

# Revealing the Mechanism of Dioxin Formation from Municipal Solid Waste Gasification in a Reducing Atmosphere

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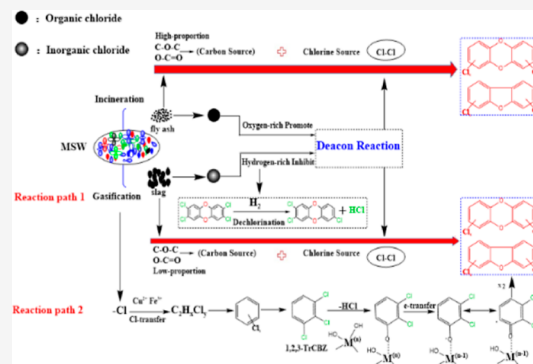
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Supporting Information

**ABSTRACT:** Gasification is an effective technology for the thermal disposal of municipal solid waste (MSW) with lower dioxin emission compared to the prevailing incineration process. Nevertheless, the mechanism of dioxin formation in the reducing atmosphere during the gasification process was seldomly explored. Herein, the effects of the atmosphere, temperature, and chlorine source were systematically investigated in terms of dioxin distribution. With  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as gasification agents, a reducing reaction atmosphere was formed with abundant  $\text{H}_2$  which effectively suppressed the generation of C–Cl, contributing to a substantial decrease of dioxin concentration by  $\sim 80\%$  compared to the incineration process. The formation of dioxin was favored at temperatures below  $700\text{ }^\circ\text{C}$  with its peak concentration achieved at  $500\text{ }^\circ\text{C}$ . It was unveiled that inorganic chlorine played a dominant role in the reducing atmosphere, with a lower proportion of C–O–C/O–C=O on residual slag compared to an oxidizing atmosphere. Additionally, the generated  $\text{H}_2$  reduced the concentration of dioxins by attacking C–Cl and inhibiting the crucial Deacon reaction for dioxin formation, validated by density functional theory calculation. Eventually, the formation route paradigm and the reaction mechanism of dioxin formation from MSW gasification were revealed, facilitating and rationally guiding the control of dioxin emission.

**KEYWORDS:** gasification, dioxins, reducing atmosphere, formation mechanism, DFT calculation



## 1. INTRODUCTION

Over the last decades, the annual disposal volume of MSW (municipal solid waste) has increased rapidly in China ( $\sim 235.11$  million tons in 2020),<sup>1</sup> and the total MSW generation is expected uphill to 3.4 billion tons by 2050 worldwide.<sup>2</sup> Incineration technology as the predominant route for MSW thermal treatment is relatively mature in China with about 463 waste incineration plants built by 2020.<sup>1</sup> However, dioxin emission emerged as the inevitable issue to hinder the global development of incineration technology in MSW treatment. Due to the intrinsic highly toxic and carcinogenic properties, dioxins are among the most toxic persistent organic pollutants listed according to the Stockholm Convention.<sup>3–7</sup> Therefore, developing an efficient and clean thermal disposal technology for MSW is essential to reduce the risk of dioxin emission toward the realization of future zero-waste sustainable cities.

Gasification technology is proposed as an alternative for MSW treatment benefiting from low pollutant emissions and high energy utilization. Distinct from the oxidizing atmosphere in the incineration process, a reducing atmosphere is formed during the gasification process with an abundant mixture of reducing gases. For example, the utilization of  $\text{CO}_2$  and steam as gasification agents can generate  $\text{CO}$  and  $\text{H}_2$  during thermal reactions. In fact, gasification technology is assumed to

effectively inhibit dioxin formation in the absence of oxygen and thereby exhibited a great difference in dioxin emission between the incineration and pyrolytic gasification process for thermal MSW treatment.<sup>8–11</sup>

In the oxidizing atmosphere during the MSW incineration process, dioxins are extremely difficult to degrade because the oxygen will accelerate the formation of chlorinated phenoxy type radicals, which are considered as the primary precursors for dioxin formation via radical–chain reactions (through radical–molecule as well as radical–radical mutual reactions).<sup>12–14</sup> Vogg et al. performed a comparative analysis of dioxin formation in fly ash with different oxygen contents (0, 1, 4, and 10%), indicating that the formation of PCDD (polychlorinated dibenzo-p-dioxins) and PCDF (polychlorinated dibenzofurans) pollutants increased with oxygen content.<sup>15</sup> Besides, temperature and chlorine source are also considered as crucial factors in the formation of dioxins during the thermal process.<sup>16</sup> At high temperature, the precursors

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**Table 1. Composition, Distribution, and Proximate and Ultimate Analyses of MSW**

Composition distribution (wt %)								
sandy soil	glass	metal	paper	plastic	cloth	vegetation	kitchen waste	white plastic
5.80	2.94	0.48	19.77	19.66	2.94	3.80	44.13	0.48
proximate analysis (wt %)					ultimate analysis (wt %)			
moisture	ash	volatile matter	fixed carbon	C	H	N	S	O
5.41	3.12	76.58	14.89	31.96	4.747	0.3	ND	39.68

incurring the generation of dioxins, such as chlorinated aromatic compounds and aliphatic compounds, would decompose in the gas phase, leading to a low dioxin concentration. Related research demonstrated that the maximum amount of dioxins was normally generated at 350 °C, while further increase of temperature will contribute to substantial inhibition of dioxin emission in contrast.<sup>17–19</sup> Most of the organic chlorine and inorganic chlorine derived from MSW is released in the gas-phase form of HCl and further converted into Cl<sub>2</sub> in an oxidizing atmosphere. Then, the generated Cl<sub>2</sub> will react with incomplete combustion products to generate dioxins via chlorination and dimerization reactions.<sup>20–22</sup>

In general, the amount of dioxins generated during gasification is 1 order of magnitude lower than that in incineration.<sup>23</sup> The reason might be attributed that the reducing atmosphere during the MSW gasification process might inhibit metal oxidation, while the ammonia gas generated in the gasification process might also affect dioxin formation by suppressing Cl<sub>2</sub>.<sup>24,25</sup> Although several studies have been performed to understand the mechanism of PCDD/F formation in MSW incineration,<sup>26–28</sup> seldom systematical work is conducted to reveal the mechanism of dioxin formation in the gasification process and its difference compared to incineration, especially the migration and transformation law of C/Cl, which is of significance to guide the rational control of dioxin emission and design thermal technologies for different MSW sources.

In this study, the effect of a reducing atmosphere on dioxins was investigated in terms of different gasification agents, temperature, and chlorine sources. Comprehensive characterization including thermogravimetric-Fourier transform infrared spectroscopy (TG-FTIR), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) was applied to analyze thermal dynamics, elemental distribution, and phase composition. Then, dithiothreitol was used to reveal the mechanism of dioxin formation in a reducing atmosphere, which indicated that the inhibitory effect of a reducing atmosphere on dioxin generation may be caused by H<sub>2</sub> attacking C–Cl. The purpose of this work was to (I) explore the effects of the atmosphere, temperature, and chlorine sources on the formation of dioxins in the gasification process, (II) identify the effect of organochlorine and inorganic chlorine on the formation of dioxins in a reducing atmosphere, and (III) reveal the difference between incineration and gasification in the de novo synthesis and precursor synthesis of dioxins.

