Amino Compounds as Inhibitors of De Novo Synthesis of Chlorobenzenes

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The inhibitory effects of four amino compounds on the formation of chlorobenzenes (CBzs) - dioxin precursors and indicators, and the inhibitory mechanisms were explored. The results show that NH4H2PO4 can decrease the total yields of CBzs (1,2di-CBz, 1,3di-CBz, 1,4di-CBz, penta-CBz and hexa-CBz) by 98.1%±1.6% and 96.1%±0.7% under air and nitrogen flow. The inhibitory effects indicated by the total yields of CBzs follow the order NH4H2PO4 > NH4HF2 > (NH4)2SO4 > NH4Br under air and nitrogen flow and NH4H2PO4 ≈ (NH4)2SO4 ≈ NH4HF2 > NH4Br under nitrogen flow. The inhibition mechanism revealed by thermal analysis that CuCl2 was converted to CuPO3 by reacting with NH4H2PO4 below 200 °C, which can block the transfer of chlorine and formation of C–Cl bonds at 350 °C. The effects of the other three inhibitors were weaker because their reactions with CuCl2, which form other copper compounds, and the reaction of CuCl2 with carbon, which forms C–Cl bonds, were almost simultaneous and competitive.

Oxygen influenced the yield of CBzs obviously, and the total yield of five CBzs sharply increased with oxygen. Because of their high efficiency, low environmental impact, low cost, and availability, amino compounds - especially NH4H2PO4 - can be utilized as inhibitors of CBzs during incineration.

Incineration is one of the mainstream technologies for treatment of wastes such as municipal solid waste (MSW), medical waste, and other hazardous wastes, due to its volume reduction ability, energy recovery and high efficiency. An important issue for environmental safety and human health is the increased stringency of environmental standards for controlling pollutions. There are still barriers for pollutions control, including toxic chlorinated aromatic compounds and dioxin-like compounds. De novo synthesis, precursor synthesis and homogeneous gas synthesis have been reported to be the main mechanisms for the formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). De novo synthesis occurs in the presence of fly ash and chlorine in the post-combustion zone, which is believed to contribute more to the generation of PCDD/Fs. Generally, temperatures that favor de novo synthesis range within 300–400 °C and the role of CuCl2 in de novo synthesis is more significant than other metal compounds. Gullett et al. proposed that CuCl2 catalyzes Cl2 generation by the Deacon reaction between HCl and O2, thus promoting dioxin formation. However, the Deacon reaction has been proven not to play such a decisive role. Complex chlorination with HCl and Cl2 on dioxin formation and observed the parallel production of PCDD/Fs. In the presence of oxygen, CuCl2 directly provides Cl, a donor for C, thus forming dioxin-like compounds; this reaction has been confirmed by another study. Takaoka et al. inferred that CuCl2 is involved in cyclic conversion via dechlorination and chlorination with oxygen and organic/inorganic chloride. Their theory was reconfirmed by Shao et al. In conclusion, CuCl2 is a potential catalyst or Cl donor that promotes the formation of chlorinated aromatic compounds.

On the basis of the known mechanism of dioxin formation, diverse inhibitors have been used in the source control or end-of-pipe removal for dioxin, including nitrogen-containing compounds (NH3, urea and (NH4)2SO4), sulfur-containing compounds (elemental sulfur, SO2, (NH4)2SO4 and coal), hydroxy-functional groups and selective catalysts for reduction (SCR). Among them, the most well-known dioxin inhibitors are highly efficient SCR, such as VOx/TiO2, V2O5/WO3 and TiO2/V2O5/WO3 catalysts, which usually require a complex preparation process and have high cost. Lundin and Jansson found that the
toxic equivalent quantity of PCDF concentration decreased by 75% when the ratio of (NH₄)₂SO₄ to HCl increased from 3:1 to 6:1. The study of Hajizadeh et al. indicated that SO₂ was more effective than NH₃ in inhibiting the formation of PCDD/Fs, while the contrast between (NH₄)₂SO₄ and CO(NH₂)₂ was contrary. In recent years, the suppression mechanisms of the formation of chlorinated aromatic pollutants by sulfur-containing and nitrogen-containing compounds have been discussed, including (1) transformation of Cl₂ to HCl, (2) sulfonation of dioxins or precursors and (3) conversion of metal chlorides (CuCl₂ or FeCl₃) with high catalytic activity to inert compounds. Yan et al. attributed the reduction of PCDD/Fs production by urea to the reaction of ammonia with active oxidant Cl₂. Shao et al. and Fujimori et al. proposed that SO₂ and H₂O can convert CuCl or CuCl₂ to CuSO₄ or CuO by detecting the residues, which was also proved by the thermodynamic equilibrium calculation. However, the fundamental information that enables an understanding of these mechanisms is still insufficient.

