

The Formation of Polychlorinated Dibenzo-p-dioxins/ Dibenzofurans From Carbon Model Mixtures Containing Ferrous Chloride

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Introduction

Processes other than combustion/ incineration and metals other than copper have the potential for the formation of polychlorinated dibenzo-p-dioxins/ furans (PCDD/F). Such processes include a variety of metallurgical and related processes (many of these operate under conditions of a low oxygen concentration in the gas phase) and metals such as iron and its compounds. In one such process, the so-called catalytic extraction process (CEP), a molten metal bath is used to transform wastes into potentially useful products¹. This process typically operates under oxygen partial pressures between 10^{-15} and 10^{-9} atm. Fine particles released contain iron compounds, carbon, and inorganic salts, including oxides. The nature of the carbons depends somewhat on the reactor conditions.

A laboratory study using model compounds based on ferrous chloride tetrahydrate was initiated. In order to produce measurable quantities of PCDD/F from these model mixtures, oxygen partial pressures of 10^{-3} atm or greater had to be used.

Material and Methods

Five carbons were obtained from various sources: activated (100 mesh), graphitic powder, two carbon blacks (CBA, CBB) and Sphero carb. These carbons were extracted in toluene for 24 hours, vacuum dried and used in model mixtures containing ferrous chloride tetrahydrate (99.995%, Aldrich) and a support matrix of aluminum, calcium and silicon oxides (12,48, and 40%, respectively). The mixture was then placed in an inverted glass thimble on a coarse glass frit. The reactor, a 152.4 cm long Pyrex tube of 3 cm ID, was heated using three ceramic heating elements while 0.9 L/min of nitrogen was passed through. The temperature at the center of the tube was controlled by three temperature controllers located within each heating section. When the reactor was within 50°C of the desired reaction temperature, the thimble with the sample mixture was inserted at the top of the reactor and heated to the desired reaction temperature. This heat-up time was kept constant at 30 minutes. At this time, the air flow corresponding to the desired concentration of oxygen was added to the total gas flow of nitrogen and oxygen. The

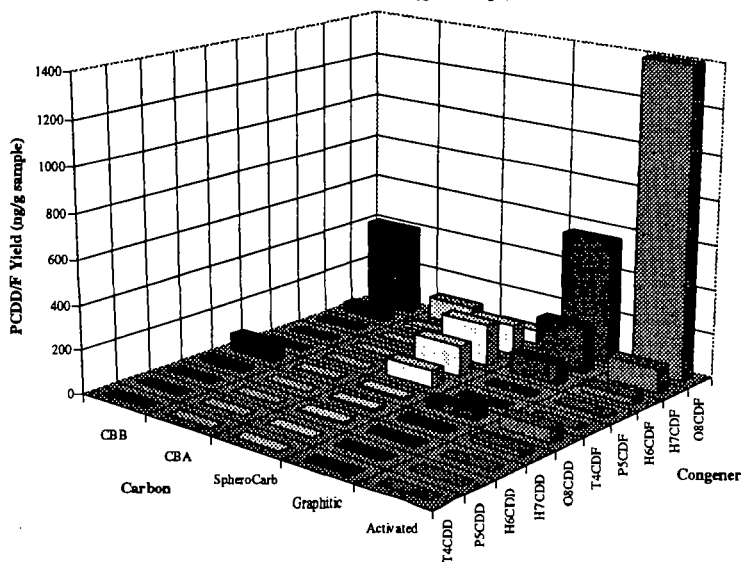
outlet gas of the reactor exited through a side arm at the top of the reactor to an ice cooled gas trap containing 250-300 ml of dichloromethane.

The gas phase and solid phase samples were purified by fractionation on alumina, as described elsewhere². A sulfuric acid wash of the samples was done prior to this procedure to remove any inorganic ferrous compounds present. The T₄CDD-O₈CDD and T₄CDF-O₈CDF were quantified via gas chromatography/ mass selective detection.

Results and Discussion

Initial experiments were performed with samples consisting of 21% ferrous chloride tetrahydrate on the support matrix and five different carbons (cf. Figure 1). With the exception of SpheroCarb, O₈CDF was the dominant product under these experimental conditions. For the two carbon blacks and activated carbon, O₈CDF accounted for approximately 85% of the total T₄-O₈CDD/F formed; the remainder being H₇CDF and H₇- and O₈CDD. A slightly greater amount of H₆- and H₇CDF was formed with graphitic carbon, however, O₈CDF was still the predominate congener. The formation of moderately chlorinated PCDF (P₅-H₇) was favored when SpheroCarb was used as the carbon source. However, the [PCDD]:[PCDF] ratio of 0.05 was in agreement with the other carbon sources used.