## 2. MATERIALS AND METHODS

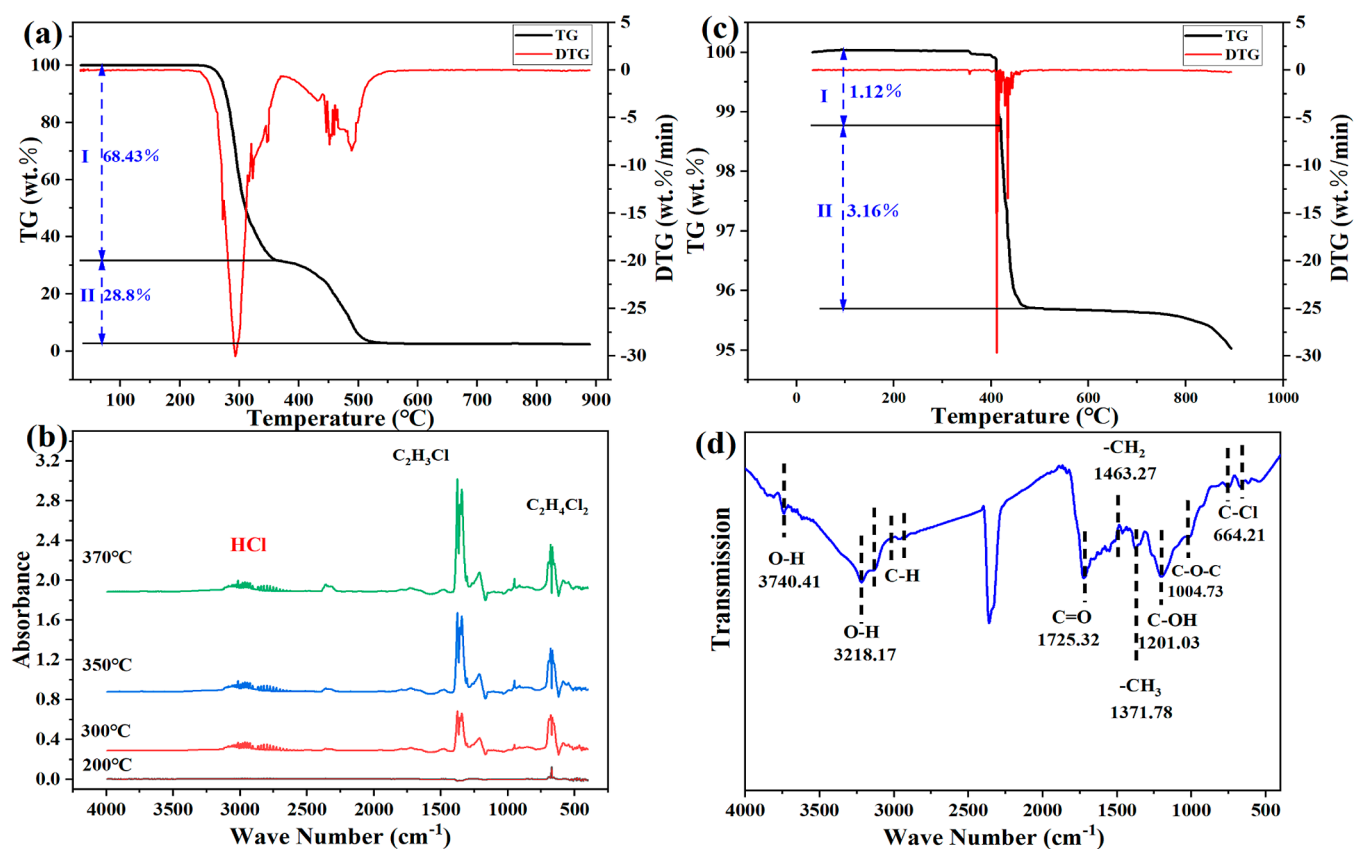
**2.1. Experimental Facility and Methods.** The MSW for gasification was collected from plant sites, while the analysis of the MSW components and industrial element analysis is shown in Table 1. A schematic diagram of the experimental device is illustrated in Figure S1 (Supporting Information). To ensure

experimental repeatability and avoid the interference caused by waste collecting, simulated household garbage was prepared according to the aforementioned analysis results in the present study. The details are as follows: wood chips were used to replace grass and wood, nylon powder was used to replace cloth, rice was used to replace kitchen waste, polyvinyl chloride (PVC) and polyethylene (PE) powder were used to replace plastic and white plastic, respectively, and iron powder was used to replace metal. The experiment was carried out in a tubular furnace with an inner diameter of 60 mm and a length of 900 mm. Ventilation was performed for 5 min before each experiment to remove air interference, and the gas flow rate used in the experiment was set of 400 mL/min. Detailed experimental conditions are listed in Table S1.

**2.2. Analytical Method.** **2.2.1. Methods for the Analysis of Dioxins and Chlorobenzene.** The process used to pretreat samples for dioxin analysis was according to the United States Environmental Protection Agency (U.S. EPA) method 1613. Dioxins were detected using a JMS800D high-resolution gas chromatography/high-resolution mass spectrometry system (JEOL, Japan). The basic processes of dioxin pretreatment were in the sequence of extraction, concentration, purification (pickling + silica gel column + alumina column), nitrogen blowing, and concentration. The gas-phase dioxins were absorbed by toluene and XAD-II, while the solid-phase dioxins were derived from the pyrolyzed ash residues. For each test, a comprehensive analysis of gas-phase dioxins/solid-phase dioxins was performed. Compared with external standards, the recovery rate of internal standards generally ranged from 60% to 110%.

The chlorobenzene (CBZ) pretreatment process applied the United States Environmental Protection Agency method-8280B. Because of the lower boiling point of CBZ and low-chlorine CBZ, the solvent was changed to dichloromethane, and the temperature was strictly controlled during the extraction process to prevent the explosion of boiling solvents.

**2.2.2. Methods for Analyzing the Solid-Phase Product.** XPS was used to measure the elemental distribution in the outermost layer of slag using a Thermo Scientific ESCALAB 250Xi instrument (16 kV/15 mA). XRD (D/max 2550PC, Japan) was used to examine the internal composition and molecular structure of the solid-phase products, with the test range of 5–90° and the scanning speed of 5°/min, respectively. The persistent free radicals were detected using electron paramagnetic resonance (EPR) spectrometry (Bruker E500 EPR spectrometer, Germany), with the typical parameters set as follows: central magnetic field, 3500.00 G; sweep time, 30.00 s; sweep width, 100 G; and modulation amplitude, 1.00 G. Thermogravimetric analysis (TGA, NETZSCH STA449F5) with evolved gas analysis using FTIR (PerkinElmer Spectrum) was employed to identify the thermal decomposition characteristics of the samples. The TG-FTIR analysis was conducted at temperatures ranging from 30 to 900 °C at a heating rate of 15



**Figure 1.** TG and FTIR spectra of the evolved gas curves. (a) TGA and (b) infrared spectrum analysis of PVC. (c) TGA and (d) infrared spectrum analysis of NaCl.

°C/min under a N<sub>2</sub> atmosphere, and the flow rate of nitrogen was regulated to 50 mL/min.

**2.2.3. Density Functional Theory Calculation.** The calculations were calculated in the “Vienna ab initio simulation package” within the framework of density functional theory (DFT). Perdew–Burke–Ernzerhof exchange–correlation functional was used to calculate the adsorption energies. The convergence criteria for the total energy and the Hellman–Feynman force are 10<sup>-5</sup> eV and 0.02 eV Å<sup>-1</sup>, respectively. Gibbs free energy for the elemental steps was calculated by the following equation

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

$E$ ,  $E_{ZPE}$ ,  $T$ , and  $S$  are defined as the DFT total energy, zero-point energy, absolute temperature (800 K), and entropy, respectively.