Amino compounds decompose at low temperature, and their reactions with CuCl₂ at low temperature are thermodynamically favorable, thereby they are generally advantageous in inhibiting CuCl₂ from donating Cl⁻ to form C–Cl bonds. In this study, we studied the inhibitory effects and mechanisms of four amino compounds on chlorobenzenes (CBzs), which are important precursors and indicators of dioxin. Except (NH₄)₂SO₄, the other three were used as inhibitor for the first time and their effects were compared with (NH₄)₂SO₄. Thermal analysis, which is beneficial to distinguishing the characteristic thermal reactions between inhibitors and model fly ash, was conducted combining with the simulated experiments, to reveal which one was more effective in inhibiting CBzs formation and why (mechanism).

**Results**

**Effect of inhibitors on CBzs formation.** The yields of the five CBzs and their total value on the mass basis of the SFA (μg/g-fly ash) are shown in Fig. 1. The total chlorine in the CBzs (equation (1)) and the degree of chlorination under air (a) and nitrogen (b) flow.

![Figure 1. CBzs yields, total chlorine in CBzs and the degree of chlorination under air (a) and nitrogen (b) flow.](image)

![Figure 2. Inhibition ratios of CBzs and total chlorine in CBzs under air (a) and nitrogen (b) flow.](image)
chlorination (equation (2)) were calculated from these yields (Fig. 1). The inhibition ratios for CBzs formation with each inhibitor were calculated through equation (3) and presented in Fig. 2.

\[ T_{\text{Cl}, j} = \sum_i \left( Y_{i, j} \times F_i \right) \]

\[ D_{\text{Cl}, j} = \sum_i \left( n_i \times \frac{Y_{i, j}}{MW_i} \right) / \sum_i \left( \frac{Y_{i, j}}{MW_i} \right) \]

\[ IR_{i, j} = 100 \times \left( \frac{Y_{i, \text{SFA}} - Y_{i, j}}{Y_{i, \text{SFA}}} \right) \]

where \( i \) is the type of CBzs, \( j \) is the type of sample, and \( T_{\text{Cl}, j} \) is the total amount of chlorine in the CBzs on mass basis of the SFA sample \( j \) (μg/g-fly ash), \( Y_{i, j} \) and \( Y_{i, \text{SFA}} \) are the yields of CBz \( i \) on the mass basis of the SFA sample \( j \) and SFA, respectively (μg/g-fly ash), \( F_i \) is the mass fraction of chlorine in CBz \( i \) (dimensionless), \( D_{\text{Cl}, j} \) is the degree of chlorination of sample \( j \) (dimensionless), \( n_i \) is the number of chlorine atoms in the CBz molecule \( i \) (dimensionless), \( MW_i \) is the molecular weight of \( i \) (mol/g), and \( IR_{i, j} \) is the inhibition ratio of CBz \( i \) for the sample \( j \) (%).

Under air flow, the yields of low-chlorinated CBzs (1,2-di-CBz, 1,3-di-CBz, and 1,4-di-CBz) were much lower than those of high-chlorinated CBzs (penta-CBz and hexa-CBz) in SFA, similar to the trends for the \( \text{NH}_4\text{H}_2\text{PO}_4 \) (I), \( \text{(NH}_4\text{)}_2\text{SO}_4 \) (II), \( \text{NH}_4\text{HF}_2 \) (III), and \( \text{NH}_4\text{Br} \) (IV) runs. This result indicated that high-chlorinated CBzs formed more easily than low-chlorinated CBzs did. A study by Fujimori et al. also showed similar distribution ratios, but the absolute yield of each CBz in the present study was higher because of the larger amount of CuCl\(_2\cdot2\text{H}_2\text{O}\) added, which is necessary for determining the mechanism. As shown in Fig. 1, chlorine from the two CBzs accounted for a large proportion of the total chlorine because of the high yield and high fraction of chlorine in penta-CBz and hexa-CBz.

