

# PROCEDURES OF OPTIMISATION OF POSTCOMBUSTION REACTIONS LEADING TO ABATEMENT OF DIOXIN EMISSIONS

*MARQUAIRE Paul-Marie, ZIEGLER-DEVIN Isabelle, BOUNACEUR Roda and BARONNET F.*

## Département de Chimie Physique des Réactions

CNRS - Nancy Université, 1 rue Grandville, BP 20451, F- 54001 NANCY Cedex - FRANCE

## Introduction

High temperature incineration and similar thermal processes lead to the formation of « dioxins » in trace amounts<sup>1,2</sup>. The optimisation of the (post-) combustion process might reduce the level of emissions not only of PCDD/Fs but also of other incomplete combustion products harmful for the environment. The objective is to destroy, by total oxidation, the dioxins and the byproducts resulting from their destruction if we want to avoid the reformation<sup>eg 3-5</sup> of dioxins by catalytic or de Novo reactions in the cooling section of the industrial units (heat exchangers, filters...). In this paper, we study the influence of the postcombustion parameters on dioxins abatement by a simulation approach using the detailed mechanism of dibenzofuran oxidation.

## Material and Methods

"Dioxins" or PCDD/Fs are a large family of 210 congeners of planar chlorinated aromatic compounds. In previous investigations<sup>6,8</sup> to study the experimental conditions leading to a total oxidation of PCDD/Fs, we have chosen 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 "dioxins"<sup>8</sup>. Furthermore, the mechanism of dibenzofuran oxidation should be very similar to the mechanism of that of PCDD/Fs.

In previous investigations<sup>6,7</sup>, we studied DBF oxidation between 800° and 950°C, at atmospheric pressure, and high dilution in helium: 0.12% of DBF; the equivalence ratio was 0.7 to 7 for oxygen, and the residence time ranged from 0.3 to 1 second. The experiments were performed in a quartz Continuous Jet Stirred Reactor. Many products were observed in fuel-rich conditions, and we were able to identify and quantify 25 carbonaceous products: CO, CO<sub>2</sub> were the major products; other reaction products were CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>4</sub>, benzene and substituted derivatives, benzofuran and substituted derivatives, indene, naphthalene and dibenzofuranol. Hydrocarbons and aromatic products ranged from 10 to 0.1 % of the DBF initial concentration. 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 combustion is obtained for oxygen in excess (an equivalence ratio > 0.8) and we can expect to avoid a catalytic or "de-Novo" formation of dioxins at lower temperature since the concentration of hydrocarbon intermediates is kept at an extremely low level. These results on dibenzofuran oxidation suggest that an optimisation 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 deduced<sup>8</sup>.

In a former study<sup>7</sup>, we proposed a radical reaction scheme which led to a better understanding of the oxidation of dibenzofuran, in qualitative agreement with the reaction products found in our experimental investigation. In a second stage<sup>9</sup>, we built a detailed radical mechanism 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 we know, there are no published data for dibenzofuran or dibenzodioxin oxidation; some data are available only for the formation of dioxins. A systematic approach was used to build the reaction mechanism, and for many elementary reactions without available data, the kinetic parameters were estimated from analogous reactions and modified by taking thermochemistry into account when it was possible.

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. The second part concerns the oxidation of toluene and benzene and it leads to the aliphatic reaction products ( $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_4$ ,...) and to the final products CO and  $CO_2$ ; this part is well-known and a published mechanism<sup>10,11</sup> is used which comprises more than 1000 elementary reaction steps including more than 190 species (molecules and radicals). This mechanism accounts for chemical species which were identified in the experimental investigation of DBF oxidation. This rather satisfactory agreement between our experimental results and the assumptions made by other research teams working on the oxidation of aromatic compounds at high temperature<sup>12</sup> confirms the proposed mechanism. By comparison with benzene oxidation<sup>13-15</sup>, the oxidation of dibenzofuran also has two parallel oxidation channels leading to different series of products, the importance of which depends on the temperature: the peroxide channel would be preponderant at temperature below 800 C, whereas for higher temperatures, the channel leading to PAHs would be more important. Despite the uncertainties on many estimated kinetic parameters, the proposed mechanism accounts reasonably well for oxidation of dibenzofuran at high temperature (900°C). The mechanism of dibenzofuran is 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).