**2.2.4. Quality Control.** Due to the formation of dioxins and CBZ during the pyrolysis and gasification process of MSW, it was susceptible to being interfered with sample collection and pretreatment, and the following measures were taken to ensure quality control.

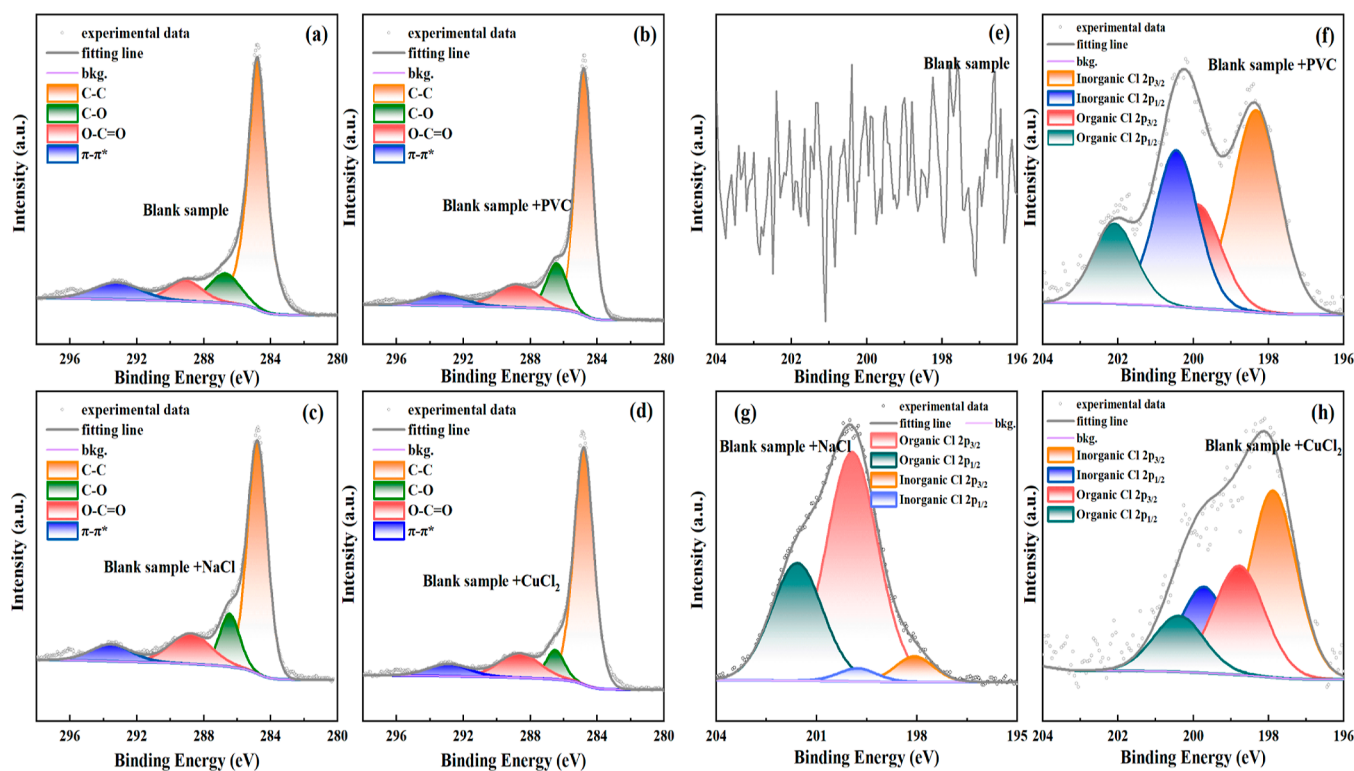
- (1) Experimental preparation stage: ensure the feasibility of the experimental scheme and accurate control of parameters during the experiment, such as temperature, time, and flow control.
- (2) At the beginning of the experiment: make good data records to ensure that the samples can be queried at any time and stored correctly.
- (3) Sample analysis stage: the sample pretreatment process must be carried out in strict accordance with the

national standard and be analyzed in time after completion to ensure a satisfactory recovery rate.

### 3. RESULTS AND DISCUSSION

**3.1. Analysis of the MSW Thermal Characteristics for Gasification.** Figure S2 shows the TG infrared analysis of MSW under nitrogen and air atmospheres. The MSW had three weight loss stages during the pyrolysis process as shown in Figure S2a. In the first stage, the weight loss temperature ranged from 30 to 250 °C, which represented the dehydration stage of MSW accompanied by a 4.94% mass loss. The weight loss temperature of the second stage ranged from 250 to 400 °C and occupied a 40.08% mass loss which was mainly attributed to the thermal degradation of cellulose (Figure S2b).<sup>29</sup> The third stage was mainly attributed to the thermal degradation of plastics (PE and PVC),<sup>30</sup> with the mass loss of ~10.84%. Similarly, the thermal characteristics of MSW during the combustion process could also be divided into three stages, as demonstrated in Figure S2c. The first stage was mainly from water evaporation, followed by the fast weight loss zone caused by the decomposition and volatile combustion of the sample (second stage). The third stage of the weight loss zone was derived from the combustion of coke and the decomposition of macromolecules (Figure S2d).<sup>31</sup>

Figure 1 demonstrates the TG and FTIR spectra of the evolved gas curves in the N<sub>2</sub> atmosphere. It was observed that the initial mass loss of PVC occurred at approximately 230 °C and ended at 550 °C (Figure 1a). The decomposition of PVC could be mainly divided into two stages. In the first stage with the temperature ranging from 230 to 400 °C, the weight loss of



**Figure 2.** XPS spectra of residual slag from blank sample and samples with PVC, NaCl, and  $\text{CuCl}_2$  [(a–d): C 1s spectra; (e–h): Cl 2p spectra].