Compared with that of SFA, the total yield of CBzs and the total chlorine in CBzs decreased by various degrees upon addition of inhibitors under air flow, especially in the case with \( \text{NH}_4\text{H}_2\text{PO}_4 \) addition. The yields of low-chlorinated CBzs (1,2-di-CBz, 1,3-di-CBz, 1,4-CBz) and high-chlorinated CBzs (penta-CBz, hexa-CBz) for the SFA–Air mixture were 1.7 and 71 μg/g-fly ash respectively, which significantly decreased to 0.28 and 1.2 μg/g-fly ash for the I\(_4\)–Air mixture. Formation of all CBzs was inhibited by 41%–100%. The total chlorine from CBzs also decreased, and the degree of chlorination changed from 5.5 to 3.3. The other three inhibitors had different effects on the yields of different CBzs. To evaluate the reduction of CBzs formation, \( \text{NH}_4\text{H}_2\text{PO}_4 \) was compared with those inhibitors. Kuzuhara found that the amount of formed PCDD/Fs decreased significantly upon addition of ammonia or urea. A possible mechanism for the suppression is a competing reaction of organic compounds with \( \text{NH}_3 \) and \( \text{CN} \) radicals, which are produced from urea or ammonia decomposition. However, they suggested that further studies are necessary to evaluate the effect of these compounds on the behavior of copper and the role in the de novo synthesis.

With I\(_4\) under air flow, the total yield of CBzs decreased by 37%, and the penta-CBz yield decreased by 92% to 3.0 μg/g-fly ash. The degree of chlorination did not decrease, but the total chlorine from CBzs declined by 36%. In Yan’s study, \( \text{(NH}_4\text{)}_2\text{SO}_4 \) reduced the yield of PCDD/Fs in the gas phase by about 93% (about 60% PCDDs and 98% PCDFs); when gaseous \( \text{SO}_2 \) was used, the yields of CBzs, PCDDs, and PCDFs were reduced by about 50%, 30%, and 50%, respectively. Thus, \( \text{(NH}_4\text{)}_2\text{SO}_4 \) and \( \text{SO}_2 \) are effective inhibitors of dioxin and CBzs formation. The mechanism of \( \text{(NH}_4\text{)}_2\text{SO}_4 \) inhibition of CBzs de novo synthesis is discussed later. Some S-containing or N-containing compounds showed inhibitory effects on dioxin synthesis, such as ethylenediaminetetraacetic acid, nitritoltriacetic acid, and \( \text{Na}_2\text{S} \). These effects were explained owing to the interaction between inhibitors and catalysts such as Cu.

Based on the inhibitory effects of the amino compounds on CBzs formation, \( \text{NH}_4\text{HF}_2 \) and \( \text{NH}_4\text{Br} \) were selected to study their potential effects on controlling CBzs. The results show that the inhibition effect of \( \text{NH}_4\text{HF}_2 \) is similar to that of \( \text{(NH}_4\text{)}_2\text{SO}_4 \) on the synthesis of low-chlorinated CBzs and penta-CBz, while \( \text{NH}_4\text{Br} \) is better on the hexa-CBz inhibition. The degree of chlorination in I\(_4\) decreased from 5.5 to 5.2 with inhibitions on penta-CBz and hexa-CBz. The effect of \( \text{NH}_4\text{Br} \) was smaller than that of the other three, but it still reduced the formation of all CBzs and the total yield of CBzs by 3%–88.7%.

Under nitrogen flow, CBzs yields in all cases were very low compared with those obtained under air flow. This difference is due to the difficulty of C–C bond scission in the absence of oxygen, which leads to formation of aromatic compounds in the presence of CuCl\(_2\cdot2\text{H}_2\text{O}\), while \( \text{(NH}_4\text{)}_2\text{SO}_4 \) showed a little less inhibition effect. In
Hajizadeh's study, both SO$_2$ and NH$_3$ were effective in inhibiting the formation of PCDD/Fs$^{27}$, and the effect of SO$_2$ was more significant than that of NH$_3$. Even though some controversies existed in the synergistic or competitive effect on PCDD/Fs inhibition by S-containing and N-containing compounds, (NH$_4$)$_2$SO$_4$ as a complex of S and N has been confirmed to have the restraint effect on PCDD/Fs$^{28}$ as well as CBzs in this study. In the contrast of (NH$_4$)$_2$SO$_4$ with NH$_4$H$_2$PO$_4$ and NH$_4$HF$_2$, especially NH$_4$H$_2$PO$_4$, showed the significant increase of inhibition efficiency on CBzs. Thus, the amino compounds can decompose and produce reactive radicals that are highly-efficient on suppressing CBzs.