## Results and Discussion

Our detailed mechanism<sup>9</sup> is used in this paper to model the abatement of dioxins by total oxidation in a postcombustion area (of municipal waste incineration for example) and to study the influence of the operating conditions or the influence of the co-reactants (methane and toluene) which are in the smoke. This approach can bring a substantial contribution to the development of an efficient post-combustion chamber. Simulations are obtained with CHEMKIN software and the postcombustion area is 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% ( $X^o(O_2)$ ), and at atmospheric pressure. The initial proportion of DBF ( $X^o(DBF)$ ) is varying between 0.1 ppm and 500 ppm. The temperature ranges from 700°C to 1050°C.

### *Influence of initial concentration of DBF on its conversion*

Figure 1 shows the influence of temperature on DBF conversion at various concentrations. First, we can observe that DBF conversion does not exceed 95% whatever the temperature, even though oxygen is brought in large excess. It is then interesting to note that the more important the initial DBF concentration is, the more efficient the DBF conversion is. For example, at 1050°C when the initial molar fraction of DBF is 0,5 ppm, only 33% of this fraction is degraded; whereas 95% of the initial concentration of 500 ppm is converted at the same temperature. We can conclude that the global kinetics of the DBF degradation does not follow a kinetic order equal to one.

The simulations show that the reactivity strongly decreases when the reactant is very diluted and the dioxins are in trace amounts. The conversions increase abruptly (like an ignition) from a minimal temperature which increases when the initial concentration decreases.

### *Influence of toluene on DBF conversion*

In flue gases, some VOCs (aromatics, hydrocarbons,...) are present. The simulations show that the reactivity is strongly increased by VOC and that they promote the abatement of dioxins by total oxidation. In Figure 2, the influence of initial toluene concentration (1 to 1000 ppm) on DBF conversion ( $X^o(DBF) = 0,1$  ppm) is shown. For example at 1000°C, the DBF conversion increases from 0% ( $X^o(\text{toluene}) = 0$  ppm) to around 50% ( $X^o(\text{toluene}) = 1$  ppm) and 80% ( $X^o(\text{toluene}) = 100$  ppm). These results are very important to show the possibility to reduce emitted dioxins by postcombustion.

### *Influence of methane on DBF conversion*

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 (1 to 1000 ppm) in flue gases when including 0.1 ppm of DBF. For example at 900°C, the DBF conversion increases from 0% (methane = 0 ppm) to around 40% (methane = 100 ppm) and 75% (methane = 1000 ppm). The effect of methane is more important at 1000°C.

### ***Influence of toluene on selectivity***

It is important to destroy the dioxins by total oxidation if we want to avoid the reformation of dioxins from the byproducts of reaction. Table 1 compares the results of oxidation at 900°C of 3 mixtures: 10 ppm of DBF, 10 ppm of DBF with 50 ppm of toluene, 50 ppm of toluene. The CO<sub>x</sub> selectivities (total oxidation) are 56%, 78% and 81 % respectively.

**Table 1: toluene influence on DBF oxidation (T = 900°C, P = 1 atm, τ = 1 s, X°(O<sub>2</sub>) = 16%)**

X° (DBF)	X° (toluene)	X (DBF)	X (toluene)	X (CO <sub>x</sub> )	% oxidation
10 E-06	0	3,72 E-06	1,66 E-06	4,2 E-05	56 %
10 E-06	50 E-06	3,68 E-06	2,82 E-06	2,6 E-04	78 %
0	50 E-06	0	5,39 E-11	2,0 E-04	81 %