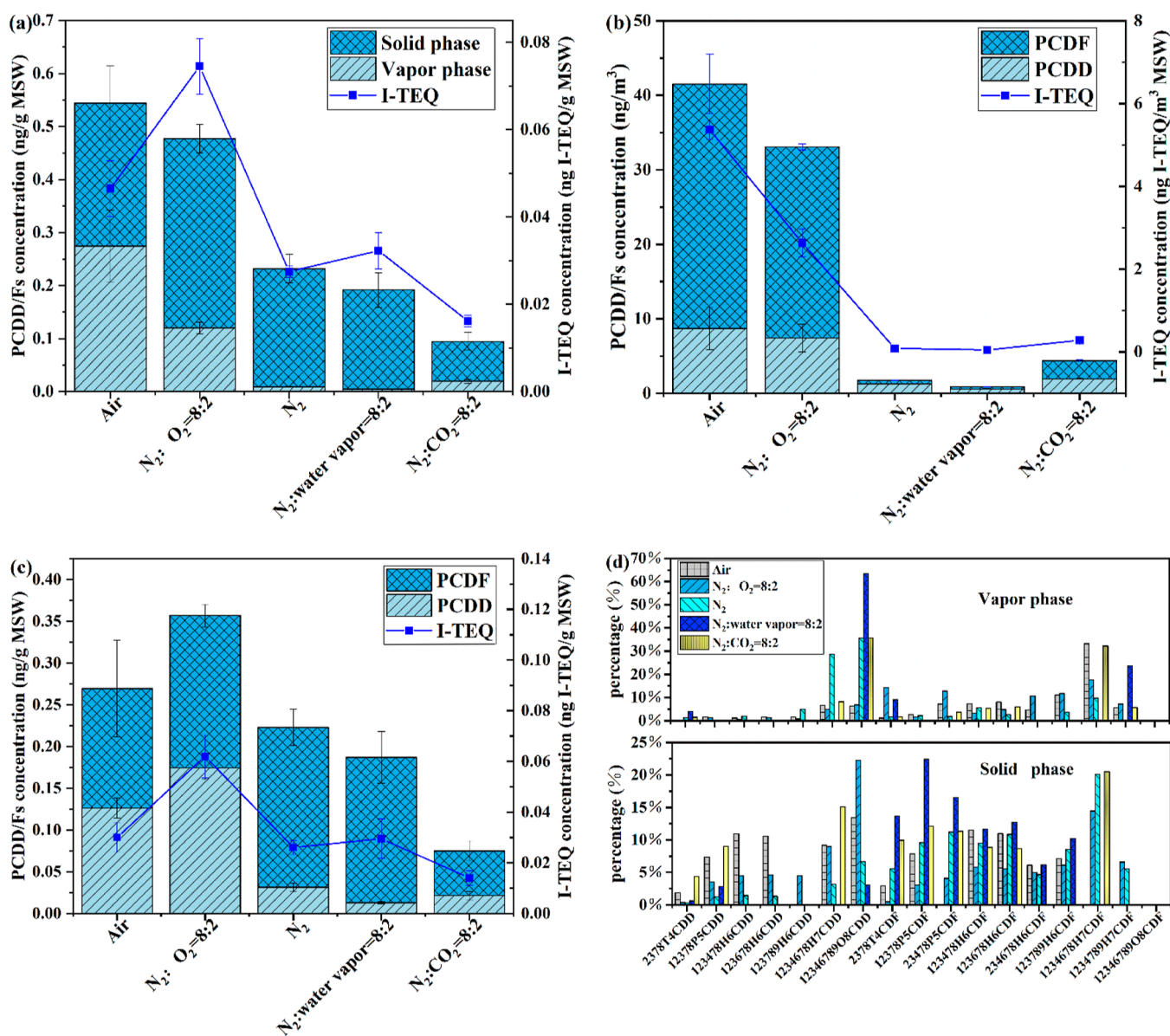
PVC approached 68.43%. In the second stage, the mass loss of PVC was approximately about 28.8% between 400 and 550 °C. The main reaction in the first stage of PVC pyrolysis might be HCl removal (Figure 1b), and almost all chlorine in PVC was transferred to HCl gas through the Deacon reaction with the temperature above 550 °C.<sup>32–34</sup> Interestingly, the theoretical mass fraction of HCl in pure PVC was approximately 56%, which was lower than the measured experimental data of 68.43%. Thus, it was speculated that part of hydrocarbons might also release in the first stage except for HCl.<sup>35,36</sup> In contrast, the weight loss of inorganic chlorine was relatively low (Figure 1c). From 30 to 800 °C, the sample with NaCl demonstrated two significant weight loss peaks with a total mass loss of 3.28%. Combined with the infrared spectrum (Figure 1d), due to the high saturated vapor pressure of alkali metal chlorides such as NaCl, they are especially easy to be vaporized and directly enter the gas phase. However, with the decrease of temperature, these alkali metal compounds will condense again and attach to the surface of slag.<sup>37</sup> NaCl is unlikely to be directly chlorinated to PCDD/Fs, but its chloride ions may first exchange with metal ions such as Fe/Cu.<sup>38</sup>

**3.2. Analysis of C/Cl Distribution Characteristics in Slag.** XPS was used for elemental depth profiling, and XRD detection was used to analyze the phase composition of pyrolysis slag. In Figures 2 and S3, XPS spectra of C and Cl from fly ash were investigated in terms of different chlorine sources and atmospheres. The typical peaks at binding energies of ~285 eV correspond to C–H or C–C bonds, and the peaks at binding energies of 287–288 eV correspond to oxygen-containing groups (such as C–O/C=O/O–C=O) (Figures 2 and S3a–d). Among these, C–C occupied the largest proportion with the value exceeding 60% (Table S2). Notably, the ratio of C–O–C and O–C=O in the oxidizing

atmosphere was higher than that in the reducing atmosphere. The carbon covering the slag in a reducing atmosphere existed in the form of organic carbon (C–O), with 19.89 mol % for PVC and 14.44 mol % for NaCl, respectively.

As shown in Figures 2 and S3e–h, four distinct peaks were identified in the Cl 2p spectra by deconvolution as inorganic chlorine  $2p_{3/2}/2p_{1/2}$  (197.88–199.88 eV) and organic chlorine  $2p_{3/2}/2p_{1/2}$  (200.18–202.03 eV), respectively. It was observed that the slag of the pyrolysis sample contained both organochlorine and inorganic chlorine. In Figure S3 and Table S3, organochlorine was dominant in the oxidizing atmosphere, while inorganic chlorine dominated in the reducing atmosphere, which implied that organochlorine played a significant role in the dioxin formation process under incineration conditions, while the inorganic chlorine might contribute to the dioxin generation during gasification conditions. With PVC and  $\text{CuCl}_2$  as chlorine sources, inorganic chlorine was the main chlorine form present on the surface of slag (accounting for approximately 60%). As shown in the XRD spectrum (Figure S4),  $\text{CuCl}_2$  and Cu are the main substances in the ash generated from  $\text{CuCl}_2$  samples. Related studies also confirmed that Cu had a strong catalytic effect on dioxins, and a high concentration of solid-phase dioxins was observed with  $\text{CuCl}_2$  added. Importantly, 90% of inorganic chlorine was converted into organochlorine with NaCl as a chlorine source. It may further indicate that  $\text{Cl}^-$  in NaCl was first exchanged with other metal ions before participating in the synthesis of PCDD/Fs.<sup>38</sup> The majority of chlorine element exists in the solid phase in the form of a solid chloride salt (Figure S4).

**3.3. Analysis of Different Influencing Factors on Dioxin Formation.** **3.3.1. Effects of the Reaction Atmosphere.** The distribution of the dioxin concentrations in different atmospheres is illustrated in Figure 3. The total

