

DECREASE OF DIOXINS EMISSIONS OF MSW INCINERATOR BY METHANE ADDITION IN POSTCOMBUSTION ZONE

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Abstract

Using a detailed mechanism of dibenzofuran oxidation, the simulations show that the reactivity strongly decreases when the reactant is very diluted and, the dioxins are usually in trace amounts. The oxidation reaction starts when the radical concentration increases with the temperature or with the reactant concentration through the initiation rate and branching steps. The methane addition induces an important increasing of radical concentration and promotes the dioxin oxidation.

Introduction

Municipal waste incineration and other thermal processes lead to the formation of "dioxins" in trace amounts. The optimization of the post-combustion might reduce the level of emissions of PCDD/Fs. The objective is to destroy, by total oxidation, the dioxins and the byproducts resulting from their destruction if we want to avoid the reformation of dioxins by catalytic or *de novo* reactions in the cooling section of the industrial units^{eg 1-3}. In this paper, we study and explain why the fuel addition (natural gas) in postcombustion aera benefits from the dioxins abatement, by a simulation approach using the detailed mechanism of dibenzofuran oxidation.

Material and Methods

In previous investigations^{4,5} to study the experimental conditions leading to a total oxidation of PCDD/Fs, we chose dibenzofuran (DBF) as a model molecule because dibenzofuran has the same structure and is more stable than PCDD/Fs. Moreover, the absence of chlorine atoms on the dibenzofuran molecule avoids any problems of dioxin toxicity and oversimplifies the products analysis. Since dibenzofuran is more stable than chlorinated dioxins or furans, reaction conditions leading to a total oxidation of dibenzofuran should also lead to a total destruction of all the other dioxins. Furthermore, the mechanism of dibenzofuran oxidation should be very similar to the mechanism of that of PCDD/Fs. DBF oxidation was studied between 800° and 950°C, at atmospheric pressure, and high dilution in helium (1000 ppm of DBF). Many products were observed in fuel-rich conditions, and we were able to identify and quantify 25 carbonaceous products: CO, CO₂ were the major products; other reaction products were CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₄, benzene and substituted derivatives, benzofuran and substituted derivatives, indene, naphthalene and dibenzofuranol. Our experimental results on the oxidation of dibenzofuran in the gas-phase at temperatures higher than 900°C show that the concentration of oxygen and the flow conditions (turbulence, back-mixing) seem to be the most important parameters ; a total oxidation is obtained for oxygen in excess (an equivalence ratio > 0.8) and a residence time of 0.5 second. These results on dibenzofuran oxidation suggest that an optimization of the conditions of the post-combustion not only lowers the amounts of PCDD/Fs but also those of other organic products and very low concentration levels are obtained. Some useful clues to design an efficient post-combustion chamber are deduced⁶.

As far as we know, there are no published data for dibenzofuran or dibenzodioxin oxidation even though a lot of data are available for the formation of dioxins^{eg 7,8}. We built a detailed gas phase radical mechanism⁹ accounting for all the reaction products found in our experimental study and also in agreement with the present knowledge on the oxidation of monoaromatic molecules. As far as the dibenzofuran oxidation is concerned (from DBF to toluene and benzene) the detailed mechanism comprises 96 elementary reaction steps including 28 molecules and 20 radicals. Some recent studies investigate several oxidation elementary reaction steps by quantum chemistry (DFT, ...) ^{10,11}. The second part concerns the oxidation of toluene and benzene and it leads to the aliphatic reaction products (C₂H₂, C₂H₄, C₂H₆, C₃H₄,...) and to the final products CO and CO₂ ; this part is well-known and a published mechanism¹² is used which comprises more than 1000 elementary reaction steps including more than 190 species (molecules and radicals). Despite the uncertainties on many estimated kinetic

parameters, the proposed mechanism accounts reasonably well for the oxidation of dibenzofuran at high temperature (900°C). The mechanism of dibenzofuran is probably the main part of the mechanism of oxidation of PolyChlorinated Dibenzofurans (PCDFs) and it must be very similar to the oxidation mechanism of PolyChlorinated Dibenzodioxins (PCDDs). A detailed mechanism is very useful to model the oxidation of dioxins and this approach can bring a substantial contribution to the development of an efficient postcombustion. Our former study show the difficulties to obtain a reaction at very low concentration of dioxins as well as the promoting effect of co-reactants (aromatics) which are in the fumes ¹³.

