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## Comparative study on the formation of toxic species from 4-chlorobiphenyl in fires: effect of catalytic surfaces

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### Abstract

This contribution compares the formation of toxic species, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) and their precursors such as polychlorobenzenes (PCBz) and polychlorophenols (PCP), during oxidation of 4-chlorobiphenyl (4-CB) in a laboratory-scale apparatus, under conditions similar to those that occur in fires and waste combustion. The experiments were conducted using two gas flow reactors made of 99.5% alumina and high purity quartz, respectively. A sampling system intercepted the gaseous products leaving the reactors, trapping the volatile organic compounds (VOC; *i.e.*, PCBz and PCP) and PCDD/F on a XAD-2 cartridge. The analysis of VOC involved high resolution gas chromatography (HRGC) – quadrupole mass spectrometry (QMS) while HRGC – ion trap (IT) MS/MS quantitated the PCDD/F produced. For the experiments using the alumina reactor, VOC analysis revealed the formation of PCBz and PCP, commencing at temperatures as low as 400 °C. Other products included benzaldehyde, naphthalene, 3-ethylbenzaldehyde, 1-chloro-4-ethynylbenzene and benzofuran. Gaseous species such as CO, CO<sub>2</sub> and HCl were detected and quantitated either by Fourier transform infra-red spectroscopy (FTIR) or ion chromatography (IC). Similar products were found to form in the quartz reactor, however, their formation commenced at 500 °C, with their yields significantly lower than those found for the alumina reactor. The present measurements indicate that surface reactions govern the oxidation of 4-CB between 300 and 650 °C for the alumina reactor, and between 450 and 600 °C for the quartz reactor. At 700 °C, both reactors operate similarly, with the oxidation process dominated by the gas phase reactions. With respect to dibenzo-*p*-dioxins and dibenzofurans, only isomers of chlorinated monochlorodibenzofuran (MCDF) and chlorinated dichlorodibenzofuran (DCDF) were found at low temperatures (300 to 450 °C), with 3-MCDF as the dominant congener. In our system, they appear to form in gas phase reactions involving 4-CB and singlet oxygen (<sup>1</sup>Δ<sub>g</sub> O<sub>2</sub>), the latter generated on the reactor walls. The present results indicate that the combustion of 4-CB in fires will be dominated by catalytic surfaces of fly ash below 600 °C, and by gas-phase kinetics above 700 °C.

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**Keywords:** Chemical fires; Toxic species in combustion; Surface effects on gas reactions

### 1. Introduction

Polychlorobiphenyls (PCB) are persistent organic pollutants, first identified as environmental contaminants in 1966 [1]. Prior to their phase-out in late 1970s [2, 3], they were widely used as coolants and insulating fluids in transformers and capacitors. They were first introduced in these applications in 1930s. PCB are toxic and accumulate in the environment. In spite of PCB production concluding in the late 1970s, these compounds persist in every part of the world, in water, soil, as well as bird and fish tissue [4]. Earlier research recognised that toxic species, such as PCDD/F and their precursors (PCP and PCBz), are produced in fires of PCB mixtures [5-7]. In this study, we investigate the formation of toxic species in oxidation of 4-monochlorobiphenyl (4-CB) under conditions similar to those of fires. This is because in recent years, more

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attention has been devoted to the fate of monochlorobiphenyls (MCB) in the environment as a consequence of their role as food contaminants. For example, MCB have been included in food monitoring programs of the European Scientific Committee for Food (SCF, Brussels, Belgium).

