Accepted Manuscript

PCDD/F-isomers signature - Effect of metal chlorides and oxides

Mengmei Zhang, Alfons Buekens, Kees Olie, Xiaodong Li

PII: S0045-6535(17)30843-3

DOI: 10.1016/j.chemosphere.2017.05.176

Reference: CHEM 19392

To appear in: *ECSN*

Received Date: 18 January 2017

Revised Date: 1 May 2017

Accepted Date: 23 May 2017

Please cite this article as: Zhang, M., Buekens, A., Olie, K., Li, X., PCDD/F-isomers signature - Effect of metal chlorides and oxides, *Chemosphere* (2017), doi: 10.1016/j.chemosphere.2017.05.176.

PCDD/F-isomers signature - effect of metal chlorides and oxides

Mengmei Zhang[1], Alfons Buekens[1,2], Kees Olie[3], Xiaodong Li[1*]

[1]State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou, China
[2]Formerly: Chemical Engineering Department, Vrije Universiteit Brussel, Brussels, Belgium
[3]University of Amsterdam, Amsterdam, the Netherlands
*Corresponding author
E-mail: lixd@zju.edu.cn. Tel.: +86 571 8795 2628; Fax: +86 571 8795 2428

Abstract

A recent paper presented the results from de novo tests, involving 11 distinct catalytic systems (oxides and chlorides of Cd, Cr, Cu, Ni, and Zn, as well as a blank sample). Their PCDD and PCDF formation activity was shown. This paper further assesses their isomer signature, with special emphasis on those congeners associated with chlorophenol precursor routes, and on 2,3,7,8- and 1,9-substituted congeners. Each metal catalyst generates a significantly different signature, also affected by the presence or absence of oxygen in the reaction atmosphere. Oxide and chloride catalysts supply distinctive signatures, suggesting singly weighted pathways. Quite a large number of data was handled, so that throughout this analysis special attention was given to testing and developing an appropriate methodology, allowing appropriate correlation analysis and statistical data treatment. The large tables resulting relate to the 11 catalytic systems, studied at 3 levels of oxygen concentration, with 94 PCDD/F-congeners considered individually. They constitute an extensive reference data bank for confronting novel experimental data with this vast data set.

Keywords: PCDD/F; Catalysis; Metal chloride; Metal oxide; Isomer distribution; CP-route.

1. Introduction

Two general pathways have been proposed for the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F): (i) precursor pathways starting from organic molecules similar to PCDD/F, either in the gas phase at temperatures between 500°C and 800°C (Yang et al., 1998; Nakahata and Mulholland, 2000; Mulholland et al., 2001; Ryu et al., 2005a), or at lower temperatures involving catalytic ash surfaces (Addink et al., 1995; Ryu and Mulholland, 2005; Ryu et al., 2005b; Nganai et al., 2014), and (ii) *de novo* synthesis mainly between 250°C and 450°C. The term 'de novo' refers to parent structures seemingly unrelated to the PCDD/F structures, and involving the chlorination and oxidative breakdown of macro-molecular carbon (Stieglitz et al., 1997; Addink et al., 1998; Hell et