Figure 1: Comparison of PCDD/F Congener Yields as a Function of Carbon Source
 1g sample (8% Carbon/ 21% Ferrous Chloride Tetrahydrate/ Al:Ca:Si Oxides)
 275 C/ 60 min/ 1.0 L/min (2% Oxygen in Nitrogen)



While the congener distribution appeared to be independent of the carbon source, the amounts of PCDD/F produced were not. Activated carbon was the most reactive of these carbons by a factor of 1.85 over graphitic carbon. The reactivities of CBB and SpheroCarb were very similar, while carbon black A exhibited little reactivity. These

results indicate that the morphology of the carbon could be important in the formation of PCDD/F.

The relative abundance of O_8 CDF produced in these experiments suggests that ferrous chloride can pre-chlorinate carbon. Therefore, the effect of the ferrous chloride concentration was investigated using activated carbon. A linear increase in the formation of PCDD/F on the model mixture was observed with increasing ferrous chloride concentration between 1 and 21% at 275°C. Increasing the concentration to 33% at 300°C had no further effect on the PCDD/F concentration. In the absence of ferrous chloride, no PCDD/F formation occurred in this system, suggesting that ferrous chloride is both a catalyst and chlorinating agent. The congener distribution was not a function of ferrous chloride concentration.

The sponsor of this work reported that the processing of some wastes yields carbons that resemble carbon blacks in certain ways. Hence, two carbon blacks (labeled CBA and CBB) were selected for further experiments. The effect of varying the reaction temperature on the *de novo* synthesis of PCDD/F with CBA and CBB is summarized in

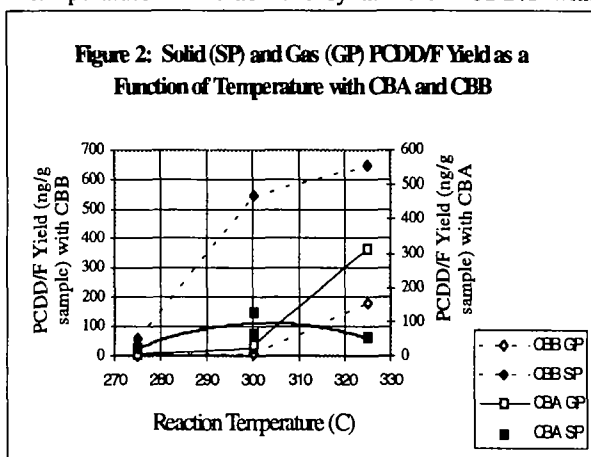
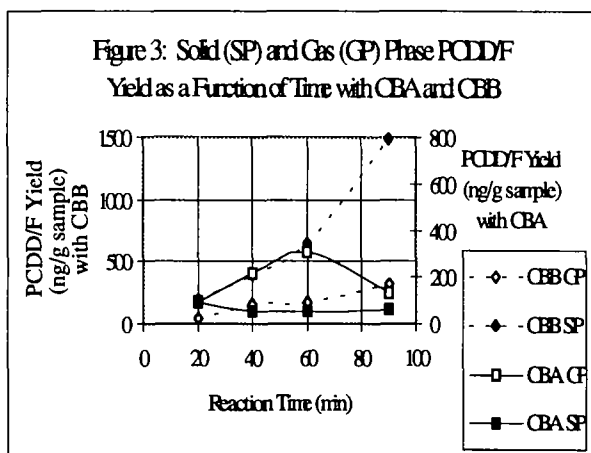
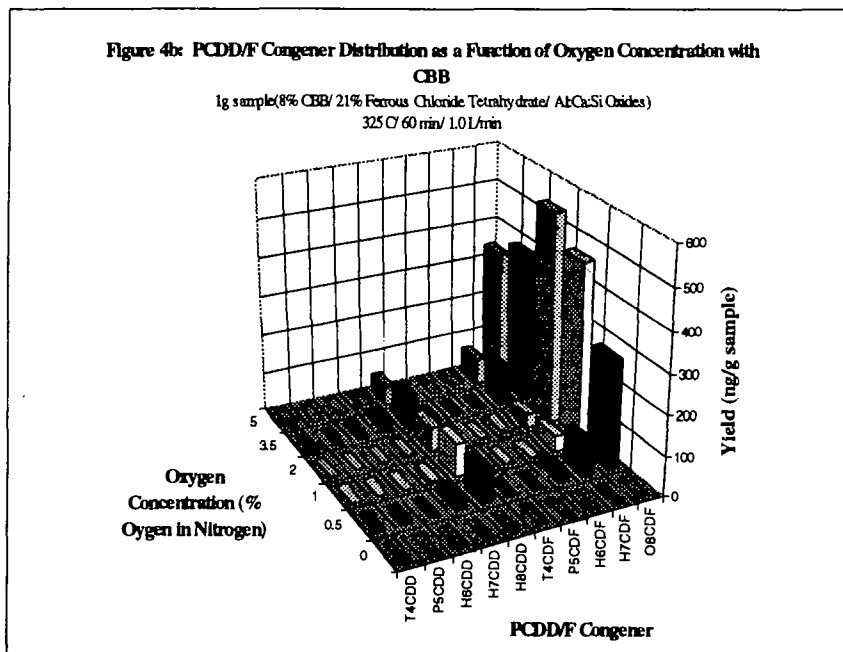
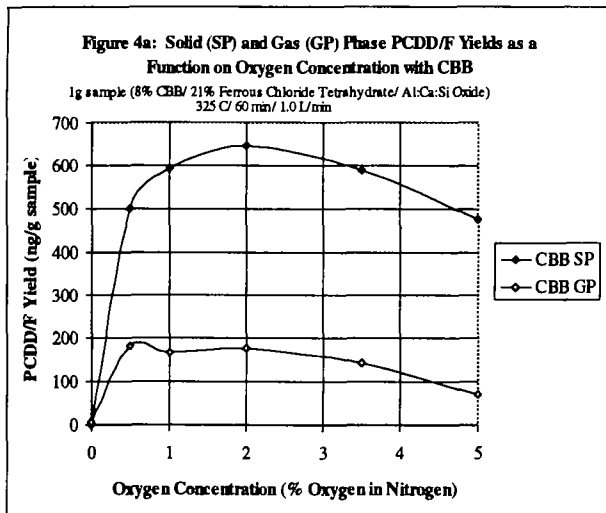