In the past 20 years, investigations focused on the removal and destruction of PCB from contaminated soil, water and industrial waste. Thermal decomposition, photodegradation, supercritical water, and indeed a range of other techniques have been studied as means to decompose PCB [8-10]. In particular, insights have been gained into the formation of PCDD/F under oxidative, catalytic and pyrolytic combustion of PCB mixtures [11, 12]. The yield of PCDD/F under oxidative conditions usually amounts to around 0.01-1 %, but it may also be as high as 6 % [13, 14]. To avoid the effect of surface reactions on gas-phase combustion, laboratory experiments normally involve high purity quartz reactors[15]. But, in previous investigations, some researchers deployed alumina reactors to study gas-phase oxidation phenomena [16, 17]. Our study demonstrates that, at temperatures below 600 °C, surface effects may govern the product distribution of oxidation of aromatic hydrocarbons. Only at temperatures above 700 °C, one may neglect the effect of the alumina walls on gas-phase oxidation reactions of aromatic hydrocarbons.

The hazards of accidental chemical fires, which may occur in production and storage facilities, necessitate a better understanding of the formation of toxic species in combustion of MCB. Lack of data on the concentration of PCDD/F formed in fires of PCB makes it difficult to evaluate risks of MCB fires to people and the environment. A study on the thermal decomposition of 4-CB would be of assistance in revealing the yield of toxic products, especially in the presence of catalytic surfaces. Real fires form large quantities of soot and fly ash, which contain catalytic particles, mostly iron present on alumina and silica surfaces. Hence, the inclusion of catalytically active surfaces in a laboratory study would lead to results of practical significance. In this study, we attempted to investigate the formation PCDD/F pollutants and their VOC precursors in gas-phase systems with and without catalytic effects; the formation of PCDD/F between 300 and 450 °C, and the emission of VOC between 300 and 700 °C. The present understanding of catalytically-assisted combustion of PCB is quite limited. By performing experiments using both alumina and quartz reactors, we explore and gain understanding of the contribution of alumina surfaces, contaminated with transition metals, to the formation of organic pollutants in fires.

## 2. Experimental

### 2.1. Experimental Set-up

Figure 1 illustrates a bench-scale apparatus to study the oxidation of 4-CB. With the details of a similar apparatus described elsewhere [18], here we only provide a brief description. The apparatus consists of three major components, a reactant vaporiser, an isothermal alumina/quartz flow reactor, and a collection system for different types of products. The oxidation reactions take place in the central zone of the alumina or quartz tube, denoted in Fig. 1 as the reaction zone.

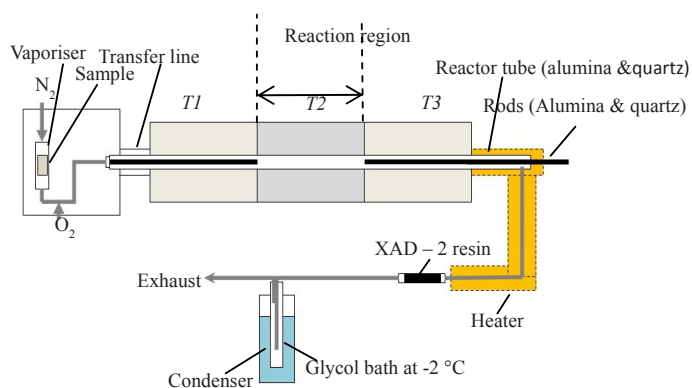


Fig. 1. A sketch of experimental apparatus

**Reactant vaporiser:** Prior to each experiment, approximately 30 mg of 4-CB (98.8 %, Apollo, UK), a white solid powder at room temperature, was placed in a polytetrafluoroethylene (PTFE) tube of 8 mm in inner diameter (i.d.), installed in an oven (Shimadzu, Japan). The impurities in 4-CB included biphenyl (1 %) and 4,4'-dichlorobiphenyl (0.5 %). The oven, maintained at 75 °C, induced evaporation of 4-CB at a rate of approximately 0.02 mg/min. The vapour was diluted in nitrogen flow and mixed with a controlled amount of oxygen prior to entering the reactor. To prevent the 4-CB vapour from

condensing prior to entering the reactor, a temperature of the transfer line was set to 175 °C with a coiled tubular heater (Helios, Australia) positioned between the reactor and the vaporiser. The concentration of O<sub>2</sub> was monitored by a Varian CP 2003 micro gas chromatograph (μGC) to ensure the O<sub>2</sub> concentration to remain constant at 6.0 ± 0.5 %, resulting in the fuel equivalence ratio of 0.07.