**Thermal analysis of the SFA samples.** As discussed above, the four amino compounds influence the profile of CBzs. However, the reason why they showed different inhibitory results, and how they affected CBzs formation were not clear, which might be related to their thermochemistry. To better understand the inhibition mechanism and to observe the physical transformation or chemical reactions, thermal analysis using TGA and DSC was conducted. The fraction of CuCl$_2$ was increased to that in real fly ash, so that the important physical-chemical changes could be observed together with the change of CBzs formation. Commonly used (NH$_4$)$_2$SO$_4$ was included in this studies for the comparison.

As shown in Fig. 3a,b, CuCl$_2$·2H$_2$O gradually underwent dehydroxylation (21 wt.%) at 50–100 °C and started to lose weight at 343 °C (air) or 348 °C (nitrogen). When the temperature reached 900 °C, the weight decreased by about 55% under air flow and by 65% under nitrogen flow. Under both atmospheres, one endothermic peak was produced at 441–445 °C. Another appeared at 471 °C only in the presence of oxygen. Under nitrogen flow at 350 °C, CuCl$_2$ dechlorinated, forming CuCl, which volatilized at 438–441 °C. Therefore, the residue formed at 400 °C and detected by XRD includes CuCl only (Fig. 4b). A similar finding was reported by Liu et al.$^{47}$ Under air flow, the residue obtained at 400 °C includes CuCl only (data not shown), whereas that obtained at 500 °C consisted of CuCl and CuO (Fig. 4a), which is in accord with the dechlorination observed by Takaoka et al.$^{22}$ The endothermic peak on the DSC curve and the smaller weight loss (10% less) compared with that under nitrogen flow suggest that oxygen oxidizes CuCl to CuO. The reactions and corresponding temperatures are indicated in equations (4)–(7). In the absence of other chlorine source, CuCl$_2$ produces chlorinated aromatic compounds, behaving as a Cl resource, transferring Cl to the C surface, and bonding with C. Takaoka et al.$^{16}$ and Fujimori et al.$^{48}$ found that the thermochemical conversion of CuCl$_2$ and thermal reaction of CuCl$_2$ with SO$_2$ occurred at below 300 °C and 280–350 °C respectively. In this study, the thermal conversion observed by DSC gave a direct and specific temperature that CuCl$_2$ decomposed, which is propitious to mechanism study.

$$\begin{align*}
100 \degree C & \quad CuCl_2 \cdot 2H_2O = CuCl_2 + 2H_2O(g) \\ 350 \degree C & \quad 2CuCl_2 = 2CuCl + Cl_2(g) \\ 430 \degree C & \quad CuCl(s) \rightarrow CuCl(l) \rightarrow CuCl(g) \\ 471 \degree C & \quad 4CuCl + O_2(g) = 2CuCl_2 + 2CuO 
\end{align*}$$

To identify the characteristic DSC peaks, AC and silica were respectively analyzed by TGA and DSC, respectively. In the presence of oxygen, AC started to combust at 400 °C (Fig. 3e), producing an intense exothermic peak. This also quickly increased the interior temperature, while the weight and heat flow remained stable under nitrogen flow (Fig. 3f). As no significant changes in TGA and DSC curves for silica were observed, they are not displayed.

The calculated weight loss of SFA consisting of AC and CuCl$_2$·2H$_2$O under air flow (according to the weight loss in TGA and mass fraction) was 9.5%, and the actual weight loss was 15%. This difference is probably caused by the greater volatilization of CuCl at higher internal temperature and the greater emission of aromatic compounds in the presence of oxygen. Under nitrogen flow, there was almost no difference in weight losses. XRD patterns (Fig. 4) show that the residue under air flow includes Cu$_4$OCl$_3$ and CuO and that under nitrogen flow includes CuCl, Cu, and Cu$_2$Cl(OH)$_3$. The presence of CuO under air flow contradicts with the results of thermal analysis in the 50–400 °C range (Fig. 3c), probably because the combustion of carbon in this system can increase the interior temperature.

