

THERMAL PROCESSES

This session is comprised of twenty six presentations addressing various aspects of dioxin and furan formation in thermal processes. The contributions cover PCDD/F formation from variety of thermal processes including incineration. The session is divided into oral and poster presentations. The oral session will have eight presentations and this will be followed by a companion poster session comprised of eighteen presentations. Presenters in this session represent ten different countries including Canada, China, France, Germany, Italy, Japan, Sweden, Spain, the United Kingdom, and the United States.

The presentations in this session report results from laboratory, pilot plant and field studies. A wide variety of experimental techniques and theoretical methods were used in these studies to investigate various aspects of dioxin formation. For many years a controversy exists about the formation routes of PCDD/F's during incineration. It seems that both the so called *de novo* and precursor formation pathways play a role during the formation. However, the exact mechanism of PCDD/F formation is not well understood for either pathway. The papers presented in this session should help answer several formation/destruction questions and should increase our understanding of PCDD/F formation in thermal processes.

The two main questions that need to be answered before PCDD/F formation mechanism can be understood are: 1) role of different metals and 2) different carbon sources. Several papers in this session were dedicated to investigating the role of metals and carbon sources in PCDD/F formation. The fact that metals (Cu) act as a catalyst during the formation is known now for a long time but now there is a contribution by Masaki Takaoka *et al* (The change in the chemical form of copper in fly ash in a suitable temperature region for *de novo* synthesis) that gives more insight in the role of copper. They conclude that: "The present results suggest that CuCl and CuCl₂·2H₂O play a vital role in the formation of chlorinated aromatics." X-ray absorption near-edge spectroscopy (XANES) was used to determine the structure of the copper compounds over the temperature range of interest. With this technique it was possible to follow the reactions that takes place with the Cu compounds during the heating of the flyash. The contribution of Nakka *et al* (Surface Catalyzed Chlorobenzene Transformation Reactions in Post-Combustion Zone) also added more information about the role of copper during transformation reactions of chlorinated benzenes. Although it is known from the beginning of the eighties that there is a very good correlation between the formation of PCDD/Fs and chlorinated benzenes. The mechanism that correlates these two formations is not known yet. One thing is for sure; the chlorinated benzenes by themselves are not precursors for the PCDD/Fs. The role of Cr was investigated by Öberg *et al* (Chromium as a potential catalyst in the thermal formation of chlorinated aromatic compounds). They concluded from the PCA analysis that Cr correlates better than Cu with PCDD/F formation.

It was shown by Grandesso *et al* (Towards the comprehension of the role of copper and iron in MSWI fly ash carbon degradation) that the carbon was completely oxidized to CO₂ in all of their model systems except in C – SiO₂ mixture. Two processes seem to play a role and the first of them needs copper as a catalyst. From the same research group there is a contribution by Collina *et al* (Model Systems for the Study of MSWI Fly Ash Thermal Degradation: Kinetics of Active Carbon-Silica Gel Mixtures). They studied the oxidation of Carbon without a catalyst and using Arrhenius and Eyring equations concluded that the pre-exponential factor, A, the activation energy, E_a, the activation entropy, ΔS^\ddagger , and the activation enthalpy, ΔH^\ddagger , depend on TOC⁰ value. Fullana *et al* (PCDF Formation from PAH Reactions) observed that large quantities of PCDF's were formed from a number of PAHs and they show that PAHs that are adsorbed on particle surface or that form the non-graphitic layer of soot are an important carbon source for PCDF emissions. These results are consistent with results of Ryan *et al* (Investigation of the Pathways

to PCDDs/Fs from an Ethylene Diffusion Flame: Formation from Soot and Aromatics) based on their experimental results concluded that the soot formed at lower temperatures contributes to the formation of PCDD/Fs and that the lower chlorinated PCDD/Fs are formed from phenols. This also validates the findings of Nordsieck *et al* (Changes in PCDD/PCDF formation Processes During Instationary Phases of Combustor Operation) which state that PCDD formation via chlorophenol condensation seems to be an important formation part during transiently impaired combustion conditions. Under normal operation conditions and during memory phases however, PCDD/F formation seems to depend on catalysed reactions from other organic compounds or from "black" carbon. Jae-Yong Ryu *et al* (Characteristic homologue and isomer patterns of polychlorinated dibenzofurans from phenol precursors) did show that not only the congener patterns but also the isomer patterns are identical for phenol and *de novo* formation. The same group also studied the formation of polychlorinated naphthalenes (PCNs).