**Reactor system:** For experiments expected to demonstrate strong wall effects, the reactor comprised an alumina tube (99.5%) with i.d. of 5 mm. Two alumina rods (4 mm o.d.) were inserted into the alumina tube to define the reactor volume and to force the reactants and products to flow in the annular space. The latter ensured the vapours to reach the reaction zone rapidly, minimising their decomposition in lower temperature regions. For experiments aimed to elucidate the gas phase reactions, we used a reactor system that constituted a high purity quartz tube (99.995%, Table 1) with i.d. of 10 mm, and two high purity quartz rods (9.5 mm). As will be presented below, this system minimised, but did not avoid, the effect of surface reactions. It afforded the same residence time at different temperatures, as attainable in the alumina flow reactor, by adjusting the inserted length of one of the rods. Both reactors were installed, one at a time, along the centreline of a three-zone furnace (Labtek, Australia) that was equipped with a temperature controller (Eurotherm 3216, Australia). The furnace was calibrated up to 800 °C with a thermocouple placed along the tube to define the location of a uniform temperature zone (about 26 cm in length). The end of either reactor tube was attached to a products collection system.

Table 1. Main impurities in alumina and quartz materials of the reactors' walls

Impurities (ppm)	Al	Si	B	Ca	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Ti	Zr	OH-	Zn
Quartz	14		<0.2	0.4	<0.05	0.2	0.6	0.6	0.1	<0.05	0.7	<0.1	<0.2	1.1	0.8	<5	-
Alumina	-	<3000	-	-	200	<3000	-	-	100	100	-	-	-	300	-	-	600

**Products collection system:** For each set of conditions, VOC (including precursors of PCDD/F) and PCDD/F themselves were collected in two separate experiments. The sampling time was set to six and three hours for PCDD/F and VOC measurements, respectively. In both experiments, 200 mg of XAD-2 resin (Supelpak-2, Sigma-Aldrich, Australia) was loaded into the glass cartridge. The connection tube, made of PTFE, was heated to 140 °C to ensure the complete trapping of all VOC reaction products by the resin. In experiments designed to collect PCDD/F products, we did not attempt to heat the connection tube to transfer all PCDD/F to the XAD-2 cartridge, as the condensation of higher chlorinated PCDD/F on the alumina and quartz tubes was difficult to avoid. We used *n*-hexane (20 mL) to fill the reactor tube and placed the tube, filled with *n*-hexane, in a shaker to dissolve the products condensed on the reactor's walls. The resulting solution was combined with the solution from washing the PTFE connection tube and analysed on the GC-QMS instrument. We also rinsed the tubes with dichloromethane, followed by acetone and baked out the tubes at 150 °C to remove any impurities which could have affected the next experiment. The gaseous products were collected in a 3 L gas bag, and then analysed on a Fourier transform infrared (FTIR) spectrometer equipped with a multipass cell. Ion chromatograph (IC) was employed to detect minor amount of hydrogen chloride present in the product gases. HCl tends to adsorb on surfaces, including those of the sampling bag and multipass cell, resulting in its inferior quantitation by FTIR.

## 2.2. Product Analysis

**HRGC-QMS analysis of VOC:** We followed the general procedure of NIOSH Method 1003 to analyse VOC products with some modification as necessary for our system. We deployed *n*-hexane rather than CS<sub>2</sub>, the latter recommended by the National Institute for Occupational Safety and Health (NIOSH) Method 1003, to desorb product species from the XAD-2 resin. *n*-Hexane provided more effective desorption of VOC from the resin. The *n*-hexane extract was filtered and injected (1 μL), at 1:10 split, into the HRGC-QMS (Varian, Australia), equipped with the VF-5ms column (30 m length, 0.25 mm i.d., 0.25 μm film thickness). Helium was used as the carrier gas flowing at a constant rate of 1.0 mL/min. The injector functioned at 260 °C. The oven temperature was held for 5 min at 35 °C, and then increased with a temperature ramp of 10 °C/min up to 245 °C, which was kept for 10 min. We operated the electron impact source at a standard value of 70 eV. Both the source and the transfer line were maintained at 250 °C. The eluted peaks were identified by matching their mass spectra with those from the NIST library, and from genuine standards.

