

Modeling the formation of precursors of dioxins during combustion of woody fuel volatiles

Elena Daniela Lavric*, Alexander A. Konnov, Jacques De Ruyck

Department of Mechanical Engineering, Vrije Universiteit Brussel, Pleinlaan, 2, Brussels B-1050, Belgium

Received 17 September 2004; accepted 21 September 2004

Available online 30 October 2004

Abstract

The emissions of polychlorinated-*p*-dibenzodioxins (PCDD) and dibenzofurans (PCDF) from waste combustion show a close correlation with the emissions of chlorinated benzenes or phenols, which could therefore be used as indicators for easier, faster and cheaper prediction of the potential dioxin emission levels. Using contemporary analytical methods, the emissions of, e.g. monochlorobenzene can be measured on-line and predictions could be made via a suitable mathematical model describing the link between these precursors and dioxins. Modeling the formation of the precursors could therefore provide an indirect possibility for the prediction of dioxins' formation and subsequent optimization of the combustion process characteristics.

A detailed combustion mechanism consisting of 3678 gas-phase reactions between 755 species including chlorine chemistry has been developed. The influence of temperature, reaction time, equivalence ratio and chlorine concentration on monochlorobenzene and monochlorophenols formation was tested for batch and well-stirred reactors. The impact of good mixing conditions, appropriate level of oxygen, chlorine contents and temperature regime on the formation of precursors of dioxins is emphasized.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Dioxin; Gas-phase kinetic mechanism; PCDD/PCDF; Surrogates; Precursors; Incineration; Biomass

1. Introduction

Although the incineration of hazardous wastes presents a means of disposal, applications of the technology have been hindered by environmental concerns regarding the stack effluent of such systems [1]. All forms of incineration (controlled or uncontrolled) are responsible for dioxins emissions, but incineration under controlled conditions is considered the most favorable destruction procedure for many wood wastes. Its advantages include [2,3] a considerable volume reduction, lower net CO₂ emissions, the possibility to substitute other fuel types for energy production and the removal of residues of environmental concern. Wood offers advantages over fossil fuels with respect to emissions because the sulfur and nitrogen contents of wood are low, thus SO_x emissions are negligible,

and, if temperature is controlled to reduce oxidation of nitrogen from the air, overall NO_x could also be low [4].

Wood combustion is at present one of the most important air emission sources for dioxins (about 25% from the total emissions), since not only natural wood but also salt-laden wood waste and woodwastes coated and treated with various types of contaminants (chromated copper arsenate, pentachlorophenol, creosote, adhesives, resins, paint and other surface coatings) has been burnt [5,6]. Unfortunately, the emissions from wood combustion, accidental fires and from the combustion and landfilling of pentachlorophenol (PCP) treated wood are difficult to assess because emission factors and corresponding activity rates are not available or highly uncertain [7,8].

The conventional measurement methods for dioxins (based on high resonance gas chromatography/high resonance mass spectrometry (HRGC/HRMS)) are time consuming and need high skills and excessive costs; even recently improved method [9], which drastically reduces

* Corresponding author. Tel.: +32 2 629 23 24; fax: +32 2 629 28 65.
E-mail address: dlavric@vub.ac.be (E.D. Lavric).

Nomenclature

HACA	hydrogen-abstraction-acetylene-addition	PCDD/PCDF	polychlorinated dibenzo- <i>p</i> -dioxin/ dibenzofuran
HRGC/HRMS	high resolution gas chromatography/high resolution mass spectrometry	PIC	products of incomplete combustion
I-TEQ	International Toxicity Equivalence Factor/Quotient	ST	Shaub and Tsang mechanism [26]
PCBzs/PCPs	polychlorinated benzenes/phenols	Φ	equivalence ratio

the operation time, hazardous solvent consumption and thus, the cost, do not provide on-line real-time results.

