Formation and Emission of Dioxins during Coking Process

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Abstract

Coking process is recognized as one of potential sources of dioxins. However, available knowledge about formation and emission of dioxins during coking process is very scarce. In this study, emission and characteristics of dioxins were presented, and formation pathway of dioxins during coking process was speculated through the available data from coke plants. De novo synthesis was assumed to be the main formation pathway of dioxins during coking process. This study may be useful for developing dioxins inventory and understanding the formation of dioxins during coking process.

Introduction

Polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs), often termed as "dioxins", are extremely harmful to human health and environment due to their high toxicity, persistence, bioaccumulation through the food web. Thermal related process including combustion sources, metal smelting and refining sources, chemical manufacturing, biological and photochemical processes are major anthropogenic dioxins sources [1]. Among these sources, thermal related processes have aroused great public's attention due to the huge industrial activity [2]. Knowledge of dioxins formation pathway could provide the basis of designing processes and reducing dioxins formation. Currently, besides homogeneous gas phase formation of dioxin, there are two dominant formation theories based on heterogeneously catalysed reactions: (i) de novo synthesis (ii) precursor theory [3]. Many studies focused on the formation pathway of dioxins in different thermal sources, such as waste incineration [4,5], sintering process [6,7], and so on. It is well known that, carbonization of coal in coke production involves many thermal reactions at high temperature. However, available knowledge about formation and emission of dioxins during coking process is still very scarce.

In previous preliminary investigation, the emission of dioxins during coking process was identified [8]. Levels and characteristics of dioxins during coking process were further presented, and the dominant formation pathway was tentatively speculated through the detected data and emission characteristics from coke plants in this study. Furthermore, for intention of comparison with other thermal sources, three types of waste incinerators (municipal waste incinerators, MSWI; medical waste incinerators, MWI; and hazardous waste incinerators, HWI) were selected as the contrasted thermal sources. This study may be useful for understanding the formation pathway of dioxin during coking process.

Materials and Methods

Coke is produced by carbonization of coal in coke ovens which coal is charged and are subjected to external

heating to about 1000 °C in absence of air, and then coke is ejected and quenched in quenching tower. Formation and emission of dioxins might occur during charging of coal (CC) and pushing of coke (PC) in coking process. In this study, four typical coke plants with different techniques of coal charging were selected. The basic information of these four coke plants were described in Table 1. The collection and analysis of stack gas samples from the coke plants followed US EPA method 23.

Table 1. The basic information of the coke plants

Denotation	P1	P2	P3	P4
Technique of coal charging	Top charging	Top charging	Stamp charging	Top charging
Air pollution control device	Bag filters	Bag filters	Bag filters	Bag filters
Segments of process for collected stack gas samples	Pushing of coke	Pushing of coke	Pushing of coke; Charging of coal	Pushing of coke

Results and Discussion

The concentrations of dioxins during coking process were converted to dry standard conditions (273 K and 101.3 kPa) and referred to 11% O_2 in stack gas. Seen from Fig.1, the formation and emission of dioxins occurred during both charging of coal and pushing of coke. The concentrations of dioxins (from tetra to octa-CDD/Fs) in stack gas samples ranged from 4553 to 34249 pg Nm^{-3}. For each plant, the concentration of PCDDs was lower than that of PCDFs. For P3 plant, the dioxins concentration during PC was lower than that of CC.

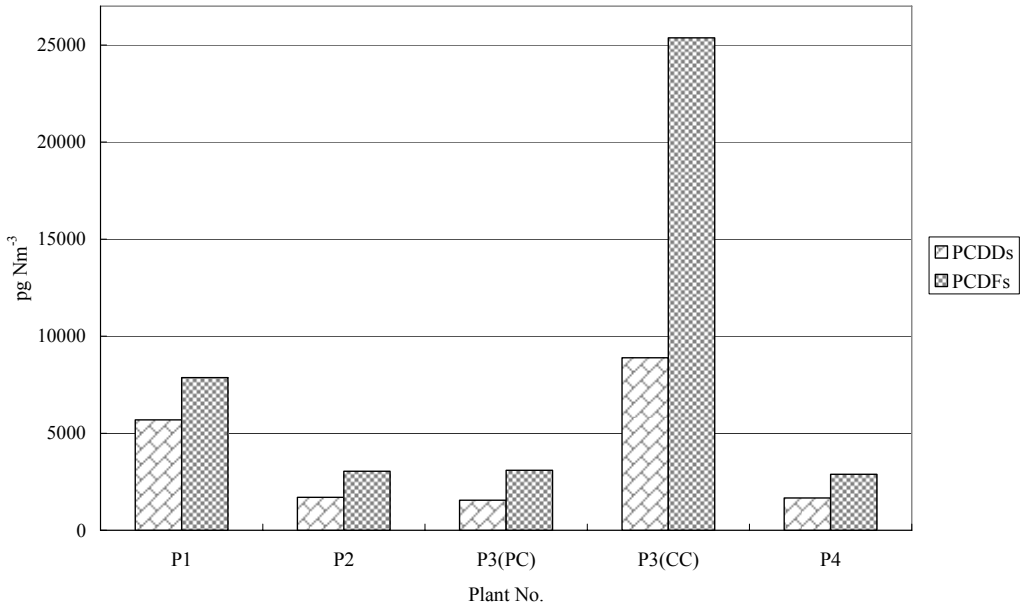

Fig.1. Concentrations of dioxins from coke plants

To concentrations of homologues of dioxins were normalized to percent of sum of PCDD/Fs (from tetra to

octa-CDD/Fs). Figure 2 demonstrated the patterns of dioxins for coking processes and waste incinerations. It could be seen that the patterns for coking processes presented very similar characteristics with that of waste incineration. Everaert and Baeyens (2002) [9] studied the fingerprints of dioxins in flue gases from different thermal processes which de novo synthesis was considered as the dominant formation pathway. Strong resemblance for characteristics of dioxins was observed among these thermal sources and coking process, which indicated possible similar formation pathway of dioxins in different thermal processes. De novo synthesis normally requires that the ratio of PCDFs to PCDDs ($R_{DF/DD}$) is greater than 1 [9]. In this study, the $R_{DF/DD}$ for coking process and waste incineration were presented in Fig. 3. It could be seen that the $R_{DF/DD}$ for coking process and waste incineration were very similar, and were larger than 1, which indicated that de novo synthesis may be the dominant pathway of dioxins formation.

