heterogeneous reaction in low temperature range (200–400°C) (Mckay, 2002; Ooi and Lu, 2011; Stanmore, 2004). The homogeneous reaction mainly contained the rearrangement of chlorophenols (CP), chlorobenzenes (CBz), and polychlorinated biphenyls (PCBs) (Cunliffe and Williams, 2009; Nganai *et al.*, 2014). The heterogeneous reaction also involved precursor compounds (e.g., CP and CBz) (Babushok and Tsang, 2003; Evans and Dellinger, 2005) as well as de novo synthesis from carbon matrix or polycyclic aromatic hydrocarbons (PAHs) (Mckay, 2002; Ooi and Lu, 2011). CP-route synthesis was considered as an important and representative precursor pathway, PCDD/Fs can be directly condensed or rearranged by three CPs (2,4,6-, 2,3,4,6- and pentachlorophenol) (Lomnicki and Dellinger, 2002; 2003). Some studies reported that the chlorination of DD/DF also contributed to the PCDD/F formation, which could follow the sequence of 2 → 8 → 3 → 7 → 1 → 4 → 6 → 9 according to the electrophilic aromatic substitution mechanism (Luijk *et al.*, 1992). The position of 2, 3, 7, and 8 in PCDD/Fs were considered as the preferable chlorination position, which could be indicators for chlorination pathway (Ryu *et al.*, 2003). The formation of PCDD/Fs were also closely related to some other factors, such as temperature, sources of chlorine and carbon, and metal catalysts (Mckay, 2002; Zhang *et al.*, 2016).

To reveal the formation characteristics and pathways of PCDD/Fs in the co-combustion process of coal and SS, this study carried out a series of experiments with different blending proportions of SS. The results pave the way for further optimization on the operation of co-combustion of coal and SS and assist in controlling the PCDD/Fs emission from co-combustion process.

2 METHODS

2.1 Materials and Pretreatment

This study collected one typical coal and one sewage sludge (SS) from a coal-fired plant in Guangdong Province, China. The SS, used for coal co-combustion, was from a domestic wastewater treatment plant located in Guangdong Province, China. The proximate and ultimate analysis information was summarized in Table S1. The moisture content of SS was 54.2%. Before experiments and analysis, the coal was dried in an oven at 105°C for over 24 h, while the SS was directly used without drying process.

2.2 Experimental Procedures

Series experiments of coal and SS were carried out in a horizontal tube furnace (Fig. 1), and the experiment scheme was listed in Table 1. This study mainly carried out five parallel experiments, including the pyrolysis of SS (S-P), the combustion of SS (S-C), the co-combustion of coal and SS with the proportion of 0%, 2.5% and 5% (M-0%, M-2.5%, and M-5%, respectively). The highest

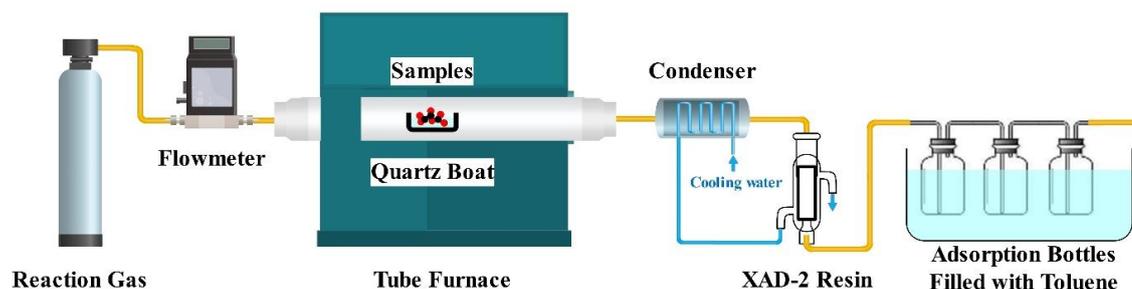
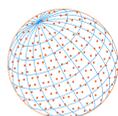


Fig. 1. Schematic diagram of the experiment devices.

Table 1. Experiments scheme.

Types	Codes	Samples	SS (g)	Coal (g)	Coal/SS weight ratio	Ambient gas (mL min ⁻¹)	Temperature (°C)
Pyrolysis	S-P	SS	10	0	1.0/0	N ₂ , 500	850
Combustion	S-C	SS	5	0	1.0/0	Air, 250	850
Co-combustion	M-0%	Coal/SS	0	2.5	0/1.0	Air, 250	850
	M-2.5%	Coal/SS	0.0625	2.4375	0.975/0.025	Air, 250	850
	M-5%	Coal/SS	0.125	2.375	0.95/0.05	Air, 250	850

blending proportion of SS was recommended as 5% in the Emission Standard of Air Pollutants for Coal & Sludge Co-fired Power Plant in Shanghai, China (Shanghai Municipal Bureau of Ecology and Environment, 2021).