Results and Discussion

In this paper, our detailed mechanism is used to simulate the abatement of dioxins by total oxidation in a postcombustion area of municipal waste incineration and to study and understand the influence of fuel addition (natural gas). Simulations are obtained with CHEMKIN software and the postcombustion area is “0 D” modeled by a simplified CFSTR (continuous flow stirred tank reactor). The modeling conditions are the following: a residence time of one second, an initial molar fraction of oxygen of 16% ($X^{\circ}(O_2)$) in large excess, and at atmospheric pressure. The initial proportion of DBF ($X^{\circ}(DBF)$) is varying between 0.1 ppm and 1000 ppm(vol). The temperature ranges from 1000 K to 1300 K.

Low reactivity for very diluted reactant

The simulations show that the reactivity strongly decreases when the reactant is very diluted and the dioxins are in trace amounts. Figure 1 shows the influence of initial concentration of DBF on its conversion at various temperatures. The conversions increase from a minimal concentration which increases when the temperature decreases. For example, at 1173 K, the DBF conversion increases from close to 0% at 1 ppm to 90% at 100 ppm. These results show the difficulties to obtain a reaction at very low concentration of pure reactant. We can conclude that the global kinetics of the DBF degradation does not follow a kinetic order equal to one (conversion independent of the concentration) and a detailed mechanism is necessary to predict the conversion.

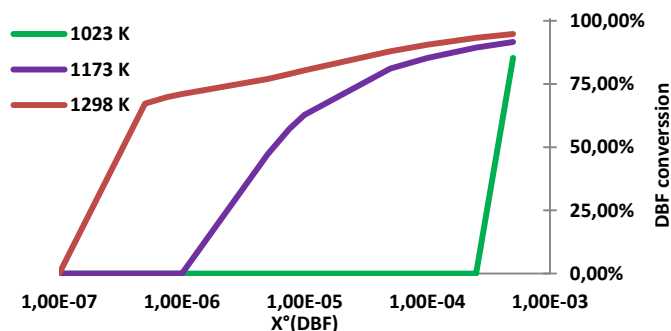


Figure 1: DBF conversion vs DBF initial concentration ($P = 1 \text{ atm}$, $\tau = 1 \text{ s}$, $X^{\circ}(O_2) = 16\%$)

The oxidation reactions are controlled by radicals such as OH, O and H. Figure 2 compares the “ignition” of reaction with these radical concentrations ; we observe (by simulation) that the reaction starts when the radical concentration increases (vs temperature) abruptly at 1250 K for an initial concentration of DBF equal to 1 ppm and 1040 K for 100 ppm. The increasing of radical concentrations depends on the initiation rate and branching steps.

Addition of methane in postcombustion zone

In order to increase the reactivity in the postcombustion zone and promote the abatement of dioxins by total oxidation, we can inject natural gas (methane). Figure 3 shows the influence of methane addition (0 or 1000 ppm) in flue gases when including 1 ppm or 100 ppm of DBF.

For an initial concentration of DBF equal to 1 ppm, the DBF conversion starts at 1250 K without methane, whereas the reaction starts at 1000 K with methane addition. The methane induces an important increasing of OH radical concentration and introduces a new important radical, the methyl radical in the reactant pool.