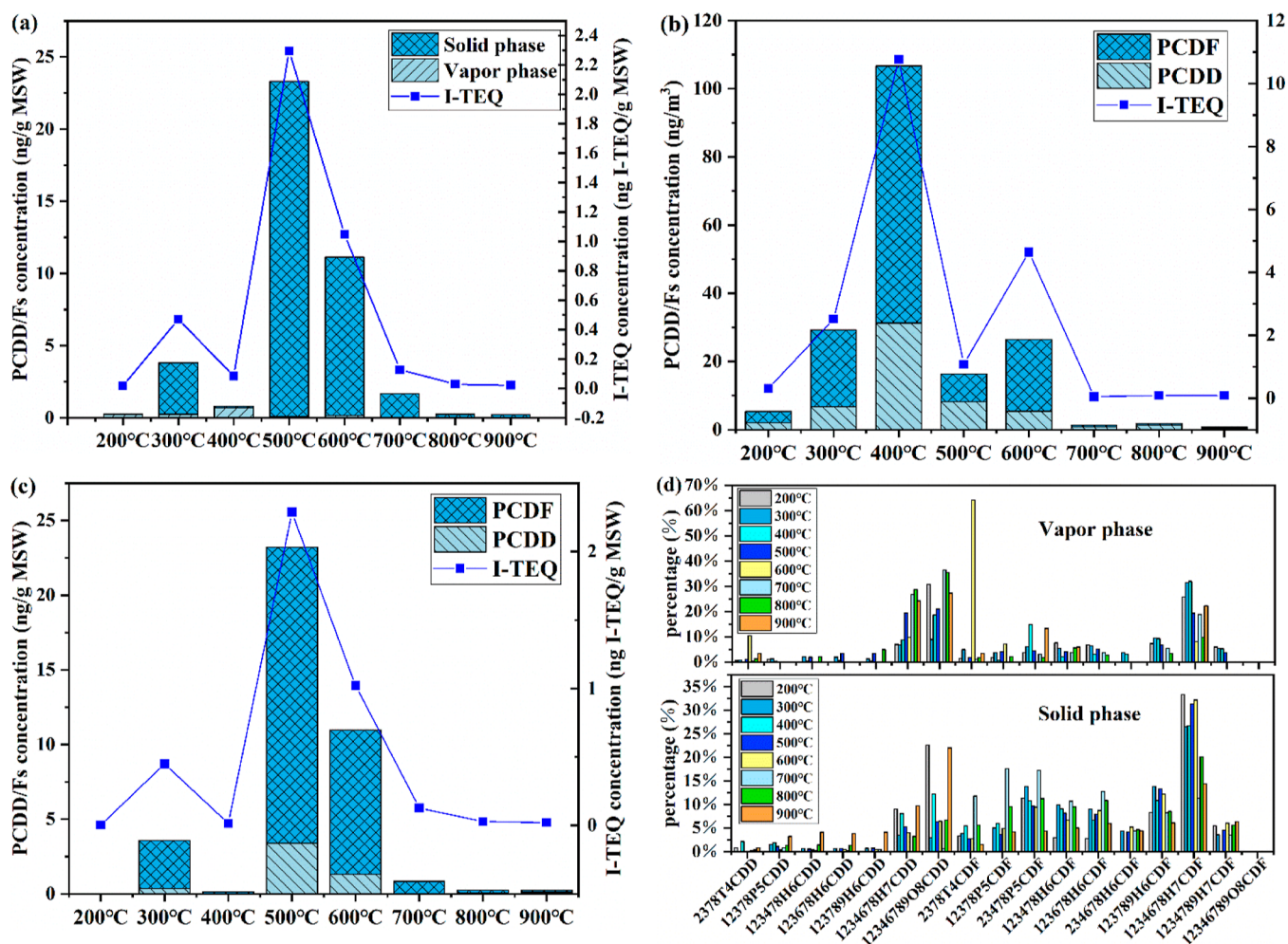


**Figure 3.** Distribution of dioxin concentrations in gas and solid phases in different atmospheres. (a) Total concentration and TEQ values of dioxins. (b) Concentration and TEQ values of dioxins in the gas phase. (c) Concentration and TEQ values of dioxins in the solid phase. (d) Concentrations of 17 PCDD/F congeners.

dioxin emissions (0.54 ng/g) under incineration conditions were significantly higher than those under gasification conditions at 850 °C (Figure 3a). With the atmosphere varying from an oxidizing atmosphere to a reducing atmosphere, the amount of total dioxin generation gradually decreased from 0.54 to 0.109 ng/g. Additionally, gas-phase dioxins decreased from 41.5 ng/m<sup>3</sup> in incineration circumstances to 1.76 ng/m<sup>3</sup> in an inert atmosphere and further decreased to 0.88 ng/m<sup>3</sup> in a reducing atmosphere (Figure 3b). The ratio of PCDD/PCDF in the gas-phase dioxins was less than 1, indicating that the de novo synthesis<sup>39</sup> (reactions between unburnt carbon and chlorine sources with metallic catalysts) dominated dioxin generation in the oxidizing atmosphere. As for gasification conditions, it was speculated that both high-temperature gas-phase generation and precursor synthesis dominated in the formation of gas-phase dioxins in a reducing atmosphere (PCDD/PCDF ratio > 1), while de novo synthesis was the dominant process controlling the generation

of solid-phase dioxins with the ratio of PCDD/PCDF < 1 (Figure 3c). By comparing the TEQ (toxic equivalency quantity) values of gas-phase dioxins in different atmospheres, the TEQ value of gas-phase dioxins in an oxidizing atmosphere was about 113 times larger than that in the reducing atmosphere. The distribution of 17 dioxin congeners in the gas and solid phases is shown in Figure 3d. Compared to the oxidizing atmosphere and inert atmosphere, part of the gas-phase dioxins in the reducing atmosphere transformed from low chlorine to high chlorine, especially in terms of H7CDD (heptachlorinated dibenzo-p-dioxins)/H7CDF (heptachlorinated dibenzofurans)/O8CDD (octachlorinated dibenzo-p-dioxins). In the solid phase, PCDF was dominant and accounted for up to 80% of the total dioxins.

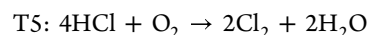
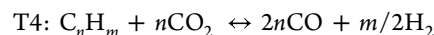
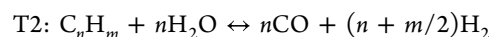
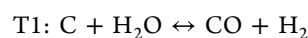
The types of gasification agents also exhibited significant effects on the dioxin concentration. Relying on the gas–solid distribution perspective, dioxins were mainly distributed in the solid phase and accounted for up to 90% of the total dioxins



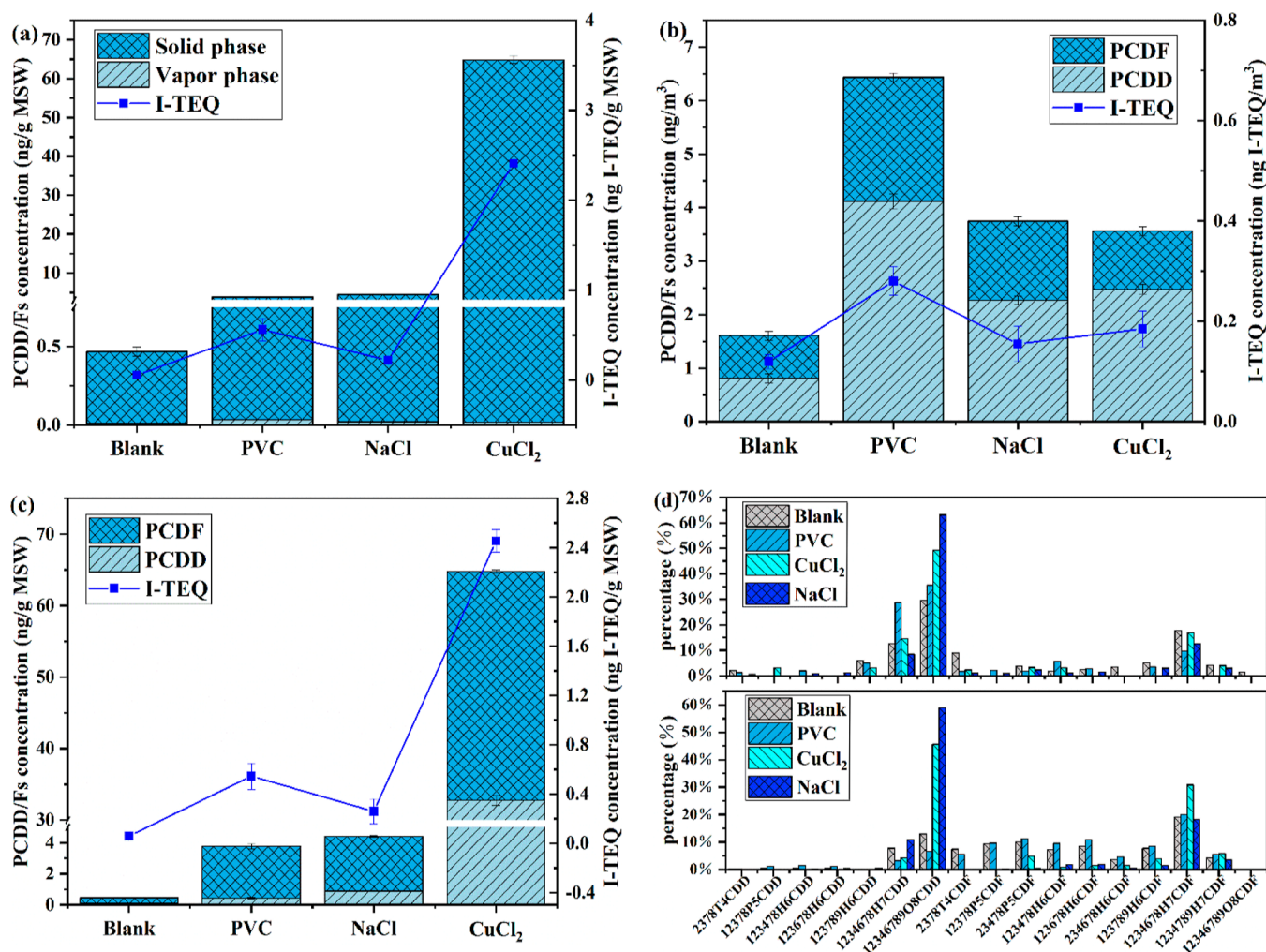
**Figure 4.** Distribution of dioxin concentrations in gas and solid phases at different temperatures. (a) Total concentration and TEQ values of dioxins. (b) Concentration and TEQ values of dioxins in the gas phase. (c) Concentration and TEQ values of dioxins in the solid phase, and (d) concentrations of 17 PCDD/F congeners.