In order to clean the PCDD/Fs, other organics, chlorides and carbon possibly adsorbed onto the inner surface of the quartz tube, it was heated at 800°C for 15 min under the sweeping of N₂ before each test. During each test, the first step was pre-heated the cleaned tube to 850°C under a heating rate of 20°C min⁻¹ with a continuous flow of reaction gas (Table 1); the second step was pushed a quartz boat loading prepared sample into the center of the quartz tube; the last step was placed each sample in the quartz tube at 850°C and reacted for 1 h, and four parts were collected for further analysis of PCDD/Fs, including (1) XAD-II polymeric resin, (2) two bottles of toluene, (3) residues in quartz boat, and (4) sampling pipes.

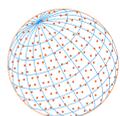
2.3 Analytical Methods

All solid and liquid samples were stored in a cooler below 4°C for further analysis. For the pretreatment and analysis of PCDD/Fs in thermally treated residues and off-gases of each sample, the pretreatment procedures followed the U.S. Environmental Protection Agency Method 1613 (U.S. EPA, 1994), which mainly contained spiking ¹³C₁₂-labelled PCDD/F standards, Soxhlet extraction, clean-up with multilayer silica gel column and basic-alumina column, quality assurance (QA), and quality control (QC). The purified samples were analyzed through a high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) (JMS-800D, JEOL, Japan) with a DB-5MS column (60 m length, 0.25 mm ID, 0.25 μm film). The recoveries of PCDD/Fs standards range from 34.2% to 100.5%, meeting the requirements of the method of U.S. EPA 1613. The international toxic equivalents (I-TEQ) were calculated with NATO/CCMS factors (Bhavsar *et al.*, 2008). More details were shown in previous studies (Chen *et al.*, 2014; Lin *et al.*, 2018).

The proximate and ultimate analysis were tested by differential thermal analyzer (DTA, 5E-IRSII, Kaiyuan Instruments Co., Ltd., China). The major elemental content of coal and SS was detected by X-ray fluorescence spectrometer (XRF, ARL ADVANT'X IntelliPower™ 4200, ThermoFisher Scientific, USA). The heavy metals (i.e., Hg, Pb, Cd, Cu, Ni, As, Cr, and Zn) in coal and SS was detected through an inductively coupled plasma combined with atomic emission spectrometry (ICP-AES, iCAP6300, ThermoFisher Scientific, USA) after the full digestion of coal and SS samples.

2.4 Statistical Analysis

In this study, total of 38 PCDD and 53 PCDF congeners was detected and analyzed, other than



the theoretical number of 49 PCDD and 87 PCDF congeners, because the peak times of some PCDD/F congeners were quite close and cannot be separated with each other.

To better evaluate the temperature effect on the distribution of PCDD/F congeners, the chlorination degree (d_c , the average number of chlorine substituents) was introduced and was calculated by following equation:

$$d_c = \frac{\sum C_j \times n_j}{C} \quad (1)$$

where $j = 4, 5, 6, 7, 8$, C_j represents the concentration of each PCDD, PCDF, or PCDD/F, n_j represents the number of substituted chlorines in each PCDD, PCDF, or PCDD/F; and C represents the total concentration of PCDD, PCDF, or PCDD/F.

The relative importance of each congener was introduced and defined by their weight percentage within their own homologue group. The relative importance of OCDD and OCDF was calculated as their weight proportions in PCDD and PCDF, respectively. The detail calculation results were summarized in Table S2.

To better investigate the formation pathways of PCDD/F in each experiment, the content of each element in M-2.5% and M-5% was calculated based on them of SS and coal and their proportion, based on the following equation,

$$C_m = C_{SS} \times P_{SS} + C_{coal} \times P_{coal} \quad (2)$$

where C_m represents the element content of mixed samples; C_{SS} and C_{coal} represent the element content in SS and coal, respectively; P_{SS} and P_{coal} represent the proportion of SS and coal.

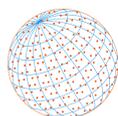
3 RESULTS AND DISCUSSION

3.1 The Element Content

In this study, the contents of basic elements and trace heavy metal elements were shown in Table 2. The sewage sludge contained abundant carbon source (C, 6.04%), chlorine source (Cl, 0.32%), metal catalysts (Fe, 2.54%; Cu, 85.49 mg kg⁻¹; Ni, 38.13 mg kg⁻¹), and inhibiting element of PCDD/Fs (S, 1.24%; Ca, 9.59%). The carbon source, chlorine source, and metal catalysts would support a lot on the formation of PCDD/Fs, while the S might inhibit the formation of PCDD/Fs. In addition, the content of all trace heavy metals was lower than the Control Standards of Pollutants in Sludge for Agriculture Use (GB 4284-2018). For coal, it contained much carbon (66.73%) but less

Table 2. Contents of basic elements and trace heavy metals of SS, coal and their mixture.