The effect and sources of Chlorine in the thermal processes were investigated in four contributions. Hatanaka *et al* (Effect of poly(vinyl chloride) and hydrogen chloride as a chlorine source on the formation of PCDDs and PCDFs in model waste incineration) confirmed that the patterns of the PCDD/Fs formed were independent from the Chlorine source. The role of PVC was also investigated by Neurath (PVC's role in dioxin emissions from open burning: New analysis of US EPA data) who came to the conclusion that by definition, uncontrolled combustion cannot be controlled. However, the types of waste materials burned are controllable, and the best way to reduce dioxins from open burning may be by reduction in PVC burning. Most of PVC in waste is packaging or low-value disposable items. Virtually all of these PVC uses have currently available cost-effective substitutes. Regulating sales of PVC products is potentially a practical and cost-effective way of reducing dioxin emissions worldwide. Fisher *et al* (Effect of chloride on the formation of PCDD/Fs and WHO-12 PCBs in iron ore sintering) came to the conclusion that during the sintering process the emissions of PCDD/Fs are linearly correlated with the Chlorine concentration. Yan *et al* (Effects of inorganic chlorine sources on PCDD/Fs formation via heterogeneous synthesis on fly ash surfaces) investigated the role of inorganic chlorine compounds and concluded that the capability of different metal chlorides to facilitate formation of PCDD/Fs should be ranked as follows: Na < Mg < K < Al < Ca. They also concluded that during heterogeneous reactions on fly ash, NaCl and MgCl₂ produced more dioxins, while KCl, AlCl₃ and CaCl₂ produced more furans.

Several papers discussed the theoretical reaction models for the formation of PCDD/Fs (Lomnicki *et al* and Dellinger *et al*) from chlorinated phenols over flyash and in gas phase. In the past degradation of PCDD/Fs on flyash and other supports has been investigated. Lower chlorinated PCDD/Fs were found but only in small amount compared to the starting material. Visez *et al* (Formation of polychlorinated dibenzodioxins, benzenes and phenols from thermal degradation of 2-chlorophenol promoted by CuCl₂) found that thermal degradation of O8CDD (≈ 0.5 mg) in presence of copper chloride (5.0 mg) at 350°C for 30 minutes produced large amounts of C₂Cl₄ along with tetrachlorocyclopentenedione and hexachlorobenzene. Trichlorobenzene, pentachlorobenzene and tetrachlorocarbon were only observed in low concentrations. The same group (Dioxins and other products from the gas-phase oxidation of 2-chlorophenol over the range 450-900°C) also investigated gas-phase dioxin formation at higher temperatures.

Prevention of formation and thermal destruction of PCDD/Fs is still a subject of great interest. Noma *et al* (Polychlorinated Naphthalene (PCNs) behaviour in the thermal destruction process of wastes containing PCNs) reported that destruction efficiencies of more than 99.5% can be achieved. The inhibition study conducted by Pandelova *et al* showed that the use of inhibitors does not influence the relationship between PCDD/Fs and chlorinated benzenes. The use of Urea as an inhibitor was investigated by Kuzuhara *et al* (Effect of Urea on PCDD/Fs Formation through De Novo Synthesis) they concluded that the suppression of PCDD/Fs formation may not be related to the changes in catalytic conditions but to the production of the NH₂ and CN radicals. The use of a pebble heater bed for the elimination of Cl and Br DD/Fs is discussed by Schlummer *et al* (Pebble Heater suppresses Synthesis of Dioxins and Furans in Off-gas generated by Incineration of Halogen-rich Fuel from WEEE). They found emissions of PCDD/Fs

in TEQ to be 0.04ng/m^3 but for the emissions of brominated compounds in TEQ were 12.3ng/m^3 . Based on theoretical study and emission data analysis Duo *et al* (Thermodynamic and Kinetic Studies of Dioxin Formation and Emissions from Power Boilers Burning Salt-Laden Wood Waste) concluded that the stack dioxin emissions increase linearly as the ESP efficiency decreases, exponentially with increasing ESP temperature, and to the second order with hog salt content.

Several other aspects of dioxin formations were also addressed by contributions to this session. Shibata *et al* discuss the "Thermodynamic Behaviours of polybrominated/chlorinated Dibenzo-p-dioxins in Flue Gas". They conclude that the bromine (Br_2 and Br) potentials are much higher than the chlorine (Cl_2 and Cl) potentials in the gas, even though the brominated dioxins are less thermodynamically stable than the PCDDs. The degradation of cotton fibres was studied by Conesa *et al* and the major degradation products were quantified. Polychlorinated terphenyls were synthesized and their thermal stability was investigated by Wichmann *et al*.

In summary, the results from all of the above discussed laboratory simulations, theoretical modeling and plant studies have enhanced our understanding of several aspects of dioxin formation in the thermal processes.

PREPARED BY
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