SUPPRESSING THE FORMATION OF POPS BY N/S-CONTAINING POLYMER INHIBITORS DURING THE IRON SINTERING

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Introduction

Chlorobenzene (CBzs), Polychlorinated Biphenyls (PCBs) and Dioxin (Polychlorinated Dibenzo-P-Dioxins/Dibenzofurans, PCDD/Fs) are a kind of persistent organic pollutants (POPs) which are ubiquitous in various environmental media and pose a serious threat to human and environmental health. These compounds are characterized by environmental persistence, long-range transport, bioaccumulation and high toxicity, so they were listed as one of the first controlled targets in "the Stockholm Convention on Persistent Organic Pollutants" signed in 2001. Incomplete combustion of carbon and chlorine during fuel combustion can produce harmful by-products, such as PCDD/Fs, which are unintentionally formed during various combustion and thermal processes[1-2]. For instance, the typical industrial thermal process of iron sintering is one of the main sources of atmospheric pollution for PCDD/Fs. The PCDD/Fs emission during the iron sintering process accounts for 57 % of the total emissions from the iron and steel industry, which is the first major industry for priority control of PCDD/Fs emissions in China. In this study, we first investigated the suppression effect of a novel polymer inhibitors, namely urea formaldehyde resin (UFR), thiosemicarbazide formaldehyde resin (TSCFR) and thiourea formaldehyde resin (TUFR), on the formation of POPs in fly ash during the iron sintering process. CBzs, PCBs and PCDD/Fs were used to explore the inhibition mechanism of POPs by N/S-containing polymer inhibitors in model fly ash (MFA).

Materials and methods

In this study, three N/S-containing polymer inhibitors were synthesized based on previous studies on the inhibitory effects of N- and S-containing inhibitors on POPs. These N/S-containing polymer inhibitors were applied in the MFA during heating experiment. The UFR inhibitor was made by condensation polymerization of urea and formaldehyde as monomers in acidic medium. TSCFR and TUFR inhibitor were made by condensation polymerization of formaldehyde with thiosemicarbazides and thioureas, respectively. The composition and ratio of MFA were determined according to the components of actual fly ash[3]. Two analytical methods, X-ray diffraction (XRD) and X-ray fluorescence spectroscopy (XRF), were used to analyze the components of actual fly ash[4]. Detailed information on the preparation of MFA were shown in Table 1.

Table 1. The detailed information of MFA preparation (g)

Groups	Fe_2O_3	AC	KCl	$CuCl_2$	SiO_2	inhibitors
Blank	2.5	0.2	0.736	0.0134	1.5506	0
UFR	2.5	0.2	0.736	0.0134	1.5006	0.05
TSCFR	2.5	0.2	0.736	0.0134	1.5006	0.05
TUFR	2.5	0.2	0.736	0.0134	1.5006	0.05

MFA (5 g) was heated by the tubular furnace with the 10 °C· min^{-1} temperature rise procedure to 350 °C (for 30 min). Synthetic air composed of 21% O_2 and 79% N_2 was passed to the tubular reactor. The total flow rate was 21 mL/min, which was controlled by a mass flowmeter. When all the gas products were allowed to enter the toluene absorption device after the heating reaction, continued to ventilate for 30 minutes.

Results and discussion

Different additives may have a significant impact on the formation of PCDD/Fs in the iron sintering process. Studies have shown that 350 ℃ is an optimum temperature for the formation of PCDD/Fs[5]. In this study, the MFA heating experiment of three N/S-containing polymer inhibitors was carried out at a temperature of 350 °C for 30 min. 5 g of MFA with an inhibitor content of 1wt% was used in the experiment. The suppression effect of N/S-based on the formation of CBzs was shown in Figure 1. It had obvious inhibitory effects on CBzs by UFR, TSCFR and TUFR. The TUFR has the highest inhibitory efficiency. When the amount of inhibitor added was 1wt%, the inhibitory efficiency of TUFR inhibitor was as high as 91.7%. Only the N element had an inhibitory effect on CBzs. Both N and S elements had inhibitory effects on CBzs, which was the difference between TUFR inhibitors and UFR inhibitors. S was the leading element for TUFR inhibitors to inhibit the formation of CBzs. N element tends to inhibit the formation of low-chlorinated products in the gas phase while S element tends to inhibit the formation of high-chlorinated products in the solid phase. The effect of TSCFR inhibitor was between UFR and TUFR inhibitor, but the inhibitory effect of N element was dominant.