**GC-(IT)MS/MS analysis of PCDD/F:** The US EPA Method 1613 was modified to include the determination of mono- to trichlorinated congeners. For each PCDD/F experiment, the products adsorbed on XAD-2 resin were extracted with toluene for 12 h in an automated Soxhlet unit (Buchi). The XAD-2 resin extract and the sample from washing the reactor and PTFE connection tubes were concentrated and analysed separately. Both samples were cleaned up to remove their matrix using glass chromatography columns loaded with basic and acidic silica gel, followed by more cleaning using columns containing

basic and acidic alumina. The solutions were concentrated prior to injections into Varian 3800 GC and Saturn 2000 ITMS for the PCDD/F analysis. The sample (1  $\mu\text{L}$ ) was introduced into an injector (280  $^{\circ}\text{C}$ ) operated in a splitless mode. Chromatographic separation was achieved with a VF-5ms capillary column (60 m length, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness) with helium as the carrier gas (1 mL/min). The oven temperature program induced 80  $^{\circ}\text{C}$  (held for one min), and then a rise to 235  $^{\circ}\text{C}$  (held for 10 min) at 10  $^{\circ}\text{C}/\text{min}$ , subsequent increase to 275  $^{\circ}\text{C}$  (held for 9 min) at 5  $^{\circ}\text{C}/\text{min}$  and then to 310  $^{\circ}\text{C}$  (held for 6 min) at 10  $^{\circ}\text{C}/\text{min}$ . We maintained the transfer line, ion trap, and manifold temperatures at 270  $^{\circ}\text{C}$ , 200  $^{\circ}\text{C}$  and 80  $^{\circ}\text{C}$ , respectively. The detection limits of HRGC-(IT) MS/MS for PCDD/F correspond to between 0.3 and 3.0  $\text{pg}/\mu\text{L}$  (except 6.0  $\text{pg}/\mu\text{L}$  for octachlorinated dibenzofuran). We have identified and quantitated PCDD/F with standards obtained from Wellington Laboratories (Ontario, Canada). Appendix lists daughter ions deployed for the PCDD/F quantitation; *i.e.*, parent minus COCl (M-COCl).

**Analysis of gaseous products analysis by FTIR and IC:** The infrared spectra were recorded on a Varian 660-IR spectrometer (Varian, Australia) with a 10-PA 10 m long permanently aligned path gas cell (Infrared Analysis, USA). The evacuated gas cell was filled with sample gas to reach atmospheric pressure. Each measurement corresponded to 10 scans in the spectral range of 4000-500  $\text{cm}^{-1}$  with a resolution of 0.5  $\text{cm}^{-1}$ . The same grade of high purity nitrogen, as used for the reaction carrier gas, was scanned as the background. The reference spectra library within QA software package afforded the identification of gaseous products. These spectra required a correction for slight frequency shifts relative to our samples. A Dionex DX-100 ion chromatograph analysed for the presence of chloride ion, with the identification of  $\text{Cl}^{-}$  based on the retention time.

### 3. Results and Discussion

#### 3.1. Comparison of VOC products in alumina and quartz reaction system

We explored the effect of temperature on the formation of VOC from the thermal decomposition of 4-CB in both reactors, and analysed products on the GC-QMS, in full scan mode. For the alumina reactor, we identified 12 major products as listed in Table 2. Only 9 were observed in the quartz reactor and the concentration of these species was lower than obtained from experiments involving the alumina reactor. For both systems, phenylethyne was the dominant product species. The chlorine containing compounds, such as 1-chloro-ethynylbenzene, appeared in the total ion count (TIC) analysis from 550  $^{\circ}\text{C}$  for the alumina reactor and from 600  $^{\circ}\text{C}$  for the quartz reactor. Some of these products, such as styrene, benzofuran, naphthalene and 1,2,3-trichlorobenzene, are classified by the International Agency for Research on Cancer (IARC) as possible carcinogens. Table 2 summarises the VOC species, observed in the combustion of 4-CB in both reactors, with Fig. 2 providing a typical TIC chromatogram. The results from the experiments performed at 650  $^{\circ}\text{C}$  were selected to show all species in the same figure that form for both reactors.