generated regardless of the reaction atmospheres, except for incineration conditions. It was because the amount of residual carbon in fly ash was reduced substantially due to complete burning of MSW within an oxygen-rich atmosphere, leading to a dramatic decrease of solid-phase dioxin formation.<sup>40</sup> However, the incomplete combustion of MSW might produce residual carbon, which will serve as the carbon source and reaction sites to accelerate both de novo synthesis and heterogeneous formation of the precursor for dioxins.<sup>41</sup> By comparing three different types of gasification agents ( $O_2/H_2O/CO_2$ ), introducing  $CO_2$  would decrease the dioxin concentration by 80% compared to the incineration condition. It was assumed the addition of  $CO_2$  promoted the reforming reaction of  $CO_2$  (T3 and T4) and generated more reducing gases like  $H_2$  and  $CO$ . Meanwhile, the extremely low  $O_2$  concentration also limited the Deacon reaction (T5) and reduced the concentration of  $Cl_2$ , which was a strong chlorination agent in the dioxin formation. With  $H_2O$  as a gasification agent, negligible dioxin was detected in the gas phase and the TEQ value of solid-phase dioxins was dominant, which was mainly contributed by P5CDF (pentachlorinated dibenzofurans). In addition, the transformation of solid-phase dioxins from high chlorine generation to low chlorine generation inhibited chlorination in the reaction process.<sup>42</sup> The presence of  $H_2O$  promoted the water–gas reaction and

the water–steam reforming reaction (T1 and T2) and effectively increased the  $H_2$  content in the MSW thermal treatment process,<sup>43</sup> and a rich hydrogen environment would inhibit the generation of dioxin validated by a substantial reduction of dioxin production in the gas phase. The following chemical reaction equations are involved in the MSW gasification process<sup>44–47</sup>



**3.3.2. Effects of the Reaction Temperature.** The distribution of the dioxin concentrations in different temperatures is illustrated in Figure 4. For MSW incineration, it is generally believed that the temperature window for dioxin formation is between 200 and 800 °C, and the maximum amount of dioxin is generally generated at about 350 °C.<sup>48</sup> The distribution of the total concentration of dioxins in the gas and solid phases under different temperature ranges is shown in Figure 4a. In the low-temperature range of 200–400 °C, the best formation



**Figure 5.** Distribution of dioxin concentrations in the gas and solid phases after the addition of different chlorine sources. (a) Total concentration and TEQ values of dioxins. (b) Concentration and TEQ values of dioxins in the gas phase. (c) Concentration and TEQ values of dioxins in the solid phase. (d) Concentrations of 17 PCDD/F congeners.

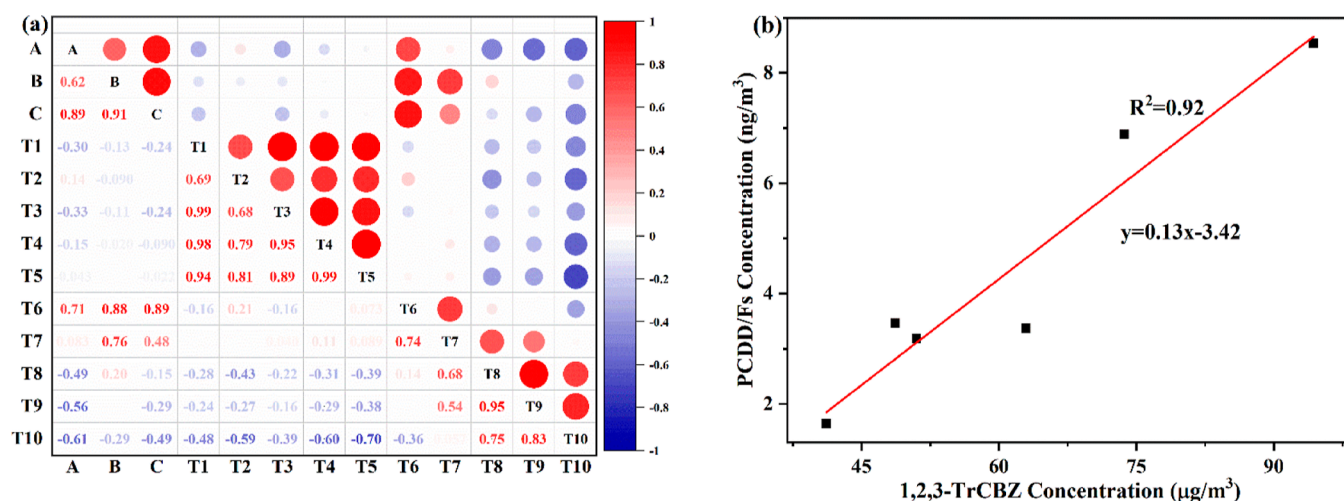
temperature of dioxins was 300 °C with the total dioxin concentration of 3.81 ng/g. By shifting the temperature range to 500–800 °C, the optimal dioxin formation temperature was 500 °C with the highest concentration achieved of 23.32 ng/g. Further increasing the temperature to 800 °C, the dioxin concentration dropped prominently with the PCDD/PCDF ratios less than 1, implying that the de novo synthesis was the main route.

