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# Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from catalytic and thermal oxidizers burning dilute chlorinated vapors

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## Abstract

Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (dioxins) have been found from 57 field tests on the oxidation of low (a few to a few hundred) parts per million levels of chlorinated and non-chlorinated volatile organic compounds (VOCs). The oxidation occurs in catalytic oxidizers with platinum, platinum/palladium or chromium(IV) oxide combustion catalysts, or in thermal oxidizers (without a catalyst). The catalyst inlet temperatures ranged from 293 to 573 °C. The thermal oxidizer operating temperatures (post-flame) were from 773 to 927 °C. Data of the toxic dioxin and furan isomers are reported and also weighted and expressed as international toxic equivalents (TEQ) of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. The maximum stack emissions, 1.07 ng/m<sup>3</sup> TEQ, occurred at 293 °C. Salient results of this field study are: (1) TEQ levels in the stack exponentially increase with a decrease in operating temperature, an empirical equation is TEQ (ng/dscm) = 8.4 exp(-0.0084*T* °C); (2) dioxin/furan production occurs at the combustion catalyst; (3) small variations in temperature cause large changes in the congener distribution of the dioxin and furan isomers; (4) molar TEQ yields from the parent compounds fed to the oxidizers are very small ( $10^{-9}$ - $10^{-13}$ ); (5) catalytic and thermal oxidizers may destroy dioxins fed from the ambient air; and (6) the oxidation of chlorinated VOCs with non-chlorinated VOCs reduces emissions of dioxins, likely due to the consumption of Cl in producing HCl. Laboratory investigations are needed to understand how dioxins are formed (and emitted) under conditions of this study.

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## 1. Introduction

The formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (dioxins), as postulated by Shaub and Tsang (1983), is less important at high temperatures (>900 °C) in gas phase combustion than from reactions on fly ash particles at lower temperatures. More recent studies on gas phase dioxin formation have been pub-

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lished by Sidhu et al. (1995), Waterland and Ghorishi (1997), Babushok et al. (2000), and Babushok and Tsang (2003). Important fundamental studies and review articles of dioxin formation have been published by Taylor et al. (1998), Olie and Schoonenboom (1998), Addink and Olie (1995), Dickson et al. (1992), Miller et al. (1989), Hagenmaier et al. (1987), Lustenhouwer et al. (1980), Altwicker et al. (1990), Stieglitz et al. (1989), Griffin (1986), Cieplik et al. (2000), and Wiater et al. (2000). These studies postulate three primary mechanisms of dioxin formation: (1) incomplete combustion of dioxins fed to the combustor, (2) formation from reactions

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of pre-cursors, and (3) "de-novo" formation from various carbon and chlorine sources. The low temperature (temperature window) formation of dioxins with transition metal catalysts (the de-novo mechanism) has been reported, but not the formation of dioxins with combustion catalysts with the exception of the recent work of Cieplik et al. (2001). The fundamentals of catalytic combustion have been studied recently by Van den Brink (1999) and others (Koltsakis and Stamatelos, 1997; Corella et al., 2000; Deutschmann, 2000; Kissel-Osterrieder et al., 2000; Mantzaras et al., 2000; Treviño et al., 2000; Van den Brink et al., 2000; Liljelind and Marklund, 2001; Padilla et al., 2002). Under certain conditions, catalytic combustion has been used to destroy dioxins, as discussed by Blanco et al. (1999) and Liljelind et al. (2001). This paper presents results from field tests that are different from all of the previous studies cited. At temperatures of 293-573 °C with platinum, Pt/Pd, and chromium(IV) oxide catalysts and 773-927 °C without a catalyst, low to several hundreds of parts per million of chlorinated VOCs gave rise to dioxins, up to a level of over 1 ng/m<sup>3</sup>.