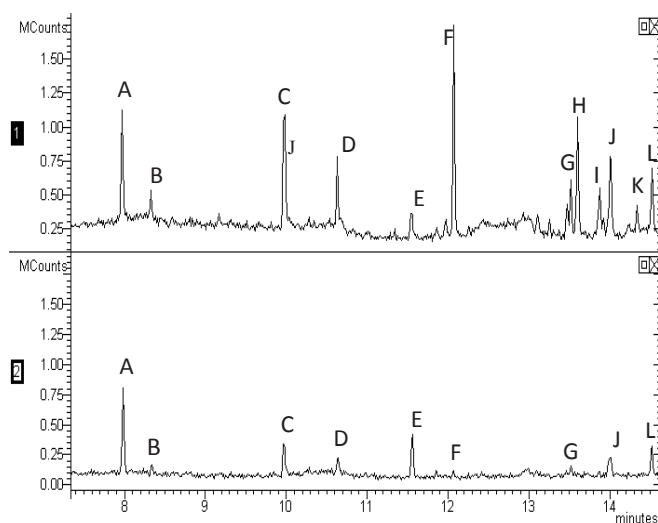














Fig. 2. Comparison of VOC products detected by GC-QMS in the experiments conducted at the same temperature (650  $^{\circ}\text{C}$ ) for both reactors; alumina (top) and quartz (bottom) reactors.

Table 2. Identified products generated in both alumina and quartz reactors

Peak	Product	Structure	R.T. (min)	Alumina reactor	Quartz reactor
A	phenylethyne		8.0	√	√
B	styrene		8.4	√	√
C	benzaldehyde		10.1	√	√
D	benzofuran		10.7	√	√
E	acetophenone		12.0	√	√
F	1-chloro-4-ethynylbenzene		12.1	√	√
G	naphthalene		13.5	√	√
H	3-ethylbenzaldehyde		13.6	√	
I	4-ethylbenzaldehyde		13.9	√	
J	1,2-naphthalenedione		14.1	√	√
K	1,2,3-trichlorobenzene		14.3	√	
L	3-phenylfuran		14.5	√	√

Under oxidative conditions, OH radicals can react exothermically with HCl to produce a relatively high abundance of Cl radicals. FTIR identified CO and CO<sub>2</sub> as the major products, whereas HCl was only detected in trace quantities. Because of the low recovery of HCl in FTIR analysis, we used 50 mL NaOH solution (pH=10) to adsorb acidic gases, followed with the XAD-2 resin cartridge. IC served to analyse the solution, detecting a minor amount of hydrogen chloride, as listed in Table 3. The concentration of HCl in the exhaust gases from both reactors increased gradually with temperature, though, the yield of HCl formed in the alumina reactor always exceeded that observed in the quartz reactor.

Table 3. Yield of HCl in both reactors

Alumina reactor (mmol/mol of 4-CB)	Quartz reactor (mmol/mol of 4-CB)
0.000	0.000
0.440	0.080
0.950	0.320
4.40	1.23
10.5	4.68

### 3.2. Comparison of yields of PCDD/F precursors in alumina and quartz reactors

As a number of studies suggested that, PCP and PCBz act as the precursors for the formation of PCDD/F under the oxidative conditions [18-20], our interests in the present investigation focused on gaining insights into the formation of these precursor species. In particular, we attempted to quantitate the yields of these precursors for both systems. In the full scan MS, we only observed small amount of 1,2,3-TCBz. To confirm the formation of other trace amounts of the PCDD/F precursors, we applied selected ion monitoring (SIM), a specialised mass spectrometric technique designed to detect and quantitate trace pollutants on quadrupole mass spectrometers. In the experiments performed between 300 and 700 °C on the alumina reactor, we identified 16 precursors of PCDD/F. However, only 6 were observed in the products leaving the quartz reactor. To confirm the retention time and to quantitate the yield for each precursor, we injected authentic standards into the

GC-QMS. Table 4 lists the identified PCDD/F precursors, their retention time and their quantitation ions for both reaction systems.