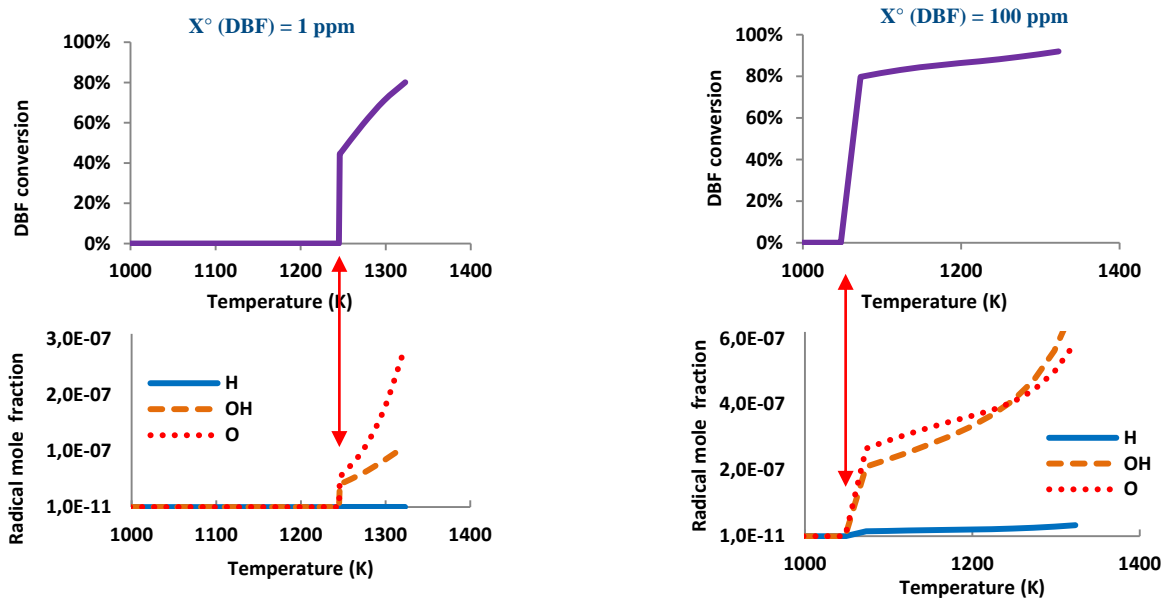


Figure 2 : DBF conversion ($P = 1 \text{ atm}$, $\tau = 1 \text{ s}$, $X^\circ(\text{O}_2) = 16\%$) and mole fraction of radicals vs temperature

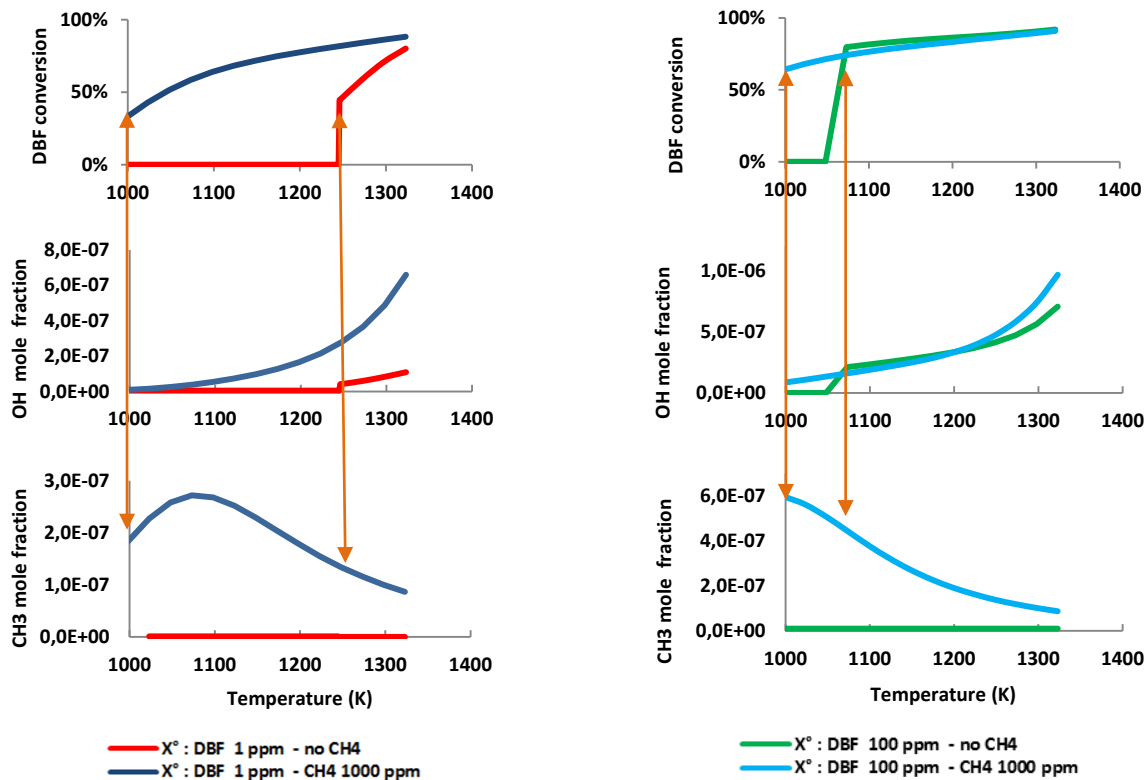
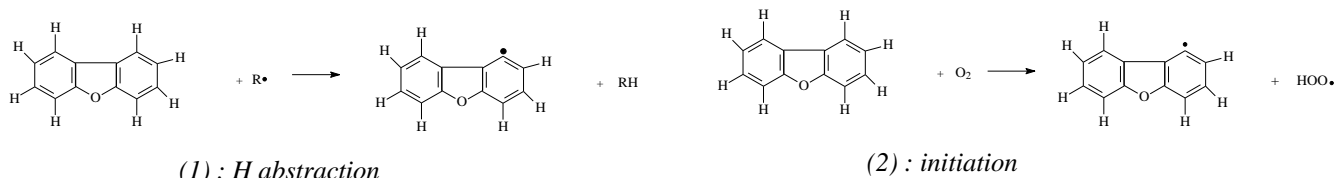