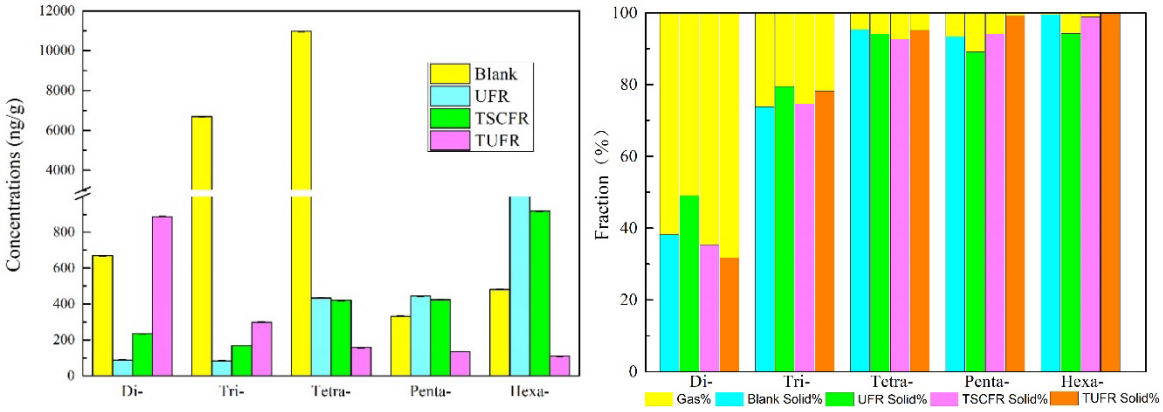

Figure 1. Suppression effect of different inhibitors on the formation and distributions of CBzs

The inhibitory effect of UFR, TSCFR and TUFR polymer inhibitors on PCBs was similar to that of CBzs. When the addition amount of thiourea-formaldehyde polymer inhibitor is 1wt%, the inhibition efficiency of PCBs was as high as 92.0%. UFR inhibitors tend to inhibit the generation of low-chlorinated PCBs. However, TUFR inhibitors tend to inhibit the production of highly chlorinated PCBs. The inhibitory effect of PCBs by TSCFR inhibitor was between UFR and TUFR inhibitor.

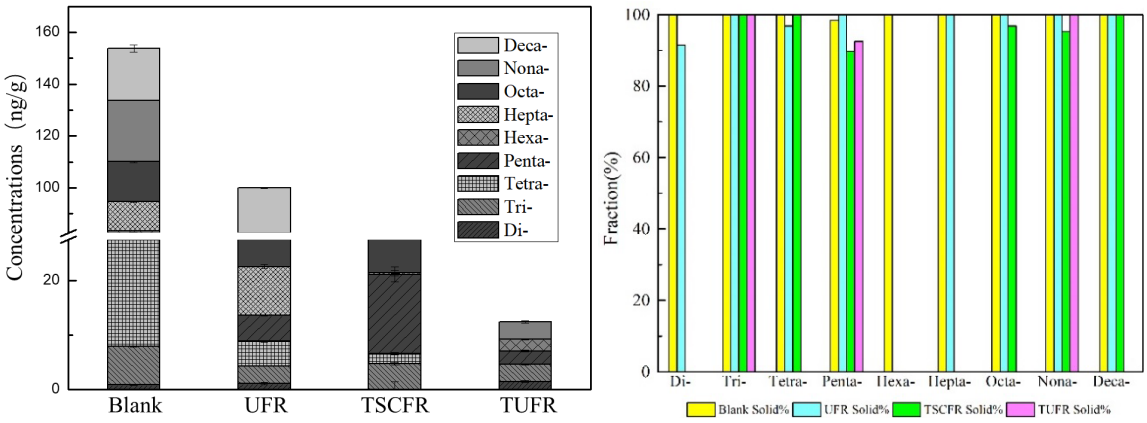

Figure 2. Suppression effect of different inhibitors on the formation and distributions of PCBs

In general, PCDFs are easier to form than PCDDs in the heat source process[6]. UFR, TSCFR and TUFR inhibitors all have obvious inhibitory effects on PCDD/Fs. Meanwhile, it's also showed significant inhibitory effects on the toxic equivalent (TEQ) concentration of PCDD/Fs. The inhibitory efficiency of TUFR was the highest. When the amount of inhibitor added was 1wt%, the inhibitory efficiency of TUFR inhibitor on PCDD/Fs was 82.6%. The three N/S- containing polymer inhibitors all tend to inhibit the formation of PCDDs.

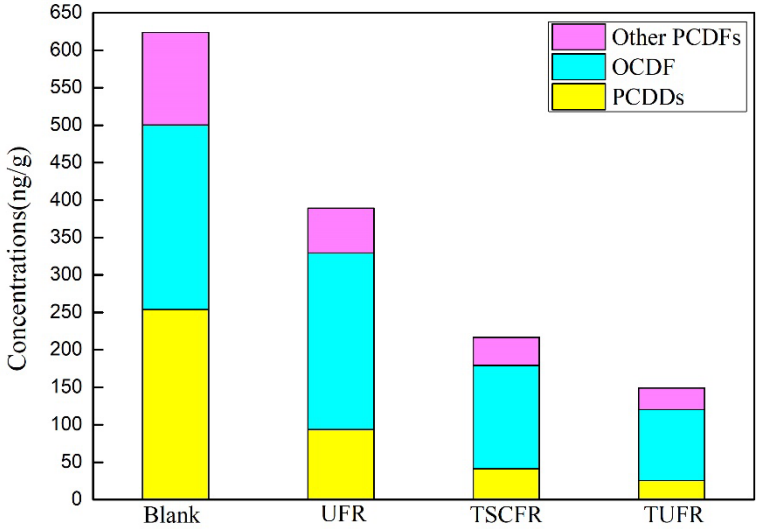

Figure 3. Suppression effect of different inhibitors on the formation and distributions of PCDD/Fs