Elements	SS	M-0% (Coal)	M-2.5%	M-5%
Basic elements (%)				
C	6.04	66.73	65.21	63.70
Cl	0.32	0.07	0.08	0.09
Fe	2.54	0.45	0.50	0.55
S	1.24	0.16	0.19	0.21
Ca	9.59	0.77	0.99	1.21
Trace heavy metal elements (mg kg ⁻¹)				
Hg	1.02	1.11	1.11	1.11
Pb	27.75	1.99	2.63	3.28
Cd	1.77	0.20	0.24	0.28
Cu	85.49	0.58	2.70	4.83
Ni	38.13	7.40	8.17	8.94
As	21.16	1.57	2.06	2.55
Cr	51.44	10.91	11.92	12.94
Zn	300.73	17.22	24.31	31.40



chlorine (0.07%), metal catalysts (Fe, 0.45%; Cu, 0.58 mg kg⁻¹; Ni, 7.40 mg kg⁻¹), and inhibiting element of PCDD/Fs (S, 0.16%; Ca, 0.77%).

After fully blending of SS and coal, the proportion of carbon was only slightly decreased with increasing proportion of SS by 2.5% and 5%, while the proportion of other chlorine, metal catalysts and inhibiting elements was increased, especially the key catalytic metal of Cu. All of which would influence a lot on the formation of PCDD/Fs.

3.2 The PCDD/F Content

3.2.1 Pyrolysis and combustion and of sewage sludge

The PCDD/F concentrations of each experiment were summarized in Table 3. In the pyrolysis experiment of sewage sludge, the concentration of PCDD/Fs was 0.59 ng g⁻¹ (0.0037 ng I-TEQ g⁻¹), dominated by PCDDs (0.38 ng g⁻¹). The chlorination degree of PCDDs ($d_{C-PCDDs}$, 4.76) show significant difference with that of PCDFs ($d_{C-PCDFs}$, 6.34), and the chlorination degree of PCDD/Fs ($d_{C-PCDD/Fs}$) was 5.30. It revealed that the existing organic pollutants (Chanaka Udayanga *et al.*, 2019), carbon source, chlorine source, and metal catalysts in SS were enough to generate PCDD/Fs, and the anaerobic atmosphere might reduce the decomposition of PCDD/Fs. In the combustion experiment of SS, the generation of PCDD/Fs was about 0.34 ng g⁻¹ (0.0019 ng I-TEQ g⁻¹), which was evenly distributed by PCDDs (0.17 ng g⁻¹) and PCDFs (0.17 ng g⁻¹). All these values were lower, compared with pyrolysis experiment. The $d_{C-PCDDs}$, $d_{C-PCDFs}$, and $d_{C-PCDD/Fs}$ were respectively increased to 5.57, 6.4, and 6.04 compared with the pyrolysis experiment, which was attributed to the introduce of oxygen.

Oxygen was an essential factor for PCDD/F formation by de novo synthesis (Pekárek *et al.*, 2001; Stieglitz, 1998). In the formation process of PCDD/Fs, oxygen can facilitate to convert inorganic chlorine into organic chlorine and the chlorination of carbon (López *et al.*, 2008; Weber *et al.*, 2001). In addition, it can also promote the oxidation of carbon structure and release PCDD/Fs (Wikström *et al.*, 2003). Since the sludge itself contained oxygen (Table S1), it should meet the needs of PCDD/F formation. However, in the combustion condition, more oxygen might promote the decomposition of dioxins at high temperature (850°C) (Mckay, 2002).

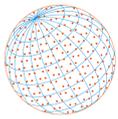
3.2.2 Co-combustion of coal and sewage sludge

Three co-combustion experiments were carried out in this study with three blending proportion of SS, i.e., 0%, 2.5%, and 5%, respectively. For experiment M-0%, the concentration of PCDD/Fs was 0.42 ng g⁻¹ (0.0022 ng I-TEQ g⁻¹), dominated by PCDFs (0.32 ng g⁻¹). That is, the generation of PCDD/Fs was higher than the emission during the combustion process of SS. The $d_{C-PCDDs}$, $d_{C-PCDFs}$, and $d_{C-PCDD/Fs}$ were further increased to 6.36, 6.49, and 6.46 compared with the combustion experiment of SS, respectively. The different chemical characteristics of SS and coal should be the major influencing factor, i.e., comparing with the abundant carbon source, chlorine source, metal catalysts, and inhibiting elements of SS, coal had much higher content of carbon source and enough support of other conditions.