Figure 4b displays the distribution of gas-phase dioxins at different temperatures. The concentration of gas-phase dioxins increased with the temperature and reached its peak at 400 °C and then decreased on further increasing the temperature. Considering the effect of temperature on PCDD/PCDF ratios, it was observed that PCDF was the dominant dioxin in the gas phase at 200–600 °C, while the gas-phase dioxins are mainly attributed by PCDD at 700–900 °C. The varying tendency of solid-phase dioxin concentration and TEQ values are similar, as shown in Figure 4c. Slightly different from gas-phase dioxins, solid-phase dioxins are dominated by PCDF from 200 to 900 °C, indicating that solid-phase dioxins are predominantly generated through de novo synthesis. By comparing the distribution of gas–solid dioxin congeners at different temperatures shown in Figure 4d, gas-phase dioxins were dominated by high-chlorinated dioxins like H7CDD/H7CDF/

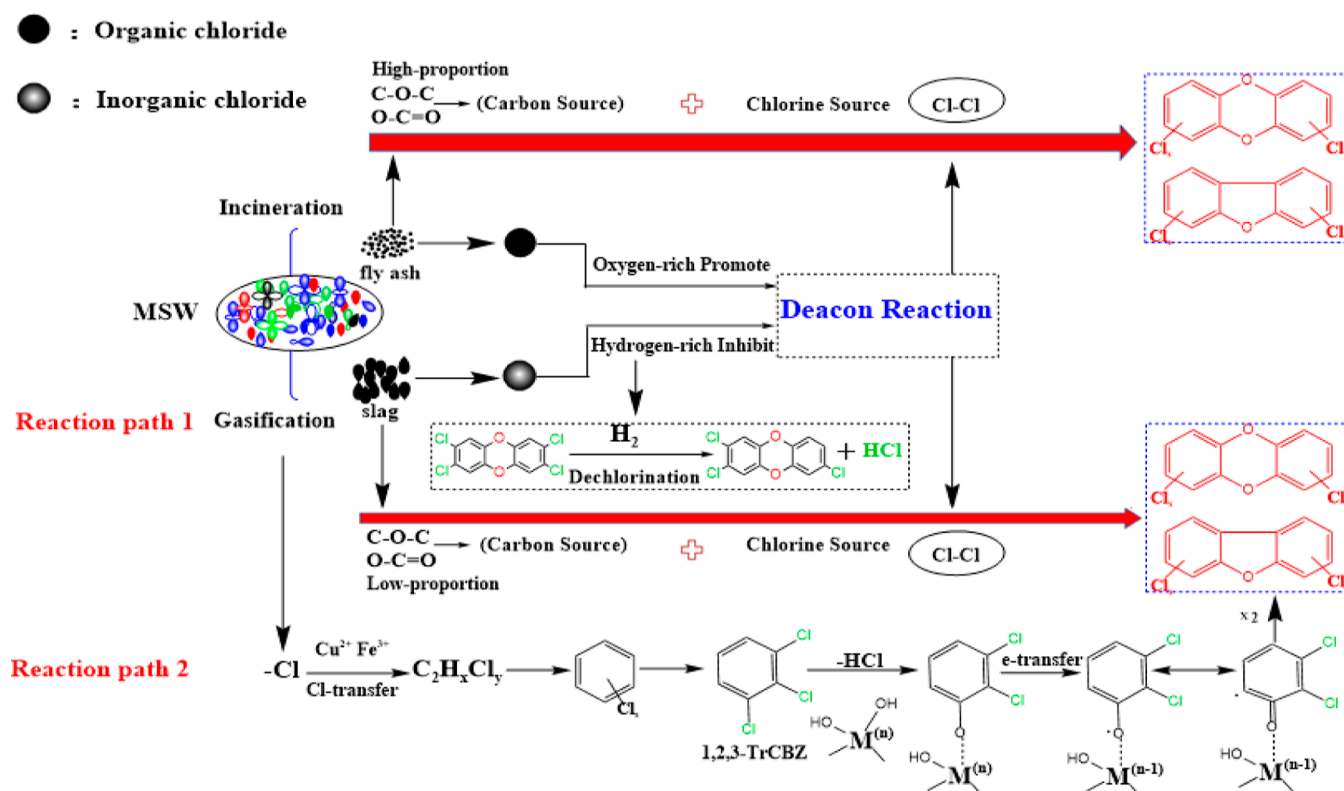
O8CDD, and solid-phase dioxins were dominated by PCDF. From the perspective of gas–solid distribution, dioxins were mainly distributed in the solid phase at high temperatures with a ratio above 90%.

**3.3.3. Effects of Chlorine Sources.** The distribution of the dioxin concentrations in different chlorine sources is illustrated in Figure 5. As shown in Figure 5a, 90% of the dioxins generated are derived from the solid-phase regardless of the types of chlorine sources. Compared to the other two chlorine sources (NaCl and PVC), CuCl<sub>2</sub> acted as both chlorine source and catalysts for dioxin formation; thus, the TEQ values increased by 22 times with the addition of CuCl<sub>2</sub>. CuCl<sub>2</sub> can not only provide the necessary chlorine source for the reaction but also catalyze the rupture of the carbon–carbon bond, release the small molecule carbon structure, and catalyze the closure of the carbon ring, thus generating PCDD/Fs.<sup>49,50</sup>

Notably, organochlorine can effectively promote the formation of gas-phase dioxins (Figure 5b), and inorganic chlorine can effectively promote the formation of solid dioxins (Figure 5c). Almost all organochlorine from PVC was released into the gas phase in the form of HCl, while inorganic chlorine only existed in the solid phase in the form of chloride salts, which was consistent with the chlorine content detected in the slag. Therefore, a large amount of chlorine remained in the slag



**Figure 6.** (a) Results of the correlation analysis of dioxins and CBZ. (A: PCDDs, B: PCDFs, C: PCDD/Fs, T1:1,4-DCBZ, T2:1,3-DCBZ, T3:1,2-DCBZ, T4: 1,3,5-TrCBZ, T5: 1,2,4-TrCBZ, T6: 1,2,3-TrCBZ, T7: 1,2,4,5/1,2,3,5-TeCBZ, T8: 1,2,3,4-TeCBZ, T9: PCBZ, and T10: HCBZ.) (b) Linear correlation model of dioxins and CBZ.



**Figure 7.** Possible reaction path analysis of PCDD/F formation in a reducing atmosphere.

after NaCl and CuCl<sub>2</sub> were added, which was consistent with the XRD detection results in Figure S4 and the detection results of chlorine content in the slag. Figure S5 demonstrates the distribution of total chlorine content in the slag under different chlorine sources. After pyrolysis, the chlorine content in the slag of PVC samples decreased, while those of NaCl and CuCl<sub>2</sub> samples increased. The congeners of both gas-phase and solid-phase dioxins were dominated by highly chlorinated O8CDD and H7CDF (Figure 5d). In this experiment, the PCDD/PCDF ratios in the gas-phase dioxins observed with the addition of chlorine sources were greater than 1, indicating that the precursor reaction was dominant, while the PCDD/

PCDF ratios in the solid-phase dioxins obtained were less than 1 in contrast, indicating that de novo synthesis was dominant.