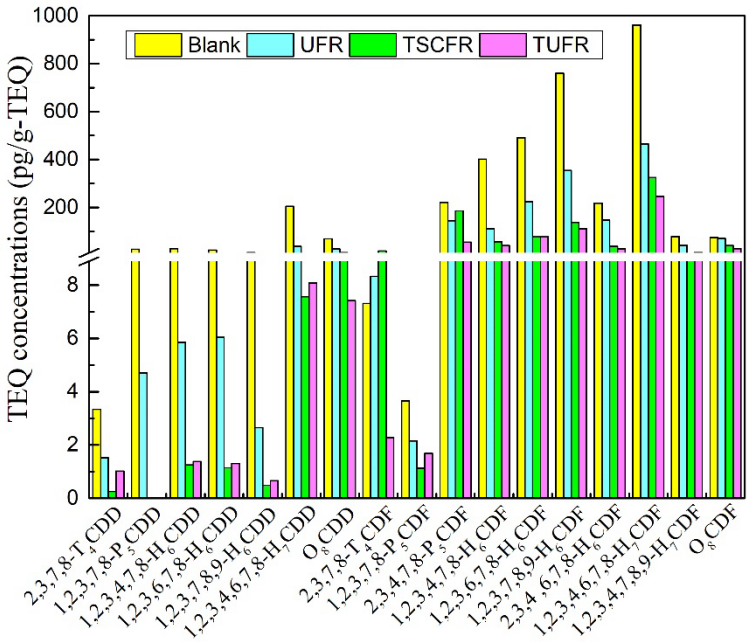

Figure 4. Suppression effect of different inhibitors on the TEQ concentration fingerprint of PCDD/Fs

Suppression effect of TUFR with different content on the formation of PCDD/Fs were shown in Figure 4. When the addition amount of thiourea formaldehyde polymer inhibitor is from 0.5wt% to 2wt%, the amount of PCDD/Fs gradually decreased with the increasing of inhibitor addition amount. While 5wt% inhibitor added, the amount of PCDD/Fs generated was slightly higher than the amount added at 2wt%. Therefore, when the inhibitor was 2 wt% added, the PCDD/Fs had the highest suppression efficiency with 99.9 %.

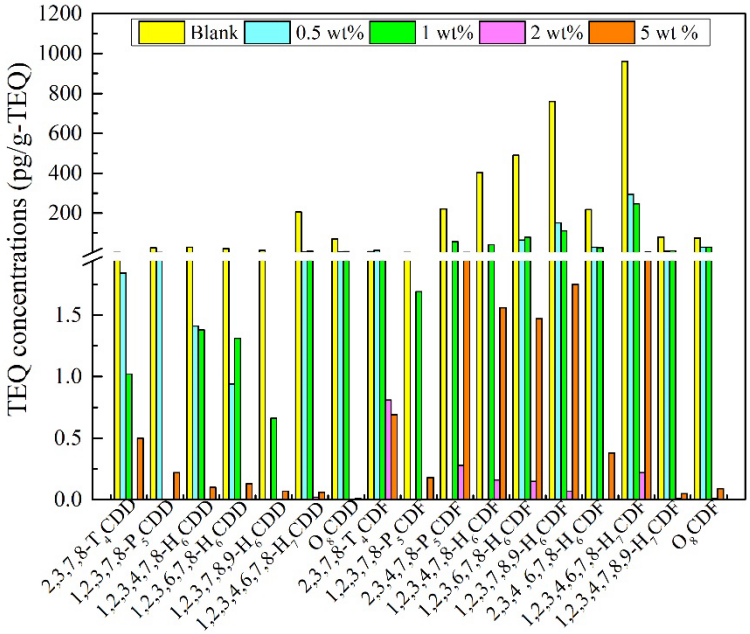

Figure 4. Suppression effect of TUFR inhibitors with different content on the formation of PCDD/Fs

Acknowledgements
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References
[1] Li Y, Chen T, Zhang J, et al. (2015) *Waste Management*. 36:130-135.
[2] Zou L, Ni Y, Yuan G, et al. (2018) *Chemosphere*. 195:491-497.
[3] Ahamad T, Alshehri S. (2012) *Journal of Thermal Analysis & Calorimetry*. 109(2):1039-1047.
[4] Zhang Y, Buekens A, Liu L, et al. (2016) *Chemosphere*. V155:300-307.

[5] Olie D K . (1991) *Chemosphere*. 23:1205-1211.
[6] Zhang C, Li X, Zhou Z. (2019) *Ecotoxicology and Environmental Safety*, 184:109615.