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Review

A review of dioxin-related substances during municipal solid waste incineration

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are among the most toxic chemicals and the main restriction on municipal solid waste incineration. To exert more effective control over the formation of dioxin homologues during municipal solid waste incineration, it is significant to investigate dioxin-related compounds. Despite the numerous studies about PCDD/Fs, a unified understanding regarding many problems has yet to be reached because the homologues of PCDD/Fs are excessive, the measurement of PCDD/Fs is difficult, and the formation mechanisms of PCDD/Fs are complicated. Firstly, this paper briefly introduces the different formation mechanisms of PCDD/Fs, including high temperature homogeneous reaction PCDD/Fs formation and low temperature heterogeneous reaction PCDD/Fs formation. Then the sources of PCDD/Fs including precursors (chlorophenols and polycyclic aromatic hydrocarbons) and residual carbon are summarized. In particular, this paper analyzes the substances that influence PCDD/Fs formation and their impact mechanisms, including different categories of chlorine (Cl_2, HCl and chloride in fly ash), O_2, copper, sulfur, water, and nitrogen compounds (ammonia and urea). Due to the high cost and complexity of PCDD/Fs measurement, PCDD/Fs indicators, especially chlorobenzenes and polycyclic aromatic hydrocarbons, are summarized, to find an effective surrogate for quick, convenient and real-time monitoring of PCDD/Fs. Finally, according to the results of the current study, recommendations for further research and industrial applications prospects are proposed.

Contents

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1. Introduction

Dioxins are generic terms for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). PCDDs and PCDFs consist of 75 and 135 homologues, respectively, as shown in Fig. 1. Dioxins are among the most toxic chemicals on the earth, and in particular, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) has the highest toxicity. US Environmental Protection Agency (USEPA) has listed dioxins as a serious cancerogen which may destroy the immune system of human body and interfere with hormone regulation (Mckay, 2002).

Municipal solid waste (MSW) incineration is one of the significant sources of PCDD/Fs in the environment. A considerable body of research about PCDD/Fs from MSW incineration has been carried out since the 1970s. Generally, researchers believe that PCDD/Fs are formed via two mechanisms. One is from homogeneous reactions, in the temperature range of 500–800 °C. The main process is the rearrangement reactions of chlorinated precursors in the gas, such as chlorophenol (CP) and chlorobenzenes (CBz). PCDD/Fs from this process are called homogeneous PCDD/Fs or high-temperature PCDD/Fs. PCDD/Fs can also be formed from heterogeneous reactions, in the temperature range of 200–400 °C. PCDD/Fs from this process are termed as heterogeneous PCDD/Fs or low-temperature PCDD/Fs. Heterogeneous PCDD/Fs may also come from CP or CBz (Addink and Olie, 1995a; Vermeulen et al., 2014), or from carbon in fly ash (Huang and Buekens, 1995). The main process is the surface catalytic effect of fly ash or soot, i.e. de novo process (Stanmore, 2004).

It remains debated whether heterogeneous PCDD/Fs come from gaseous precursors or carbon in fly ash. The experiments of Dickson et al. (1992) show that, under the same conditions, the PCDD/Fs formation rate from precursors is 72–99,000 times higher than the formation rate from carbon in fly ash. Therefore, precursors are thought as the main source of PCDD/Fs. Luijk et al. (1994) also thought the PCDD/Fs formation from precursors was approximate 3000 times faster than the de novo process from activated carbon. In a review article, Tuppurainen et al. (1998) also argued that precursors were the main source of PCDD/Fs formation. However, the experiments of Dickson et al. and Luijk et al. had some limitations. The CP concentration was too high—much higher than the real concentration in flue gas of incineration. Moreover, the characteristics of synthetic fly ash were quite different from that of real fly ash, and the reactivity of real fly ash was higher.