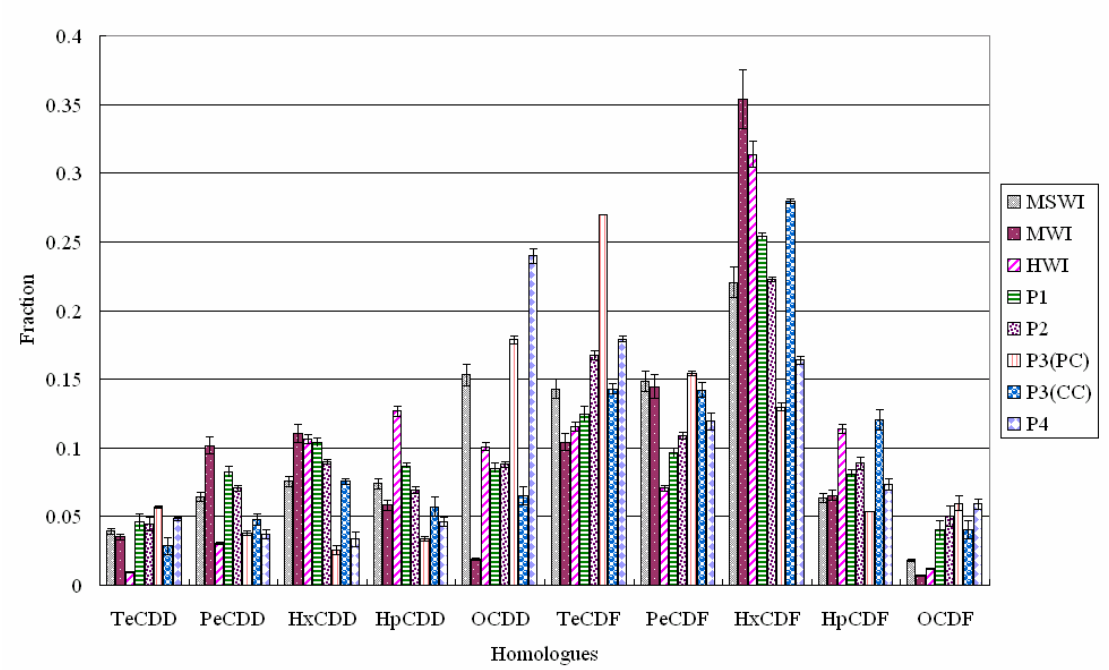

Fig. 2. Characteristics of dioxins during coking process and waste incineration.

For precursor formation theory, chlorobenzenes are suggested to be the important precursors for dioxins formation [3]. In this study, several chlorobenzenes were detected, and the correlations of chlorobenzenes and PCDD/Fs were investigated by linear fitting. Table 2 showed the correlation coefficients of chlorobenzens and PCDD/Fs, and no strong correlation was observed, which supported the view from another aspect that de novo synthesis may be the dominant pathway for coking process. However, more detail reactions for dioxins formation during coking process are still unclear. In order to explore the explicit pathway of dioxins formation during coking process, much further studies are needed.

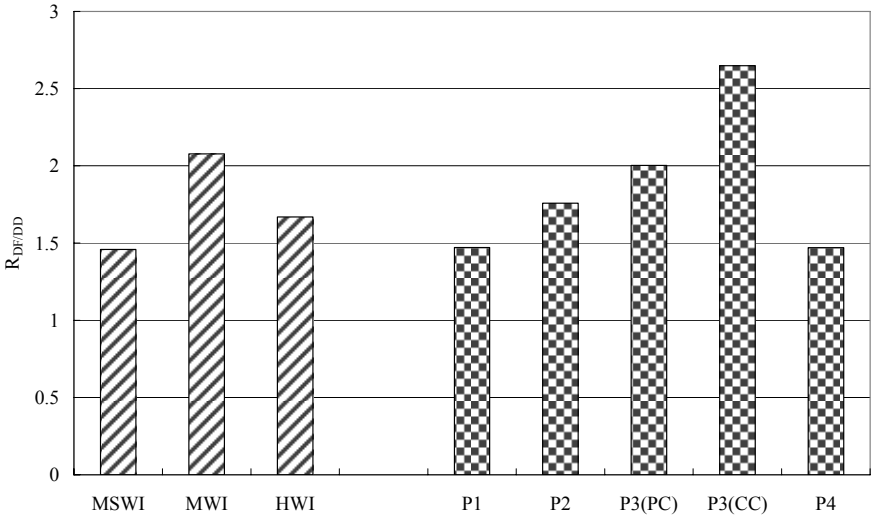

Fig. 3. The $R_{DF/DD}$ for coking process and waste incineration

Table 2. Correlation coefficients (R^2) of chlorobenzens and PCDD/Fs for coking process

Homologues	1235-TeCB	1245-TeCB	1234-TeCB	PeCB	HCB
∑PCDD/Fs	0.03	0.05	0.21	<0.01	<0.01

Acknowledgments

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