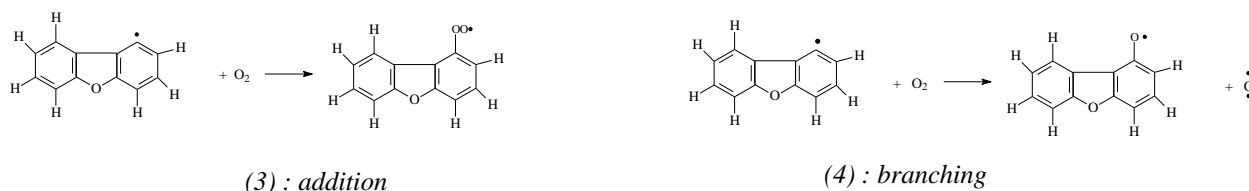
Figure 3 : DBF conversion vs temperature ($P = 1 \text{ atm}$, $\tau = 1 \text{ s}$, $X^\circ(\text{O}_2) = 16\%$)
mole fraction of OH and CH_3 radical vs temperature

These radicals promote the DBF oxidation by formation of dibenzofuranyl radical (DBF•) through metathesis reactions (H abstraction by a radical R•) (1) which are more efficient than DBF initiation step (2).

The key reactions controlling the DBF conversion (with or without methane addition) are the following; only the reactions on one site are represented, but equivalent reactions are possible on the three other positions and taken into account in the detailed mechanism:



The DBF oxidation is controlled by the formation of dibenzofuranyl radical (DBF•). Then, these radicals are consumed by two reactions (3,4) with oxygen leading to the formation of new radicals. These new aromatic radicals are then progressively destroyed to lead finally to the final products CO and CO₂.



At low conversion of DBF and methane, the methyl radicals are the most important and they decrease later with the consumption of methane. At higher initial concentration of DBF (100 ppm), similar results are observed, but the benefit effect of the addition of methane is less important and its consumption faster.

A detailed mechanism is used to model the oxidation of dioxins in a postcombustion area of municipal waste incineration; some simplifications were used; indeed, PCDD/PCDF families are represented by the dibenzofuran and the postcombustion area is 0 D modeled (CFSTR reactor).

But this simplified approach brings a substantial contribution to understand these complex reactions and to allow the development of an efficient post-combustion (abatement of dioxins by total oxidation). The simulations of DBF oxidation show that the reactivity strongly decreases when the reactant is very diluted. The key parameter is the concentration of radicals which is controlled by the initiation rate and branching steps; the oxidation reaction starts when the radical concentration increases. The addition of methane (natural gas) in low quantities induces an important increasing of radical concentration and promotes the dioxin oxidation very efficiently.

Acknowledgements

This work has been funded by the CNRS and the Région Lorraine

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