



# Chemical-looping combustion of plastic wastes for *in situ* inhibition of dioxins

Haibo Zhao\*, Jinxing Wang

State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

## ARTICLE INFO

### Article history:

Received 24 March 2017

Revised 5 October 2017

Accepted 22 December 2017

### Keywords:

Chemical looping combustion

Waste management

PCDD/Fs

Dechlorination

Chlorine substitution

## ABSTRACT

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) as toxic by-products are inevitably emitted during conventional air incineration processes of chlorine containing wastes (typically, plastic wastes). The presence of O<sub>2</sub> in the conventional waste incineration not only participates in carbon gasification and rearrangement as an oxygen source during the *de novo* synthesis process of PCDD/Fs, but also promotes chlorination through generating more active Cl<sub>2</sub> via Deacon reaction. Chemical looping combustion (CLC), which creates an O<sub>2</sub>-free atmosphere in the fuel reactor, was proposed to dispose plastic wastes. Comparative experiments [conventional PW incineration vs. *in situ* gasification-chemical looping combustion (*iG*-CLC) using CaO-decorated Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> as oxygen carrier] were conducted to measure the distribution properties of 17 toxic PCDD/Fs congeners. The total amount and toxic equivalency quantity of PCDD/Fs have been reduced by 94 % and 89 %, respectively, in *iG*-CLC. The absence of O<sub>2</sub> in fuel reactor and lower Cl<sub>2</sub> yield (due to the restriction of Deacon reaction and effective dechlorination by CaO) lead to the significant inhibition of the PCDD/Fs formation. Chlorine substitution modelling also demonstrated that the chlorine substitution probabilities for the formation of 7 toxic congeners of PCDDs and 10 toxic congeners of PCDFs are significantly reduced in *iG*-CLC.

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## 1. Introduction

A fast industrial development has led to increased amounts of municipal solid waste (MSW) [1]. These solid wastes, if not properly disposed, are serious threats to the environment and public health [2–4]. On the other hand, MSW is potentially valuable fuel due to its high calorific value and embodied energy. Among the existing waste treatment technologies, incineration has been broadly adopted [5]. However, serious attention has been paid to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) as secondary contaminations, especially for the incineration of chlorine containing polymers such as non-renewable and non-recyclable plastic wastes (PWs) [6]. Consequently, the problem of MSW disposal urgently needs to be addressed and solved.

To date, it has been verified that many factors (such as O<sub>2</sub> concentration, chlorine source, carbon residue and catalytic metal oxide) could affect the formation of PCDD/Fs in the waste incineration processes [7–10]. In particular, chlorine and oxygen sources play an important role in the formation of PCDD/Fs [7–9]. Although the PCDD/Fs formation pathways have not been fully un-

derstood, it is generally believed that precursor conversion (high-temperature homogeneous reactions or low-temperature catalytic-assisted heterogeneous reactions) and *de novo* synthesis are two major mechanisms [7–9]. In the precursor conversion mechanism, organic molecules combine to form PCDD/Fs. Chlorobenzenes (CBzs), chlorophenols (CPs), polychlorobenzenes (PCBzs), polychlorophenols (PCPs), etc. have been considered as main chlorinated precursors [7–10]. The *de novo* synthesis is involved with the breakdown of a carbonaceous matrix with simultaneous oxidation and chlorination under the influence of metal catalysts (such as copper) [7–9].

In recent decades, effective means for controlling PCDD/Fs emission and meeting stringent emission regulations have been developed, including activated carbon injection (ACI) [11], and the addition of suppressants such as calcium-based additives [12] and sulphur-containing compounds [13]. However, ACI technology only transfers gaseous PCDD/Fs to the solid phase (in fly ash), without reducing the total emission of PCDD/Fs [14]. The addition of suppressants will increase operation cost. The most cost-effective way of reducing PCDD/Fs emission is to minimize their generation rather than to destroy or collect them after they have been generated. Therefore, it is essential to explore novel approaches to inhibit their formation *in-situ*, based on their formation mechanisms.

\* Corresponding author.

E-mail addresses: [klinmannzjb@163.com](mailto:klinmannzjb@163.com), [hzhao@mail.hust.edu.cn](mailto:hzhao@mail.hust.edu.cn) (H. Zhao).