**3.4. Correlation Analysis of the Gas-Phase Dioxin Concentration and CBZ Concentration.** Precursors, including PAHs, CBZ, chlorophenol, and other heterogeneous compounds, are important components correlated with the catalytic generation of dioxins. CBZ was recently proposed as both the precursor and indicator for dioxin formation. It was because the emission level of CBZ was 100 or even 1000 times higher than trace organic dioxins.<sup>51,52</sup> Therefore, the formation-indicator relationship between CBZ and dioxins

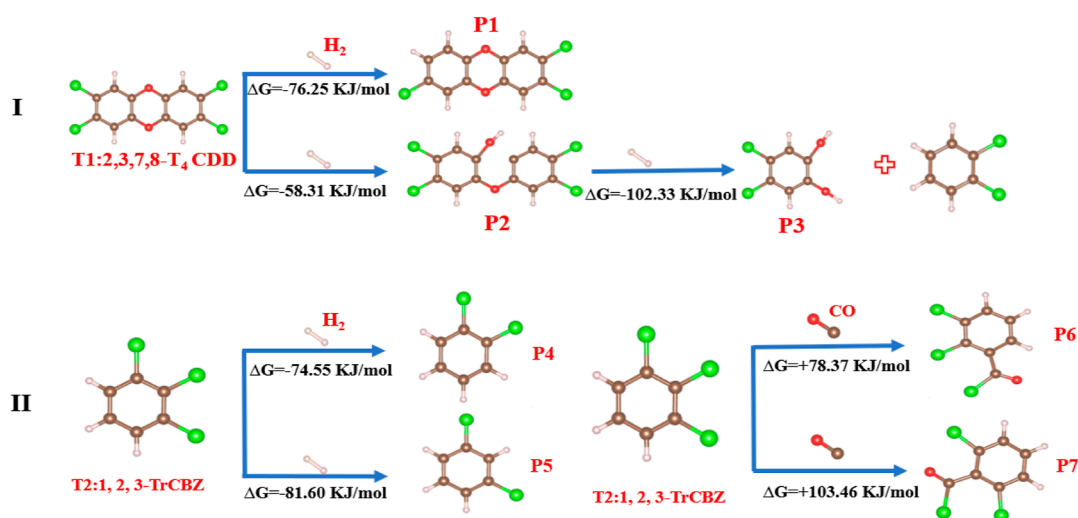


Figure 8. DFT path simulation.

was studied to determine the mechanism of dioxin formation during MSW gasification.

Due to the low recovery rate of solid-phase CBZ, only dichlorobenzene and hexachlorobenzene achieved the target recovery rate, even though it exhibited a weak correlation with solid-phase dioxins. Herein, the correlation analysis was only focused on gas-phase dioxins by considering 11 forms of CBZ. The results of the correlation analysis are shown in Figure 6a. Dioxin concentrations demonstrated a strong correlation with the 1,2,3-TrCBZ concentration but a poor correlation with the concentrations of other CBZ forms. In the flue gas generated from MSW pyrolysis, PCDD/Fs had a closer relationship with trichlorobenzene, which was better than the other CBZ forms. Therefore, 1,2,3-TrCBZ was assured as the preferred indicator of dioxins in MSW pyrolysis gasification flue gas. The correlation model of the PCDD/F concentrations and 1,2,3-TrCBZ concentrations in the flue gas is shown in Figure 6b. A linear correlation model with  $R^2 = 0.92$  was established between gas-phase PCDD/Fs and 1,2,3-TrCBZ. This discovery could provide an effective method to indirectly characterize the dioxin formation during gasification to facilitate the understanding of the dioxin formation mechanism.

**3.5. Mechanism of Dioxin Formation during Gasification.** The potential mechanism of dioxin formation in a reducing atmosphere is speculated in Figure 7. Under incineration conditions, complete combustion of MSW was achieved due to the sufficient oxygen provided. Almost all organochlorine and inorganic chlorine in MSW were released in the form of HCl, which promoted the Deacon reaction accompanied with the generation of Cl<sub>2</sub> and promised stronger chlorination ability than HCl in terms of the dioxin formation. Under the pyrolysis and gasification conditions, CO/H<sub>2</sub> was generated during MSW pyrolysis in a reducing atmosphere, which inhibited the Deacon reaction and consequently reduced the generation of Cl<sub>2</sub>, resulting in the inhibition of the de novo synthesis of dioxins. On the other hand, as the bond energy of H–Cl (431 kJ/mol) was more stable than that of C–Cl (337 kJ/mol), Cl tended to bind to H to form the more stable molecule HCl in the reaction process. Thus, the hydrogen-rich environment during gasification eliminated C–Cl and the concentration of the chlorine-containing precursors.<sup>53</sup> To distinguish the effect of H<sub>2</sub> and CO, DFT calculation was carried out for 2,3,7,8-T<sub>4</sub>CDD (the most toxic

compound in dioxin homologues) using VASP software. By calculating the bond dissociation energy, C–Cl and C–O were more prone to be cleaved than C–H. As shown in Figure 8, Gibbs free energy of paths I were both negative, indicating that the reaction was spontaneous in the positive direction, and H<sub>2</sub> was prone to attack C–Cl than C–O. Besides, the degradation reaction path of the precursors like 1,2,3-TrCBZ at high temperature is shown in Figure 8 II. The calculation results of both reaction routes demonstrated that H<sub>2</sub> high-temperature degradation of 1,2,3-TrCBZ has negative Gibbs free energy, and the reaction can proceed spontaneously. The two paths of CO participation have positive Gibbs free energy, and the degree of spontaneous reaction is low. Therefore, this also shows from the side that our previous path of exploring the formation mechanism of dioxins in the reducing atmosphere is correct.

In the presence of transition metal ions such as Cu<sup>2+</sup>/Fe<sup>3+</sup>, chlorine ligands were transferred to carbon atoms with macromolecular structures to form organic C–Cl bonds over the surface of fly ash. Then, aliphatic compounds were generated through a cyclization reaction, and CBZ was chlorinated as a precursor. Dioxins were generated by removing small molecules of CBZ and reacting with free groups adsorbed to the metal surface. This route was also validated by EPR test to detect the formed radicals over the metal surface as shown in Figure S6. The radicals resembled aromatic-type, carbon-centered radicals with relatively low *g* values (2.0025–2.0030) that may form during the tautomerization of oxygen-centered adsorbed radicals into carbon-centered radicals; this type of transformation may occur on the surface.

**3.6. Low-Temperature Dioxin Resynthesis.** To verify the hypothesis that the concentration of dioxin formed in a reducing atmosphere was lower than that formed in an oxidizing atmosphere, dioxin regeneration experiments were performed. Relevant studies showed that the maximum amount of dioxin was generated at the temperature of 350 °C. The distribution of regenerated dioxin concentrations is shown in Figure S7. The concentration and TEQ values of dioxins produced in a reducing atmosphere were lower than those produced in an oxidizing atmosphere, and more dioxins were derived from de novo synthesis, indicating that a reducing atmosphere indeed inhibited the generation of dioxins.

According to the analysis described above, we validated that the inhibitory effect of a reducing atmosphere on dioxin production may be caused by H<sub>2</sub> attacking C–Cl, enabling Cl free radicals to interact with H to form the more stable molecule HCl and subsequently reducing the generation of C–Cl.

#### 4. IMPLICATIONS

Herein, the effects of temperature, atmosphere, and external chlorine source on the dioxin formation during pyrolysis and gasification processes were systematically studied, and the possible mechanism of dioxin formation in a reducing atmosphere was explored. We realized that an important inhibitory mechanism in a reducing atmosphere is for H<sub>2</sub> to attack C–Cl bonds. Besides, dioxins in the liquid phase may be an important part of its formation mechanism as well. Furthermore, in the mechanistic analysis, chlorophenol and PAHs may also affect the generation of dioxin. Therefore, the mechanism of dioxin formation in a reducing atmosphere requires further study. If the relevant values are creditable, the total amount of MSW will increase to billions of tons in future decades. Without effective thermal disposal technologies, increasing dioxin emissions will be inevitable and the environment will be greatly threatened. The choice between incineration and gasification is clear. As a promising thermal disposal technology, gasification is not only effective in controlling dioxin emissions but also effectively increases the efficiency of power generation. Therefore, gasification will be very important for controlling dioxin emissions in the future.

#### ■ ASSOCIATED CONTENT

##### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.2c05830>.

Experimental setup, slag-related characterization analysis (XRD/XPS/EPR/TG-FTIR), and chlorine content detection results (PDF)

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#### Notes

The authors declare no competing financial interest.

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