For experiment M-2.5%, the PCDD/F concentration was increased to 0.54 ng g⁻¹ (0.0030 ng I-TEQ g⁻¹), dominated by PCDF (0.38 ng g⁻¹). The emission of PCDDs and PCDFs were both increased by 0.06 ng g⁻¹. The $d_{C-PCDDs}$, $d_{C-PCDFs}$, and $d_{C-PCDD/Fs}$ were further increased to 6.31, 7.12,

Table 3. PCDD/F concentrations of different experiments (ng g⁻¹ for PCDDs, PCDFs and PCDD/Fs; ng I-TEQ g⁻¹ for toxic PCDD/Fs).

	S-P	S-C	M-0%	M-2.5%	M-5%
PCDDs	0.38 ± 0.02	0.17 ± 0.01	0.10 ± 0.01	0.16 ± 0.02	1.11 ± 0.08
PCDFs	0.20 ± 0.01	0.17 ± 0.01	0.32 ± 0.02	0.38 ± 0.01	0.59 ± 0.09
PCDD/Fs	0.59 ± 0.02	0.34 ± 0.01	0.42 ± 0.01	0.54 ± 0.02	1.70 ± 0.09
Toxic PCDD/Fs	0.0037 ± 0.0004	0.0019 ± 0.0002	0.0022 ± 0.0002	0.0030 ± 0.0002	0.0305 ± 0.0006
PCDFs/PCDDs	0.52	1.02	3.26	238	0.54
PCDFs/(PCDD/Fs)	0.34	0.50	0.77	0.70	0.35
$d_{C-PCDDs}$	4.76	5.57	6.36	6.31	4.70
$d_{C-PCDFs}$	6.34	6.49	6.49	7.12	7.28
$d_{C-PCDD/Fs}$	5.30	6.04	6.46	6.88	5.60



and 6.88 compared with the combustion experiment of SS, respectively. For experiment M-5%, the concentration of PCDD/Fs was further increased to 1.70 ng g^{-1} ($0.0305 \text{ ng I-TEQ g}^{-1}$), dominated by PCDDs (1.11 ng g^{-1}). The $d_{c\text{-PCDDs}}$, $d_{c\text{-PCDFs}}$, and $d_{c\text{-PCDD/Fs}}$ were further increased to 4.70, 7.28, and 5.60 compared with the combustion experiment of SS, respectively. Herein, the emission of PCDD/Fs was increased with the increasing proportion of SS, especially from 2.5% to 5%, which was mainly caused by more discharge of PCDDs (0.95 ng g^{-1}). In addition, the $d_{c\text{-PCDDs}}$ was decreased as the blending proportion of SS increased, while the $d_{c\text{-PCDFs}}$ was increased. All of which can attributed to the well support of oxygen and the increasing amount of chlorine source, metal catalysts (Fe and Cu) (Table 2).

3.3 Influence on PCDD/Fs Congeners/Homologues Distribution

3.3.1 Pyrolysis and combustion of sewage sludge

Figs. 2(a) and 2(b) showed the distribution of PCDD/Fs homologues on concentration and proportion, respectively. In pyrolysis experiment of SS, low-chlorinated homologues, TCDDs (0.2359 ng g^{-1} , 40%) and PeCDDs (0.0864 ng g^{-1} , 15%), were the major parts of PCDDs, while PCDFs showed less difference between low-chlorinated homologues and high-chlorinated homologues and was dominated by PeCDFs (0.0543 ng g^{-1} , 9%) and OCDF (0.0832 ng g^{-1} , 14%). Compared with the pyrolysis process of SS, low-chlorinated homologues, TCDDs (0.0389 ng g^{-1} ,