Table 4. Identified PCDD/F precursors formed in both reaction systems

Name	Quantitation ions (%)	Retention time (min)	Alumina reactor	Quartz reactor	Name	Quantitation ions (%)	Retention time (min)	Alumina reactor	Quartz reactor
phenol	94(100)	10.3	√	√	MCBz	112(100)	7.2	√	√
	66(30-35)					114(35)			
	63(10)					77(45)			
2-CP	130(35)	10.5	√	√	m-DCBz	146(100)	10.8	√	√
	128(100)					148(65)			
	64(35)					111(30)			
2,4-DCP	162(100)	13.65	√		p-DCBz	146(100)	11.0	√	√
	164(65)					148(65)			
	98(40)					111(34)			
2,6-DCP	162(100)	14.2	√		o-DCBz	146(100)	11.4	√	√
	164(65)					148(65)			
	98(25)					111(35)			
2,4,6-TCP	196(100)	16.36	√		1,2,3-TriCBz	180(100)	14.4	√	
	198(95)					182(96)			
	200(30)					184(31)			
2,4,5-TCP	196(100)	16.44	√		2,4,5-TriCBz	180(100)	15.6	√	
	198(95)					182(96)			
	200(30)					184(31)			
1,2,3,5-TetraCBz	214(81)	16.0	√		1,2,3,4-TetraCBz	214(81)	16.7	√	
	216(100)					216(100)			
	218(51)					218(51)			

The results presented in Table 4 illustrate that only MCBz and DCBz formed in the quartz reactor system. For both reactor systems, MCBz was the dominant precursor species, with the yield of MCBz initially increasing slowly with temperature. *p*-DCBz dominated the DCBz isomers, followed by *o*-DCBz and *m*-DCBz. As for MCBz, concentrations of the three isomers of DCBz increased gradually with temperature, in both reactors. In gases emitted from the alumina reactor, we also detected small amounts of 1,2,3-TriCBz and 1,2,4-TriCBz, starting from 500 °C. In addition, TeCBz formed in a temperature range of between 625 to 700 °C. Fig. 3(a) shows the total yield of PCBz for both reactors. Note the differences in the trends. The formation of PCBz in the alumina reactor commences at low temperature, but rises sharply at 575 °C to reach a maximum at 625 °C. However, the yield of PCBz in a quartz reactor only exhibits a steep increase at temperatures above 650 °C.

With respect to phenols, only 2-CP and phenol itself were detected in the products exiting the quartz reactor. Minor amounts of DCP (2,4-DCP and 2,6-DCP) and TriCP (2,4,6-TriCP and 2,4,5-TriCP) were also detected in experiments involving the alumina reactor. Fig. 3(b) presents the total yield of PCP from each of the reactors. The trends are similar to those of PCBz. Evidently, the yield of the precursors in the exhaust of the alumina reactor significantly exceeds that of the quartz reactor at low temperature (400 to 550 °C). This means that the initiation reactions involve species formed on the alumina surfaces. At high temperature, the total yield of precursors in both reactor systems appears similar, indicating the importance of gas-phase reactions in that temperature range.

In Table 5, we plot the conversion of 4-CB as function of the reactor temperature. Clearly, catalytic wall effects appear to govern the conversion of 4-CB up to 600 °C for both reactors, but the magnitude of these effects is significantly higher for the alumina reactor. Above 700 °C, gas phase reactions control the oxidation behaviour, with both reactors showing similar operation, in terms of conversion and selectivity. At temperature below 450 °C, only the alumina reactor appears to be



catalytically active, though between 450 and 600 °C even the surfaces of the quartz reactor seem to exhibit minor surface activity.