#### 2. Description of field experiments

Many sites with soils contaminated with chlorinated VOCs are cleaned by soil vapor extraction, by applying a vacuum to an underground vapor well. The higher the compound's vapor pressure, the more readily it will be transported to the gas phase from the soil. Because of this, typically only VOCs are found in the extracted gas. A blower causes the extracted gas to be transported from the soils to the wells and ducts. The contaminated gas may contain chlorinated VOCs and non-chlorinated VOCs, and is then burned in a catalytic oxidizer or thermal oxidizer, prior to release through a stack.

For a catalytic oxidizer, the vapor stream is normally pre-heated first by a heat exchanger in the catalyst exhaust, and then introduced downstream (post-flame) of an auxiliary burner fired by propane or natural gas. The vapors are then introduced into the catalyst bed, in which the active catalyst may be platinum, platinum with other precious metals (palladium), or chromium(IV) oxide. The catalyst is normally on an alpha-alumina support. The thermal oxidizers in this study burn the vapors with auxiliary fuel in a porous ceramic burner or in a conventional burner. The presence and concentration of chlorinated and non-chlorinated VOCs is determined by a grab sample of the extracted vapor, and analyzed by a standard gas chromatograph (GC). Prior to this, soil samples are taken to characterize the full extent of contamination. The contaminants identified are then target analytes for sampling of the extracted gas. Dioxins were sought for, but were not detected in the soils. This investigation produced 45 discrete

data for catalytic oxidizers and 12 more for thermal oxidizers.

In the first group 12 tests concerned a Degussa 'HDC' catalyst (0.15%Pt+0.15%Pd on alumina), 13 tests were with Pt/alumina catalysts, and in 20 tests a Wheelabrator 12%Cr<sub>2</sub>O<sub>3</sub> + 2%CrO<sub>3</sub> on alumina catalyst was employed. The catalyst inlet temperatures ranged from 293 to 573 °C. Further details are available on request, including the oxidation unit type, site location and date of test, operating temperature, TEQ values and concentrations of the 17 dioxin and furan congeners. The thermal oxidizer operating temperatures (postflame) are from 773 to 927 °C. The gas flow rates in the oxidizers are 6-57 standard m<sup>3</sup>/s. Residence times in the catalyst are approximately 0.5 s, and are 0.5-1 s for the thermal oxidizers. The stack (and catalyst inlet)  $O_2$ concentration is approximately 18% for all of the oxidizers. The dioxin sampling method used is US EPA's Method 23 sampling train (see www.epa.gov/ttnemc01/ promgate/m-23.pdf) or equivalent, which is an extractive sorbent technique that is run for approximately a fourhour period. The analytical methods are high resolution gas chromatography followed by high resolution mass spectroscopy. Depending on the dioxin congener, detection limits are on the order of 10<sup>-3</sup>-10<sup>-4</sup> ng/m<sup>3</sup> except for OCDD and OCDF which can be as low as  $10^{-7}$  ng/m<sup>3</sup>. The methods incorporate internal standard recoveries and blanks to insure data quality. Besides dioxins, other products of incomplete combustion are not determined during this study.

## 3. Results

This study produced 45 discrete data points for catalytic oxidation and 12 for thermal oxidizers. The 45 data representing catalytic oxidizers (25 using platinum and platinum/palladium, and 20 using chromia), were taken at different locations under different conditions, and do not represent controlled experiments. Even though no direct causal relationships may be obtained from these field data, some insights have been gained.

The first is that toxic equivalents of 2,3,7,8-TCDD (TEQ) appear to exponentially increase with a decrease in operating temperature, presented in Fig. 1. There is an apparent temperature effect, but because these were not controlled laboratory experiments, other factors may have contributed to the exponential rise in dioxins with decreasing operating temperature. Some of these factors could have been the amount of dioxins in the inlet of the device, the age and amount of fouling and deactivation of the catalyst, the specific design of the catalytic oxidizer, the presence of nanometer-sized particles and reactions on their surface, and other factors. One of the most important factors that vary for these data is the design of the oxidizer system, and the types of