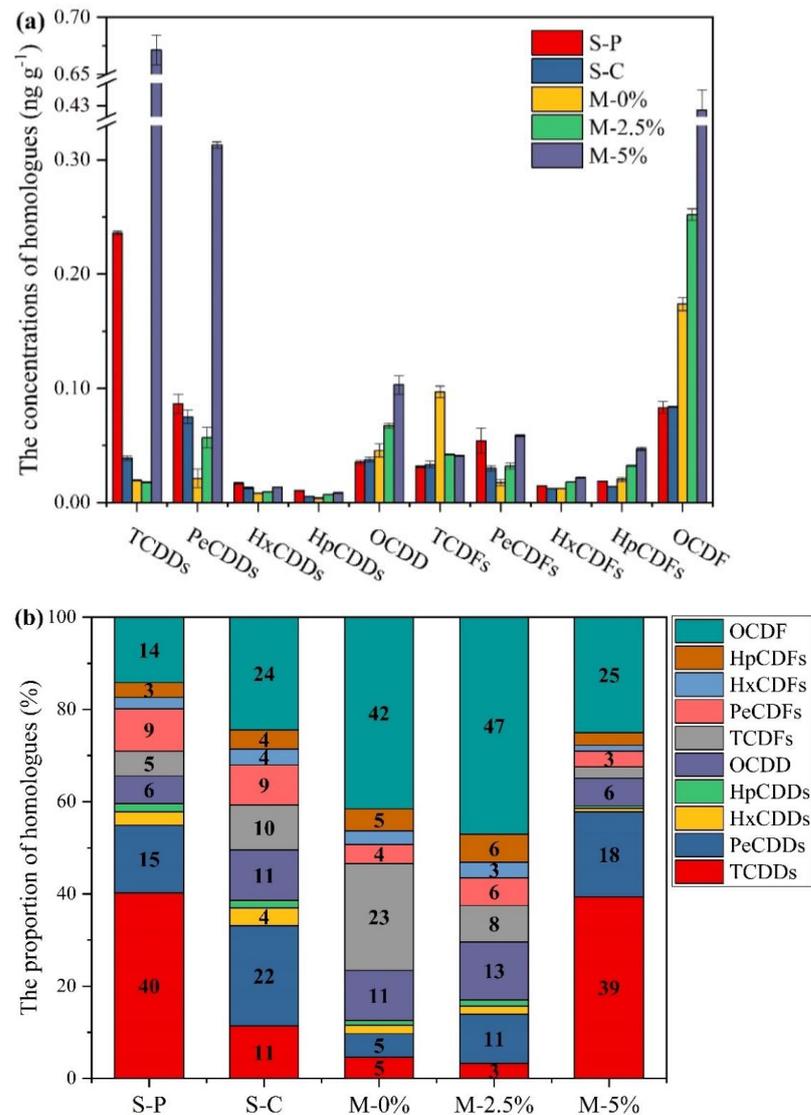
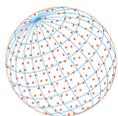


Fig. 2. The concentration and proportion of PCDD/F homologues.



11%) and PeCDDs (0.0749 ng g⁻¹, 22%), were still the domination of PCDDs in the combustion process of SS, but the proportion of OCDD was increased from 6% to 11%. Except OCDD, the concentrations of other four PCDD homologues were decreased with varying degrees. The total proportion of PCDFs had increased from 34% to 51%, mainly divided by TCDFs (0.0333 ng g⁻¹, 10%), PeCDFs (0.0299 ng g⁻¹, 9%), and OCDF (0.0837 ng g⁻¹, 24%). All these changes resulted in the increasing of $d_{c-PCDDs}$, $d_{c-PCDFs}$, and $d_{c-PCDD/Fs}$.

3.3.2 Co-combustion of coal and sewage sludge

In co-combustion experiment of M-0%, PCDFs was the absolutely dominant part (77%) as mentioned above, resulting from the high concentration and proportion of TCDFs (0.0968 ng g⁻¹, 23%) and OCDF (0.1737 ng g⁻¹, 42%). The PCDDs mainly consisted of TCDDs (0.0194 ng g⁻¹, 5%), PeCDDs (0.0212 ng g⁻¹, 5%), and OCDD (0.0456 ng g⁻¹, 11%). Compared with the combustion of SS, the lower concentration of PCDDs in experiment M-0% was caused by the decreasing concentration of TCDDs, PeCDDs, HxCDDs, and HpCDDs, while the higher concentration of OCDF was resulted from the significant increase of TCDFs and OCDF. After increasing the blending proportion of SS from 0% to 2.5%, the concentrations of PeCDD/Fs, HxCDD/Fs, HpCDD/Fs, and OCDD/F, especially the PeCDDs (from 0.0212 ng g⁻¹ to 0.0568 ng g⁻¹), OCDD (from 0.0456 ng g⁻¹ to 0.0674 ng g⁻¹), and OCDF (from 0.1737 ng g⁻¹ to 0.2520 ng g⁻¹), were all increased with varying degrees, which resulted in the increased concentration of total PCDD/Fs. Only the concentrations of TCDDs and TCDFs showed decreasing trend, especially TCDFs (from 0.0968 ng g⁻¹ to 0.0422 ng g⁻¹). Meanwhile, the proportions of PeCDD/Fs, HxCDD/Fs, HpCDD/Fs, and OCDD/F were increased with varying degree, and the proportions of TCDD/Fs decreased. After further increased the blending proportion of SS from 2.5% to 5%, almost the concentrations of all PCDD/F homologues increased other than TCDFs, resulting the huge increase of total concentration of PCDD/Fs. Among the them, TCDDs contributed most (from 0.0177 ng g⁻¹ to 0.6713 ng g⁻¹); PeCDDs contribute much (from 0.0568 ng g⁻¹ to 0.3131 ng g⁻¹); and OCDF also contributed a lot (from 0.2520 ng g⁻¹ to 0.4261 ng g⁻¹). At the same time, the proportions of TCDDs and PeCDDs also increased a lot to 39% and 18%, respectively. However, due to the huge increase of TCDDs and PeCDDs, the proportions of other homologues decreased with varying degrees.