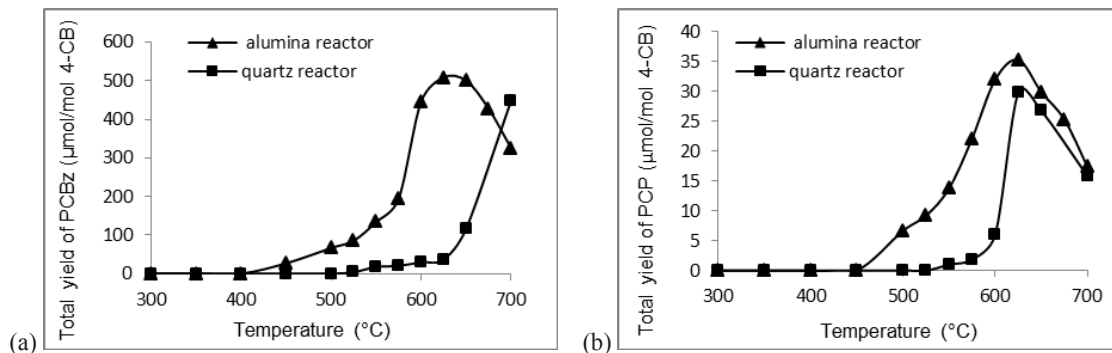


Fig. 3. Total yield of PCBz (a) and PCP (b) in both alumina and quartz reactors.

Table 5. Conversion (%) of 4-CB in both reactors

Temperature (°C)	300	350	400	450	500	550	600	650	700
Alumina reactor	0.0036	0.0065	0.0371	0.0683	0.124	0.148	0.276	0.869	1.37
Quartz reactor	0.0000	0.0000	0.0001	0.0169	0.0328	0.0505	0.115	0.640	1.43

### 3.3. Comparison of yields and distribution of dioxin products at up to 450 °C in both reactors

The identification of CDD/F congeners follows the injection of genuine standards and the published elution order [21, 22]. MCDF was the most abundant CDD/F homologue group. Table 6 records the yield for each identified MCDD/F congener, with Fig. 4 illustrating a typical chromatograph of the elution order of all MCDF congeners. 3-MCDF was the most abundant congener in the MCDF homologue group, followed by 2-MCDF, 1-MCDF and 4-MCDF. At low temperature, only MCDD/F and DCDF congeners were found in the experiments. We detected 1-MCDD in the exhaust from the alumina reactor at 450 °C but not in the product gases from the quartz reactor. Trace quantities of three DCDF congeners were also detected. They might have been formed from 4,4'-dichlorobiphenyl (4,4'-DCB), an impurity in 4-CB. The total yield of MCDD/F at 450 °C corresponded to 29 and 38 ng/g of 4-CB, for the quartz and alumina reactors, respectively.

Figure 5 compares the yield of PCDD/F at temperatures from 300 to 450 °C. PCDD/F were observed at 300 °C in an alumina reactor, with a small yield of 0.59 ng/g of 4-CB. At the same temperature, in the emissions from the quartz reactor, the yield of PCDD/F corresponded to 0.02 ng/g of 4-CB; *i.e.*, the same level of PCDD/F as in a blank experiment, probably due to contamination in the Soxhlet extraction system. The yield of PCDD/F increased with temperature in both systems, with the PCDD/F formation in the alumina reactor being always greater than in the quartz reactor.