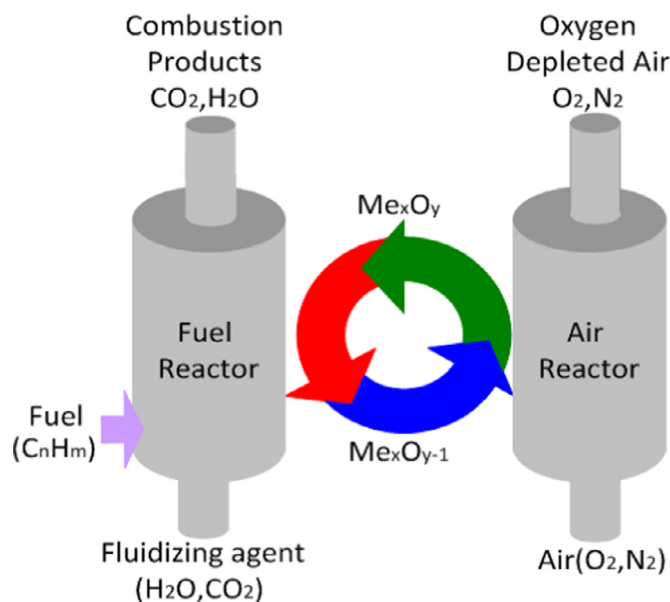


Fig. 1. Schematic description of chemical looping combustion technology.

It is widely believed that  $O_2$  participates in carbon gasification and rearrangement as an oxygen source during the *de novo* synthesis process of PCDD/Fs [7–9]. Therefore,  $O_2$ -deficient condition is very beneficial to inhibit the formation of PCDD/Fs via the *de novo* synthesis route. On the other side, the absence of  $O_2$  will effectively suppress the metal-catalyzed Deacon reaction (R1)  $4HCl + O_2 \leftrightarrow 2Cl_2 + 2H_2O$  [15]. As known,  $Cl_2$  has a higher activity for chlorination than  $HCl$ , and the chlorination of the benzene ring by  $Cl_2$  is an essential step in both precursor conversion and *de novo* synthesis [7–9]. Therefore, a low  $Cl_2$  amount (which is due to the  $O_2$ -free condition) is expected to help the inhibition of PCDD/Fs. To sum up, creating an  $O_2$ -free atmosphere during the combustion of chlorine containing solid wastes may be very advantageous from the perspective of PCDD/Fs inhibition.

Chemical-looping combustion (CLC) [16], which has been emerging as a promising next-generation  $CO_2$  capture technology with the advantages of inherent  $CO_2$  separation, cascaded utilization of energy and low  $NO_x$  [17], utilizes an oxygen carrier (OC, usually a metal oxide) to transport oxygen from the air to the fuel, avoiding direct reaction between fuel (PW here) and air and, indeed, creating an  $O_2$ -free atmosphere for fuel combustion. We [18] therefore proposed CLC as a promising waste management technology for *in situ* inhibition of PCDD/Fs. The designed CLC prototype usually consists of two separate reactors: an air reactor (AR) and a fuel reactor (FR) [19], as shown in Fig. 1. Here  $Me_xO_y$  denotes the OC in the oxidized form and  $Me_xO_{y-1}$  in the reduced form. In the FR, fuel will react with  $Me_xO_y$  to generate  $CO_2$  and  $H_2O$  via reaction (R2)  $C_nH_m + (2n+m)Me_xO_y \rightarrow nCO_2 + mH_2O + (2n+m)Me_xO_{y-1}$ . In the AR, the reduced OC,  $Me_xO_{y-1}$ , is re-oxidized to its originally oxidized form by air according to reaction (R3)  $O_2 + 2Me_xO_{y-1} \rightarrow 2Me_xO_y$ .