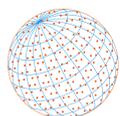
3.4 The Formation Pathway of PCDD/Fs

As mentioned above, the homogeneous reaction mainly involved the rearrangement of chlorinated precursors, such as CP, CBz, and PCBs (Cunliffe and Williams, 2009; Nganai *et al.*, 2014). The heterogeneous reaction involved not only precursor compounds (CP and CBz) (Babushok and Tsang, 2003; Evans and Dellinger, 2005), but also the de novo synthesis (from carbon matrix or from PAHs) (Mckay, 2002; Ooi and Lu, 2011). In addition, the experiment temperature was stably hold on 850°C, which could better support the homogeneous reaction. Herein, this study tried to reveal the potential formation pathway and key influence factors of PCDD/Fs in the co-combustion process of SS and coal.

3.4.1 Precursors synthesis

As for the CP-route, the representatives of PCDD and PCDF congeners were 1,3,6,8- and 1,3,7,9-TCDDs, and 2,4,6,8- 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, respectively. As mentioned above, these congeners can be directly condensed or rearranged by three CPs (2,4,6-, 2,3,4,6- and 2,3,4,5,6-chlorophenol) (Weber and Hagenmaier, 1999). Previous studies also identified 2,4,6,8- 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, 1,2,4,6,8/1,2,4,7,9-, 1,2,3,6,8- and 1,2,3,7,9-PeCDDs, and 1,2,3,4,6,8/1,2,3,4,7,9-HxCDD as representative congeners based on their high correlation with 1,3,6,8- and 1,3,7,9-TCDDs (Zhang *et al.*, 2017b; Chen *et al.*, 2018). To obtain reliable mechanism by means of data analysis, the relative importance of these representatives was introduced in this study, which was calculated through their proportions (%) within their own homologue group (Table 4). The results showed an average contribution of 22.38%–27.96% was from the CP-route representatives in PCDD side, while it only contribute about 6.86%–7.99% in PCDF side. In addition, the contribution to PCDDs and PCDFs were both decreased as the blending proportion of SS increased.

Based on the homologue profiles, the PCDD/F congeners were also analyzed by principal

**Table 4.** The relative importance of CP-route congeners (%).

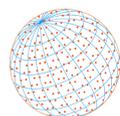
Congeners	S-P	S-C	M-0%	M-2.5%	M-5%
1,3,6,8-TCDD	3.42	19.29	41.11	33.92	2.20
1,3,7,9-TCDD	2.37	10.36	22.00	20.84	3.39
Sum of TCDD	5.79	29.65	63.11	54.76	5.59
1,2,4,7,9/1,2,4,6,8-PeCDD	91.55	87.80	69.10	87.59	88.66
1,2,3,6,8-PeCDD	0.62	5.03	10.29	3.85	0.67
1,2,3,7,9-PeCDD	2.58	3.54	7.21	2.87	2.24
Sum of PeCDD	94.75	96.38	86.60	94.31	91.56
1,2,3,4,6,8-HxCDD	37.74	62.59	18.02	14.85	37.13
Average of PCDD	23.05	31.44	27.96	27.32	22.38
2,4,6,8-TCDF	8.73	4.34	10.09	2.87	2.68
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	18.77	21.64	5.89	12.31	11.05
Sum of TCDF	27.49	25.98	15.99	15.18	13.72
Average of PCDF	13.75	12.99	7.99	7.59	6.86
Average of PCDD/F	20.72	26.82	22.97	22.39	18.50

component analysis (PCA) (Fig. S1). The data characteristics of TCDD, PeCDD, HxCDD and TCDF congeners were well explained by Factor 1 and Factor 2 with the total variance of 100%. However, the distribution of six CP-route representatives were not consistent with our previous studies (Zhang *et al.*, 2017b; Zhan *et al.*, 2019; Wang *et al.*, 2020) excepting of 1,3,6,8- and 1,3,7,9-TCDDs, and other congeners were not all distributed in the lower left quadrant and close to each other. All of which indicated that the CP-route would not be the major formation pathway of PCDDs and PCDFs, and higher proportion of SS reduced the potential contribution of CP-route.

As for the pyrolysis of SS, the contribution of CP-route representatives was lower than those in the co-combustion of coal and SS, indicating the CP-route could also not the major formation pathway of PCDD/Fs. In contrary, the contribution of these representatives in the combustion process of SS was higher than the co-combustion process of coal and SS, which could attribute to the more abundant organic pollutants in SS than coal (Chanaka Udayanga *et al.*, 2019).