Table 6. Yield of MCDD/F congeners in both reactors

MCDD/F congeners	Yield for the quartz reactor (ng/g 4-CB)	Yield for the alumina reactor (ng/g 4-CB)
1-MCDF	0.030	0.340
3-MCDF	28.4	35.7
2-MCDF	0.570	1.62
4-MCDF	0.040	0.250
1-MCDD	0.000	0.080

At 400 °C, we observed a miniscule concentration of PCDD/F precursors and no formation of soot on the walls of the reactors, leading us to believe that the classical mechanisms of synthesising PCDD/F, *i.e.* the phenoxy condensation and the

de novo pathways, do not operate in our system [23-25]. Since we also detected the formation of PCDD/F, we concluded the existence of a new pathway that had not been reported in literature. This pathway is likely to involve a gas-phase reaction between 4-CB and singlet oxygen, with the latter forming catalytically on alumina and quartz surfaces (Fig. 6). Our preliminary quantum chemical calculations for the non-chlorinated biphenyl confirm the viability of this new mechanism of formation of PCDD/F [26].

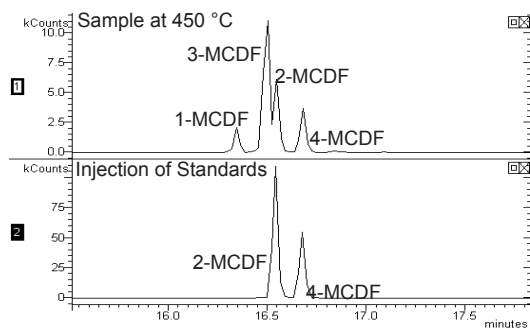


Fig. 4. Distribution of MCDF congeners at 450 °C

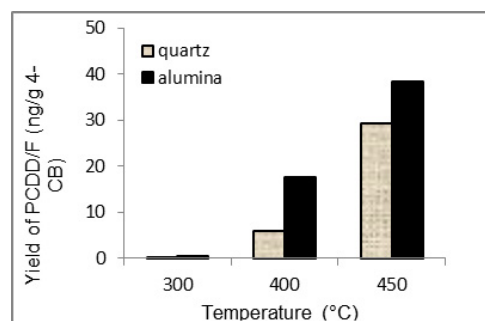


Fig. 5. Comparison the total yield of PCDD/F in both reactors.

#### 4. Conclusions

We studied the thermal decomposition of 4-CB in two reactor systems comprising the alumina and quartz flow reactors, with a sampling train to capture a wide range of toxic species. The results presented in this contribution confirm the role of catalytic surfaces on the initiation reactions in the gas-phase oxidation of 4-CB. The identification and quantitation necessitated the application of several analytical techniques, including HRGC-QMS, FTIR, HRGC-(IT)MS/MS and IC. We have been able to identify and quantitate the PCDD/F and VOC, by injecting the authentic standards, and, in the case of VOC, by comparing the spectra with those in the NIST database. Up to 650 °C, the alumina reactor yielded more products and at higher concentration, compared with the emissions from the quartz reactor. Especially, the emissions of PCBz were significantly higher from experiments conducted using the alumina reactor than the quartz reactor. We observed the formation of possible VOC carcinogens but no formation of toxic PCDD/F congeners. At temperatures up to 450 °C, mono- and dichlorinated CDD/F formed by reactions of surface generated singlet oxygen with 4-CB and its impurity 4,4'-DCB, rather than from PCBz and PCP precursors. The present measurements indicate that surface reactions govern the oxidation process between 300 and 650 °C for the alumina reactor, and between 450 and 600 °C for the quartz reactor. Though, the surface activity of quartz always falls significantly below that of alumina. At 700 °C, both reactors display similar operation governed by the gas phase reactions. Thus, the combustion of 4-CB in fires will be dominated by catalytic surfaces of fly ash below 600 °C, and by gas-phase kinetics above 700 °C.

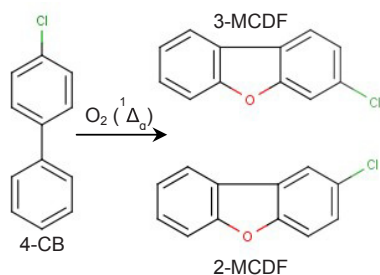


Fig. 6. Proposed singlet oxygen pathway for the formation of MCDF.



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