Bi et al. [20] measured the formation characteristics of PCDD/Fs in the CLC of polyvinyl chloride (PVC) pyrolysis gas using  $CaSO_4$  as OC in a two-stage reactor, where PVC was pyrolyzed in  $N_2$  atmosphere in the 1st reactor and then the pyrolysis gas was carried by  $N_2$  to the 2nd reactor to react with  $CaSO_4$ . Although PCDD/Fs or their precursors were generated in the 1st pyrolysis reactor, the yield and International Toxicity Equivalent Quantity (I-TEQ) of PCDD/Fs after the CLC reactor were significantly lower than those in air incineration, which is attributed to the absence of  $O_2$ . How-

ever, the syngas/pyrogas-CLC technique requires another separate gasification/pyrolysis reactor, which will increase the complexity and operation cost of CLC system. Furthermore, using  $CaSO_4$  as oxygen carrier may suffer from  $SO_x$  emission and particle abrasion/fragmentation [21]. Considering plastic wastes [usually containing a very high volatile content (e.g., 93%)] are quite easier to be pyrolyzed or gasified than other solid fuels (e.g., coal char, petroleum coke, or even biomass char), we first proposed to utilize *in situ* gasification-CLC (iG-CLC, where the pyrolysis/gasification of fuel and the reduction of combustible gases by OC occur in the same reactor) to dispose PW [22,23]. The performance of iG-CLC using PW as fuel and iron oxide as oxygen carrier was evaluated in a batch-operated fluidized bed reactor, and very high carbon conversion (up to 98%) and  $CO_2$  yield (up to 97%) can be attained [22,23]. Further dechlorination through adsorbent-decorated OC was examined, and the dechlorination efficiency can reach ca. 80% [18], which will further constrain the presence of  $Cl_2$  and other active chlorine sources. We [23] also measured the organic compounds in the exhaust gases during the iG-CLC of PWs, and discovered that utilizing  $CaO$ -decorated iron ore as OC can effectively reduce the emission of chlorobenzene (as an indicative intermediate of PCDD/Fs), which is attributed to the effective dechlorination via chlorine adsorbent (i.e.,  $CaO$ ). Although these encouraging results provided indirect evidence to *in-situ* inhibition of PCDD/Fs by CLC, to the best of our knowledge, the distribution properties of 17 toxic PCDD/Fs congeners as the direct evidence have not been measured during the iG-CLC process of PWs to date. More importantly, the formation and inhibition mechanisms of PCDD/Fs in iG-CLC based on the experimental measurement have not been investigated previously.

In order to examine the feasibility of the CLC technique for *in situ* inhibiting the formation of PCDD/Fs, the following questions should be addressed. (1) How are 17 toxic PCDD/Fs congeners distributed in the iG-CLC process, especially when compared to the conventional PW incineration? (2) How are the PCDD/Fs formed and inhibited in iG-CLC, respectively? To address the first question, the 17 toxic PCDD/Fs congeners from conventional PW incineration and iG-CLC using  $CaO$ -decorated  $Fe_2O_3/Al_2O_3$  as OC were sampled and quantified by a high-resolution gas chromatography/high-resolution mass spectrometer (HRGC/HRMS). Then, in order to explore the formation and inhibition mechanisms of PCDDs and PCDFs in iG-CLC, a chlorine substitution model was proposed to calculate the chlorine substitution probability based on the PCDD/Fs measurements. Also, the  $Cl_2$  yield measurement via methyl orange spectrophotometry, the organic matter analysis via Fourier-transform mass spectrometry, as well as particle (oxygen carrier and fly ash) characterization via ESEM-EDX and XPS were conducted to help understand the formation and inhibition mechanisms of PCDDs and PCDFs in iG-CLC.

## 2. Experimental

### 2.1. Materials

A medical perfusion tube (which is made of polyolefin thermoplastic elastomer. Polyethylene and polybutylene are the main components, and a small amount of chlorine is also added to improve its performance) was selected for this study as a typical PW sample. The ultimate analysis of PW shows that the contents (wt%, d.a.f.) of C, Cl, O, S, N and H are 73.89 %, 4.92 %, 3.39 %, 0.16 %, 0.72 % and 10.82 %, respectively. Besides, the proximate analysis components of PW includes volatile (93.79 wt%), ash (6.1 wt%), fixed carbon (0.08 wt%) and moisture (0.03 wt%). In addition, the ash analysis of PW shows that the contents (wt%) of  $SiO_2$ ,  $Fe_2O_3$ ,  $CaO$  and  $Al_2O_3$  are 34.92 %, 19.23 %, 19.54 % and 15.63 %, respectively.

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