The signal intensity of 2,3,7,8-substituted congeners were summarized in Table 5. Some studies reported that the chlorination of DD/DF could follow the sequence of 2 → 8 → 3 → 7 → 1 → 4 → 6 → 9 (Luijk *et al.*, 1992). The average signal intensity of 2,3,7,8-substituted PCDDs significantly decreased from 16.22% to 15.15%, and 11.03% with the increasing blending proportion of SS in co-combustion experiments (0%, 2.5%, and 5%, respectively), while those of 2,3,7,8-substituted PCDFs was slowly increased from 15.25% to 15.67%, and 16.67%, respectively. All of which indicated that the chlorination pathway of DD/F could not be the major formation pathway of PCDDs, but it partly contributed to the formation of PCDFs. As for the pyrolysis and combustion process of SS, the average signal intensity of 2,3,7,8-substituted PCDDs and PCDFs was generally lower than those in the co-combustion process of coal and SS, which could explain the less contribution of the chlorination pathway of DD/F.

As mentioned above, the PCDD/F concentration decreased after introducing oxygen into combustion process of SS, and the proportion of precursor pathway obviously increased. However, the chlorination pathway only increased slightly. However, these two formation pathways of PCDD/Fs reduced with increasing proportion of SS in co-combustion experiments, although the PCDD/F formation obviously increased. In pyrolysis and combustion process of SS, the decreasing concentration of PCDD/Fs and decreasing proportion of precursor and chlorination pathway could also influenced by the high content of S in SS, which can inhibit PCDD/F formation by following aspects: (1) decreasing chlorine source through convert Cl₂ into HCl (Ma *et al.*, 2021; Raghunathan and Gullett, 1996), (2) decreasing Cu/CuO or other metals/metal oxides through convert them into sulfate (Ma *et al.*, 2021; Shao *et al.*, 2010). As for the decreasing contribution of precursor and chlorination pathways in co-combustion process, which could attribute to the increasing performance of de novo synthesis reaction. It reflected the introduced S could not inhibit the formation of PCDD/Fs. In addition, it also revealed that higher blending proportion of SS would result in higher PCDD/F formation and emission.

**Table 5.** PCDD/F-Hagenmaier profile in each experiments (%).

Congeners	S-P	S-C	M-0%	M-2.5%	M-5%
2,3,7,8-TCDD	0.59	0.91	2.55	4.94	4.00
1,2,3,7,8-PeCDD	2.10	0.56	1.06	1.02	0.92
1,2,3,4,7,8-HxCDD	2.79	2.83	2.44	3.41	3.43
1,2,3,6,7,8-HxCDD	8.19	5.02	4.42	4.75	4.66
1,2,3,7,8,9-HxCDD	7.99	5.19	8.32	7.83	7.01
1,2,3,4,6,7,8-HpCDD	51.75	52.04	48.35	41.66	47.89
OCDD	9.14	22.08	46.42	42.47	9.28
PCDD average	11.80	12.66	16.22	15.15	11.03
2,3,7,8-TCDF	1.80	1.69	3.38	2.49	3.23
1,2,3,7,8-PeCDF	1.14	2.13	5.81	4.19	2.50
2,3,4,7,8/1,2,4,8,9-PeCDF	0.83	3.07	4.87	3.49	1.09
1,2,3,4,7,8-HxCDF	9.28	8.40	7.16	6.79	6.84
1,2,3,6,7,8-HxCDF	10.03	8.84	8.52	8.01	9.66
2,3,4,6,7,8/1,2,3,6,8,9-HxCDF	4.06	4.04	3.16	2.46	3.07
1,2,3,7,8,9/1,2,3,4,8,9-HxCDF	11.16	10.82	7.78	8.06	7.61
1,2,3,4,6,7,8-HpCDF	60.96	60.10	47.16	43.02	50.26
1,2,3,4,7,8,9-HpCDF	11.01	10.07	10.50	11.26	10.77
OCDF	41.17	48.35	54.23	66.91	71.71
PCDF average	15.14	15.75	15.25	15.67	16.67
PCDD/F average	13.77	14.48	15.65	15.46	14.35

3.4.2 Correlation analysis

To better reveal the formation pathways and influence factors of PCDD/Fs in the co-combustion process, this study also analyzed the relationship among the PCDD/F homologues, chlorination degree, and key elements in coal and SS based on the data in Table 2, Table 3, and Fig. 2(a), and the analysis results were shown in Fig. 3. These factors distributed in the lower left quadrant (TCDF, C, Hg, $d_{c-PCDDs}$, and $d_{c-PCDFs}$) and higher right quadrant (other factors), which mean the correlation between factors in lower left quadrant and other factors in higher right quadrant was not strong. The reason could be attributed to the influence of inhibition element (S) in higher right quadrant. In the higher right quadrant, chlorine source (Cl), metal catalyst (Fe), and most PCDD/F homologues excepting TCDFs distributed closely and showed important relationship between each other, which was closely related to the formation mechanism of PCDD/Fs. In addition, the points of Cu and some other factors were not found in Fig. 3, which indicated their less relationship or even contribution to the formation of PCDD/Fs in the co-combustion process. Overall, the de novo synthesis should be the major formation pathway of PCDD/Fs in the co-combustion process of coal and SS.