**Discussion**

According to Fig. 3i,j, NH$_4$H$_2$PO$_4$ started to decompose at 203 °C under either air or nitrogen flow. An endothermic peak appeared at almost the same temperatures. NH$_4$H$_2$PO$_4$ decomposed into gaseous NH$_3$ and H$_2$O and solid-phase HPO$_4$, as shown by the weight loss (~30%) and by thermodynamic calculation (equation (8)). The weight loss for I$_2$ under air flow was calculated by summing the respective weight losses of silica, AC, CuCl$_2$·2H$_2$O, and NH$_4$H$_2$PO$_4$. The sum should be ~20% if there was no interaction between CuCl$_2$ and NH$_4$H$_2$PO$_4$. The real weight loss was 10% less than the calculated value, indicating the occurrence of interaction. In addition, endothermic peaks were produced at 100 °C and 191 °C under both atmospheres (Fig. 3k,l) and an exothermic peak was produced at 400 °C under air flow. Both indicate dehydration, a reaction between NH$_4$H$_2$PO$_4$ and CuCl$_2$, and carbon combustion. According to the XRD results (Fig. 4), the products included Cu$_4$P$_2$O$_7$ (Cu(PO$_3$)$_2$·CuO) (air), as well as CuCl and Cu(PO$_3$)$_2$ (nitrogen), which suggest that CuCl$_2$ reacted with NH$_4$H$_2$PO$_4$ (equation (9)). In contrast to SFA, CuCl$_2$ converted to CuPO$_3$ at a lower temperature instead of transferring Cl to C; thus, CBzs formation was restrained significantly. This not only explains the mechanism, but also suggests that CuCl$_2$ was the main Cl source. The diminution of the total chlorine in CBzs when NH$_4$H$_2$PO$_4$ was applied was caused by the decrease in the yield of CBzs and the degree of chlorination.
Figure 3. TGA-DSC of CuCl$_2$·2H$_2$O, AC, SFA, NH$_4$H$_2$PO$_4$ and I$_7$ under the air (a,c,e,g,i,k) and nitrogen (b,d,f,h,j,l) flow.
The suppression effects of (NH₄)₂SO₄, (NH₄)₂S₂O₃, CO(NH₂)₂S, and SO₂ on the formation of PCDD/Fs have been studied, but the mechanisms with these inhibitors are not as clear as that with SO₂. One proposed mechanism is the conversion of copper into non-reactive sulfates. Partial sulfation of CuCl₂ by SO₂ in the presence of O₂ to CuSO₄ and Cl₂ has been reported. Below 400 °C in this study (Fig. 5), (NH₄)₂SO₄ completely decomposed into gaseous NH₃, H₂O, and SO₃, producing endothermic peaks at 293 °C (air) and 297 °C (nitrogen) (equation (10)). Upon addition of (NH₄)₂SO₄ to SFA, endothermic peaks were produced at 100, 260, and 312 °C under air flow, as well as at 100, 263, and 312 °C under nitrogen flow. An exothermic peak at 400 °C was also produced under air flow. The characteristic peaks at 260–263 °C under both atmospheres do not correspond to the constituents of IS, indicating that a reaction between CuCl₂ and remaining (NH₄)₂SO₄ occurred with this endothermic phenomenon (equation (11)). When there was no interaction between SFA and (NH₄)₂SO₄, the calculated weight loss was 9% less than the experimental value, suggesting that some products remained in the residues. The XRD results show Cu₂OCl₂, CuO, and weak CuSO₄·H₂O peaks, which indicate that dechlorination and sulfation were simultaneous, with dechlorination being dominant. Therefore, the inhibitory effect was weaker than that of NH₄H₂PO₄. Although the total yield of CBzs and the total chlorine in CBzs decreased, the degree of chlorination did not decline because hexa-CBz easily formed with the stable structure.

\[
\begin{align*}
203 °C & \quad \text{NH}_4\text{H}_2\text{PO}_4 = \text{NH}_3 + \text{H}_2\text{O} + \text{HPO}_3 \\
191 °C & \quad \text{CuCl}_2 + 2\text{NH}_4\text{H}_2\text{PO}_4 = \text{Cu}(\text{PO}_3)_2 + 2\text{HCl} + 2\text{NH}_3 + 2\text{H}_2\text{O}
\end{align*}
\]