Due to the low concentration of precursors in flue gas, Huang and Buekens (2000) studied the proportional distribution of PCDDs and PCDFs, and concluded that the main origin of heterogeneous PCDD/Fs was the de novo process of the carbon in fly ash. Everaert and Baeyens (2002) reviewed the incinerator of MSW, wood and industrial waste, coal boiler, and metallurgical furnace, and obtained the same conclusion. Stanmore and Clunies-Ross (2000) also deemed that all the PCDD/Fs from MSW incinerator were related to fly ash. Their conclusions have been proved by the experiments by Hell et al. (2000) and Tame et al. (2003) and the model established by Stanmore (2002a).

However, some researchers contend low chlorinated PCDD/Fs are from gas phase catalysis or non-catalytic flame reactions, while high chlorinated PCDD/Fs are mainly from de novo reactions of fly ash (Wikstrom et al., 2004a). Xhrouet et al. (2001) found that the ratio of PCDFs to PCDDs was larger than 5 in simulated de novo reactions, and the same results have been replicated in other studies (Everaert and Baeyens, 2002; Addink and Olie, 1995b; Pekarek et al., 2001; Chang and Huang, 2000). Thus it is believed that PCDFs are mainly from de novo reactions, while precursors play an important role on the formation of PCDDs. Moreover, during the heterogeneous PCDD/Fs formation from trichlorophenol (TrCP), the ratio of PCDDs to PCDFs is much larger than 1 (Hell et al., 2000; Qu et al., 2009).

Given the PCDD/Fs formation mechanisms are complicated and the measurement of PCDD/Fs is difficult, continuous research efforts have been devoted to this area and a universally accepted result has yet to be obtained (Stanmore and Clunies-Ross, 2000). After the heterogeneous formation mechanisms of PCDD/Fs were discovered, most of the research focuses on heterogeneous PCDD/Fs (Alderman et al., 2005; Vehlow, 2012). With the application of advanced industrial dust removal equipment, the formation of heterogeneous PCDD/Fs is controlled to some extent (Kim et al., 2007a; Lin et al., 2008). Accordingly, the percentage of homogeneous PCDD/Fs is increased, thus more researchers have turned to investigating the formation of homogeneous PCDD/Fs (Qu et al., 2009).

PCDD/Fs may be generated from the condensation of CP and CBz, the chlorination of polycyclic aromatic hydrocarbons (PAHs), or the de novo reactions of fly ash. The present article reviews three important sources of PCDD/Fs: CP, PAHs and residual carbon, and summarizes the influences of chlorine, O_2, copper, sulfur, water, and nitrogen compounds on PCDD/Fs formation. Since conventional PCDD/Fs measurement in incinerators is complicated and costly, many researchers are seeking for PCDD/Fs indicators (Pandelova et al., 2006), i.e. to find a simple method to measure PCDD/Fs emissions during incineration process. Therefore, the last part of this paper reviews the possibility of CBz and PAHs and other compounds as PCDD/Fs indicators.

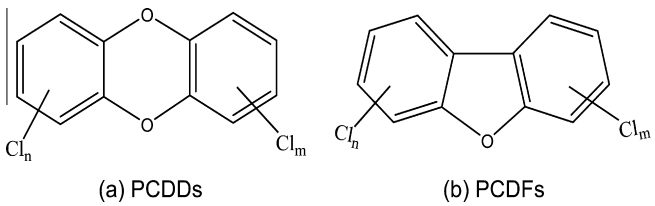

Fig. 1. The structure of PCDD/Fs.

2. The sources of PCDD/Fs

2.1. Chlorophenol

Among many precursors, CP has the most similar structure with PCDD/Fs, and CP is the easiest to form PCDD/Fs (Xu et al., 2010; Pan et al., 2013).

Both the homogeneous and heterogeneous reactions of CP are very important for PCDD/Fs formation (Tuppurainen et al., 2003). Many studies have identified the total amount and categories of PCDD/Fs using CP as an origin at elevated temperature (Hell et al., 2000), including high-temperature homogeneous PCDD/Fs formation (Kim et al., 2007b; Khachatryan et al., 2003a) and low-temperature heterogeneous catalytic PCDD/Fs formation