Efforts were done to develop robust screening techniques to simplify the determination of PCDD/F concentration in flue gases. One of the possible screening strategies for the prediction of the International Toxicity Equivalent (I-TEQ) of stack gases is to measure and correlate a surrogate chemical (i.e. a compound other than PCDDs and PCDFs, but which is representative for the emission of the latter) against corresponding PCDDs and PCDFs [10–12]. Various components were analyzed in the same time with PCDD/Fs, to identify the suitable surrogate. Correlations between products of incomplete combustion (PIC), e.g. chloroaromatic compounds, can be used to characterize the emissions from combustion processes. Statistically good relations were found between PCDD/F (expressed as concentration or as I-TEQ) and polychlorinated benzenes (PCBz) [11,12]. All the observed chlorobenzenes roughly well correlate with I-TEQ. Monochlorobenzene in particular was found to be a very sensitive surrogate [11,12], which is suited for on-line detection using mobile resonance-enhanced multiphoton ionization time-of-flight mass spectrometry. If the correlation between a surrogate (like monochlorobenzene) and dioxins established for an installation could be used together with a model accurate enough to describe the formation/consumption of that surrogate, then the control of the incineration processes should be possible. From this point of view, such a model is very useful. Modeling the formation of the precursors could therefore provide a direct possibility for the dioxins' prediction and optimization of the combustion process characteristics.

In the present work a short review of the formation mechanism of dioxins and corresponding kinetic models is first given. A new mechanism for homogenous gas phase formation of monochlorobenzene and monochlorophenols is next presented. The influence of temperature, reaction time, equivalence ratio and initial chlorine concentration will be discussed for batch and for well-stirred reactors.

2. Dioxins formation mechanisms

Many studies trying to elucidate the formation mechanism(s) of PCDD/Fs and the affecting factors are available. The wide variability of organic material incinerated

and the wide range of combustion technologies that have variable temperatures, residence times, and oxygen requirements make this problem very complex, however. The precise mechanisms by which PCDD/F are formed in thermal processes such as combustion, incineration and other non-specific thermal events have not been clarified yet [13,14], but several theories are in development [13,15–17].

It is generally accepted that three primary mechanisms lead to formation of PCDD/Fs in combustors: (1) homogenous gas-phase reactions involving chlorinated organic precursors such as chlorobenzenes and chlorophenols; (2) heterogeneous reactions between chlorinated organic precursor compounds and fly ash-based metallic catalysts such as copper; and (3) de novo synthesis involving fly ash-bound carbon, a chlorine source and metallic catalysts [18]. These three main mechanisms should not be regarded as excluding each other. The relative importance of the precursor (heterogeneous) and de novo mechanisms is still highly controversial [19].

Homogenous formation of PCDD is governed by the concentration of chlorophenols and that of PCDF by chlorophenols and chlorobenzenes concentrations [20]. According to Weber and Hagenmaier [21], only phenols with chlorine in *ortho* position are capable of forming dibenzodioxins, while *para*-chlorophenol is responsible for PCDF formation.

All pathways have been proven in laboratory scale experiments. Routes (2) and (3), highly investigated, are heterogeneous catalytic processes, occurring on the fly ash surface in the incinerators temperature range of 250–450 °C. Both show the same optimum temperature for PCDD/F formation revealed by laboratory experiments, which emphasized copper as an essential catalyst for both processes. This might be an indication that macromolecular carbon species are first cleaved to chlorobenzenes and chlorophenols, which are further converted to PCDD/F in the rate determining step [22]. The preferred locations where generation of PCDD/F occur are in the economizer and in the equipment for dedusting, especially the electrostatic precipitator. The precursor theory is supported by the existence of a relationship between the concentrations of chlorobenzenes and chlorophenols and the concentration of PCDD/F in the flue and stack gas of incinerators. Some studies [23,24] indicate that the precursor theory can be extended to C-2 precursors like acetylene, ethylene, etc.

Download English Version:

<https://daneshyari.com/en/article/10273319>

Download Persian Version:

<https://daneshyari.com/article/10273319>

[Daneshyari.com](https://daneshyari.com)