# DE NOVO synthesis of polychlorinated dibenzofurans on fly ash from a Belgian sintering belt and its inhibition.

Céline XHROUET, Catherine PIRARD, Edwin DE PAUW

University of Liege, Mass Spectrometry Laboratory, B6c Sart Tilman, B-4000 Liege, Belgium
C.Xhrouet@ulg.ac.be

## *INTRODUCTION*

Since the discovery of polychlorodibenzo-p-dioxins (PCDD) and polychlorodibenzofurans (PCDF) in the flue gas and the fly ash of municipal waste incineratiors by Kees Olie et al. in 1977[1], the formation of these toxic compounds has been studied intensively. Recent reviews summarized the most important trends and results[2,3].
About the thermal formation, like in the waste incinerators or other combustion processes, two main formation routes have been postulated[4] : the 'De Novo' synthesis from carbon and the synthesis from precursors (like chlorophenols).
Although iron and steel industries are known to be an important source of PCDD/F in different countries, most studies concerning the formation of these highly toxic compounds deal only with municipal waste incineration. All laboratory experiments use incinerator fly ash[5-16] or model mixtures[12,13,17-18].
This study describes the thermal behavior of fly ash from a sinter plant relating to the De Novo synthesis of PCDF. The isomer distribution are also looked in order to get a better understanding of the formation mechanisms. On the other hand, the inhibition of the formation of these toxic compounds are also investigated. Three different inhibitors are tested: triethylamine, triethanolamine and urea.

### *Materials and methods*

**Fly ash.** Fly ashes were collected in the electrostatic precipitator of a Belgian sintering belt.
**Experimental apparatus.** Fly ash (5 g) was packed into a horizontal glass tube reactor (16 cm long, 3 cm diameter) with glass wool as plugs. The samples were heated at different temperatures (between 250°C and 450°C) under a flow of technical air (100 ml/min) for different reaction times (30 min until 6h). Products evaporating from the fly ash were collected using two cold traps (toluene cooled with ice). Cold traps were combined with the toluene used for the soxhlet extraction. All experiments were conducted with extracted fly ash in order to minimize potential interferences from adsorbed organic precursors and native PCDD/F's. Prior to experiments, all fly ashes were soxhlet extracted with toluene (2x24h), rinsed with hexane, and air-dried at room temperature. Each experiment was performed in duplicate or triplicate.
**Cleanup.** The method used has already been described elsewhere[19].
**Analysis.** All analyses were performed by HRGC/HRMS using VG-Autospec-Q high resolution mass spectrometer and Hewlett Packard 5890 Series II gas chromatograph. The GC conditions were optimized to separate most of the PCDF's: SP 2331 capillary column (Supelco) for all PCDF except HpCDF on J & W DB-5ms (30m).

**Identification and quantification.** Most of the $T_4$CDF-HpCDF congeners were analyzed. Native concentration was determined by isotopic dilution using the 2,3,7,8 Cl-substituted labeled PCDD/F's to quantify all the native isomers within homologues assuming equal response for all isomers within an isomer group. The isomers were identified according to Ryan et al.[20].

## *RESULTS AND DISCUSSION*

### Formation of PCDF as a function of the temperature.

In a first set of experiments, the formation of PCDF has been studied between 250 and 450°C during 2 hours. The results of these experiments are presented in fig 1.
The formation of PCDF on this kind of fly ash seems to reach its maximum around two different temperatures (340°C and 400°C). The maximum temperatures observed are likely due to competing formation and destruction reactions. The presence of two different maximum temperatures could be explain by two different formation mechanisms which reach their maximum at different temperature. The optimum temperatures found are in agreement with the temperatures found by Stieglitz[13] ( 400°C for the PCDF and 350°C for the PCDD), Addink[14] (350°C for the PCDD/F). Somewhat lower optimum temperature were found on incinerator fly ash for the PCDD/F: Vogg[21] found 300°C. However all the authors found only one optimum temperature and never speak about two different optimum temperatures. In addition of the fly ash nature, differences in reaction conditions could also explain the various optimum temperatures found in the literature.

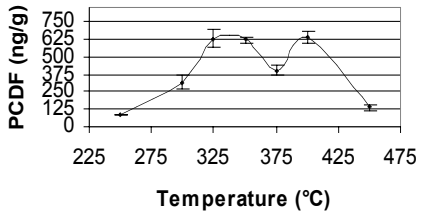


Fig 1. Formation of PCDF as a function of the temperature ; air (100 ml/min), reaction time 2h.

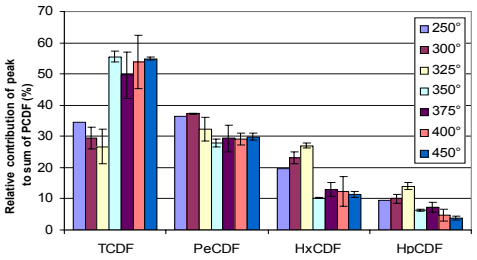


Fig 2. Homologue distribution as a function of the temperature ; air (100 ml/min), reaction time 2h.