Figure 2. While a peak in solid phase formation was observed at ca. 300°C with CBA, no distinct peak occurred up to 325°C for CBB. A phase shift occurred between 300 - 325°C with CBA, indicating that desorption becomes important above this temperature. Although the gas phase:solid phase ratio did increase with increasing temperature for CBB, the ratio climbed no higher than 0.26. This indicates that the adsorptivity of CBB is greater than that of CBA, thus limiting the role of desorption with CBB. The greater overall reactivity of CBB over CBA is apparent.



A comparison of the effect of reaction time at 325°C is presented in Figure 3. A peak in overall formation with CBA is observed at 60 minutes. Since the solid phase PCDD/F remained constant for all times studied, destruction of the gas phase PCDD/F became important after 60 minutes at

325°C, while the desorption rate increased up until this time. With CBB, no optimum occurred within 90 minutes. In both the temperature and time study, the PCDD/F congener patterns were unaffected. For the data in Figures 2 and 3, one gram samples of 8% CBB or CBA, 21% ferrous chloride tetrahydrate and the remainder Al:Ca:Si oxides powder was reacted at 325°C in a flow of 1 L/min of 2% oxygen in nitrogen for the specified reaction times.



The effect of oxygen concentration on the system with CBB was studied for concentrations up to 5% (cf. Figure 4a and 4b). A peak in formation at 325°C occurs at 2% oxygen in nitrogen, while the congener distribution and gas phase:solid phase ratio were both independent of the oxygen concentration. Recent experiments suggest that this decrease may be due to the oxidation and vaporization of the ferrous chloride; however, more work is necessary to determine the importance of this effect.

Conclusions

A model mixture containing ferrous chloride tetrahydrate and an inorganic oxide matrix was studied using five different carbon sources. With the exception of Sphero carb, O₈CDF was the major PCDD/F congener formed via the *de novo* synthesis. This trend proved to be independent of the ferrous chloride concentration, perhaps suggesting that this compound is an effective chlorinating agent. Of the two carbon blacks, CBA was less reactive than CBB under all conditions studied, as well as less adsorptive. More information about the properties of these carbon blacks is necessary for a more complete analysis. The reaction temperature and time had no effect on the PCDD/F congener distribution. Furthermore, a decrease in formation with CBB was observed at oxygen concentrations greater than 2%, however, the congener distribution remained unchanged. The insensitivity of the congener distribution to these other parameters points to the possibility of a "simplified" mechanism of PCDD/F formation via catalysis and chlorination by ferrous chloride.

Acknowledgments

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