Fig. 1. All data from field tests, dioxin/furan stack emissions as toxic equivalents of 2,3,7,8-TCDD (with non-detects taken at 0.5 of detection limit), plotted against the operating temperature of the catalyst or thermal oxidizer.

concentrations of contaminants fed to the oxidizers. Also, for the majority of these data, there was no sampling of the inlet to the oxidizer for dioxins. Because of this lack, it is unknown if or how much dioxin was fed to the inlet of the oxidizers for most of these data. Besides ambient sources of dioxins nearby, there is a small amount of dioxins found as "background" in the US ambient air. Ambient concentrations of dioxins can be added to the feed stream from two major sources. One source is the dilution air that is used in most catalytic oxidizers. In order to reduce concentrations of contaminants fed to the device, ambient air is fed prior to oxidation. This is done so that operating temperatures are not exceeded. Typical urban ambient concentrations have been measured in California, and are on the order of 0.0005 ng/m<sup>3</sup> (29). Using a feed rate of ambient air on the order a 10% by volume, the amount of dioxins fed to the device would be on the order of  $0.0001 \text{ ng/m}^3$ .

Fig. 2 presents an Arrhenius-type plot of the data, which indicates a low activation energy assuming that emissions can be modeled by a global pseudo-first-order reaction rate.

#### 3.1. Treatment of non-detects in calculating TEQ values

There is no published standard on the treatment of congeners that are not detected, and how these values



Fig. 2. Arrhenius-type plot of all TEQ data at ND = 0.5 (pseudo-first-order).

are used in calculating a TEQ value. However, a standard that is used in some areas of health risk assessment is to use 1/2 of the reported detection limit in calculating emissions. For data sets with the majority or all of the isomers non-detects, using 1/2 of the detection limit may excessively "penalize" the calculation of the TEQs. For data sets with all or the majority of isomers greater than the detection limits, there is very little or no difference in the calculated TEQs. Nevertheless, there needs to be a standard approach to deal with non-detect values. For a reported congener concentration of non-detect, the actual concentration can be 0 up to the limits of detection. From this, the uncertainty can range from 0 for data with no non-detects, up to 1/2 of the detection limit (equal to 9.00E-03 ng/m<sup>3</sup> for this study) for data with all non-detect concentrations for each of the 17 congeners. In addition, there is an uncertainty associated with the sampling and analytical methods of the data, on the order of 50%.

# 3.2. Pt and Pt/Pd catalytic oxidizer congeners of toxic PCDD/F

Figs. 3 and 4 present the congener distributions at the catalyst inlet temperatures of the Pt and Pt/Pd catalytic oxidizers. Labels of the 17 toxic congeners for Figs. 3-11 are listed in Table 1. An average of all the Pt and Pt/Pd congener distributions at an average inlet temperature of 439 °C is in Fig. 3. Hepta and octa dioxins and a hepta furan and octa furan dominate. At the lowest inlet temperature in the study (293 °C), the congener distribution is in Fig. 4a from the oxidation over a platinumonly catalyst, and again favors the hepta and octa dioxins, a hepta furan (1234678-HpCDF), and octa dioxin (OCDF). At 430 °C, over a platinum-only catalyst, Fig. 4b shows an entirely different congener pattern favoring the tetra through hexa furans (123678-HxCDF) and a hepta furan isomer (1234678-HpCDF). This is for a fixed bed unit with only TCE at 7 ppm in the feed. For the 454 °C Pt/Pd catalyst, the congener distribution is in Fig. 4c, and the predominant isomer is 1,2,3,7,8-PeCDD.



Fig. 3. Average congener distribution for average Pt and Pt/Pd catalyst at average 439  $^\circ$ C inlet temperature.



Fig. 4. Average congener distributions over (a) Pt catalyst at 293 °C, (b) Pt catalyst at 430 °C, (c) Pt/Pd catalyst at 454 °C, (d) Pt/Pd catalyst at 480 °C, (e) Pt/Pd Catalyst at 492 °C, (f) Pt/Pd catalyst at 510 °C.