In fig 2, the homologue distribution of PCDF as a function of the temperature is shown ($\Sigma$TCDF-HpCDF=100%). There are some changes in the homologue distribution when increasing temperature. The lower chlorinated specie (TCDF) shows a great increase between 325 and 350°C while the PeCDF remain constant and the most chlorinated (Hx and HpCDF) decrease. This suggests that with increasing temperature dechlorination reactions become more important.
Fig 3 presents a part of the tetraCDF distribution. All the homologue distributions were calculated by setting the sum of each homologue to 100% and calculating the relative contribution of each peak. From fig 3, we can conclude that the isomer distribution for the tetraCDF is nearly independent of the temperature. Actually, the differences found as a result of increasing the temperature are small and in the same order of magnitude as the variation between replicates. Similar results were found for all the homologues (not shown). From fig 3, we can also notice that the differences between the isomer distribution of the non-treated (original) fly ash, reflecting the formation under the industrial process, and the one found after the thermal treatment are small.

Although the formation from precursors must play a role in the PCDF formation in the industrial process, the De Novo formation can explain the quantity and the pattern found in the original fly ash.

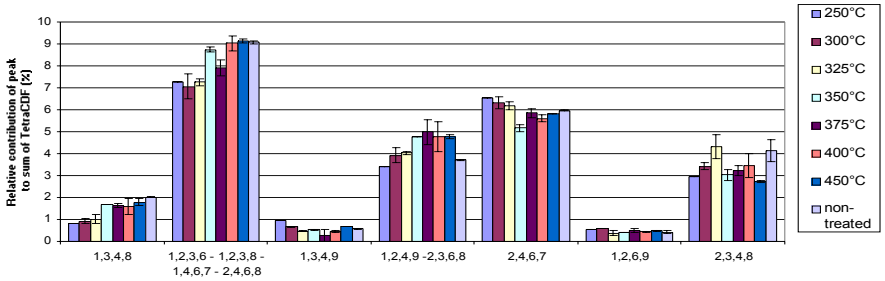


Fig 3. Isomer distribution (TetraCDF) as a function of the temperature ; air (100 ml/min), reaction time 2h

**Formation of PCDF as a function of the reaction time.**

A series of experiments was carried out to study the influence of the reaction time on the formation of PCDF. The results obtained at 400°C are presented in fig 4. Already after 30 min, a great quantity of PCDF is formed ( 682 ng/$g_{of\ fly\ ash}$). The fast increase is followed by a slower formation between 2 and 4 hours. At longer reaction time, the formation slows down and dechlorination/decomposition become important. Considering a typical collected particle residence time in an ESP of 20-30 min, the amount formed is sufficient to explain the levels found in the non-treated fly ash ( 611 ng/$g_{of\ fly\ ash}$).

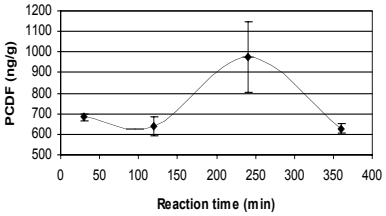


Fig 4. Formation of PCDF as a function of the reaction time ; air(100ml/min), 400°C.

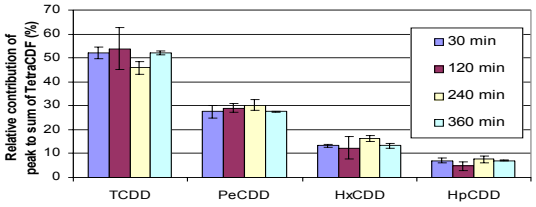


Fig 5. Homologue distribution as a function of reaction time ; air(100ml/min), 400°C.

Fig 5 shows the influence of reaction time on the homologue distribution at 400°C. There is no clear tendance. The homologue distribution seems to be independent of the reaction time at 400°C. Fig 6 shows the influence of the reaction time on the isomer distribution for the TetraCDF family. The isomer distribution is independent of the reaction time. As explained by Addink[10], the time independence of the PCDF formation is an argument in favor of the thermodynamic control of the isomer distribution within homologue during De Novo formation.

**Inhibition of the PCDF formation.**

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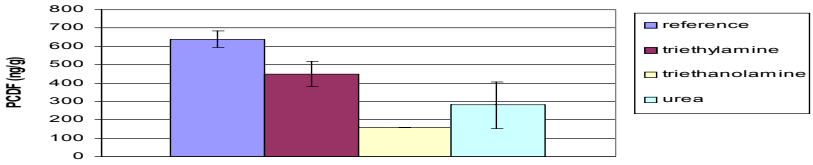


O Fig 6. Isomer distribution (TetraCDF) as a function of the reaction time, air(100ml/min), 400°C.
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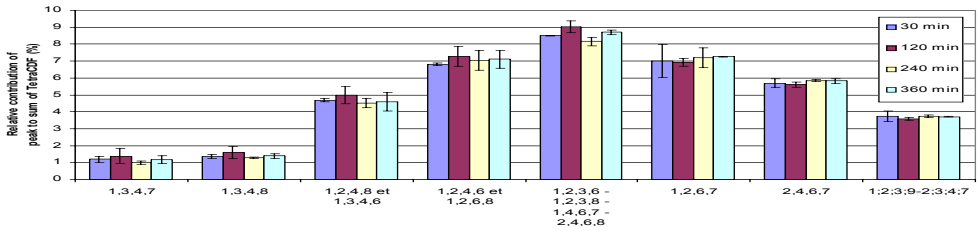


Fig 7. Inhibition of PCDF formation, air(100ml/min), 400°C, 2h, inhibitor

tested was mixed with the treated fly ash. The temperature and reaction time used in this set of experiments were 400°C and 2h. The results are presented in fig 7.

As it can be seen, all the three compounds have an inhibition activity on the PCDF formation. The best results are obtained with the triethanolamine with a reduction of 75%. More experiments are still in progress in our laboratory to confirm these results.

***ACKNOWLEGMENT***

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