A detailed mechanism is very useful to model the abatement of dioxins by total oxidation in a postcombustion chamber and to study the influence of the co-reactants which are in the smoke (VOCs). This approach can bring a substantial contribution to the development of an efficient post-combustion chamber. Our results show the difficulties to obtain a reaction at very low concentration of dioxins as well as the promoting effect of co-reactants which are in the smoke (aromatics) or added in the flue gases (natural gas). In conclusion, the postcombustion process, which improves the design of furnace structures, is one way of dioxin abatement. It could be economically interesting to compare this solution to other thermal processes which can reduce the dioxin emissions. For instance, we can quote the feasibility of a process of abatement of dioxins by using a plasma<sup>16,17</sup>.

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Figure 1: Conversion of DBF with temperature and concentration (P=1 atm,  $\tau=1$  s,  $X^{\circ}(O_2) = 16\%$ )

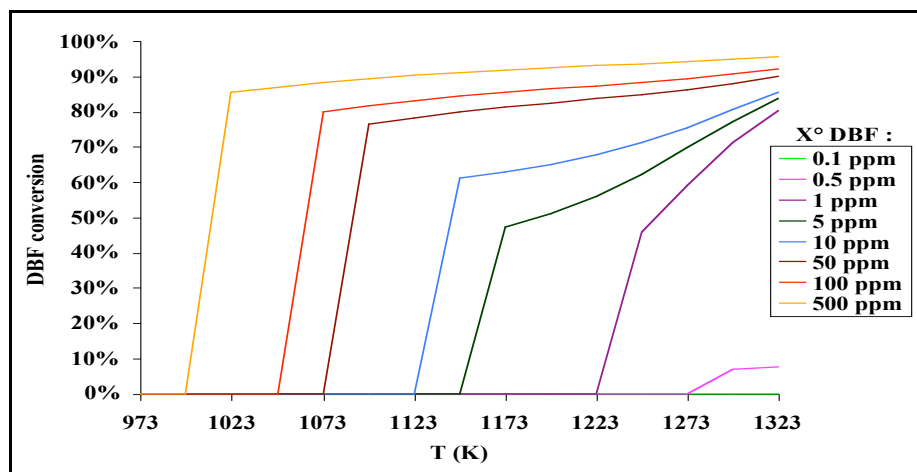


Figure 2: Influence of toluene on DBF concentration vs temperature (P=1 atm,  $\tau=1$  s,  $X^{\circ}(O_2) = 16\%$ )

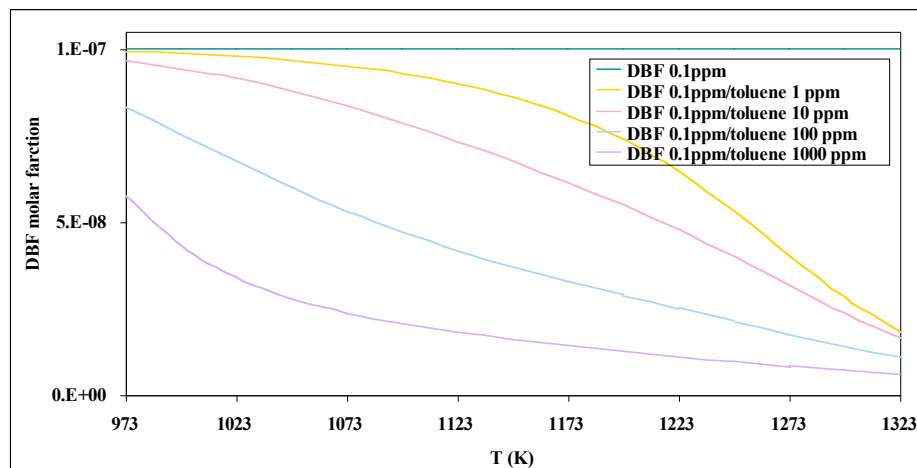


Figure 3: Influence of methane on DBF concentration vs temperature (P=1 atm,  $\tau=1$  s,  $X^{\circ}(O_2) = 16\%$ )