At 480 °C with Pt/Pd (Fig. 4d), all of the seven dioxin congeners are in significantly higher concentrations than the furans. At 492 °C with a platinum/palladium catalyst (Fig. 4e), the hepta and octa dioxin congeners are dominant, as well as a hepta furan. At 510 °C (Fig. 4f), three of the furans are dominant with Pt/Pd.

# 3.3. Cr oxide catalytic oxidizer congeners of toxic PCDD/F

In Fig. 5, the catalyst is now chromium(IV) oxide, and the average operating temperature is  $550 \,^{\circ}$ C. In this case the congener that is produced in most abundance on average is 2,3,7,8-tetrachlorodibenzofuran (2378-TCDF). According to the operator, the catalyst is regularly changed out with fresh catalyst about every 6 months. At 506 °C, the most dominant congener is OCDD, as seen in Fig. 6a. Fig. 6b shows the congener distribution at 549 °C is almost identical to that of



Fig. 5. Average congener distribution for average Cr catalyst at average  $550 \, ^{\circ}$ C inlet temperature.

the average distribution at 550 °C. At 568 °C (Fig. 6c), the three most abundant congeners are hepta and octa dioxin and tetra furan. Another test at 571 °C (see Fig. 6d) results in 2,3,7,8-TCDF being most abundant. Comparing chromia and Pt catalysts at 510 °C, show that Pt/Cr ratios are on the order of 15–30, on average.



Fig. 6. Average congener distributions over Cr catalyst at (a) 506 °C, (b) 549 °C, (c) 568 °C, (d) 571 °C.



Fig. 7. Average congener distribution for average thermal oxidation unit at average 885 °C operating temperature.

#### 3.4. Thermal oxidizer congeners of toxic PCDD/F

There are 12 data taken from three different thermal oxidizers. Average congener data for the non-catalytic thermal oxidizers at 885 °C is presented in Fig. 7. The congener distribution mainly favors OCDD in this case. At 778 °C tetra and penta dioxin and a penta furan are most abundant (refer to Fig. 8a). At 871 °C, OCDD is most important, demonstrated in Fig. 8b. At 927 °C, OCDD is again most important (see Fig. 8c).

Molar conversions from the parent compounds fed to the oxidizers to the toxic equivalents of 2,3,7,8-TCDD are very small. Based on the parent compound trichloroethene (TCE) that was in each of the field tests, the fractional molar conversions are on the order of  $10^{-9}$ - $10^{-10}$  for catalytic units and  $10^{-12}$  for thermal units. Based on total volatile organic compounds to the inlet of the oxidizers, the fractional molar conversions are between  $10^{-10}-10^{-11}$  for catalytic units and  $10^{-11}-10^{-13}$  for thermal units. It only takes a few ppm of a parent TCE to produce measurable amounts of dioxins, assuming that dioxin emissions are by-products from the oxidation of parent compounds and not from unburned dioxins from ambient dilution air fed to the oxidizers.

There are also parameters that apparently have very little effect on dioxin emissions. These parameters were not varied during the field tests in a rigorous manner. Parameters with little correlation with dioxin emissions include the total inlet concentration of volatile organic compounds (VOCs), the inlet concentration of TCE, the gaseous inlet volumetric flow rate, and the oxygen concentration.

#### 4. Discussion of results

# 4.1. Issues which may influence the chemical reaction formation mechanism or pathway

Given the fact that these data were taken in field experiments, there is much unknown information which is essential to understand the chemical reaction formation pathways and mechanism(s) of the polychlorinated dioxins and furans. There are many uncertainties about the causes of dioxin emissions in this study, and the relative importance of surface chemistry and homogeneous gas phase chemistry. There is most likely competition between chlorination and oxidation, and ultimately between formation and destruction of dioxins that can



Fig. 8. Average congener distributions for thermal oxidation at (a) 778 °C, (b) 871 °C, (c) 927 °C.