**Figure 4.** XRD patterns of the residues under air (a) and nitrogen (b) flow.

\[
\begin{align*}
290 °C & \quad (\text{NH}_4)_2\text{SO}_4 = 2\text{NH}_3 + \text{H}_2\text{O} + \text{SO}_3 \\
240 °C & \quad \text{CuCl}_2 + (\text{NH}_4)_2\text{SO}_4 = \text{CuSO}_4 + 2\text{NH}_3 + 2\text{HCl}
\end{align*}
\]
ranges of 72–114 °C, 158–216 °C, and 325–400 °C under air flow, as well as at 75–112 °C and 159–297 °C under nitrogen flow. These weight losses correspond to hydration, a reaction between CuCl₂ and NH₄HF₂, and carbon combustion. The residue (Fig. 4) formed under air flow was a mixture of CuO, Cu₂OCl₂, and CuF₂, whereas that formed under nitrogen flow consisted of CuF₂. The reaction temperature for equation (13) was higher than that for NH₄HF₂ decomposition. In addition, the amount of the functional radical of F⁻ did not exceed that of Cu²⁺, thus decreasing the degree of conversion and the inhibitory effect. The yields of CBzs and the degree of chlorination of IF were lower than those of IP, indicating low degree of conversion.

\[
\begin{align*}
130 ^\circ & \text{C} & \quad \text{NH}_4\text{HF}_2 = \text{NH}_3 + 2\text{HF} \\
210 ^\circ & \text{C} & \quad \text{CuCl}_2 + \text{NH}_4\text{HF}_2 = \text{CuF}_2 + \text{NH}_3 + 2\text{HCl}
\end{align*}
\]

Similar to NH₄HF₂, NH₄Br is an unstable amino compound below 400 °C, producing an endothermic peak at 155 °C (Fig. 7). From 180 to 375 °C, NH₄Br started to decompose (equation (14)) and lost weight completely. As the TGA curves show, two-step weight losses occurred at 179–313 °C and 350–400 °C under air flow, and one-step loss occurred at 176–350 °C under nitrogen flow when NH₄Br was added to SFA. The DSC curves obtained under air flow show weak endothermic peaks at 144 and 268 °C and intense peaks at 400 °C. Those obtained under nitrogen flow have peaks at 100, 146, and 277 °C. New peaks at 268 °C (air) and 277 °C (nitrogen) are characteristic of the product IBr, indicating that there was an interaction between SFA and NH₄Br. This interaction is also evidenced by comparison between the actual and calculated weight losses. The residues obtained under air flow (Fig. 3) and under nitrogen flow consisted of CuO and CuBr, respectively. Consistent with the results of thermal analysis and XRD, CuCl₂ could react with NH₄Br during its decomposition (equation (15)). As these two changes occurred under almost same temperature ranges, the inhibitory effect decreased.

\[
\begin{align*}
180 ^\circ & \text{C} & \quad \text{NH}_4\text{Br} = \text{NH}_3 + \text{HBr} \\
270 ^\circ & \text{C} & \quad 2\text{CuCl}_2 + 2\text{NH}_4\text{Br} = 2\text{CuBr} + 2\text{NH}_3 + 2\text{HCl} + \text{Cl}_2
\end{align*}
\]
Methods

Materials. The mass composition of the simulated fly ash (SFA) in each experiment is shown in Table 1. The inhibitors were added at Cu/H$_2$PO$_4$$^-$$^-$, Cu/SO$_4$$_2$$^-$$^-$$^-$$^-$, Cu/HF$_2$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^-$$^
The GC was equipped with a HP-5MS column (30 m × 0.25 mm ID) (Agilent, USA) and an electron capture detector. The oven temperature program was set at: 40 °C for 1.5 min, 10 °C/min to 100 °C with 3 min holding time, 10 °C/min to 240 °C with a final hold of 1 min. The carrier gas was helium (30 mL/min), the detector temperature and transfer line temperature were set at 300 °C and 250 °C respectively. The analysis of 1,2 di-CBz, 1,3 di-CBz as well as 1,4 di-CBz were splitless, penta-CBz and hexa-CBz were split with split ratio 10:1. The yields of 1,2 di-CBz, 1,3 di-CBz, 1,4 di-CBz, penta-CBz, and hexa-CBz were calculated on the mass basis of fly ash. The recovery ratios for the analysis of CBzs in the resins ranged within 70%–130%.

Thermogravimetric analysis (TGA) and differential scanning calorimeters (DSC) (Q600 SDT, TA instrument, USA) were used for thermal analysis of the samples. Heating was done at a rate of 10 °C/min from 50 °C to specified values, at which the temperature was maintained for more than 60 min. The flow rate of air or nitrogen was adjusted to 100 mL/min.
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**Author Contributions**
S.J.W. and H.Z. designed the experiments, S.J.W. and W.T.L. performed the experiments and wrote the paper with the help of H.Z., P.J.H. and L.M.S. All authors reviewed the manuscript.

**Additional Information**
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