AN OVERVIEW OF DIOXIN FORMATION IN COMBUSTION PROCESSES

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1. Introduction

In 1977 the full range of polychlorinated dibenzo-p-dioxins and their corresponding furan compounds (PCDD & PCDF) were first found in the flyash of a municipal incinerator in Amsterdam by the Hutzinger group. The extensive research work that followed on the occurrence of PCDD/PCDF and their formation mechanisms in municipal waste incinerators (MSWI) throughout the world established that their presence was a universal phenomenon with a common origin. Early concepts favored formation of PCDD/PCDF in the combustion zone, but research very quickly pointed to flyash as the agent of formation in the 200-400 C degree zones of the incinerator. Catalytic surface reactions on the flyash from adsorbed precursors seems to be the major formation mechanism. Since the flyash is a very complex matrix of numerous inorganic compounds with trace amounts of adsorbed organic compounds several theories have been advanced to explain the observed data. The precursor concept permits any number of several hundred possible organic precursor compounds to be the starting point [1]. The de-novo concept proposes that organic particulate carbon is the starting precursor and that PCCD/PCDF are produced through a series of unknown reactions [2]. Recent and continuing work is developing more insight into these pathways. This is important in that it leads to development of methods to prevent formation in this large source of environmental PCDD/PCDF pollution.

2.Discussion

Figure 1 summarizes the potential formation pathways one finds in the literature. If the de-novo concept were a major pathway then reducing the carbon content of the flyash should reduce the amount of PCDD/DF formed, but this does not seem to be the case. Recent work with C^{13} labeled charcoal indicates that the PCDD generated in the de Novo experiments could be explained on the basis of originating from organic precursors retained by the powerfully adsorbing charcoal [3]. Although some have reported that CO and CO_2 in the presence of HCl may be viable precursors, other experimental work does not support this.

Recent definitive work by Froese (see Fig.3) shows that chlorinated benzenes and phenols, which are proven precursors, can be formed from ethylene and acetylene in the presence of HCl as combustion reactions [4]. It is quite logical that these combustion products represent the most basic molecules in the catalytic pathways to PCDD/DF.

It is difficult to understand how and why flyash acts as a specific catalyst to produce PCDD/DF. It does not have the surface and pore size characteristic of a typical catalyst. The particle size distribution differs from one MSWI to another and the elemental composition varies as well. The metals such as Cu and Fe incorporated into the flyash surface has been postulated as the active elements in the catalytic reactions. Various attempts have been made to correlate the amounts of different metals with catalytic activity of the flyash with little success [5]. This is to be expected since catalytic activity would depend upon the detailed valence state and surrounding of the metallic sites and the overall effect would be the sum effect of some metals that enhance activity and others, such as Pb, that retard it. There is a correlation with the amount of PCDD/DF found on a flyash and the catalytic activity measured and also with the temperature of the Electrostatic precipitator. There is no correlation between chlorine content of the waste incinerated, HCl in the gases and PCDD/DF formed. Inorganic chlorides in the flyash can provide the chlorine.

The flyash catalyzed reactions of precursors whatever they may be is the most important concept in formation of PCDD/DF in MSWI. It has lead to a method of determining activity of a given flyash using C-13 labeled pentachlorophenol that shows maximum activity occurs at 300-350 C degrees. A method of preventing formation of PCDD/DF by contacting the active sites on the flyash with an inhibitor chemical such as ethanol amine has been developed [6]. This dioxin Inhibition technique has been thoroughly tested in the laboratory and successfully tested in several large scale MSWI sites where reduction of PCDD/DF of about 90 % of PCDD/DF content have been achieved. Recently optimized MSWI tests have achieved even higher reductions. Widespread application of this simple and economical technology to MSWI could produce a significant reduction in the PCDD/DF load on the environment.

3. References

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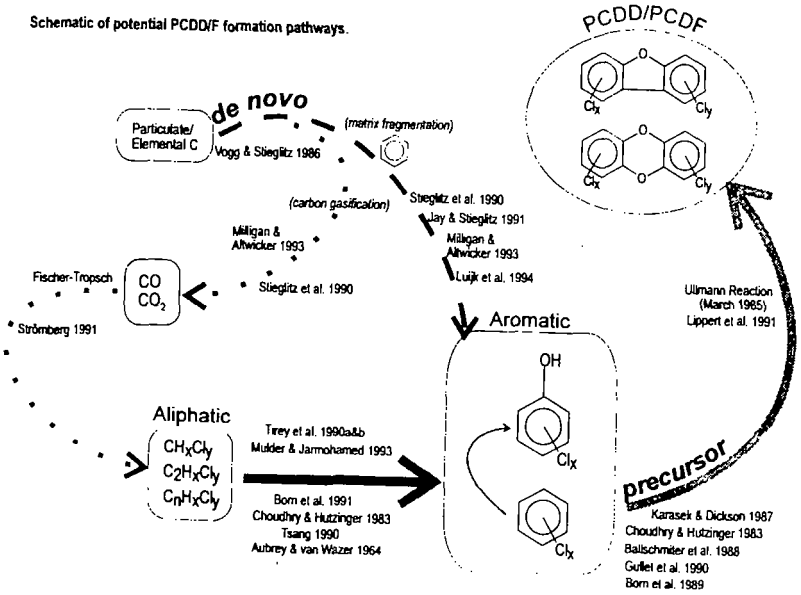

Figure 1. Potential PCDD/F formation routes based on recent literature. Some key literature references are provided