Fig. 9. Dioxin measurements (TEQ ng/m<sup>3</sup>) at Pt catalyst inlet and outlet, heat exchanger outlet, and stack (for 3 runs *T* approximately 492 °C).

affect the emissions concentrations reported in this study. Although there are 57 congener distributions from the 57 sampling events, there are no clear patterns of chlorination from these distributions that could lead to an understanding of the dioxin formation chemistry. However, operating temperature appears to be a key factor in dioxin emissions.

#### 4.2. Role of operating temperature

The only parameter in this study found (and studied) to affect dioxin emissions is operating temperature. Although the data do not give fundamental relationships on such important information on elementary reaction rates, an Arrhenius form  $(k = AT^n \exp(-E/RT))$  of a rate equation can be used as a simplified empirical equation based on inspection of all of the data:

$$TEQ = 8.4 \exp(-0.0084T) \tag{1}$$

where TEQ is the dioxin concentration in ng/dscm, and T is the operating temperature (°C). The data do not conform with the temperature window phenomena reported with "de-novo" synthesis of dioxins.

Van den Brink (1999) found at high temperatures that for a  $Cr_2O_3$  catalyst, chromium chlorides and oxychlorides can leave the surface. Thus at higher temperatures these catalysts will be deactivated. On the other hand, he documented that platinum catalysts experience deactivation below 400 °C because of the formation of platinum(IV) chlorides and oxides. Heating the platinum catalyst above 400 °C will restore the surface. He also found that palladium catalysts led to more by-products. On alumina (the primary type of support in this study), Cl is adsorbed at low temperatures. At higher temperatures, Cl reacts with H to form HCl, and is released from surface to allow free sites for combustion. However, in this study, the concentration of free Cl is very small.

### 4.3. Issues with catalysts and support

A reasonable hypothesis is that different reaction mechanisms or at least different pathways exist for dioxin formation and destruction with platinum, platinum/ palladium, chromium catalysts and without catalysts. This can be observed in part by the different congener distributions for the different oxidation systems. Some of the issues that need to be examined are different catalyst particle size and concentrations, deactivation of the catalyst and support, reactivation, and relative importance of heterogeneous surface reactions and homogeneous gas phase reactions. Some of the important reactions may actually take place on the alpha-alumina support.

# 4.4. Field study of dioxin concentrations at inlet, outlet of catalyst, outlet of heat exchanger and stack

Figs. 9 and 10 show the data from one field study in a catalytic (platinum/palladium) oxidizer. Fig. 9 shows the dioxin/furan TEQ levels at the catalyst inlet and outlet (which is the heat exchanger inlet), the heat exchanger outlet, and at the stack. The inlet TEQ concentrations



Fig. 10. Congener distributions across Pt catalyst and heat exchanger (T = 492 °C).

Table 1 Labels of the 17 toxic congeners used in Figs. 3–11

2,3,7,8-TCDD	D4
1,2,3,7,8-PeCDD	D5
1,2,3,4,7,8-HxCDD	D6a
1,2,3,6,7,8-HxCDD	D6b
1,2,3,7,8,9-HxCDD	D6c
1,2,3,4,6,7,8-HpCDD	D7
OCDD	D8
2,3,7,8-TCDF	F4
1,2,3,7,8-PeCDF	F5a
2,3,4,7,8-PeCDF	F5b
1,2,3,4,7,8-HxCDF	F6a
1,2,3,6,7,8-HxCDF	F6b
2,3,4,6,7,8-HxCDF	F6c
1,2,3,7,8,9-HxCDF	F6d
1,2,3,4,6,7,8-HpCDF	F7a
1,2,3,4,7,8,9-HpCDF	F7b
OCDF	F8