4 CONCLUSIONS

This study carried out five parallel experiments, including the pyrolysis of SS, the combustion of SS, the co-combustion of coal and SS with the proportion of 0%, 2.5% and 5%, respectively.

As the blending proportion increased, the emission concentration of PCDD/Fs respectively increased from 0.42 ng g⁻¹ (0.0022 ng I-TEQ g⁻¹) to 0.54 ng g⁻¹ (0.0030 ng I-TEQ g⁻¹) and 1.70 ng g⁻¹ (0.0305 ng I-TEQ g⁻¹). The dominant part was also changed from PCDFs (0.32 ng g⁻¹ in M-0%, 0.38 ng g⁻¹ in M-2.5%) to PCDDs (1.11 ng g⁻¹ in M-5%). In addition, the PCDFs was always dominated by OCDF (25%–47%) and TCDFs (8%–23%), while PCDDs was always dominated by TCDDs (3%–39%), PeCDDs (5%–18%), and OCDD (6%–13%).

The formation concentration of PCDD/Fs in the combustion process of SS was about 0.34 ng g⁻¹ (0.0019 ng I-TEQ g⁻¹), which was evenly distributed by PCDDs (0.17 ng g⁻¹) and PCDFs (0.17 ng g⁻¹). In the pyrolysis process of SS, the concentration of PCDD/Fs was 0.59 ng g⁻¹ (0.0037 ng I-TEQ g⁻¹), dominated by PCDDs (0.38 ng g⁻¹). The TCDDs, PeCDDs, OCDD, TCDFs, PeCDFs, and OCDF were the dominant homologues.

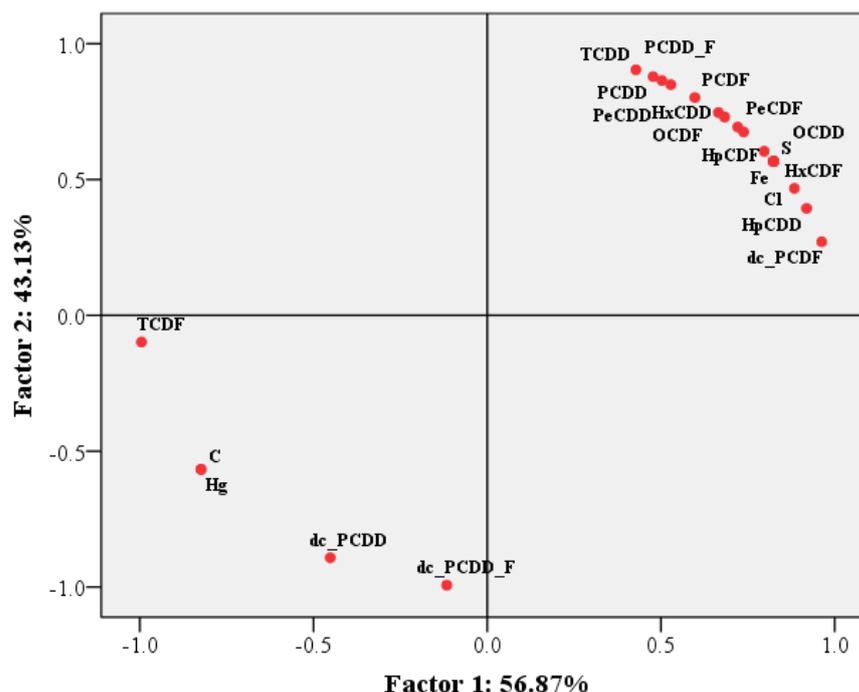
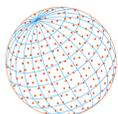


Fig. 3. Principal component analysis results of PCDD/F homologues, chlorination degree, and key elements.

The de novo synthesis should be the major formation pathway of PCDD/Fs in the co-combustion process of coal and SS. The relative importance analysis revealed that the CP-route and the chlorination of DD/F were not the major formation pathway of PCDD/Fs. On the basis of sufficient carbon sources, the PCA analysis revealed the chlorine source (Cl) and metal catalyst (Fe) should contribute a lot on the formation of PCDD/Fs.

The results pave the way for further optimization on the operation of co-combustion of coal and SS and assist in controlling the PCDD/F emission from co-combustion process.

ACKNOWLEDGMENTS

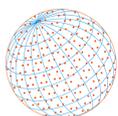
This study was supported by the National Key Research and Development Program of PCDD/F China (2020YFC1910100).

SUPPLEMENTARY MATERIAL

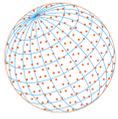
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