show ambient levels of dioxins are fed to the oxidizer, probably due to local source of dioxins, since data indicate that the soil did not contain dioxins as a contaminant. The dilution air fed to a catalytic oxidizer can be significant (up to 50% of the total gas flow, depending upon the contaminant loading), and would be the probable source of dioxins in the inlet to the oxidizer. TEQ concentrations increase dramatically over the catalyst, and then decrease over the heat exchanger and at the stack. As temperatures slowly cool, the dioxin/furan chemistry changes to cause TEQ concentrations to decrease. Although there was a substantial increase in TEO concentrations over the catalyst, the emissions of TEQ decreased from the inlet to the stack. These specific data indicate that further research on these issues are needed: how the amount of dioxins in the inlet affect the stack emissions of dioxins, and how dioxins might decrease in a duct or air pollution control equipment due to relaxation by homogeneous gas phase kinetics or heterogeneous gas-wall interactions. On cooler surfaces, there is a possibility of some condensation occurring for some of the heavier congeners. However, there should be an equilibrium reached for condensation and evaporation at some point. In Fig. 10, the congener distributions of the toxic isomers that contribute to the TEQ values are plotted. The catalyst inlet shows a relatively high concentration of the hepta and octa dioxins, and a hepta furan (1234678-HpCDF). At the catalyst outlet, which also is the heat exchanger inlet, the congener patterns shift to a higher concentration of the hepta and octa dioxins, and tetra through hexa furans. A redistribution occurs of the congeners in the heat exchanger outlet, with a decrease in the tetra through hexa furans, but an increase in the tetra and penta dioxins, and in 1234678-HpCDF. Prior to the stack is a wet scrubber that removes dioxins to a certain degree. In principle, the lower vapor pressure congeners would be removed better than higher vapor pressure congeners. Fig. 10 shows primarily a reduction in tetra-hepta dioxins and heptaocta furans. Changes in chemistry may account for these differences. At the stack, a further redistribution of the congener occurs so that the major congeners are the hepta and octa dioxins and 1234678-HpCDF. It appears that a slight variation in temperature across the catalyst and across the heat exchanger contributes to a dramatic change in the dioxin and furan chemistry. There is virtually no production of four of the congeners (2 dioxins and 2 furans) across the platinum supported catalyst, but a large production of the rest of the congeners. The highest production is in the tetra through hexa furans, and in the 1234789-hepta furan (HpCDF). These data indicate that small variations in temperature apparently



Fig. 11. Comparison of TEQ emissions at two different sites with and without non-chlorinated vapors.

cause large changes in the congener distribution of the dioxin and furan isomers.

## 4.5. Effect of non-chlorinated organics

Van den Brink et al. (2000) found a reduction or elimination in by-products by removal of Cl from surface by the addition of alkanes. Comparing data using the same type of catalytic oxidizer with and without the addition of non-chlorinated VOCs, this phenomenon also occurred in this study. TEQ concentrations are shown in Fig. 11 with and without non-chlorinated VOCs. Even at lower catalyst inlet temperatures, the TEQ emissions are much lower with the addition of the non-chlorinated VOCs. Congener concentrations are nearly non-detect for the co-firing of non-chlorinated VOCs. This may be due to consumption of Cl by the non-chlorinated VOCs to form HCl. An interesting issue is the formation of non-chlorinated VOCs (such as benzene) as by-products from the burning of methane in the auxiliary burner, and how these by-products may interact in the dioxin formation pathways.

#### 5. Conclusions

The results of this field study indicate that:

- Toxic equivalents of 2,3,7,8-TCDD (TEQ) exponentially increase with a decrease in operating temperature. An empirical equation is TEQ (ng/dscm) = 8.4 exp(-0.0084T °C).
- Dioxin/furan production occurs at the combustion catalyst.
- Catalytic and thermal oxidizers may be destroying dioxins fed from the ambient air.
- Small variations in temperature cause large changes in the congener distribution of the dioxin and furan isomers.

- Molar yields from the parent compounds fed to the oxidizers to the toxic equivalents of 2,3,7,8-TCDD are very small (10<sup>-9</sup>-10<sup>-13</sup>).
- The oxidation of chlorinated VOCs with non-chlorinated VOCs reduces emissions of dioxins.

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